



Hybrid hydrogels as model nanocomposites : reinforcement mechanisms by analogy with filled rubbers

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Hybrid hydrogels as model nanocomposites : reinforcement mechanisms by analogy with filled rubbers

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analogy with filled rubbers

Anne-Charlotte LE GULLUCHE

Greetings

Cette thèse a été réalisée en partenariat entre le laboratoire Science et Ingénierie de la Matière Molle (SIMM) à l'ESPCI Paris et le laboratoire Polymères et Matériaux Avancés (LPMA) de l'entreprise Solvay à Saint-Fons, petite ville méconnue mais fort charmante de la région nouvellement nommée Auvergne-Rhône-Alpes. Elle s'est déroulée sous la direction scientifique d'Alba Marcellan (SIMM) et de Paul Sotta (LPMA) et l'aspect industriel de ce travail a été supervisé par Olivier Sanséau (Solvay).

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Summary

Hydrogels are soft and elastic solid materials mainly composed of water. Owing to their ability to interact with their environment through drastic volume change, hydrogels already find a wide range of applications, as superabsorbants, in pharmaceuticals as drug delivery systems and more recently, as sensors and actuators, widening even more the possible use of soft materials as structural or load-bearing materials. Hence, providing gels with high mechanical performances is of major importance to meet these demanding applications.

Efficient toughening can be achieved by combining inorganic and organic materials linked by physical and/or chemical interactions. In such nanocomposite materials, the reinforcement depends on the interactions between the polymer and the filler and of the dispersion state of the fillers, allowing to reach the full extent of reinforcement. Hybrid hydrogels based on poly(*N*-alkylacrylamide) and nanosilica demonstrating great mechanical reinforcement at large strain as well as self-healing capabilities were designed by Hourdet and Marcellan . The drastic improvement of the mechanical behavior is attributed to the reversible adsorption of the polymer onto silica surface. Viscoelastic properties of such hybrids gels have been extensively studied but few studies were carried out to understand and quantify the interactions at the solid/liquid interface. Likewise, the behavior beyond viscoelastic regime of such materials remains scarcely investigated.

A first part of this study focused on the synthesis and the adsorption behavior of linear polymer chains of polyacrylamides, more precisely poly(acrylamide) (PAAm), poly(*N,N*-dimethylacrylamide) (PDMA) onto silica nanoparticles with controlled surface chemistry. It evidenced the non-interacting behavior of PAAm towards silica surface, justifying its choice as a non-interacting polymer. A second part dealt with the modulation of particle/polymer interactions in hybrid gels either by substituting the interacting monomer (DMA) with a non-interacting one (AAM) or by tuning the surface chemistry of the nanoparticles. Then, the study of their structure and mechanical properties was conducted with a special focus on the non-linear behavior. The role of polymer adsorption for gel reinforcement was evidenced and more specifically the importance of the silanol groups at the silica surface for PDMA/silica interactions. The contribution of the dispersion state of silica on the structure and the mechanical response of hydrogels was then addressed and the non-linear domain of the resulting hydrogels was investigated using Large Amplitude Oscillatory Shear experiments. The impact of the chosen monomer and of the dispersion state of the fillers was investigated at large strain, allowing a more precise analysis of the reinforcement mechanisms, by analogy with filled elastomers.

Key-words: hydrogel, silica, adsorption, reinforcement, poly(acrylamides), reversible interactions

Résumé

Les hydrogels sont des matériaux intrinsèquement mous, fragiles et élastiques, majoritairement composés d'eau. Leur capacité unique à interagir avec leur environnement se traduit par une grande variation de leur volume initial et en font l'objet d'applications variées dans de nombreux domaines tels que le secteur biomédical, l'industrie agro-alimentaire et cosmétique. Plus récemment, des hydrogels ont été développés pour des secteurs de pointe comme la robotique ou l'ingénierie tissulaire, permettant d'élargir le spectre d'utilisation de la matière molle en tant que matériau structural. De ce fait, la conception d'hydrogels mécaniquement performants représente un enjeu majeur au développement futur de ces applications.

L'élaboration de matériaux nanocomposites incorporant des nanocharges à un réseau organique réticulé de façon covalente s'est avérée une stratégie de renfort efficace. Le renforcement dépend alors des interactions existantes entre le polymère et les charges ainsi que de l'état de dispersion des nanoparticules au sein du réseau. Des hydrogels hybrides, à base de poly(*N*-alkylacrylamides) et de nanoparticules de silice ont ainsi été mis au point, démontrant une amélioration significative des propriétés mécaniques (déformation à la rupture, capacités d'auto-réparation). Ce phénomène est attribué à l'adsorption réversible du polymère à la surface des nanoparticules. Si les propriétés viscoélastiques de ces composés ont été largement étudiées, peu de travaux ont été effectués sur la caractérisation et la quantification des interactions à l'interface solide/liquide. De même, le comportement au delà du domaine linéaire ne reste que peu étudié à ce jour.

La première partie de ces travaux a été dédiée à la synthèse de chaînes linéaires de poly- (acrylamide) (PAAm) et poly(*N,N*-diméthylacrylamide) (PDMA) ainsi qu'à l'étude de leurs capacités d'adsorption sur la silice tout en contrôlant la chimie de surface des nanoparticules. Cela a permis de mettre en évidence le peu d'affinité du PAAm envers la surface de silice, justifiant ainsi son emploi en tant que monomère 'inerte'. En second lieu, il s'est agi de moduler les interactions entre le polymère et la silice au sein des hydrogels hybrides en substituant le polymère interagissant avec l'adsorbat (PDMA) par un polymère peu apte à s'adsorber sur la silice (PAAm). La structure de ces composés ainsi que leur comportement mécanique ont été explorés avec un intérêt marqué pour le domaine non linéaire. Le rôle de l'adsorption dans le renfort mécanique a ainsi été confirmé et plus précisément l'importance des groupements silanols à la surface de la silice. La contribution de l'état d'agrégation des nanoparticules sur la structure et les propriétés mécaniques ont ensuite été étudiés. Le comportement non-linéaire aux grandes déformations des hydrogels synthétisés a notamment été investigué par des expériences de rhéologie aux grandes amplitudes de cisaillement (LAOS), permettant une caractérisation plus poussée des mécanismes de renfort, par analogie avec les élastomères chargés.

Mots-clés: hydrogel, silice, adsorption, renforcement, poly(acrylamides), interactions réversibles

List of symbols and abbreviations

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Abbreviations

AAm Acrylamide

APS Ammonium persulfate

ATRP Atom Radical Transfer Polymerization

CRP Controlled Radical Polymerization

DLS Dynamic Light Scattering

DMA *N,N*-dimethylacrylamide

FID Free Induction Decay

FRP Free Radical Polymerization

KPS Potassium persulfate

LCST Lower Critical Solubility Temperature

MBA *N,N'*-methylenebis-acrylamide

Me₆TREN Tri[2-(dimethyl)ethyl]amien

MeCrCl Methyl-2-chloropropionate

MQ Multiple Quanta

MSE Magic Sandwich Echo

NMR Nuclear Magnetic Resonance

NPs Nanoparticles

PAAm Poly(acrylamide)

PAMPS Poly(2-acrylamido-2-methyl-1-propanesulfonic acid)

PDMA Poly(*N,N*-dimethylacrylamide)

PHEMA Poly(hydroxyethylmethacrylate)

PNIPAm Poly(*N*-isopropylacrylamide)

PVP	Poly(vinylpyrrolidone)
SANS	Small Angle Neutron Scattering
SAXS	Small Angle X-Ray Scattering
SEC	Size Exclusion Chromatography
SEM	Scanning Electron Microscopy
SPS	Sodium metadisulfite
SR	Swelling ratio
TEMED	N, N, N', N' -tetramethylethylenediamine
TOC	Total Organic Carbon

Greek Symbols

Δ	Width of the square well
δ_e	Plane shear position
ϵ	Strain
ϵ_T	True strain
ϵ_0	Vacuum dielectric constant
ϵ_e	Free energy gain
ϵ_i	Molar extinction coefficient
ϵ_p	Perturbation factor
ϵ_r	Dielectric constant
η	Viscosity
η_i	Intriseq viscosity
Γ	Adsorbed polymer amount
γ	Strain amplitude
Γ''	Generalized loss modulus
Γ'	Generalized storage modulus
λ	Strain ratio
λ_D	Debye length
λ_l	Wavelength
μ_e	Electrophoretic mobility

ν	Scaling factor to describe the polymer/solvent interactions
ν_e	Cross-linking density
ν_{crack}	Crack propagation velocity
ω_0	Larmor frequency
Φ	Electrostatic forces
ϕ_f	Filler volume fraction
ϕ_0	Polymer volume fraction in the preparation state
ϕ_{eq}	Polymer volume fraction at swelling equilibrium
Ψ	Surface potential
ρ_{Si}	Silica density
Σ_c	Surface density of chains across the fracture plane
σ_{int}	Hard sphere diameter
σ_{Mooney}	Reduced/Mooney stress
σ_N	Nominal stress
σ_T	True stress
τ	Interpulse NMR delay/ mixing time
τ_{int}	Stickiness factor
τ_{MSE}	Interpulse NMR MSE delay
Θ	Surface coverage
ξ	Correlation length
ξ_c	Polymer network mesh size
ξ_{eff}	Effective cross-linking density
ζ	Zeta potential

Other Symbols

$\vec{R}$	End-to-end vector
a_T	Time-temperature superposition shift factor
A_{abs}	Absorbance
C_p	Equilibrium polymer concentration
D_{res}	Average residual dipolar coupling constant

E_d	Dissociation energy
f	Functionality
k_B	Boltzmann constant
M_e	Entanglements molecular weight
q	Wave vector modulus
Q_0	Swelling at preparation state
Q_e	Swelling equilibrium
r_f	Filler radius
r_{Si}	Silica nanoparticles radius
S_b	Dynamic order parameter of polymer backbone
S_{spe}	Specific surface
T_M	Torque
$^{\circ}\text{C}$	Celsius degree
a	Khun length
b	Statistical segment length
C_m^*	Overlapping concentration
D	Adsorbed thickness layer
DP_n	Average Degree of Polymerization
E	Linear tensile/ Young's modulus
e	Electronic charge
E_{VdW}	Van der Waals forces
G	Shear modulus
G''	Loss modulus
G'	Storage modulus
G_0	Fracture energy required to propagate a crack
G_c	Fracture energy
G_x	Contribution of covalent bonds to the shear modulus
I	Ionic force
I_0	Initiator

J	Joule
J_r	Energy required to break a covalent bond
K	Kelvin
L	Contour length
M	Monomer concentration
M_0	Monomer molecular weight
M_n	Polymer number average molecular weight
M_w	Polymer weight average molecular weight
N	Number of monomer units
N_{CL}	Number of monomer units between two cross-linking points
N_a	Avogadro constant
p	Probability of growing chain
p_b	Fraction of protons bond to an interface
Pa	Pascal
R_2^0	Reference relaxation rate
R_2^{sp}	Specific relaxation rate
R_g	Gyration radius
r_H	Hydration radius
T	Temperature
T_2	NMR transverse relaxation time
U	Interaction potential
$\mathbb{D}$	Polymer dispersity

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General Introduction

This PhD thesis was carried out in the Laboratoire Science et Ingénierie de la Matière Molle at the ESPCI PARIS (SIMM, UMR 7615) and at the Laboratoire Polymères et Matériaux Avancés (LPMA, UMR 5268), a joint research unit between the CNRS and the Solvay company.

Hydrogels are soft and elastic materials mainly composed of water. Their unique ability to absorb and/or release a high quantity of water combined with their elastic properties make them used in numerous industrial domains: agriculture, cosmetics and food science first. Nowadays, increasing prospective uses in biology, biomedicine, microfluidics and energy harvesting are emerging. They can be found in our everyday life in health-care products, pharmaceuticals or food products as diapers, drugs targeted-delivery system, contact lenses, food additives, artificial snow but also as part of state of the art applications such as actuators, sensors, batteries.

Synthetic polymer hydrogels can be considered as active matter as they are able to interact with their external environment through their ability to absorb, store or release solvent. Their properties can be tuned through external stimuli like temperature, pH, ionic force, magnetic or electric fields, pressure or light.

Despite their very promising properties, their range of applications as load bearing systems remains limited because of their extreme softness (and brittleness) due to their high content of water and also to the combined effects of frozen inhomogeneities of the polymeric network coupled with the non-operating viscoelastic losses.

Strategies of reinforcement were first inspired by biological systems. Indeed, such systems often possess both good elastic properties and toughness and are able to adapt to hostiles conditions such as jelly fish, anemones, joint cartilage or agarose. Investigations at the micro and nanoscale have revealed complex multiscale morphologies and structures that have inspired new ways to design hydrogels with advanced macroscopic responses. Reinforcement of hydrogels has been a field of extensive research for the past decades and remains very active today.

The ongoing strategies for gel toughening can be divided into two main tendencies: reducing the inhomogeneities of the polymer network, i.e. potential defects or weak points by elaborating well-defined macro molecular structures like the tetra-PEG gels developed by Sakai [Sakai et al., 2008] or the slide-rings gels designed by Okumura and Ito in Japan [Okumura and Ito, 2001], or by introducing the sacrificial bond concept, as pioneered by Gong in 2003 with double networks (DN) gels [Gong and Osada, 2003] that dissipate energy through covalent bond breaking. The basic concept here is to promote dissipative processes which would allow the material to store and dissipate a large amount of energy before breaking. Another way to promote dissipative processes is to design

nanocomposites (NC) gels, combining inorganic and organic materials linked by physical or chemical interactions or by both to obtain gels with enhanced mechanical properties. It is known that the hybridization of nano-objects with polymer networks allows to design materials displaying specific mechanical, electrical, thermal or anti-microbial properties. In the field of material engineering, a good example are elastomers filled either with nanosilica or carbon black possessing tremendously enhanced mechanical properties such as stiffness, toughness, wear and rupture resistance [Berriot et al., 2002; Charlesby et al., 1969]. As with elastomers, in NC gels, the reinforcement depends on the interactions between the polymer and the filler and of the dispersion state of the fillers.

Hybridization between hydrogel network and nanoparticles has been developed first in 2002 by Haraguchi who designed hydrogels with poly(*N*-alkylacrylamide) filled with clay nanosheets [Haraguchi, 2002]. Since then, research on hybrid nanocomposites remains highly active. Following the work of Lafuma et al. on semi-dilute solutions [Lafuma et al., 1991], hybrid hydrogels based on poly(*N*-alkylacrylamide) and nanosilica were designed by Hourdet and Marcellan [Carlsson et al., 2010; Rose et al., 2013] demonstrating great mechanical reinforcement at large strain as well as self-healing capabilities. Drastic improvement of mechanical behavior compared to the corresponding organic poly(*N*-alkylacrylamide) is attributed to the reversible adsorption of the polymer onto silica surface. More recently, Leibler and Marcellan [Rose et al., 2014] developed a new method for gluing gels and biological tissues using solid nanoparticles suspensions as adhesive. Beyond the promising results for surgery, this concept had opened up a new paradigm for adhesion: gluing without polymers, but using solid nanoparticles solutions.

Viscoelastic properties of nanocomposite gels have been extensively studied but only few studies were carried out to understand and quantify the interactions at the solid/liquid interface.

Hydrogels reinforced with nanoparticles present strong similarities with filled elastomers which non linear behavior was extensively studied by Sotta et al. [Papon et al., 2012; Perez-Aparicio et al., 2013]. Still, discriminating the contributions arising from the dispersion state of the filler and the particle/polymer interactions remains a difficult issue to address. In the meantime, the work developed by Hourdet and Marcellan on PDMA hybrid gels has revealed that the silica dispersion state as well as the interactions between PDMA and silica nanoparticles could be independently tuned. These results gave the idea to use these networks as model systems to investigate first the impact of polymer/filler interactions and secondly, of the aggregation state of the nanoparticles. Polymer/filler interactions have been tuned by comparing systems based on PDMA with systems synthesized with an homologous polymer, poly(acrylamide) (PAAm) which possesses supposedly a very different adsorption behavior onto silica nanoparticles. Therefore, the purpose of this study is to better understand these contributions and to explore the non-linear domain using new methods of investigations inspired by the work conducted on filled elastomers [Leblanc, 2002].

This manuscript is divided into five chapters. The first one is dedicated to a survey about hydrogels with a specific interest on the role played by adsorption onto solid surface as reinforcement mechanism. The main characteristics of hydrogels as well as the major reinforcements strategies developed are addressed, followed by a review about polymer adsorption onto solid surface. Filled elastomers are also briefly introduced by analogy with hybrid hydrogels.

The second chapter describes the study conducted on adsorption of linear polymer chains of PAAm,

PDMA and P(AAm-co-DMA) onto silica nanoparticles. The synthesis of linear polymer chains of PDMA and PAAm, the characterization of the silica nanoparticles and the several techniques developed to investigate adsorption are described. As result of this study, it was assessed that adsorption can indeed be tuned in a quite versatile way.

The third Chapter deals with the modulation of particle/polymer interactions in hybrid gels and the study of their structure and mechanical properties, with a special focus on the impact of such tuning.

In Chapter four, advanced NMR methods have been used to characterize further the impact of the polymer-silica interactions on the polymer dynamics and gel network structure, in relation to the mechanical behavior.

In Chapter five, the contribution of the dispersion state of silica on the structure and the mechanical response of hybrid gels is addressed. Then, the behavior in the non-linear domain is investigated using Large Amplitude Oscillatory Shear experiments. The time-scale effects are discussed and also the analogy between hydrogels and filled elastomers

Finally, the main contributions of this work will be recalled and summarized in a concluding part, along with the perspectives.

Each chapter has been structured as a self-contained study which could potentially be submitted to publication. This choice implies some degree of redundancy between the different chapters.

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Chapter I

State of the art

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1 General survey on hydrogels and reinforcement mechanisms

1.1 Synthetic polymer hydrogels: definition and applications

1.1.1 Hydrogels as smart and active materials

Gels can be defined as two- or multi- component three-dimensional network, able to be highly swollen with liquid filling the space between the solid content. Usually, they are composed of inorganic colloids or polymer chains connected to each other into a percolating network at sample scale [Flory, 1974]. Gels are complex and responsive matter that behaves like soft solids, yet mainly composed of fluid.

Depending on the solvent nature, polymeric gels are often categorized: the hydrogels (swollen with water), the organogels (containing organic solvents) and the aerogels (without liquid component) [Shibayama, 2008]. More recently a fourth category has emerged, the ion gels, made of ionic liquids [Le Bideau et al., 2011; Ding et al., 2017]. This chapter will mainly address hydrogels, as they are the main focus of this work.

The concept of hydrogels appeared at the end of the XIXth century with colloid gels composed of inorganic compounds [Chirani et al., 2015]. Still, the first record of a synthetic polymer hydrogel described by its typical properties, one of all the high water affinity, was first reported by Wichterle and Lim who designed polyhydroxyethylmethacrylate (PHEMA) gel to serve as biological scaffold in the 60's [Wichterle and Lim, 1960].

Hydrogels are usually composed of a very low content of hydrophilic polymer chains (from 1 wt % to 7 wt%) percolating through the network, able to hold a large amount of water without disowning in the timescale of observation. The solid-like behavior of such materials even in swollen state relies on chemical or physical cross-linking of individual polymer chains, as illustrated in figure I.1.

Chemical gels contain irreversible permanent bonds between polymer chains that permanently fix the network topology and confer to the material an infinite gel life-time. They do not flow and behave as elastic solids. Physically cross-linked gels are constituted of chains interacting with each other through associative, physical interactions: Van der Waals forces [Rubinstein and Dobrynin, 1999], hydrogen bonds [Ilmain et al., 1991], hydrophobic [Guo et al., 2016] and ionic interactions [Karakasyan, 2010]), with a life-time longer than the observation scale. Due to the reconfigurable interactions, physical gels may undergo a reversible transition from liquid state to gel state called *sol gel transition* in response to a change in the environmental conditions such as pH, temperature or ionic concentration, as it was evidenced for gelatin gels [Djabourov et al., 1988].

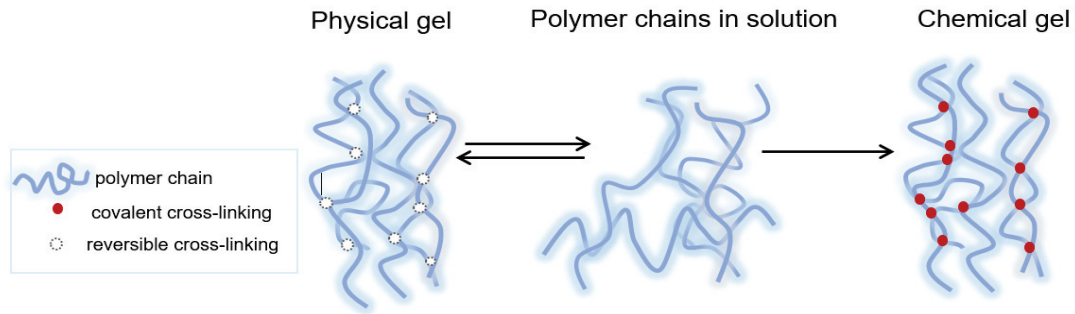


Figure I.1 – *On the left, schematics of physical hydrogel, on the right schematic illustration of chemical hydrogel.*

Hydrogels are able to interact with their environment through their ability to absorb and/or release solvent. Moreover, playing with polymer/water phase transition, gels may respond to external triggers through drastic volume changes. Numerous applications have been developed using this feature: they are commonly used as superabsorbants due to their swelling ability [Buchholz and Graham, 1997], as biomedical scaffolds [Leon-Mancilla et al., 2016] since they offer properties close to those of natural tissues, and as drug delivery systems [Li et al., 2017]. Since water can diffuse through them, they may carry active molecules that are released under proper stimulation [Qiu and Park, 2001].

More recently, owing to hydrogels' soft, wet and biocompatible nature, hydrogel-based actuators and robots have been developed opening the way to transformative applications in areas as diverse as biomedicine [Shepherd, 2011], soft robotics [Dong et al., 2006], energy harvesting and soft electronics and machines [Bauer, 2014]. Gels can also find applications in fuel cells as polymer electrolytes membranes [Page, 2012].

An example of that is the poly(acrylamide) - alginate dually cross-linked system developed by Yuk et al., able of high-speed, high-force actuation with optical and sonic transparency in water [Yuk et al., 2017]. The authors designed bio-inspired hydrogel-based soft hydraulic actuators which were mostly fabricated with silicone elastomers until then, as hydrogels structure could not maintain the robustness and functionality under cyclic hydraulic actuations. The principle relies on the assembly of chemically and physically cross-linked hydrogels, grafted to elastomeric structures (tubing and baseframe) to form serially-connected actuators units, as displayed in figure I.2. Actuation force and/or actuation frequency of such hydrogel actuators can be orders of magnitude higher than the typical performance of osmotic hydrogel actuators responsive to pH, ionic force or temperature.

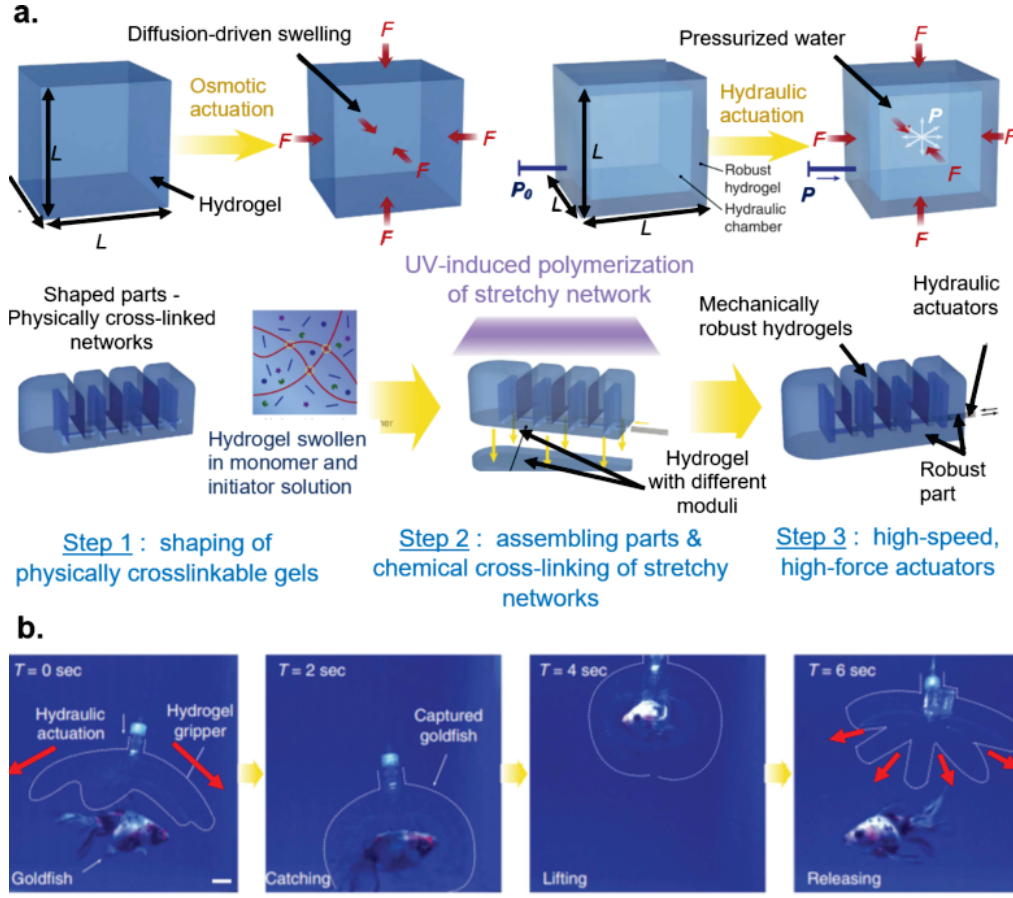


Figure I.2 – **a.** Schematic illustration of osmotic-driven actuation of hydrogels and hydraulic-driven actuation of hydrogels. Below, schematic illustration of the fabrication of complex and robust hydrogel structures for hydraulic hydrogel actuators. **b.** Goldfish capture performed by hydraulic actuators. The hydrogel-based actuator is underlined in white, from [Yuk et al., 2017]

1.1.2 Structure-property relationship

For these materials possessing both solid- and liquid-like properties, industrial perspectives are highly promising. In order to fulfill these expectations, hydrogels need to combine mechanical resistance and toughness besides other properties of interest so as to be easily manufactured at the industrial scale. Their properties are closely related to their bulk structure. Therefore, it is of the uppermost importance to be able to finely tune the network architecture.

To do so, it is necessary to identify the relevant parameters that define the polymer network structure such as the number of monomer units between two cross-linking points N_{CL} [Kahn et al., 2016], the polymer network mesh size ξ_c [Peppas et al., 2000], and the volume fraction of polymer in the swollen state ϕ_{eq} [Singh et al., 2018]. They all relate to the cross-linking density of the polymer matrix that has a marked effect on the obtained properties. For example, highly cross-linked networks display enhanced stiffness along with reduced swelling ability [Canal and Peppas, 1989], indeed, as cross-links reduce the polymer chain mobility, the mesh size will be tighter and the overall network less likely to absorb a large quantity of solvent. The polymer/solvent affinity also deeply impact the mechanical behavior of hydrogels [Obukhov et al., 1994].

In their book *Polymer Physics*, Colby and Rubinstein proposed a classification of gels and hydrogels

based on gelation mechanisms [Colby and Rubinstein, 2003], extended later to the associated preparation methods by Gulrez and *al* as depicted in figure I.3 [Gulrez et al., 1999]. Synthesis method directly impacts network structure hence the mechanical response.

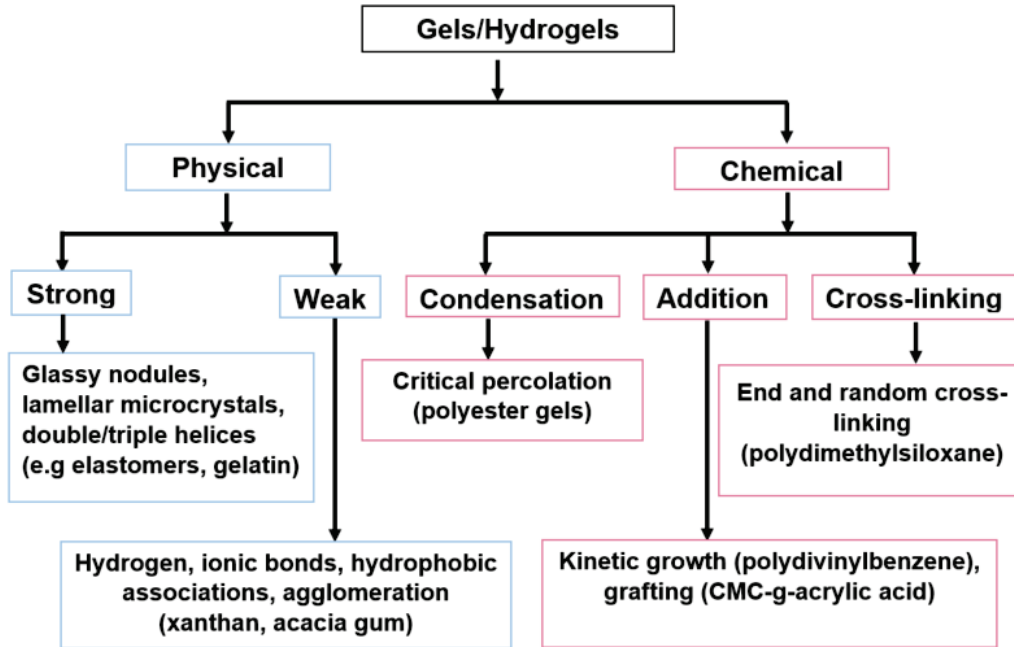


Figure I.3 – *Classifications of gelation mechanisms and relevant examples, adapted from [Gulrez et al., 1999]*

Nowadays, numerous methods exist to chemically cross-link polymer chains, such as radical polymerization, free or controlled, addition and condensation reactions, enzymatically catalyzed polymerization, each of them resulting in a different density and distribution of cross-linkings points in the network [Canal and Peppas, 1989; Dong et al., 1994; Anseth et al., 2016]. The overall network topology as well as the chemical nature of the polymer segments play a major part on the gel response both to mechanical loading and to external environmental parameters. The synthesis path defines important factors for the resulting gels, such as cross-linking density and distribution, concentration of elastically active chains, initial concentration of polymer and solvent content.

1.1.3 Frozen inhomogeneities within the network

Cross-linking allows to permanently fix the network topology and conformation but inevitably brings along inhomogeneities, that is, non-relaxing frozen concentration fluctuations [Ikkai and Shibayama, 2007].

Inhomogeneities in chemicals gels, identified for the first time in 1983 [Hsu et al., 1983] have been extensively studied since they greatly impact the mechanical, optical and other physical properties of hydrogels [Shibayama, 2011], especially in the swollen state as demonstrated by Leibler and Bastide [Bastide and Leibler, 1990].

Nature of inhomogeneities

The defects can be regrouped in three types [Ikkai and Shibayama, 2007] that can be defined as:

- Spatial inhomogeneities corresponding to the uneven distribution of cross-linkers within the network. For chemical gels, these disparities in cross-linking distribution are permanent while for physical gels as the interactions are reversible, they can disappear, following topological rearrangement.
- Topological inhomogeneities, that correspond to the non-elastically active chains of the network (dangling chains, loops).
- Connectivity inhomogeneities, linked to the size and distribution of branched polymer clusters with perhaps a non-elastically active fraction of sol.

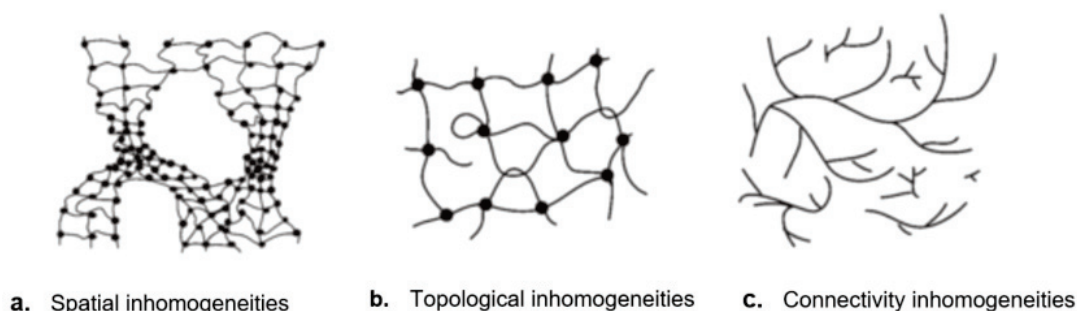


Figure I.4 – *Inhomogeneities in gels* [Ikkai and Shibayama, 2007]

Origins of inhomogeneities

Several factors impacting the density of defects within networks have been identified. For instance, Okay et al. demonstrated that the nature of the initiator system influences greatly the density of inhomogeneities in acrylamides-based gels synthesized via radical polymerization. The density of inhomogeneities can be lowered when ammonium persulfate - N, N', N' -tetramethylenediamine (APS-TEMED) redox couple is replaced by APS-sodium metabisulfite (SPS) redox initiators [Orakdogan and Okay, 2007]. Moreover, several experiments underlined the link between cross-linker concentration and inhomogeneities. Using SANS and DLS experiments, Shibayama demonstrated that when the polymer is in good solvent, increasing the cross-linker concentration leads to an enhancement of the network defects in chemical gels [Shibayama, 1998, 2011], with the existence of a cross-linker threshold concentration [Norisuye, 2002].

The decrease of network inhomogeneities when charged groups are present was evidenced by Okay et al. [Kizilay and Okay, 2003]. They later showed that inhomogeneities in acrylamides-based gels were more pronounced for poly(acrylamide) (PAAm) gels than for poly(N, N -dimethylacrylamide) (PDMA) gels in the same preparation conditions, due to a delayed onset of gelation for PDMA with respect to the critical overlap concentration [Orakdogan et al., 2005]. The impact of monomer concentration on swelling behavior and effective cross-linking density on chemical poly(N -dimethylacrylamide) gels was evidenced by Gundogan et al. They found that for high polymer concentrations, the effective cross-linking density was decreased, probably due to steric hindrance of the vinyl side groups [Gundogan et al., 2003].

Defects are intrinsically present in chemical hydrogels, i.e. permanently cross-linked, their density and type driving the mechanical response. However several models have emerged to depict the mechanical properties of hydrogels, often based on ideal network, without such inherent defects.

1.1.4 Mechanical properties of chemical hydrogels

Mechanical behavior

Regarding the polymer network as a collection of chains that are dynamically flexible, the elasticity is entropy-driven. Several models have been proposed, based on the rubber elasticity comparing the entropy of the network at rest and under stress state, such as the phantom or affine models [Treloar, 1973; Flory and Rehner, 1943b]. Indeed, hydrogels can be compared to cross-linked rubbers networks [Anseth et al., 1996] displaying lower mechanical characteristics regarding those of unfilled rubbers with elastic modulus of the order of 10 kPa (vs 1 MPa for rubbers), strength around 100 kPa (against 2 MPa for rubbers [Bueche, 1957]) and fracture resistance of 10 J/m² [Calvert, 2009] while values around 10 kJ/m² are reported for rubbers [Hoo Fatt et al., 2011].

Role of polymer/solvent interactions

As polymer chains interact with the surrounding solvent, hydrogels possess a maximum swelling degree described by the Flory-Rehner theory [Flory and Rehner, 1943a], that considers several parameters such as the affinity between solvent and polymer, the concentration of the monomer and the cross-linker functionality. The polymer/solvent affinity, combined with the network topology complexifies the mechanical response [Obukhov et al., 1994]. The uptake of solvent accounts for the difference between rubbers and gels, as increasing solvent content favors the negative impact of existing defects that do not contribute to the mechanical behavior of the material. Higher cross-linking density increases hydrogels stiffness (linear tensile modulus $E \simeq \nu_e k_B T$, with ν_e the cross-linking density) as well as the swollen state that brings polymer chains in an extended conformation at the expenses of the gel stretchability.

Fracture properties

Hydrogels are known to be fragile compared to rubbers, their fracture behavior was described by the Lake and Thomas model [Lake and Thomas, 1967] initially developed to calculate the threshold value of fracture energy G_0 , needed to propagate a crack according to the following formula:

$$G_0 = \Sigma_c J_r N_{CL}$$

where Σ_c is the surface density of chains across the fracture plane, N_{CL} is the number of monomer units between cross-links and J_r is the energy required to break a covalent bond. This model is based on the hypothesis that the load sustained by the network brings each bond of polymer strand crossing the interface close to the dissociation energy of the weakest bond of the monomer unit. It does not take into account dissipative properties and remains an elastic prediction.

For elastomers, the fracture energy is described as the combination of two main contributions, the first being an interfacial one and the second one is due to viscoelastic losses linked to internal frictions of monomers in the vicinity of the crack tip [Gent, 1996] :

$$G_c = G_0 [1 + f(a_T \nu_{crack})]$$

where G_0 is linked to the interface chemistry and $[1 + f(a_T \nu_c)]$ is related to the crack propagation velocity ν_{crack} and to the time-temperature superposition and shift factor a_T , and depends on the mechanical dissipation in the volume. Hydrogels are also known to be brittle, without efficient

dissipative process characterized by a loss modulus G'' much lower than the storage modulus G' . Chemical hydrogels have low dissipative properties, G_c values are of the same order than G_0 . Conversely, rubbers G_c values can be higher than G_0 by a two to three orders of magnitude as the viscous contribution is much stronger.

To sum up, on one hand hydrogels are characterized by their ability to contain a large amount of solvent, leading to smart and responsive materials. On the other hand, they lack mechanical strength because of its solution-like nature, i.e., low density of polymer chains and small friction between the polymer chains and the inherent heterogeneity of the network structure.

1.2 Strategies of mechanical reinforcement for chemical hydrogels

Hydrogels have been often disregarded as structural or load-bearing materials, the first applications being rather dedicated to absorption and actuation due to their weak mechanical properties.

For the last decades, extensive efforts have been devoted to improve the mechanical behavior, ending up with gels displaying outstanding improvement of strength, toughness and/or recovery processes. The usually developed strategies consist in either reducing the cross-linking inhomogeneities, since this is one major source of hydrogels weak mechanical behavior, or introducing mechanisms of energy dissipation.

1.2.1 Delaying damage initiation: improvement of chemical gel architecture

The work led on conventional hydrogels evidenced the fact that homogeneous networks lead to stiffer and highly stretchable materials. As the load can be allocated over a larger fraction of elastically active chains, homogeneous networks display higher strength and extensibility than heterogeneous gels with the same cross-linking density.

Tetra arm gels

Following the aim of ideal network, Sakai *et al.* designed homogeneous structures consisting in the combination of two symmetrical tetrahedron-like structure of the same size alternately connected [Sakai *et al.*, 2008]. They are composed of tetra-amine-terminated PEG (TAPEG) and tetra-NHS-terminated PEG (TNPEG) synthesized using controlled anionic polymerization in stoichiometric ratio either in aqueous solution (TAPEG) or in organic solvent (TNPEG). These star-shaped macromonomers possess functional groups able to react with each other at the end of each arm, providing homogeneous hydrogels networks displaying very high compressive strength and deformability, with a maximal compressive strength up to 27 MPa for polymer concentration of 14 wt% using units of 20 kg/mol and maximum stretchability up to 1 100% for units of 40 kg/mol [Matsunaga *et al.*, 2011]. A representative scheme of tetra PEG gel is illustrated in figure I.5.

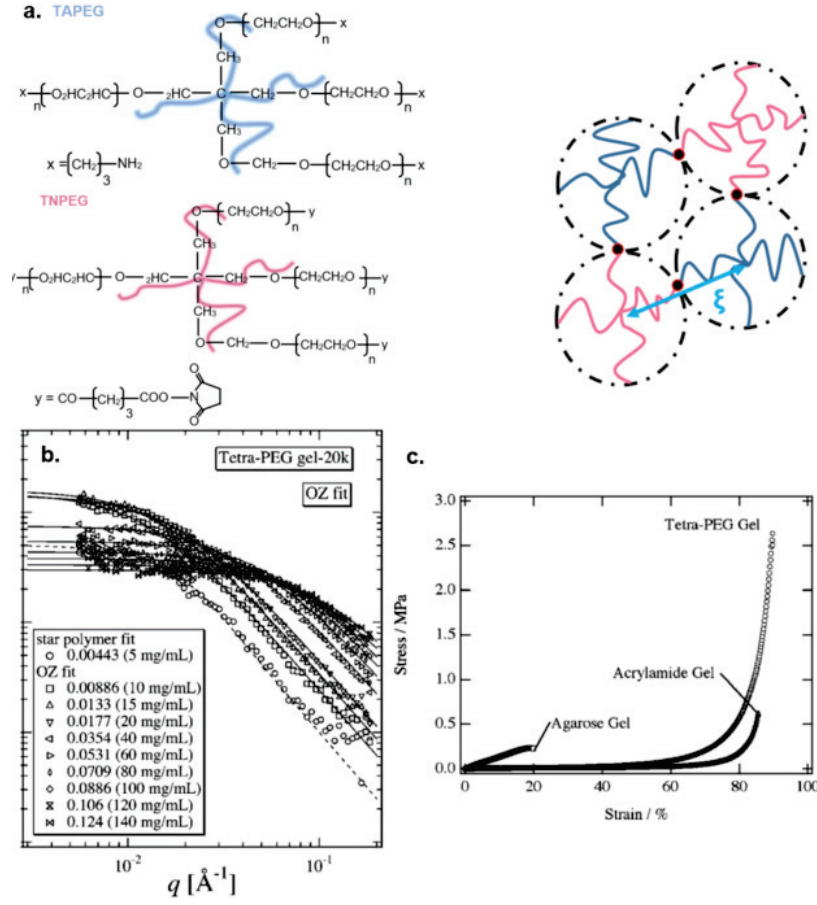


Figure I.5 – **a.** Scheme of tetra-PEG gel composed of TAPEG and TNPEG units with ξ , the mesh size, adapted from [Sakai et al., 2008]. **b.** SANS curves of tetra-PEG of 20 kg/mol of different polymer concentrations. Dashed lines are fitted functions for imperfect gels at low polymer concentrations and solid lines correspond to fit functions using Ornstein-Zernike model [Matsunaga et al., 2009a]. **c.** Compression curves of tetra-PEG 20 kg/mol for polymer concentrations of 14wt%. Curves of pure chemical poly(acrylamide) and alginate are also displayed as a comparison [Sakai et al., 2008].

Scattering studies conducted on those materials confirmed the homogeneity of the networks without any increase of scattered intensity contrary to corresponding conventional gels and low concentration fluctuations [Akagi et al., 2010; Matsunaga et al., 2009b]. The unique sphere-like behavior of star-shaped tetra-PEG units in semi-dilute solution prevents the onset of topological defects at the micro scale, thus providing nearly ideal networks. In spite of the increased strength, these gels remain fragile as they do not display efficient process to dissipate the energy, with fracture energies G_c smaller than 50 J/m^2 for 40 kg/mol units tetra-PEG gels (14 wt% polymer concentration) [Akagi et al., 2013].

Slide-rings gels

Around twenty years ago, Ito et al. developed a novel kind of gel, different from physical or chemical gel, called *topological networks* or *slide-rings* gels [Okomura and Ito, 2001].

The idea was to introduce mobile cross-linking, which was only described theoretically before [Ed-

wards and Vilgis, 1986; Rubinstein and Panyukov, 2002]. These gels are composed of polymer chains with bulky end groups, covalently interlocked with a double cycling molecule able to move freely along the polymer chains. The bulky end groups act as stoppers preventing the dissociation of the sliding cross-links molecules. This unique architecture allows to equalize the tension of the threading polymer chains based on the *pulley* effect. These materials can be obtained from chemical cross-linking of polyrotaxane chains with α -cyclodextrin molecules forming a figure-of-eight junctions between the polymer chains as displayed in figure I.6.

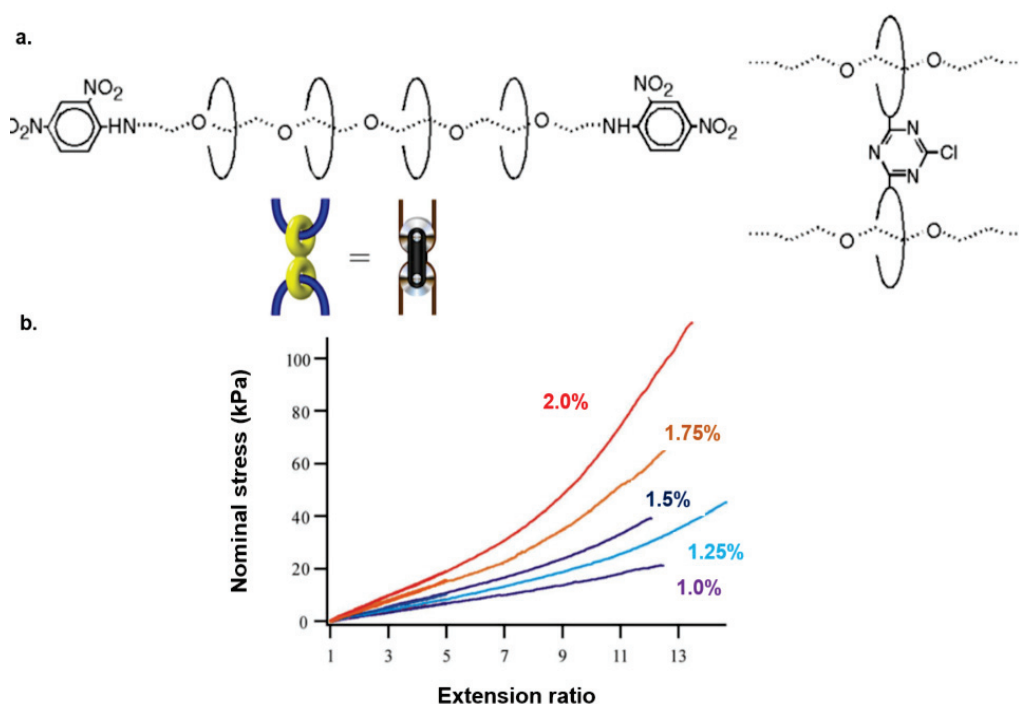


Figure I.6 – **a.** Schematics of polyrotaxane chain with cyclodextrin molecule around it. On the right, "figure-of-eight" junction, made of chemically cross-linked cyclodextrins, from [Okomura and Ito, 2001]. Below, illustration of the pulley effect, from [Ito, 2007]. **b.** Stress-strain curves of gels at 10wt% polymer concentrations with several concentrations of cross-linker (used for chemically modified polyrotaxane chains) [Ito, 2010].

Their genuine structure provide these gels a high swellability, about 500 times their original weight. They are also highly stretchable, reaching strain of 2 000% [Ito, 2010]. These unique properties are due to the homogeneity of the network that was evidenced by neutrons scattering and DLS studies [Karino et al., 2006].

The mechanical behaviour of slide-rings gels differs from conventional polymer networks, leading to the elaboration of a novel theory of entropic elasticity that takes into account the sliding transition from a rubber state to a sliding state, due to the entropic contribution of rings. [Mayumi et al., 2012]. Despite their high extensibilities at break and swelling abilities, slide-rings gels remain soft, exhibiting poor fracture resistance, without any efficient energy dissipation mechanism [Ito, 2007].

1.2.2 Promoting dissipative processes

Topological and tetra-PEG gels are good examples that well-structured synthetic hydrogels can exhibit exceptional mechanical behaviour. Elastic gels are known to be brittle and notch-sensitive [Hui et al., 2003], to enhance their fracture resistance along with other properties, dissipative processes need to be introduced in the network.

Double network gels: reaching mechanical reinforcement through sacrificial bonds

In 2003, Gong et al. [Gong and Osada, 2003] pioneered the domain of tough polymeric gels. They designed materials consisting in two covalently cross-linked interpenetrating networks, synthesized in a two-step process: first by forming a tightly cross-linked polyelectrolyte hydrogel network (PAMPS) using radical polymerization in aqueous medium then by swelling this gel in an aqueous solution of monomers with a low content of cross-linking agent before performing another polymerization as illustrated in figure I.7. The first swollen network is highly stretched, while the second neutral network (PAAm) is loose. The key-point is to find the proper combination between the rigidity and brittleness of the first network and the extensibility and ductility of the loose network. Here, the strategy relies on introducing dissipative mechanism at the molecular level by bond-breaking [Tominaga et al., 2007].

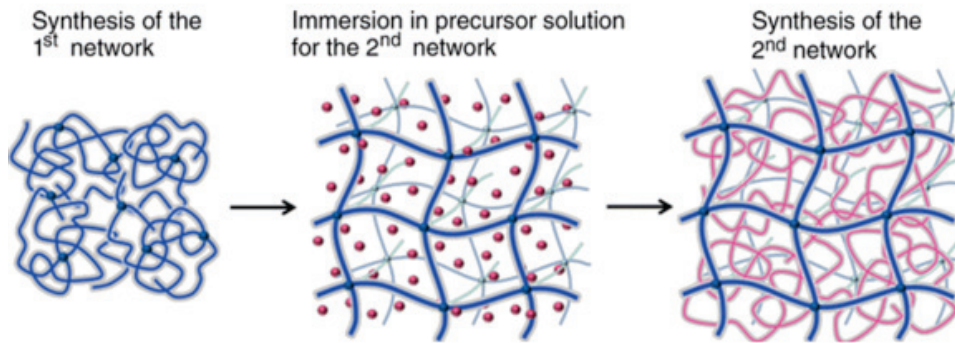


Figure I.7 – Schematic representation of the two step-synthesis of double network hydrogels and their structure, from [Kobayashi and Mullen, 2015].

Double networks can achieve extremely high toughness ($100\text{--}4400\text{ J/m}^2$) [Haque et al., 2012] with fracture energy of the same order as rubbers and load-bearing soft tissues ($5\,000\text{ J/m}^2$) as well as high compressive strength around 17 MPa for a water content of 90% [Gong and Osada, 2003]. The mechanical properties of double networks are way better than that of the individual networks but an optimal cross-linker concentration for the two networks as well as the molar ratio of the second network to the first are crucial parameters for reaching drastic mechanical reinforcement [Tanaka et al., 2005; Nakayama et al., 2004; Webber and Creton, 2007]. Several studies were conducted to elucidate reinforcement mechanisms of double networks [Tanaka, 2007; Nakajima et al., 2009; Brown, 2007].

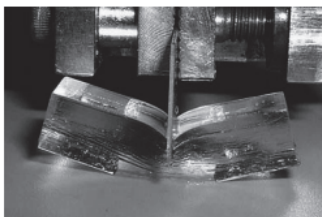


Figure I.8 – Pictures demonstrating the strength of a DN hydrogel that resists slicing with a cutter, from [Gong, 2010].

Since then, other types of double networks have been developed with various structure, including anisotropic double networks [Wu et al., 2010], tetra PEG double networks, raising the issue of the role of the first network homogeneity in reinforcement mechanism [Nakajima et al., 2013], hydrogels including mineralized part [Nonoyama and al, 2016] so as to widen the applications scope of hydrogels as structural materials.

1.3 Beyond the sacrificial bond concept using reversible interactions

Another way to promote dissipative processes is to introduce sacrificial reversible interactions as transient cross-linkers. This strategy allows to overcome the challenges inherent to network homogeneity. Indeed, the reversible associations grant rearrangements to polymer networks contrary to frozen covalently cross-linked polymer chains [Furukawa et al., 2003], thus delaying fracture propagation [Wu et al., 2011]. Furthermore, the breaking and re-formation of the transient bonds dissipate the energy efficiently, which greatly increases the toughness of the network. The reversibility of such bonds leads to recovery processes, providing materials with self-healing abilities. Likewise, secondary physical interactions contribute to the enhanced strength and deformability of these polymer networks. As these weak interactions can be tuned by environmental conditions, it opens the way to the conception of responsive hydrogels.

Usually, versatile reversible interactions involved in hydrogel reinforcement are weak compared to covalent bonding (E_d , the dissociation energy of covalent carbon-carbon bond = 347 kJ/mol [eds, 2005]), comprising hydrogen bonds (E_d = 8-35 kJ/mol), crystallization, ionic bond ($E_d \approx 10^2$ kJ/mol), Van der Waals and hydrophobic interactions (E_d =1-10 kJ/mol [Luo, 2009]) as illustrated in figure I.9.

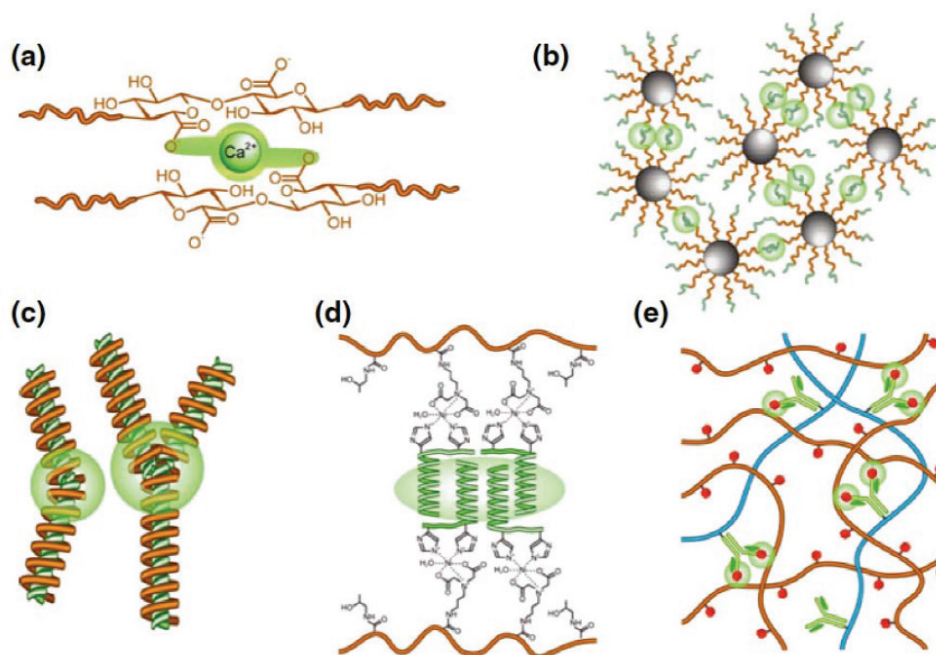


Figure I.9 – Schematic representation of physically cross-linked hydrogels via (a) ionic interactions, (b) hydrophobic interactions, (c) self-assembling, (d) coiled-coil interactions, (e) specific molecular recognition, from Ebara et al. [Ebara et al., 2014].

1.3.1 Ionic hydrogels

Supramolecular associations of polymer chains using weak reversible interactions as cross-linkers points allowed to investigate the potential of hydrogels as strong structural materials, expanding widely their scope of applications by combining their intrinsic properties (swelling, elasticity, environmental response) along with interesting mechanical properties. Playing with the scope and affinity of these interactions, it is possible to design sophisticated architectures. It highlighted the fact that weak interactions can bring strong reinforcement mechanisms such as recovery process, toughness, strength.

Polyampholyte gels composed of randomly polymerized anionic and cationic monomers are purely physical cross-linked compounds, formed of intra- and inter-chains ionic interactions with a wide distribution of strength [Sun et al., 2013]. The "strong ones" provide the network integrity while the weaker ones act as sacrificial bonds, serving several mechanical purposes: toughening and dissipative processes with the presence/rupture of reversible interactions, recovery processes and fatigue resistance by the re-forming of bonds and shock absorbance thanks to the high internal frictions generated. Their structure is illustrated in the figure I.10.

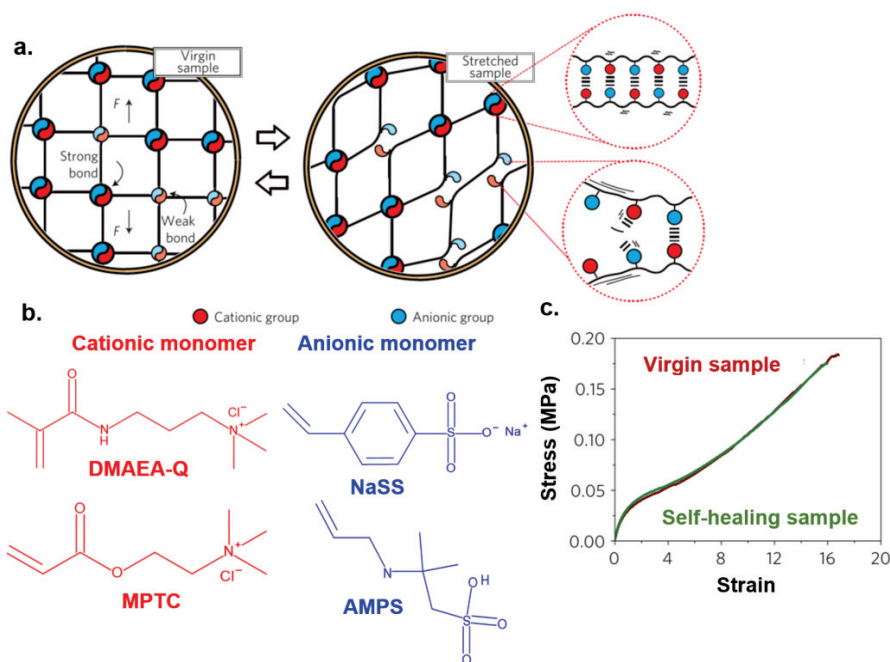


Figure I.10 – **a.** Schematic illustration of polyampholyte networks with ionic bonds of different strengths. Strong bonds act as permanent cross-linkers while weak bonds serve as reversible sacrificial bonds breaking under deformation **b.** Chemical structures of the constitutive monomers: cationic monomer: [3-(Methacryloylamino)propyl]trimethylammonium chloride (MPTC) or dimethylaminoethylacrylatemethylchloride (DMAEA-Q), anionic monomer: sodium styrenesulfonate (NaSS) or 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) **c.** Stress-strain curves of virgin and self-healed samples at 25 °C for 24 hours in water, from Gong et al. [Sun et al., 2013].

They possess a supramolecular structure, and contain 50–70 wt% of water at equilibrium state, which is much lower than that of conventional hydrogels. Synthesized gels display high linear tensile modulus E ranging from 0.01 to 8 MPa, high fracture energy (4 000 J/m²) as well as full recovery of the mechanical behavior after a few hours. As their mechanical properties are closely related to their structure, polyampholytes gels are tunable through the chemistry used. Still, the sample preparation remains challenging. While bulky hydrophobic combination yielded strong and tough gels, the hydrophilic combination such as acrylamido-2-methylpropanesulphonic acid (AMPS) with cationic DMAEA-Q was shown to completely impede the gelation.

Another approach is to design networks based on polyelectrolytes polymers bearing cations to induce the ionic cross-linking. The polyelectrolyte network can be either synthetic like poly(methacrylic acid) or natural (chitosan, alginate). Following this idea, dually cross-linked hydrogels were designed by Suo et al. [Sun et al., 2012]. These hydrogels were composed of covalently cross-linked poly(acrylamide) (PAAm) network together with ionically cross-linked alginate network comprising divalent cations (Ca²⁺) for a water content close to 90%. The chemical PAAm network is intrinsically soft and weak whereas the ionic alginate-Ca²⁺ is rigid but fragile. The resulting double-network displays very high toughness (9 000 J/m²) due to the combination of crack-bridging mechanisms brought by the covalent PAAm network and strong energy dissipation processes by bond breaking of the ionic network. They are also highly stretchable and able to recover their mechanical behavior due to the re-forming of the ionic bonds. Nevertheless, those materials remain soft, with tensile

strength of 160 kPa and the recovery processes are only effective after a long period of rest, around one day at 80 °C.

Those drawbacks were later overcome by Zhou *et al.* who introduced acrylic units into a chemically cross-linked PAAm network, containing 60-70 wt% of water, to form a homogeneous macromolecular structure on which a secondary ionic cross-linking was imposed, using Fe^{3+} cations, as illustrated in figure I.11 [Lin *et al.*, 2015]. The resulting materials possess remarkable properties such as ultrahigh tensile strength (of ≈ 6 MPa), large stretchability (>7 times its original size), ultrahigh toughness (≈ 27 MJ/m³) along with good self-recovery properties within hours at room temperature.

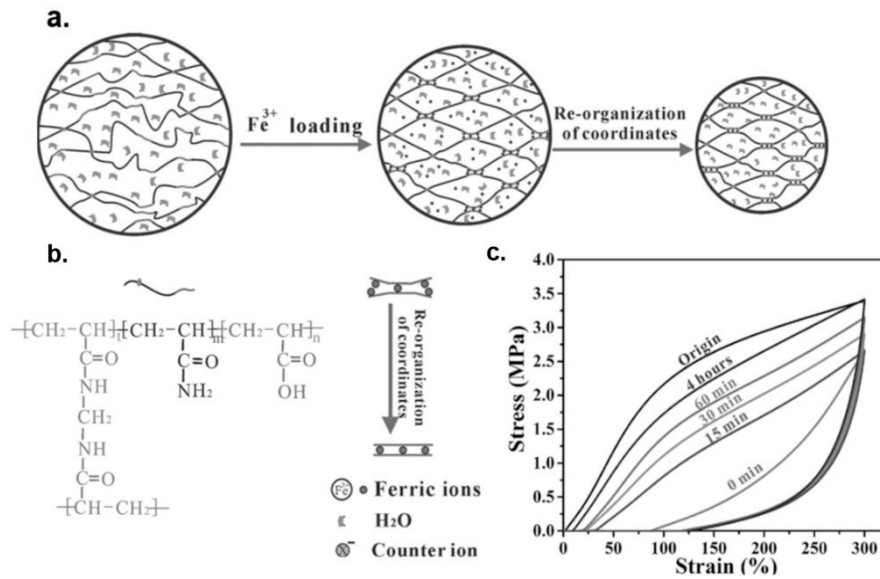


Figure I.11 – **a.** Preparation of dually cross-linked hydrogel: *in situ* polymerization is performed to form a single-component chemically crosslinked network, the Fe^{3+} coordination-physically cross-linked network was formed after Fe^{3+} loading and the reorganization of the coordinates. **b.** Schematics of the poly(AAm-co-acrylic acid) polymer. **c.** Stress-strain curves showing the self-recovery of the as-prepared samples (from Zhou *et al.* [Lin *et al.*, 2015].)

Although enhanced properties can be reached in this way, ionically cross-linked networks are vulnerable to mobile ions present in electrolyte solutions, which limit their application in physiological environment [De Silva *et al.*, 2015].

1.3.2 Hydrophobic associations

Materials using hydrophobic interactions as physical cross-linkers have also been developed. Hydrogels are mainly hydrophilic, so the driving force for hydrophobic associations is the interactions that arise to minimize the contact with water.

These associations were first explored using complex synthesis of triblock copolymers of poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) [Brown *et al.*, 1992] or by performing hydrophobic modifications of poly(acrylic acid) (PAA) [Miquelard-Garnier *et al.*, 2006].

A simpler method was then developed consisting in micellar copolymerization of hydrophobic compounds solubilized in micelles in presence of an hydrophilic monomer. Okay *et al.* used this

method to design polyacrylamides and PAA gels comprising hydrophobic associations in NaCl solutions possessing very interesting properties [Abdurrahmanoglu et al., 2009; Tuncaboğlu et al., 2011]. The authors designed hydrogels formed through hydrophobic interactions between *N*-alkyl units (C18 or C22) forming bilamellar lipidic structures displaying good stiffness with a Young's modulus ranging from 180 to 600 kPa and shape memory with a recovery ratio of 100% , along with good toughness and self-healing properties [Algi and Okay, 2014; Gulyuz and Okay, 2014]. The strong associations between the alkyl groups promote the gel structure even under chemical changes of the environment (pH, salts) while the dynamic junctions between the network allow for the self-healing properties.

Inspired by the lamellar lipidic bilayer of cell membranes that are both strong and multi responsive to their environment, Gong et al. designed anisotropic gels containing stratified lamellar bilayers composed of chemically cross-linked PAAm and dodecylglyceryl itaconate (DGI) as a surfactant. They obtained gels with laminated structure, as illustrated in figure I.12, possessing a very interesting combination of properties.

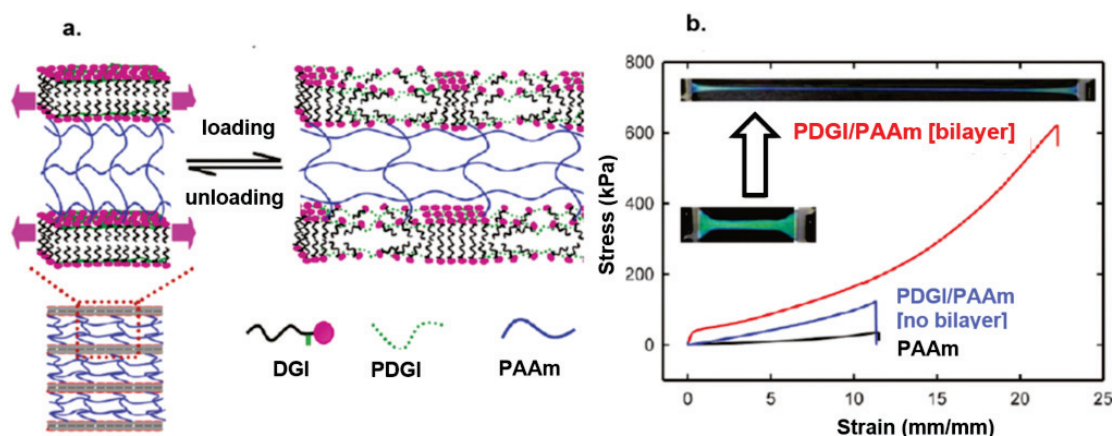


Figure I.12 – *a.* Schematics of PAAm gels with PDGI hydrophobic layer at rest and under stress. *b.* Tensile curves of the parents polymers and of PAAm-PDGI bilayered (from Gong et al. [Haque et al., 2011].)

The lipid-like mobile nature of bilayers and their reversible molecular dissociation serve as a reversible sacrificial bond, providing self-recovery and persistent fatigue resistance. They also provide hysteresis as energy dissipation mechanism, enhancing thus the toughness. Moreover, these gels are able to diffract visible light to provide iridescent materials that were later used to synthesize tough photonic gels [Yue et al., 2014].

Another interesting path for reinforcement using hydrophobic associations was explored by Hourdet and Marcellan using thermoresponsive organic nanocomposites hydrogels composed of poly(*N*-isopropylacrylamide) (PNIPAm) and poly(*N,N*-dimethylacrylamide) (PDMA) [Guo et al., 2016].

1.3.3 Nanocomposite hydrogels

The aforementioned examples clearly illustrated that the mechanical response of hydrogels is drastically improved with the introduction of secondary interactions.

Another strategy revolves around the design of hydrogels including inorganic compounds: nanocomposites gels. Still pursuing the aim to strengthen hydrogels by introducing dissipative processes and

following the strategy used to reinforce natural rubbers, the impact of nano-fillers in the polymer matrix was investigated, first by Haraguchi et al. They designed hybrid hydrogels composed of chemical poly(*N*-isopropylacrylamide) (PNIPAm) matrix and anisotropic exfoliated clay platelets [Haraguchi, 2002] without organic cross-linker using *in situ* polymerization. The clay platelets, said to be fully exfoliated, are uniformly dispersed in the matrix act as multi- functional cross-linkers connecting the PNIPAm chains, as illustrated in figure I.13.

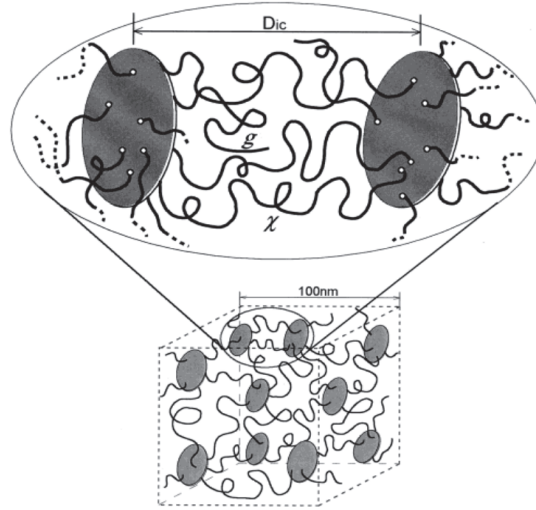


Figure I.13 – *Schematics of PNIPAm/clay platelets nanocomposite structure, from [Haraguchi et al., 2002].*

The novel structure of these gels was vastly investigated using SANS, SAXS and DLS measurements at rest and under uniaxial elongation in order to understand the gelation process and the reinforcement mechanisms [Miyazaki et al., 2007; Shibayama et al., 2005, 2004]. A gelation mechanism was proposed, based on the initiation of the polymerization at the surface of the platelets, followed by polymer chains growth resulting in micro gels clusters, composed of polymer chains surrounding the platelets. The gelation occurs when the percolation threshold between the clusters is reached [Miyazaki et al., 2007].

The scattering measurements evidenced the fact that a polymer layer of 1 nm in thickness is always present at the surface of the platelets, regardless of the clay concentration, as numerous polymer chains can interact with a single platelet and each polymer chains can interact in multiple points. This polymer/clay interactions were ascribed as non-covalent bonds between the amide groups of the polymer and the silanols (-SiOH) groups at the surface of the platelets.

The resulting inorganic/organic compounds displayed extraordinary mechanical properties compared to organic gels for increasing clay content as shown in figure I.14, such as good deformability (up to 1 000% of strain) with near-complete recovery, increased modulus, toughness and a large swelling equilibrium [Haraguchi, 2002].

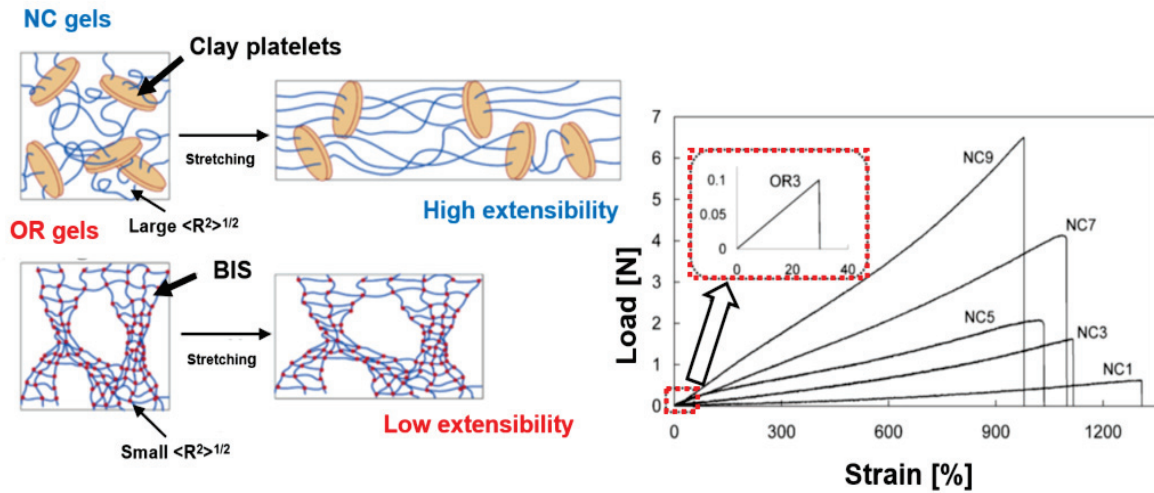


Figure I.14 – Deformation model of nanocomposite (NC) gels and of organic (OR) gels. PNIPAm chains in NC gels are effectively bridging clay platelets, and the molecular weight between cross-links is rather high compared with those of OR gels. Under deformation, the clay platelets align and at high strains, a residual alignment is observed after the release of stress, from [Shibayama et al., 2005]. On the right, stress/strain curves at several platelets content. Chemical PNIPAm gel tensile curve (OR3) is also displayed as a comparison, from [Shibayama et al., 2005].

The mechanical properties were found to be highly dependent of synthesis conditions (concentrations of polymer and clays) [Haraguchi, 2002] and of the complex mechanisms of platelets alignments under elongation [Haraguchi and Li, 2005]. The high deformability is attributed to the fact that the effectively active physical cross-linking is quite low, with typical chain length between cross-links of 5 000 g/mol. It was also evidenced that a high clay content was able to prohibit the PNIPAm phase transition above the Lower Critical Solubility Temperature (LCST), probably due to the steric hindrance of the PNIPAm chains [Haraguchi et al., 2002].

Due to the adsorption/desorption processes of the polymer onto the clay platelets, enhanced fracture resistance and long time relaxation were reported, as well as good self-healing properties [Haraguchi et al., 2011]. The behavior at rest and under elongation was then studied via SAXS experiments to follow the structural change through time [Nishida et al., 2012].

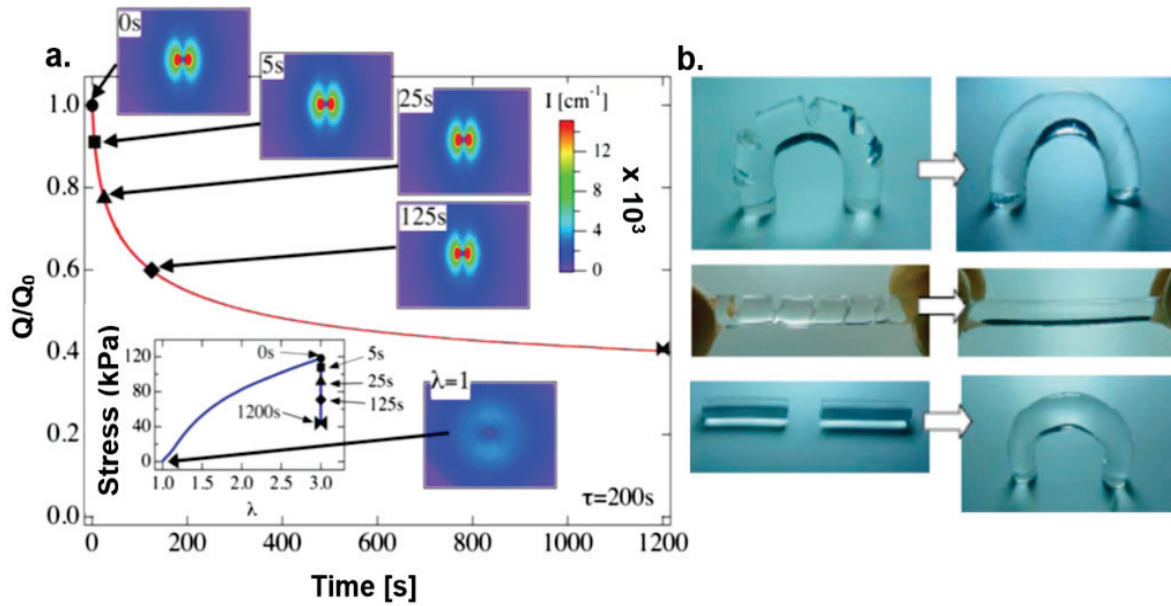


Figure I.15 – **a.** The stress relaxation curve at 0 s, 5 s, 25 s, 125 s., with corresponding 2D-SAXS scattering patterns plotted with normalized intensity as a function of time . Before elongation (0 s), the scattering pattern is isotropic and diffuse. By stretching the gel to $\lambda=3$, a two-lobe butterfly pattern (red and green) and an outer elliptic pattern (blue) were observed. The outer elliptic pattern means that the clay platelets orient parallel to the stretching direction and the two-lobe butterfly pattern shows that the inter-clay distance is different for the parallel and perpendicular directions to the stretching direction, from [Nishida et al., 2012]. **b.** Self-healing of nanocomposite PNIPAm/clay platelets gels after several hours of rest, from [Haraguchi et al., 2011].

Nevertheless, the self-healing of such compound needs heat treatment to be effective, and an instantaneous residual strain was observed, probably due to the platelets residual alignment undergone under the stress observed on the 2D-SAXS measurements, as depicted in the figure I.15.

Hydrogels comprising clay platelets were intensively studied those last years so as to improve even more their mechanical properties. Attempts to combine platelets with hydrophobic (2-methoxyethyl acrylate) (MEA) and hydrophilic (N,N-dimethylacrylamide) (DMA) were performed, generating micro and macro-phase separation during polymerization process whereby creating a new kind of multi-responsive (pH, temperature, solvent) and tough nanocomposites [Nishida et al., 2012]. Furthermore, improvements of the structure were made with the incorporation of clay platelets into a well-defined tetra-PEG structure, giving interesting mechanical properties but only for a sharp concentration range of clay. Indeed, clay platelets can disrupt the homogeneity of the network, hence decreasing the mechanical response [Haraguchi et al., 2010].

The impact of chemical cross-linker on the nanocomposite networks was also a axis of interest to create hybridly cross-linked gels. It led to an improvement of the stiffness but at the expense of the maximum strain at break.

Very recently, Haraguchi et al. succeeded in creating a ternary PNIPAm-silica nanoparticles-clay network, chemically and physically cross-linked with a polymer content of 10wt%. Those gels displayed highly enhanced mechanical behavior with very high tensile moduli (around 4 MPa) and

strength (≈ 2 MPa) along with very well-defined swelling/deswelling behavior which expands greatly the range of tunable mechanical properties of that kind of nanocomposites [Li et al., 2018].

These nanocomposites opened the way to the design of materials using reversible interactions between polymer and inorganic fillers as reinforcement mechanisms. Since then, research have been carried out using polymer adsorption onto solid surface so as to introduce efficient dissipation processes in hydrogel networks besides other promising properties such as adhesion.

Work conducted by Schmidt et al. on chemically and physically cross-linked nanocomposites gels containing anisotropic clay platelets nicely evidenced the crucial role played by physical interactions between the polymer and the filler that impart viscoelasticity to the gel [Loizou et al., 2005]. They suggested, using cryo-SEM analysis that these reversible interactions between Laponite clays and poly(ethyleneoxide) (PEO) and poly(propyleneoxide) (PPO) triblock copolymer diacrylates were responsible for rearrangement of the network structure at high deformations (up to 1200%) [Wu et al., 2011]. Also, the studies conducted on nanocomposites hydrogels made from chemically cross-linked poly(ethyleneoxide) (PEO) and clay platelets provided good insight on the use of polymer adsorption to induce self-healing abilities but also to the possibility of enhancing the bioactivity and the stickiness properties of hydrogels along with the improved mechanical response [Gaharwar and Schmidt, 2011].

1.3.4 Our approach: using polymer adsorption as reinforcement mechanism

The idea of organic/inorganic nanocomposites has been generalized to other type of inorganic fillers, using cellulose nano-crystals [Zhou et al., 2011], enzymatically-produced calcium phosphate [Rauner et al., 2017], graphene carbon or iron oxides [Cha et al., 2014; Jaiswal et al., 2016], and silica nanoparticles. The latter has been widely studied since silica is a well-known, commercially available compound that presents several advantages such as isotropy, chemical stability and well-controlled, easily fonctionnalisable surface chemistry.

At a first glance, the strategy was to develop Haraguchi's approach and with the concepts of double network and sacrificial bonds pioneered by Gong. The idea relies on using polymer adsorption on nanoparticles (NPs) to promote reversible cross-links and to combine such "physical" network with a covalently cross-linked one to control the recovery processes. Based on pioneering studies on semi-dilute solutions [Portehaut et al., 2006], hybrid assemblies have highlighted the adsorption properties of poly(*N*-alkylacrylamides) chains as poly(*N*, *N*-dimethylacrylamide) (PDMA) or poly(*N*-isopropylacrylamide) (PNIPAm) on aqueous suspensions of silica nanoparticles, that were evidenced using depletion method and calorimetric studies [Petit, 2007]. The resulting physical gels remained soft, with a modulus of the order of the kPa. Likewise, Hihara et al. used silica nanoparticles (NPs) as a multifunctional cross-linker to design gels composed of a poly(vinylpyrrolidone) (PVP) backbone grafted with trimethoxysilyl groups. The PVP backbone can interact physically with the silica through hydrogen-bonding while the side groups are able to form covalent bonds with silica surface groups, serving as anchoring groups [Takafuji et al., 2011].

Extending the same concept, it was found that a variety of mechanical properties can be enhanced by the introduction of silica nanoparticles into an interacting polymer matrix like poly(*N*, *N*-dimethylacrylamide) (PDMA) as shown in figure I.16. Tough gels were designed, seeking to drasti-

cally increase both the concentration of silica and polymer, using *in situ* free radical polymerization of DMA monomers and silica nanoparticles. In such hybrid networks, the silica NPs are well-dispersed in the chemically cross-linked polymer matrix, serving as physical cross-linkers through specific adsorption of PDMA chains onto silica surface, forming a transient secondary network [Rose et al., 2013b].

Marcellan et al. explored the abilities offered by the reversible bonding between covalently cross-linked poly(*N,N*-dimethylacrylamide) and silica nanoparticles to induce strong bulk reinforcement on the mechanical behavior at large strain [Carlsson et al., 2010].

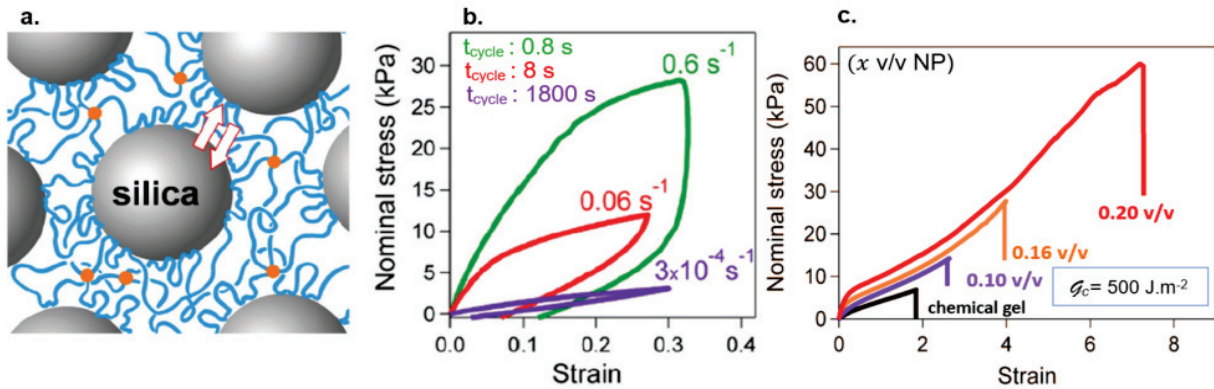


Figure I.16 – **a.** Schematics representation of hybrid hydrogels combining covalent bonds (orange dots) and exchangeable bonds, symbolized by the arrows. Polymer adsorption onto silica NPs serves as reversible cross-linkers. **b.** Strain rate impact on hybrid gels containing 20% volume fraction of silica NPs: loading/unloading cycles for varying strain rate, for a PDMA content of 12 wt% with a molar chemical cross-linker ratio of 0.1 mol% towards the initial DMA content. **c.** Stress-strain curves of PDMA hybrid gels for increasing silica content up to 20 vol%. Chemical gel (without silica) is also displayed, from [Rose et al., 2013a].

The addition of silica nanoparticles led to simultaneous enhancement of the stiffness and the strain at failure, that can be tuned by changing the amount of NPs and/or of the organic cross-linker introduced. As physical interactions are reversible in nature, it was shown that the mechanical response is directly dependant of the dynamics of the adsorption/desorption processes [Rose et al., 2015]. Still due to the reversible bonds between silica and the neutral hydrophilic polymer network, those gels displayed increased fracture resistance with energy dissipation mechanisms brought by the rupture and re-forming of hydrogen bonds as well as efficient self-healing properties and rapid recovery processes within a short range of time (1-10 seconds) [Rose et al., 2013a].

The behavior at rest and under uniaxial deformation was then investigated using scattering experiments and showed that at rest, as the silica particles remain well-dispersed so the dynamics of interactions are indeed prevailing on the mechanical response. Also, they observed the deformation mechanisms, with first an affine deformation at small strain (from 10 to 45%) followed by a non affine deformation at higher strain (from 75 to 200 %) reflecting particles/particles interactions. NPs become closer to each other in the perpendicular direction, producing shear due to transverse compression. NPs show irreversible residual displacement at high tensile strains, due either to par-

ticle aggregation or breaking of polymer chains [Rose et al., 2015].

Despite several attempts using contrast-variation small-angle neutron scattering (CV-SANS), no clear evidence of dense adsorbed gel layer was obtained. Shibayama et al. studied the local structure on a parent system, made of PNIPAm and silica particles of different sizes [Suzuki et al., 2009]. They were able to observe the aggregation mechanism of silica for small-sized nanoparticles (20-30 Å radius) together with the observation of an adsorbed layer of thickness ranging from 4 nm (small-sized particles) to 13 nm (large-sized particles of 100-150 Å radius) as illustrated in figure I.17.

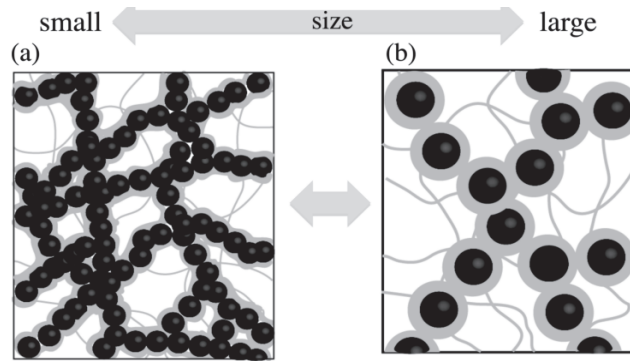


Figure I.17 – Size dependence of the schematic models of PNIPAm/silica hybrid gels. The silica spheres and polymer network are designated by black spheres and gray lines, respectively. The polymer chains that are adsorbed onto the silica surface are indicated by the gray area, from [Suzuki et al., 2009].

The adsorption abilities of polymer onto silica was also used to provide adhesion at gel interface. Indeed, Marcellan and Leibler explored another way to glue hydrogels using only nanoparticles solutions. They demonstrated that two chemical PDMA layers could be efficiently attached together using silica nanoparticles solution as adhesive, without affecting substantially the rigidity or permeability of the assembly [Rose et al., 2014]. The adhesion arises from the nanoparticles ability to adsorb readily onto gel surface through relatively weak interactions, meaning that the free energy gain ϵ_E is comparable to the thermal energy $k_B T$. Adsorption promotes dissipative mechanisms through exchanges processes as demonstrated in nanocomposites hybrid gels illustrated in figure I.18.

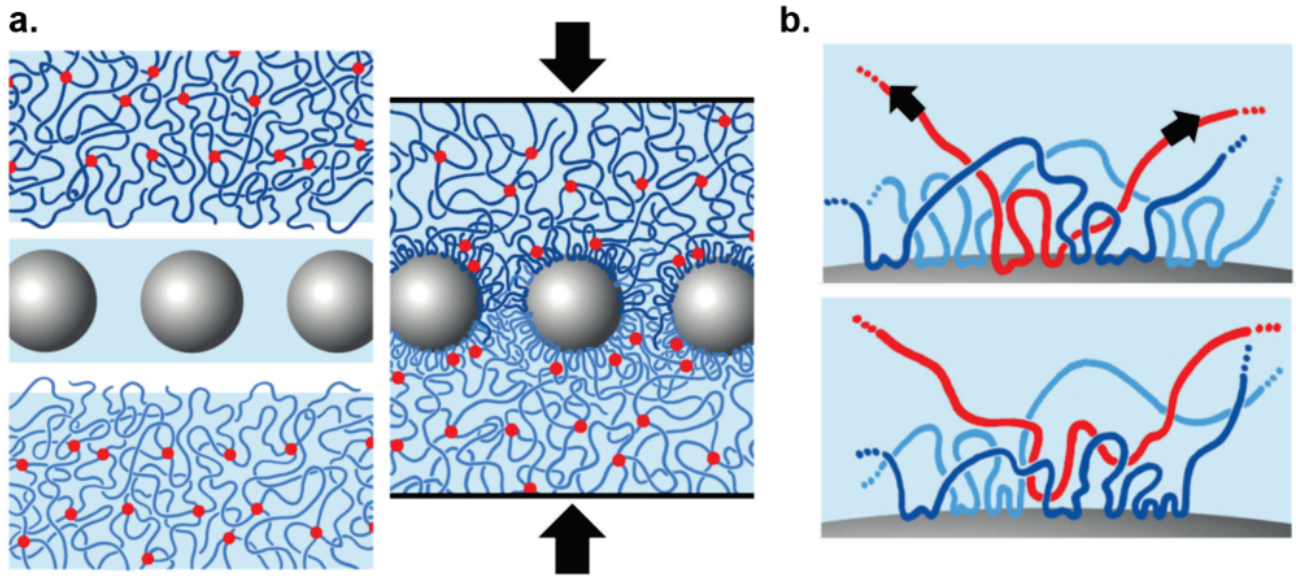


Figure I.18 – **a.** Schematic illustration of the concept of gluing swollen polymer networks together using silica NPs. The nanoparticles diameter is comparable with the gel network mesh size. The adsorbed PDMA segments onto the NPs provide anchoring to the gel layers. **b.** Polymer adsorption is irreversible because the NPs are attached to the gel network by numerous junctions (red, light- and dark-blue strands). At adsorption equilibrium or when submitted to a tension (symbolized by the black arrows), a segment of the polymer chain detaches from the surface and can be replaced by another one, belonging to the same chain or from a different strand. This dynamic process is at the core of the reinforcement of hybrid gels, from [Rose et al., 2014].

Here, the polymer chains act as bridges between the different particles and the NPs as connectors for the two gel pieces. They also evidenced the reinforcement of mechanical behavior at the junction, able to sustain large deformation with failure happening outside the junction zone. The improved resistance of the junction is still due to the adsorbed chains onto the silica surface that are able to detach under strain to release the tension, hence dissipating the energy. Since the dissipated energy is much higher than ϵ_e , the nanoparticles are able to ensure both adhesion and local reinforcement.

The importance of the particles surface chemistry was also underlined with the possible adhesion performed on cellulose nanocrystals, usually inert towards silica surface, grafted with sulphate groups. This work opened the way for efficient and simple adhesion methods with many prospective applications in the field of biomedicine and suture of soft tissues with research further extended to *ex vivo* and *in vivo* soft tissues closure [Meddahi-Pelle et al., 2014].

The reversible segment adsorption is the origin of the significant enhancement of bulk or interface mechanical properties in hybrid hydrogels.

So as to be able to tackle the mechanisms at stake in hybrid gels reinforcement a brief survey about silica nanoparticles is of interest. Then, relevant facts about polymer adsorption will be quickly exposed so as to better understand the interactions taking place between PDMA and silica

nanoparticles (commercial precipitated silica Ludox TM-50) in the materials studied in this report.

2 Generalities about silica solutions

Silica or silicon dioxide SiO_2 is one of the most commonly used oxides. It can be either crystallin or amorphous, synthesized or found as natural supply, with an extensive use in a large number of fields ranging from tire engineering as a reinforcing filler [Mark and Erman, 2005]) or optical industry for its antireflecting properties [Dimitrov et al., 1999], to food industry as an anticaking agent [Villota and Hawkes, 1986].

A main focus will be dedicated to amorphous silica since the nanoparticles used in this study are amorphous ones. Amorphous silica of submicron size displays unique physical and chemical properties and gathers a wide array of silica. Their properties depend mainly on their manufacturing process (pyrogenic vs liquid synthesis) that strongly influences the obtained surface composition.

2.1 Surface chemistry of silica nanoparticles

2.1.1 Silanols groups

Silica is composed of four oxygen atoms surrounding a silicon atom in a tetrahedral arrangement, with an average of two oxygen atoms shared by one silicon to constitute a three-dimensional poly tetrahedral network with an highly disorganized surface structure [Vansant and Vrancken, 1995]. At the surface, the network terminates either with a silicon atom engaged in siloxane bond with oxygen atoms Si-O-Si with the oxygen near the surface, or with silanol bond between silicon and hydroxyl group, Si-OH as illustrated figure I.19.

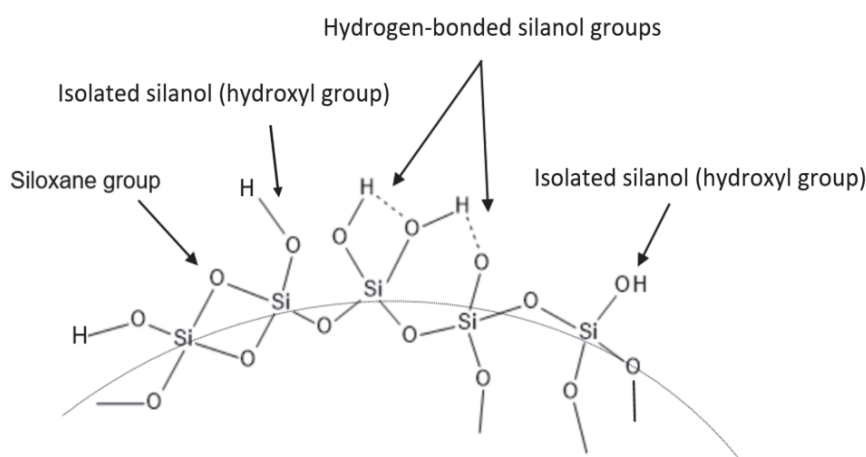


Figure I.19 – *Schematics of silica surface*

Identified in silica structure for the first time by Kiselev and Hoffman in the 30's, silanol groups drive not only the surface charge but also the chemical reactivity of silica. Therefore it is necessary to review the general aspects of silanols, from their structure to their quantification in order to control the grafting or adsorption reactions that might occur at the surface of silica.

Influence of pH on silanol groups

Silanol groups are sensitive to their chemical environment and especially to pH since hydroxyl groups exist under protonated and deprotonated forms. Silanols are more acidic than the corresponding alcohols and possess acid base properties in water with the following equilibrium reactions illustrated in figure I.20:

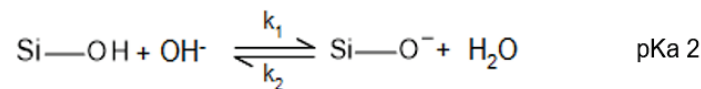
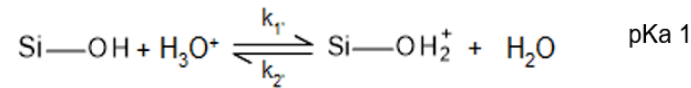


Figure I.20 – Acid base equilibrium of silanol groups in water

Wide disparities are found in the literature concerning the pKa values, ranging from -4.6 to -1 for pKa 1 [Legrand, 1998] and from 5.5 to 9.8 for pKa 2 [Engelhardt et al., 2005; L. and Hertl, 1970; Iler, 1979]. The pH rules the different protonation states of silica surface, as shown on the figure I.21. The iso electric point of silica is at pH 2-3 [Iler, 1979], beyond that value, silanol groups can be fully deprotonated. They are then called siloxide or silanolate. The protonated form, silanolium, only exists at low pH (< 1). The stability domain of dispersed sol of silica corresponds to pH values between 8.5 and 10.5. Beyond that point silica starts to dissolve, increasing the ionic force of the suspension.

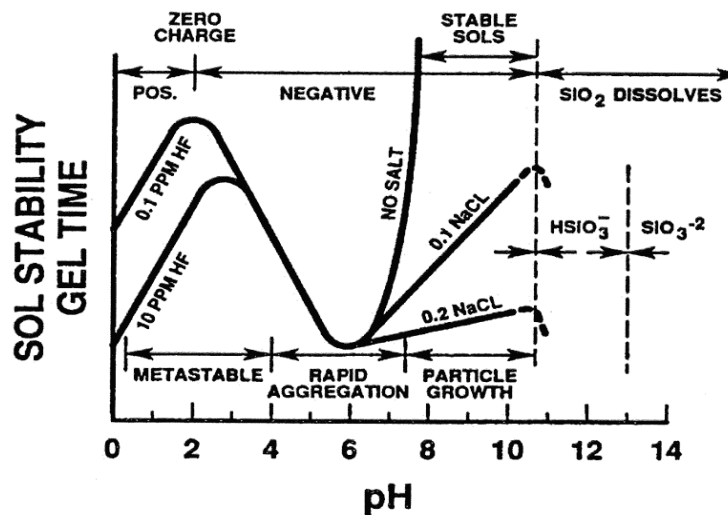


Figure I.21 – Sol stability diagram of silica as a function of pH, from [Iler, 1979]

Dissolution of silica

Silica in water can dissolve under acidic (hydrofluoric acid) or basic conditions (hydroxydes ions,

(OH⁻). In his book *The Chemistry of Silica*, Iler proposed a dissolution mechanism based on the chemisorption of the catalyst at the surface, increasing the coordination number of silicon and weakening the bonds with oxygen atoms as displayed in figure I.22. Silicates are released in the solution and will either stay under ionized form or turn into silicic acid Si(OH)₄ depending on the pH. Several factors influence dissolution of silica, among them pH, and temperature are the more important ones. At higher temperatures solubility increases and the critical pH is switched towards acid values [Iler, 1979].

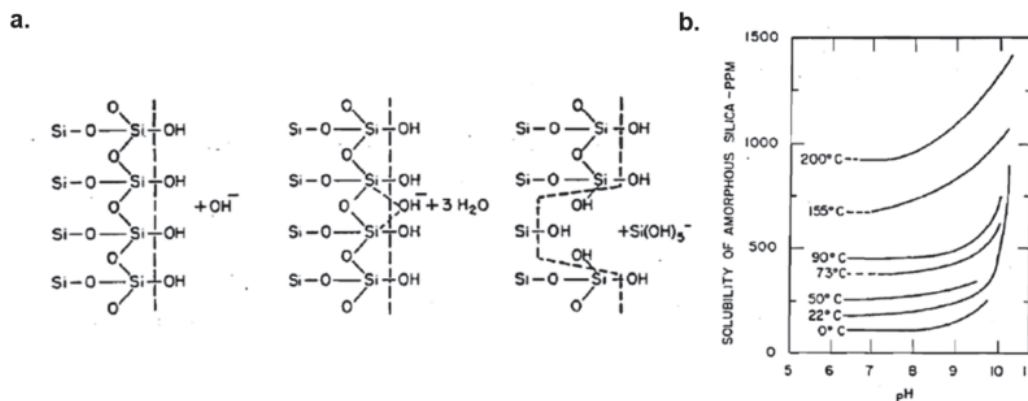


Figure I.22 – *a. Dissolution mechanism of silica in basic conditions. b. Evolution of solubility with temperature as a function of pH, from Iler [Iler, 1979]*

2.1.2 Hydroxylation and dehydroxylation of silica surface

The surface of silica is covered to varying degrees by hydroxyl groups or ions which play an important role in the adsorption processes. Water surrounding the particles can react with the silicon atoms of the surface engaged in siloxane bonds to create silanols groups through a condensation reaction as depicted in figure I.23

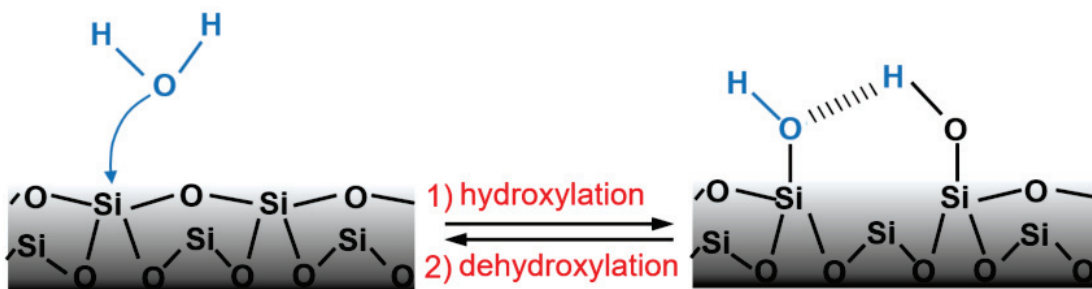


Figure I.23 – *Hydroxylation/dehydroxylation processes at silica surface. Water molecule forms covalent bond with the silicon atom of the surface*

A complete coverage can be achieved, meaning that the surface is fully *hydroxylated*. Likewise the surface can be *dehydroxylated* under high temperature implying that all silanols groups condensated to leave a surface composed only of siloxane groups. Hydroxylation/dehydroxylation is a reversible

process that depends on several parameters, the more important being temperature and humidity.

Hydroxylation must not be confused with *hydration* of the surface which is the uptake of physically adsorbed water at the surface [Vansant and Vrancken, 1995]. The amount of physisorbed water and hydroxylated can be assessed through Thermo Gravimetric Analysis, ATG as illustrated in figure I.24.

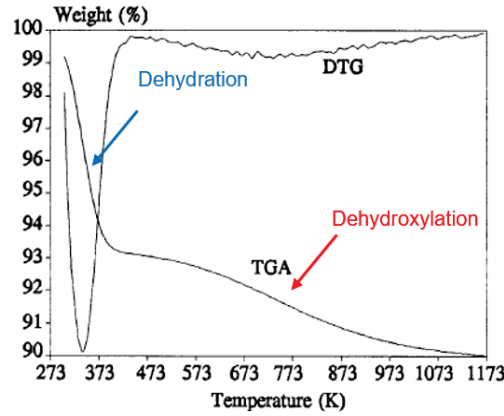


Figure I.24 – TGA thermogram of silica from [Vansant and Vrancken, 1995]

Hydroxylation processes depend on the activation energy required for the chemisorption of water onto the surface. This activation energy is weak when a silanol group is already present but extremely high when the considered surface is completely dehydroxylated as depicted in figure I.25.

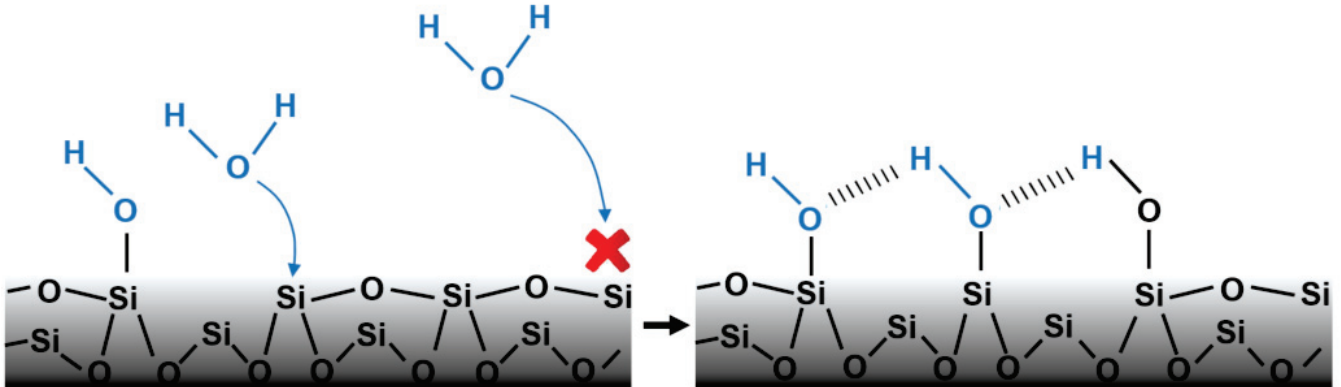


Figure I.25 – Hydroxylation of silica surface favored by the presence of silanol groups.

The hydroxylation degree is strongly linked to the initial silanol groups density which is directly related to the thermal treatments endured by the silica [Vansant and Vrancken, 1995].

Zhuravlev studied the surface density of hundreds of fully hydroxylated amorphous silica leading to the conclusion that the surface density of silanols depends neither on the synthesis way nor on the morphology and that the average value is 4.6 SiOH/nm^2 [Zhuravlev, 1987, 1993]. This value is known as the Kiselev-Zhuravlev constant. In his book, Iler referenced several studies confirming

that the surface concentration of silanol groups was about 5 silanol groups per nm^2 [Iler, 1979] for precipitated silica.

2.2 Stability of colloidal suspensions

Derjaguin, Landau, Vervy and Overbeek (DLVO) developed a theory of colloidal stability which is still the basis of the understanding of interactions between colloidal particles and their aggregation behavior. It is a good approximation for diluted systems where there is no correlations between the particles. The theory describes the interaction potential between two particles as the sum of two additive contributions: Van der Waals forces (E_{VDW} , attractive) and electrostatic forces (Ψ , repulsive). Van der Waals interactions result from interactions of the rotating or fluctuating dipoles in presence. They originate from the asymmetric repartition of the electronic cloud surrounding atoms and molecules. Electrostatic forces are linked to the repartition of ions around a charged particle. When they approach each others, their electronic clouds generate repulsive forces that contribute to the colloidal stability.

As shown in figure I.26, the system reaches a metastable state in the secondary minimum when the potential barrier ΔV is high.

Lowering the Debye length λ_D by increasing the ionic force allows to decrease the potential barrier. At some point, thermal agitation is sufficient to reach the stable state, leading to particles aggregation.

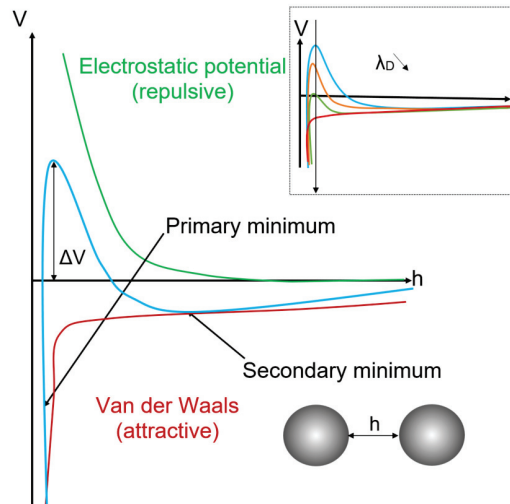
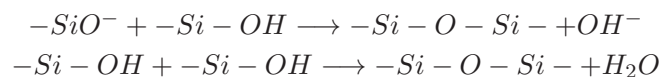


Figure I.26 – Interaction potential V between two particles as a function of their surface to surface distance. The influence of λ_D on the potential barrier ΔV is also shown (see insert).

2.3 Aggregation of silica

As discussed before, the stability of nanosilica in water can be interpreted as a balance between attractive and repulsive interactions or condensation reactions.

As they are submitted to Brownian motion, silica nanoparticles can come in contact with each other and the surface groups can undergo the following reaction:



These condensation reactions are irreversible. The first one happens more frequently at basic pH with an optimum at 9 and the second one occurs less frequently, at acid pH conditions catalyzed with hydrofluoric acid [Iler, 1979]. Flocculation can appear under the influence of several other factors such as pH, ionic force, temperature, presence of polymer chains in solution.

The chemical environment plays a major part in silica stability. As previously detailed, pH drives the surface density of charges and monovalent salts are able to screen these charges. Colloidal stability is promoted for pH values > 7 and weak ionic force, as displayed in figure I.21. Flocculation is most important for pH values ranging from 4 to 7 since surface potential is weak and is no longer efficient enough to prevent condensation reactions. Around the isoelectric point, although electrostatic repulsions nearly vanish and the collision rate is quite high, the suspension appears quite stable. This metastability is believed to be due to the weak condensation process between silanol groups without catalyzer and also to repulsive hydration forces. At low pH catalyzed by hydrofluoric acid, aggregation is fast and irreversible. Adding salts to the suspension, especially polyvalent salts or cationic polyelectrolytes [Hoogeveen et al.], decreases the Debye length which also causes destabilization of the colloidal suspension.

2.4 Ludox TM-50[®]: specificity and uses

Silica colloidal suspensions are complex systems which stability and reactivity are driven by their chemical environment. The silica sol used throughout this study is precipitated silica Ludox TM-50[®], produced by Grace.

2.4.1 Precipitated silica

Production of precipitated silica occurs through supersaturation and polymerization of silicic acid $\text{Si}(\text{OH})_4$ to get either gel networks or discrete particles, like every other liquid state silica synthesis methods, such as the Stober method [Stober and Fink, 1968] or the microemulsion process.

Precipitated silica are synthesized in aqueous medium by neutralization of a preheated sodium silicate solution Na_2SiO_3 under acidic conditions. The first step of the reaction is the nucleation of the germs, followed by the growth step during which the colloidal suspensions or the aggregates of silica are obtained. The size and morphology can be tuned depending on the operating conditions (pH, ionic force, stirring, kinetics of reactants, temperature). To synthesize monodispersed and stable sol, the system is maintained at basic pH to ensure electrostatic repulsion between particles and at weak ionic force to minimize screening of the surface charges by the salts. Particles grow until the desired size is reached, between 5 and 100 nm [Persello, 1999]. Precipitated silicas are characterized by a specific surface ranging from 30-800 m^2/g and a mean diameter around 30 nm [Hyde, 2016]. The resulting colloidal suspension is then concentrated through evaporation to provide 30 to 50wt% sol. Liquid synthesis methods lead to fully hydroxylated silica surfaces contrary to pyrogenic synthesis methods that imply high temperature processes.

2.4.2 Ludox TM-50[®]

Ludox TM-50[®] is a charged (52 wt %, 33 vol%) aqueous dispersion of silica particles in the low nanometer size range (13.5 nm radius verified through SAXS measurements) that typically exhibits

narrow particle size distribution, which stability is ensured by negative charges at the particles surface (pH ranging between 8.5-9.5) at weak ionic force, with Na^+ as counter-ion. The silica nanoparticles surface is thus believed to be fully hydroxylated with mixture of silanols/silanolates groups at its surface.

It is mostly used as inorganic binder (catalyst washcoats), reinforcing and strengthening agent (functional coatings), flocculating agent (beer clarification) and surface modifier (paper manufacture). Its specific behavior upon dilution for several concentrations is investigated in the Chapter 2.

2.5 Polymer/silica interactions

Generally speaking, hybrid inorganic–organic composite materials have attracted increasing attention since the resulting composites can potentially benefit from the combined properties of both as exemplified by the use of silica nanoparticles and/or carbon black in the tire industry.

Polymer chains can have a strong impact on colloidal suspensions, acting either as a stabilizer or as a flocculant depending on the surface coverage, the polymer molecular weight and solvent conditions [Babayan et al.; Lafuma et al., 1991].

2.5.1 Chemical grafting onto silica nanoparticles

Covalent interactions between silica and polymers have been developed to tune the properties of silica such as its hydrophilic behavior for chemical separative processes [Czaun et al., 2008] or to tune silica interactions with polymers when embedded in elastomer or gel matrix. Takafuji et al. designed hydrogels based on polymer chains containing trimethoxysilyl groups able to react both covalently and physically with precipitated silica surface [Takafuji et al., 2011]. Another example is the design of responsive materials containing silica nanoparticles. Coradin et al. developed collagen fibrils linked to modified-Stober silica network in which the polymer organization is strongly depending on the pH [Aime et al., 2012].

2.5.2 Reversible interactions between polymer and silica

Reversible interactions between polymers and silica can also take place as shown in the second part of this chapter with the example of PDMA/silica hybrid gels. Hybrid hydrogels have also been developed with polyacrylamide (AAm) as monomer, leading to no specific mechanical reinforcement, highlighting the key role of polymer/fillers interactions in mechanical reinforcement [Lin et al., 2011; Rose et al., 2013b]. In this case, the silica nanoparticles act as non-interacting fillers and these materials can be compared to filled elastomers [Kalfus et al., 2012].

3 Polymer adsorption at solid/liquid interface

Understanding adsorption mechanisms onto solid surface is of major importance so as to be able to control better the mechanical properties of hybrid hydrogels using adsorption as cross-linking mechanism.

Using the tools and knowledge developed for the understanding of adsorption of polymer chains in solution on solid surface is thus necessary to go deeper in the understanding of hydrogels behavior at solid interface, as highlighted by Joanny et al. [Joanny et al., 2001]. Adsorption of polymers

have been widely studied both experimentally and theoretically and now a good picture of flexible macromolecules at solid interfaces can be drawn from experimental records.

3.1 Physics of polymer chains in solution

It is first necessary to introduce a few concepts developed to explain the behavior and properties of polymer chains in solution and the associated models.

3.1.1 Ideal linear polymer chain in solution

A single polymer chain is constituted of N , number of segments of size a , the Kuhn length, with a contour length $L = Na$. The simplest description of polymer chain is the *Freely-Jointed Chains* model, depicting ideal Gaussian polymer chain where each units is allowed to rotate freely (random walk). In this model, monomer-monomer interactions are neglected. The mean squared end-to-end vector is directly proportional to the number of units as follow:

$$R^2 \approx \langle R^2 \rangle = Na^2 = La$$

It is also useful to introduce the *gyration radius*, R_g which is the rms of the squared average distance of all monomers to the center of mass of the polymer in solution. It is calculated as follow:

$$\langle R_g^2 \rangle = Na^2/6$$

The R_g parameter can be used to describe the size of the statistical chain that varies proportionally to the square root of the molecular weight. It is important to notice that gyration radius R_g is different from the *hydration radius* r_H which represents the radius of the structure polymer chain including the hydration layer around it as illustrated in figure I.27 and accounts for the hydrodynamic interactions in a solution.

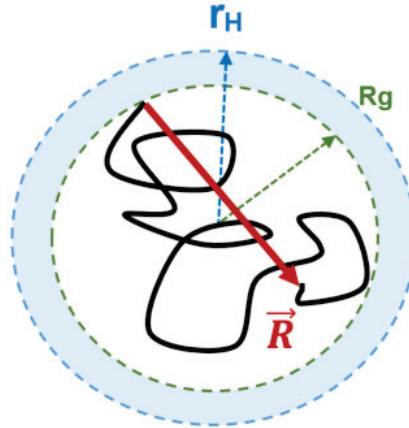


Figure I.27 – *Illustration of a simplified ideal polymer chain with its end-to-end vector $\vec{R}$ represented (in red). Gyration radius, R_g (in green) and hydration radius, r_H (in blue) of a single polymer chain are also represented.*

The shape factor R_g/r_H is sometimes used to characterize on the anisotropy of a molecule, for example a shape factor for a compact sphere (such as a microgel) is around 0.77 and for rod-shaped structures, it increases to values about 4 [Muthukumar, 2016].

3.1.2 Free energy of ideal chain

The entropy of the chain S is the product of Boltzmann constant k_B with the logarithm of the number of accessible conformations of the chain constituted of N monomers of size b depicted by the end-to-end vector $\vec{R}$. For random distribution of the monomers and considering an extension much smaller than the maximum extension length R_{max} , i.e. $|\vec{R}| \ll R_{max}$, the entropy becomes:

$$S(\vec{R}, N) = -\frac{3}{2}k_B \frac{\vec{R}^2}{R_0^2} + S(N, 0)$$

where $S(N, 0)$ depends only on N and not on the end-to-end vector $\vec{R}$. The free energy of the system is defined by $F = U - TS$ with U not related to $\vec{R}$ since interactions between the monomers are neglected. It gives:

$$F(\vec{R}, N) = \frac{3}{2}k_B T \frac{\vec{R}^2}{R_0^2} + F(N, 0)$$

Therefore the force necessary to hold the chain ends can be obtained by partial derivation of the free energy over the end-to-end vector $\vec{R}$:

$$\vec{f} = \frac{3k_B T}{Na^2} \vec{R}$$

where $3k_B T/Na^2$ is the *entropic spring constant* of an ideal chain.

Hence, polymers are characterized by the entropic nature of their elasticity [Colby and Rubinstein, 2003]. The force increases linearly with $\vec{R}$, following the Hooke's law at small strains. Above $|\vec{R}| \ll R_{max}$, the dependence becomes strongly non-linear.

3.1.3 Describing polymer/solvent interactions

To describe the behavior of real polymer chains, it is important to take into account the interactions between monomers as well as the polymer/solvent ones. A real chain conformation depends on the balance between effective repulsion energy between monomers that tends to swell the chain and the loss of entropy due to the deformation.

One of the most simple model describing the conformation of a real chain depending on the solvent condition is the Flory theory that considers a polymer chain swollen to size R , constituted of N monomers of Kuhn length a , uniformly distributed within the volume R^3 without any correlation between them. Under those conditions the end-to-end radius R becomes

$$R = \sqrt{\langle R_N^2 \rangle} \approx aN^\nu$$

Where ν is a scaling parameter, that varies depending on the solvent conditions. Three main types of solvents can be depicted, depending on the specific chemistry that drives the monomer-solvent interactions and on the temperature: good, bad and theta solvents.

Theta solvent can be seen as an intermediate between good and bad solvent conditions which is characterized by a scaling parameter $\nu = 1/2$. This consideration is only valid because in this situation, the effective attraction between monomers in the solvent cancels the steric repulsion. An example of that is the poly(N,N-dimethylacrylamide) which has been depicted in theta condition when solubilized in water.

In *good* solvent, the monomer-solvent interactions are stronger than the monomer-monomer interactions. The scaling parameter is equal to $\nu = 3/5$. The chain adopts a swollen conformation, with

a larger than that of ideal chain in theta condition $aN^{1/2}$.

In *bad* solvent conditions, the effective monomer-monomer interactions are attractive which leads to the collapse of the chain and to the precipitation as depicted in figure I.28. Consequently, the polymer can be seen as a three-dimensional embedded object in solvent with $N \sim R^3$ so $\nu = 1/3$.

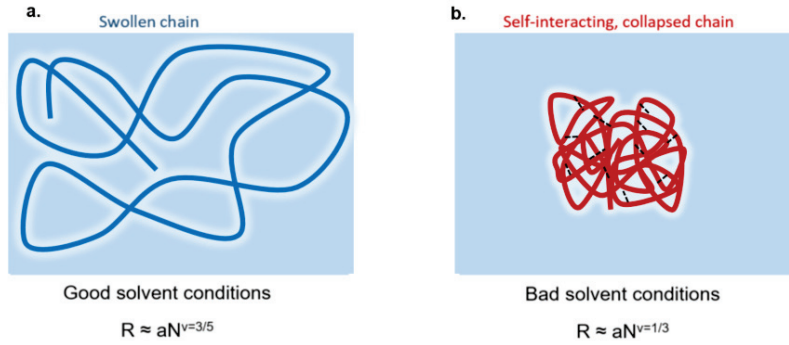


Figure I.28 – **a.** Schematic illustration of a polymer chain in good solvent, swollen and interacting mainly with its solvent. **b.** Bad solvent conditions, self-interacting polymer chains through weak bonds (dashed black lines), in collapsed state.

3.2 Adsorption of polymer chains

The comprehension of adsorbed polymer layer is of fundamental importance for many applications because the presence of polymer chains can affect many bulk properties of colloidal systems.

Extensive works have been conducted to depict theoretically and experimentally the physics of polymer adsorption, notably by P. G. de Gennes, Pefferkorn and Cohen-Stuart [De Gennes, 1987; Cohen-Stuart et al., 1986]. It is influenced by several parameters as solvent condition, temperature, molecular weight, adsorbing surface, polymer composition and architecture.

3.2.1 Conformation of adsorbed polymer chains

Contrary to the adsorption of single molecules, the adsorption of polymer chains is largely driven by the reduction of the number of conformations of chains adsorbed at the surface of the substrate [Simha et al., 1953]. Macromolecules can adopt several conformation at the solid surface, adsorbed segments are found in a broad distribution of segments either in flat conformation onto the surface, called *trains*, or broken up into short sequences with *loops* (two points of contact) or *tails* (one point of contact and free end of the chain) of segments out of it [Scheutjens et al., 1986; Fleer et al., 1988; Johner and Rubinstein, 1993] as illustrated in figure I.29.

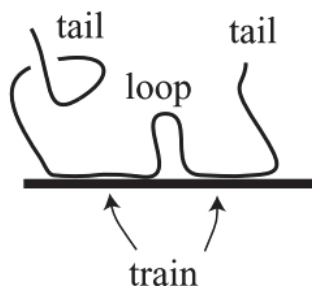


Figure I.29 – Schematics of adsorbed polymer chain conformation at a solid surface, from [Netz and Andelman, 2003].

Simplified view for adsorbed polymer conformation

The interaction potential between an adsorbing compound and a flat surface can be seen as an attractive well of depth V_0 and width A , in $k_B T$ units. The distance A , corresponds to the range of attraction. Then the potential tends exponentially towards the potential of the bulk solution.

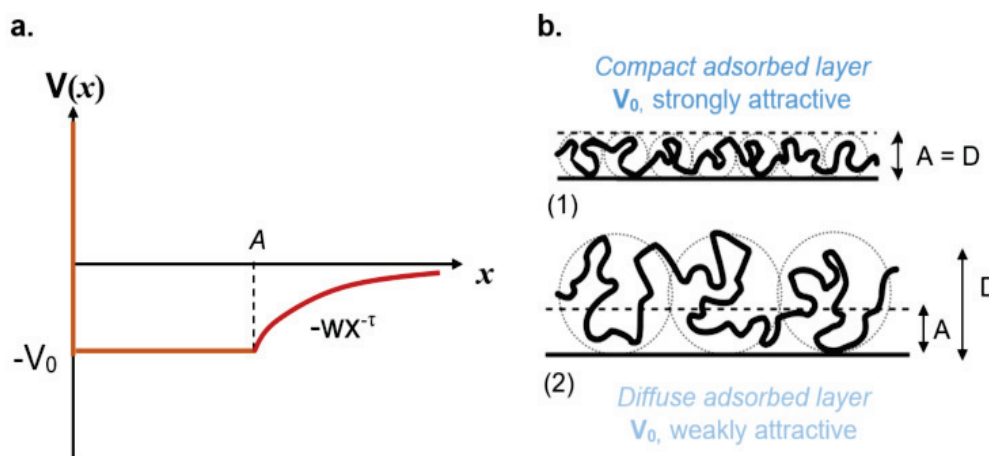


Figure I.30 – **a.** Surface potential felt by a monomer as a function of the distance x from an adsorbing flat surface. Firstly, the surface is impenetrable, $V = \infty$. The attractive potential is V_0 of range distance A .

Then the attraction decreases with the distance according to $-wx^{-\tau}$. **b.** Possible conformation of an adsorbed polymer chain, (1), for V_0 strongly attractive, (2) for V_0 weakly attractive, adapted from [Netz and Andelman, 2003].

When the attractive potential A is high compared to $k_B T$, the chain is completely adsorbed and the thickness of the adsorbed layer, D , is within the width A of the attractive well. If the potential is weaker, D is more diffuse and larger than the potential range, as depicted in figure I.30. As seen for the case of ideal linear polymer chain, very long and flexible chains have different spatial rearrangement at small and large length scale. The adsorbed polymer chain can be divided into decorrelated blobs linked to each other of size ξ , that corresponds to the adsorbed layer thickness D in figure I.31 (in dotted circles) [De Gennes, 1987]. For scale lengths inferior to D , the polymer conformation appears unperturbed while for larger scales the overall chain conformation changes.

The adsorption behavior of a polymer chain results from the competition between the attractive potential V_0 that tends to bind the monomers to the surface and entropic repulsion that tends to repel a large fraction of monomers away from the surface to maximize the entropy. Hence, in the adsorbed state, each blob leads to an entropy loss of the order of one $k_B T$ so that the total entropy loss F_{rep} of the chain, using a scaling relation $D = an^\nu$ [De Gennes, 1979] with n , the number of monomer units within a blob, a the Kuhn length, ν the scaling parameter, is:

$$F_{rep} = N \left(\frac{a}{D} \right)^{1/\nu}$$

The attractive term is calculated using *mean-field theory* arguments (which, very roughly described, implies that each monomer is placed in a field generated by the external potential plus the average interactions with all the other monomers). Assuming that the polymer chain is confined within an average thickness D , the full free energy F_{ads} can be expressed as the sum of the repulsive entropic term and the average potential:

$$F_{ads} = N \left(\frac{a}{D} \right)^{1/\nu} + NV$$

with the potential value V depending on the distance from the interface as depicted in figure I.30.

Self-similar structure

Neutral linear polymer chain in good solvents at an interface adsorb with a self-similar structure as developed by De Gennes [De Gennes, 1987]. Polymer at a distance x of an interface is assimilated to a semi-dilute solution of correlation length $\xi[\phi(x)]$ assumed to be equal to x , with $\phi(x)$ the volume fraction. This model allows to estimate the polymer concentration profile according to $\phi(x) = (a/x)^{4/3}$, for $a < x < R$, with a , the Kuhn length, and $R = aN^{3/5}$ the Flory radius in good solvent. This theory was later confirmed by Auvray and Cotton [Auvray and Cotton, 1987] using contrast variation scattering experiments conducted at adsorption equilibrium on poly (dimethylsiloxane) (PDMS) of large molecular weight in presence of silica nanoparticles. They have shown that the neutral polymer near the semi-dilute regime adsorbs onto surface with self-similar structure through weak interaction between surface groups of the silica and siloxane groups of PDMS (hydrogen bonding and Van der Waals interactions) [Auroy and Auvray, 1996].

De Gennes translated the simple qualitative description of polymer adsorption into clear quantitative predictions of the density profile of adsorbed polymer chains. Three regions of the density profile can be distinguished: the proximal region close to the surface has the highest concentration of polymer chains (trains) and is affected most directly by the exact nature of the polymer-surface interactions. Secondly, the central region, made up of loops and tails with a density that decreases following a power law, and the distal region, dominated by tails, with an exponentially decreasing density [De Gennes, 1981, 1979].

It is relevant to dissociate here the case of polyelectrolytes polymers that of neutral polymers. Polyelectrolytes behavior is governed by electrostatic interactions while for neutral polymers, diffusion is the main force driving adsorption [Chaplain et al., 1995]. The case of polyelectrolytes will not be discussed further in this section.

3.2.2 Adsorption: a low-energy but irreversible process

Adsorption occurs when the energy gain ϵ_e of the adsorbed monomers overcomes thermal energy $k_B T$, meaning that the interaction between the polymer and the surface is more favorable than that of the solvent with the surface. However the energy gain is counter-balanced by the loss of entropy due to confinement of the chains at the solid surface.

Considering the interaction energy between segment units and adsorption sites, adsorption energy is weak, around $k_B T$ but the contribution of numerous chain segments can lower the enthalpy sufficiently to balance the loss of entropy, making adsorption irreversible. Indeed, for sufficiently long polymer chains, the adsorbed layer cannot be removed by solvent washing, as shown by Granick *et al.* [Frantz and Granick, 1994]. To displace an adsorbed polymer, it is necessary to introduce a competitor, by bringing in a polymer with greater affinity for the surface for instance [Kronberg *et al.*, 1986; Char *et al.*, 1988]. Another way is to disrupt the polymer-surface interactions either by introducing a better solvent [Chaplain *et al.*, 1995] or with a change of the chemical environment.

3.2.3 The impact of chain concentration on polymer adsorption

As this study involves the use of polymer at several concentrations, from very dilute to concentrated (in gels) the impact of chain concentrations on adsorption is of interest.

The concentration of polymer chains can be considered as *dilute*, *semi-dilute* or *concentrated* as shown in figure I.31.

The *dilute regime* is defined when the monomer concentration C_m is inferior to C_m^* , which is the concentration where the chains start to overlap. This concentration tends to decrease for increasing polymerization index. For very dilute bulk solutions, it was shown that the surface coverage of the adsorbate was proportional to the bulk concentration. When the concentration increases and starts to approach C_m^* , the surface coverage increase only logarithmically with bulk volume concentration [Bouchaud and Daoud, 1987].

The semi-dilute regime corresponds to a wide range of concentrations comprised between the overlap concentration C_m^* and C_m^{**} , the monomer concentration reached inside a Gaussian blob, under good solvent conditions. This regime is thus important for typical application. It was shown that the surface coverage remained constant with an extension of the adsorbed concentration profile for increasing concentrations. For concentrated polymer solutions, the blobs do not adsorb onto the surface and the regime is closer to the one of melts [Bouchaud and Daoud, 1987].

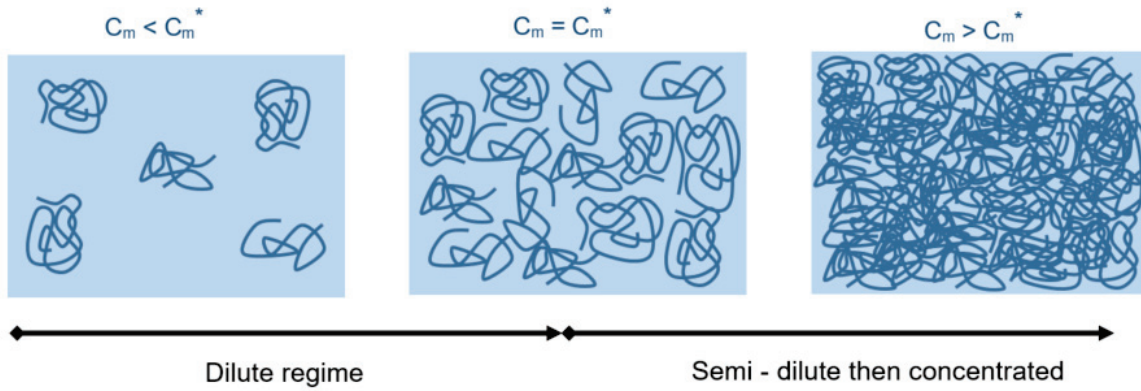


Figure I.31 – Schematics of polymer chains for $C_m < C_m^*$ (dilute), $C_m = C_m^*$ (semi-dilute) and $C_m > C_m^*$ (concentrated)

3.3 Assessment of polymer adsorption

Relevant parameters to discuss polymer adsorption are the adsorbed amount of polymer, expressed as Γ in mg/m^2 , the surface coverage Θ and the thickness layer D (in m).

For neutral homopolymers in good solvent conditions, the maximum adsorbed amount Γ is of the order of mg of polymer per m^2 of surface.

Several techniques have been developed to assess the adsorbed amount of linear polymer chains on a solid surface that can be depicted by adsorption isotherms, illustrating the mass or number of adsorbed monomer/surface area. An example of that are the depletion methods that consist in putting the polymer in contact with the adsorbate before removing either the adsorbed polymer or the free polymer chains allowing then to calculate the remaining quantity, coupled with spectroscopy method such as phosphomolibdic acid coupled with UV spectroscopy [Chaplain et al., 1995; Wisniewska, 2012] or FT-IR spectroscopy [Frantz and Granick, 1994; Liu and Xiao, 2008], TOC measurements [Hourdet and Petit, 2010; Mathur and Moudgil, 1997], precipitation and turbidimetry [Malmsten et al., 1992], drying and thermogravimetric analysis [Liu and Xiao, 2008]. Hydrodynamic measurements [Rose et al., 2013b] and ellipsometry [Charmet and De Gennes, 1983] can be used to investigate the thickness layer as well as scattering experiments or evanescent waves [Tassin et al., 1989].

Other techniques can be used to assess polymer adsorption on a surface such as zeta potential measurements that allows to follow adsorption through a change in the shear plane of a charged particle Liu and Xiao [2008], or NMR measurements that are of use to evidence the presence of an immobilized adsorbed polymer fraction both qualitatively through its dynamics [Papon et al., 2011] and quantitatively using solvent relaxation [Nelson et al., 2002].

3.4 Relevant parameters for polymer adsorption

3.4.1 Impact of molecular weight on adsorption

As seen previously, the conformation of a polymer at an interface is determined by a balance of entropic and enthalpic factors. For sufficiently long enough polymer chains, the loss of conformational freedom will dominate the total entropy loss so that for adsorption to take place, there must be a

net enthalpy gain.

The adsorbed amount was found to increase along with molecular weight until it reaches a limit where no dependency can be observed, as it has been shown for adsorbing poly(ethylene oxide) (PEO) at silica surface, in water [Liu and Xiao, 2008; Mathur and Moudgil, 1997]. The decrease of the adsorbed amount for very high molecular weights was also anticipated theoretically by Joanny *et al.* who considered the equilibrium adsorption of linear polymers using a mean field approach (extended to good solvent conditions through scaling analysis as developed by P. G. de Gennes [Semenov *et al.*, 1996]). Hence, increasing M_w lead to rearrangement from train to loops and tails, increasing the thickness layer until it reaches a threshold where the adsorbed amount starts to decrease due to the tails contributions.

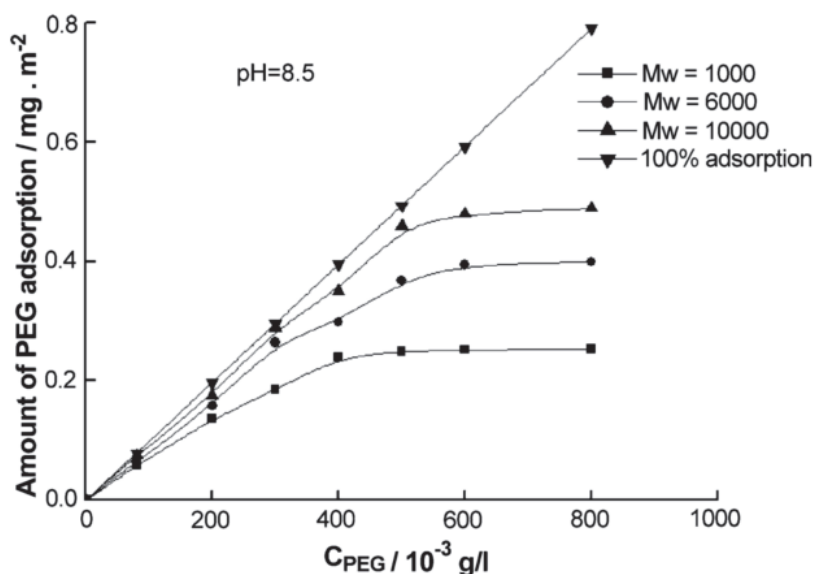


Figure I.32 – Adsorption isotherms of PEO with different M_w (expressed in g/mol) on zinc oxide nanoparticles. The adsorbed amount increases along with M_w , due to the greater participation of loop and tail segments at the interface from [Liufu *et al.*, 2004].

Liufu *et al.* assessed polymer adsorption of PEO onto zinc oxide nanoparticles using thermogravimetric analysis evidencing the impact of M_w . The isotherm shown in figure I.32 demonstrate the marked influence of the PEG molecular weight on the extent of adsorption. They also evidence the increase of the thickness of the adsorbed layer for both increasing M_w and polymer concentration, underlying the change of conformation from trains to more loops and tails that play the main role for the thickness of adsorbed layer [Liufu *et al.*, 2004].

3.4.2 Role of chemical environment

Ionic strength

The thickness of the adsorbed layer of non-ionic polymer was also shown to be strongly dependent of the ionic force of the medium as first theoretically evidenced by Cohen-Stuart *et al.* who developed a model for neutral polymer at a charged surface [Cohen Stuart *et al.*, 1984] then later investigated on poly(ethyleneoxide)/silica nanoparticles systems by Cosgrove *et al.* [Flood and Cos-

grove, 2006] using Photon Correlation Spectroscopy, ^1H NMR and adsorption isotherms.

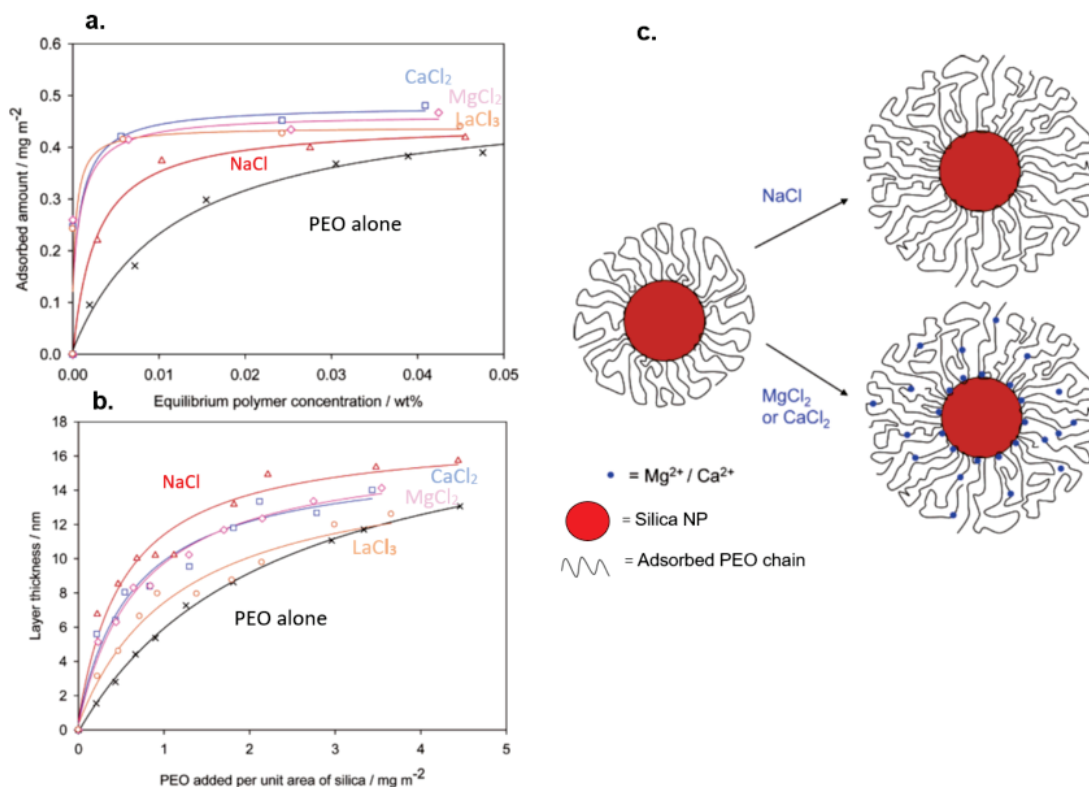


Figure I.33 – **a.** Adsorption isotherms of PEO onto silica without and in presence of metal ions. Surprisingly, the total amount adsorbed remains almost the same, perhaps slightly increased by the presence of salts. **b.** Evolution of the thickness layer in presence of the same ions. **c.** Schematics of the evolution of the adsorbed layer without, and in presence of mono- and divalent salts, from [Flood and Cosgrove, 2006].

The impact of salts on the polymer conformation was observed through several aspects, the first being that it increases the affinity of the polymer for the surface, probably due to a decrease of solvent affinity and to a change of the surface chemistry of the particles consequently to an increase of the concentration of the divalent counterions close to the surface as illustrated in figure I.33. Consequently, the layer thickness was found to increase with the valency and concentration of salts. NMR solvent relaxation times measurements allows identifying train density at the surface of particles. For PEO/silica systems, it showed that the conformation was greatly impacted by the polyvalent ions, with an increase of the train density (weaker in the presence of NaCl).

pH effect on adsorption

Similarly to ionic strength, pH is known to impact adsorption. Studies conducted on the PEO/silica system in water have demonstrated that adsorption was disfavored for high pH values with a critical desorption pH around 10.4 -10.8 [Van der beek and Cohen-Stuart, 1991; Van der Boomgaard et al., 1987]. The phenomenon can be explained by the increase of negative charges at silica surface, impairing the hydrogen bonding between the ether group of PEO and the surface groups of

silica. Studies conducted by Griot and Kitchener on the interactions between poly(acrylamide) and silica in water also evidenced the critical importance of the surface chemistry of silica for polymer interactions [Griot and Kitchener, 1965a,b]

3.5 Probing the dynamics of polymer adsorption

Adsorption is a multi-segmental, dynamic process for an energy gain of the order of $k_B T$. It proceeds through exchanges of polymer chains detaching and re-attaching at the considered surface, implying continuous rearrangements until the adsorption equilibrium is reached.

Thus, the adsorption process can be described according to the following scheme depicted in figure I.34: diffusion of the incoming chains from the bulk solution (for neutral polymers) to the interface, which is rapid at the experiment time scale, then bounding at the surface, and conformational equilibration that involves longer time scales. At the latter stage, polymer chains may be expected to be bound more tightly to the surface with more potential adsorption sites [De Gennes, 1990].

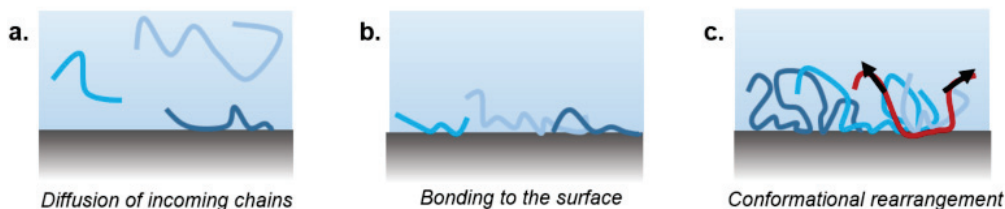


Figure I.34 – **a.** Schematics illustration of polymer chains approaching the surface (diffusion). **b.** Adsorption of polymer in flat conformation. **c.** Rearrangement of polymer chains driven by multi-segmental exchanges until equilibrium is reached

Varoqui et al. genuinely investigated the dynamics of adsorbed polymer using radioactive labelled-polymers. They notably evidenced the fact that the adsorbed polymers exchange poorly with the solute molecules, reaching thermodynamic equilibrium very slowly, according to second-order kinetics [Peffekorn et al., 1985]. This phenomenon is certainly due to the fact that adsorption of polymer chain is multi-segmental, meaning that one chain attaches in multiple junction points and thus relaxes very slowly.

This was confirmed by the adsorption kinetics studies conducted by Fritsch et al. [Frisch et al., 1959] and later by Granick et al., who used polymer exchange between deuterated-poly(styrene) (PS) and protonated-PS as a probe for polymer dynamics. They also proposed a model for the time dependence of the distribution of conformation for unrestricted chain mobility. They used a single time constant, τ_{off} to describe polymer displacement and found the following exponential variation of the rearrangement time with molecular weight that was compared with experimental results: $\tau_{off} \sim \exp(\Delta F/k_B T) \sim \exp(\alpha M_n/M_0)$, where ΔF is the free energy variation, α is a scaling parameter that considers the polymer-surface interaction. [Frantz and Granick, 1994].

The lowest energy configuration of the polymer is characterized by the characteristic equilibrated time constant τ_{eq} , which appears to be independent of external conditions such as polymer concentration. However, the rearrangement time τ_{off} needed to reach τ_{eq} varies greatly with experimental conditions such as temperature and molecular weight as shown in figure I.35.

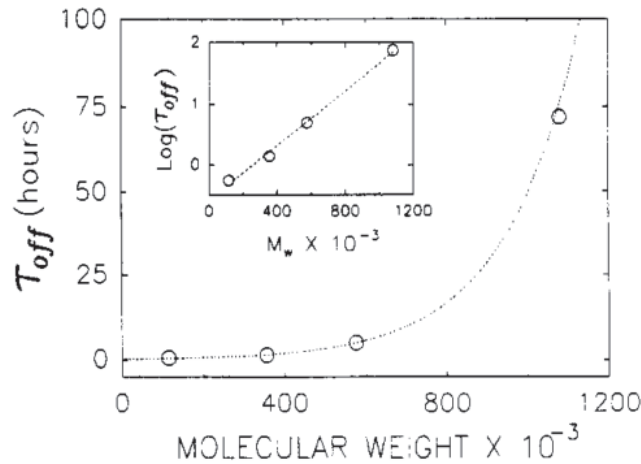


Figure I.35 – Evolution of τ_{off} (in hours) as a function of the molecular weight, from [Frantz and Granick, 1994]

Indeed, τ_{off} rose from 30 minutes for low molecular weight of 10^5 g/mol, to almost three days for high molecular weight of 10^6 g/mol. This could be due to the dependence of the displacement kinetics between protonated-PS and deuterated-PS on the residence time. As the adsorbed layer occupies the surface, the time constant for desorption increases, indicating that it becomes increasingly more difficult for the adsorbed chains to detach from the surface.

The self rearrangement of polymer chains at the interface with a solid surface at constant chemical environment was also investigated, at the plateau region and in the high adsorption zone (low coverage) [Peffekorn et al., 1989]. The kinetics revealed great differences between the two regimes, linked to the specific conformations of the polymer. Poly(styrene) (PS) is able to strongly interact with hydroxyl groups of silica through hydrogen bonding in stoichiometric conditions. As such, for low coverage, it adsorbs readily in flat conformation. When adsorption increases, the polymer forms loops and tails and slow exchanges take place between adsorbed polymer chains at the surface and polymer chains in solution, highlighting the fact that adsorbed polymers have a long life-time in the adsorbed state. Moreover, desorption kinetics were shown to increase for increasing polymer concentration in solution, confirming the presence of exchanges.

4 Towards an analogy between hybrid gels and filled elastomers

Similarly to hydrogels, elastomers are polymers networks formed either by supramolecular associations [Cordier et al., 2008] such as small glassy or crystalline domains or by permanent covalent bonds. Rubbers exhibit enormous extensibility up to several hundreds per cent, compared with a few per cent for ordinary solids, and have the ability to recover their original shape.

Originally the introduction of fillers was linked to a reduction of costs. Nowadays, prime importance is attributed to selecting active fillers in order to introduce specific improvements in physical properties. Filled elastomers are complex polymer systems exhibiting a number of singular properties. Although the reinforcement by fillers is a well-recognized phenomenon the term ‘reinforcement’ is not well defined and includes the improvement in abrasion, tear, cutting and rupture resistance, in stiffness and hardness, with modulus values far beyond the values expected on the basis of the Einstein-Guth and Gold theory [Jovanovic et al., 2010]. It takes into account the effects caused by

colloidal spherical particles (hydrodynamic effect) as well as the modifications in mechanical and flow properties whose origin is assigned to strong interactions between the elastomer and the filler. Silica reinforcement is of high interest since the recognition of the benefits of surface treatments with silanes that promote interactions with the polymer chains, allowing to enhance dispersion and/or mechanical coupling by covalent or non-bonded interactions [Leblanc, 2002].

Interfacial interactions and interphases play a key role in all multicomponent materials and for rubbers, filler distribution is also a key parameter to consider to understand the reinforcement mechanisms to be able to finely tune the resulting properties of the material.

Mechanical properties of filled rubbers are driven by the interactions between the filler and the matrix and the aggregation state of the fillers. Decorrelating the two contributions is thus necessary to fully understand the mechanisms at stake. From this point of view, hybrid gels can be seen as model systems with the advantage of the tunability of the dispersion state and/or interactions of the matrix/filler interactions.

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Chapter II

Adsorption of linear polymer chains of polyacrylamides onto silica nanoparticles

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1 Introduction

The adsorption of polymer from solution onto solid surfaces plays an important role in many industrial processes, involving colloid stabilization, lubrication or adhesion [Johner and Rubinstein, 1993]. Strong and rapid adhesion of soft materials relying on polymer adsorption was recently achieved using nanoparticles solutions on hydrogels surface [Rose et al., 2014].

The adhesion relies on the ability of the polymer to adsorb onto nanoparticles through multiple and reversible bonds. This method was used to efficiently attach together pure hydrogels layers based on *N,N*-poly(dimethylacrylamide) (PDMA), an hydrophilic neutral polymer, as well as biological tissue (calf's liver) [Meddahi-Pelle et al., 2014]. However the attempts to glue together poly(acrylamide) (PAAm) gel layers using this technique remained unsuccessful. This difference of behavior is believed to be due to the lack of interactions between silica nanoparticles and PAAm. Numerous data on the adsorption behavior of acrylamides polymers have been published and are all consistent with adsorbing behavior of poly(*N*-alkylacrylamides) onto silica nanoparticles [Petit, 2007] that are believed to interact with silica through hydrogen bonding between the carbonyl function of the amide group and silanol group of silica surface and through hydrophobic interactions which strength depends on the moieties [Zhang and Ren, 2004], as illustrated in figure II.1.

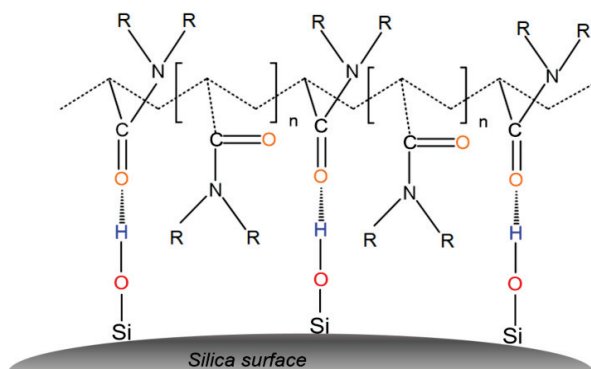


Figure II.1 – *Schematics of interactions between silica surface and poly(*N*-alkylacrylamides). Reversible interactions occur through hydrogen bond between silanol groups and the amide groups of the polymer. The strength and range of the hydrophobic interactions depend on the size of the alkyl group (*R*).*

When it comes to poly(acrylamide), data differ greatly in the literature, with great disparities found in the reported experimental adsorbed amount, Γ , ranging between 0 (no adsorption) [Guevellou et al., 1995; Bjelopavlic et al., 2001] and 2.7 mg/m² [Al-Hashmi et al., 2012] and few explanations are available to rationalize these contradictions. Yet, interactions between polymer chains and fillers are a key-aspect for nanocomposites elastomers [Perez-Aparicio et al., 2013] and hydrogels reinforcement [Haraguchi et al., 2002; Wu et al., 2011].

Strong but reversible adsorption of poly(*N*-alkylacrylamide) polymer chains onto the surface of silica nanoparticles has been demonstrated to be responsible for the self-healing abilities of hydrogels as well as for the improvement of fracture toughness and stretchability [Rose et al., 2013b] while the use of PAAm in such hydrogels (in their swollen state) does not lead to any significant reinforcement of the mechanical properties in the viscoelastic regime [Rose et al., 2013a]. Thus a better under-

standing of the mechanisms driving poly(acrylamide) adsorption onto silica seems to be important for the engineering of strong and tough nanocomposites materials.

Polymer adsorption is a complex process that depends on several parameters such as solvent condition, chemical conditions [Flood and Cosgrove, 2006; Van der beek and Cohen-Stuart, 1991; Van der Boomgaard et al., 1987], temperature, molecular weight [Semenov et al., 1996] and composition of the adsorbate surface [Griot and Kitchener, 1965a; Peffekorn et al., 1985]. It is important to consider every aspects of the chemistry governing polymer adsorption so as to disentangle the impact of each compounds.

Looking more accurately to the reported data concerning PAAm adsorption onto silica, it appears that the disparities found in the literature can be explained by several factors such as the generalization of the term "poly(acrylamide)" regrouping neutral, hydrolyzed (containing acrylic acid groups) and chemically-modified poly(acrylamide) [Peffekorn, 1999], the variation in the chemical conditions (pH and ionic force) [Guevellou et al., 1995] or the nature of the adsorbate (meaning either the alteration of the silica surface with the inclusion of others oxides [Graveling et al., 1997] or a change in silica surface groups composition [Zhuravlev, 1993; Griot and Kitchener, 1965b]).

Those data show that precise statement of the experimental conditions is of major importance to evaluate polymer adsorption but remain too often overlooked. Very recently, Bessaies-Bey and *al.* drew a general review of adsorption abilities of neutral and hydrolyzed PAAm of high molecular weight onto silicate surfaces and for once, clearly depicted the impact of experimental conditions and of the nature of the adsorbate on assessed adsorbed amounts [Bessaies-Bey et al., 2018].

The purpose of this chapter is to evaluate the adsorption abilities of linear polymer chains of defined molecular weight of poly(acrylamide) and poly(*N*-alkylacrylamides) onto pure silica nanoparticles under constant chemical conditions. Adsorbed amounts are measured using ^1H NMR (solvent relaxation time measurements), Total Organic Carbon analysis and zeta potential measurements to provide insight on the adsorbed quantity as well as on polymer conformation and on the thickness of the adsorbed polymer layer.

The experiments have been conducted on homopolymers of poly(acrylamide) (PAAm), poly- (*N*, *N*-dimethylacrylamide) (PDMA) and and statistic copolymers of PAAm and PDMA that were obtained by synthetic route using Atom Transfer Radical Polymerization. In the following, the principle of the used techniques will be briefly described and the synthesis route developed to synthesize the different polymers will be dealt with. Then the adsorption abilities of the several polymers synthesized onto silica nanoparticles will be assessed and discussed.

2 Principles and techniques

In the following section, the principles of the synthesis route developed and of the used analysis techniques are presented, for the reader's convenience and the self-consistency of the chapter. A skilled reader can skip this section and go directly to the 3rd section, Materials and Methods.

2.1 Polymer synthesis

2.1.1 Conventional Free Radical Polymerization: principle and limits

Conventional Free Radical Polymerization (FRP) is a method of chain growth polymerization, along with anionic, cationic and coordination polymerization. Contrary to other polymerization processes, it does not require stringent process conditions and can be used for the (co)polymerization

of a wide range of vinyl monomers (containing carbon-carbon double bonds, like AAm and DMA) in aqueous or organic solvents at moderated temperatures and is easily adaptable at industrial scales [Matyjaszewski and Davis, 2002]. Facile statistical copolymerization is also one of the main advantages of free radical polymerization since the reactivities of the monomers for many systems are relatively similar contrary to ionic polymerization [Matyjaszewski and Gaynor, 2000]. The polymer grows by successive addition of the monomer units via the breaking of a double bond of the monomer unit, converting it into an active propagating radical [Moad et al., 2005]. Free radical polymerization occurs through a chain mechanism consisting of four different types of reaction summarized in figure II.2.

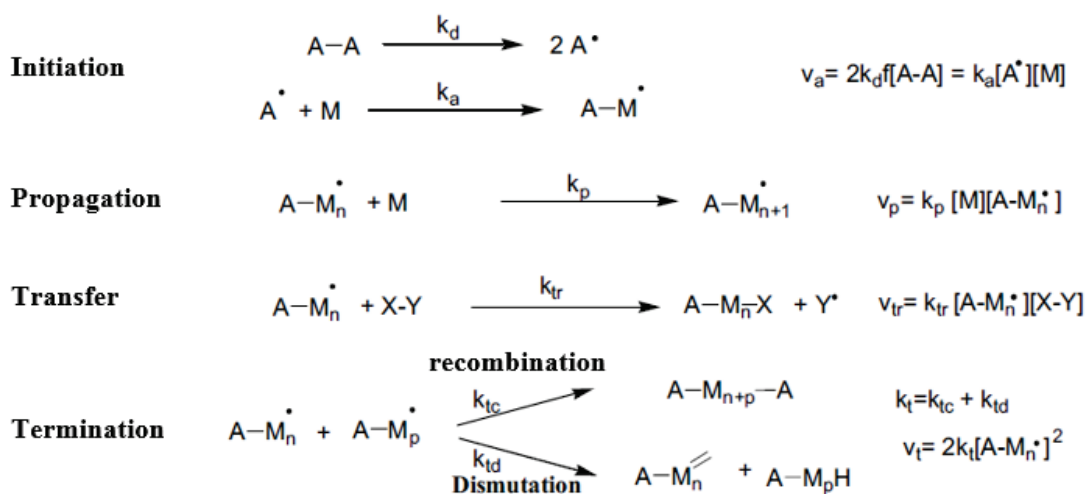


Figure II.2 – General scheme of Free Radical Polymerization, adapted from [Matyjaszewski and Davis, 2002]

The major encountered drawback lies in the transience of created radicals. Initiation, propagation and termination steps are happening at the same time which can lead to polymer with high molecular weight distribution. Despite FRP many benefits and its wide spread use, the high reactivity of propagating radicals combined with the existence of concomitant modes of chain deactivation have long been considered a barrier for obtaining polymers with controlled architecture. Hence, the major limitation of FRP is poor control over some of the key elements of the process that would allow the preparation of well-defined polymers with controlled molecular weight, dispersity, composition, chain architecture, and site-specific functionality. Therefore another path of synthesis allowing a controlled radical polymerization process of the desired polymers has to be considered.

2.1.2 Controlled radical polymerization

Controlled Radical Polymerization (CRP) has thus emerged to overcome the limitations of conventional FRP. First initiated by Tatemoto et al. in the late 70's and by Otsu et al. who reported the use of perfluoroalkyl iodides and thiuram disulfide iniferters as a way to reversibly deactivate the polymer chain growth, later extended to the reversibility of chain termination, CRP has become one of the most explored fields in macromolecular science [Matyjaszewski and Davis, 2002; Otsu and Yoshida, 1982]. This process requires establishing and selecting conditions that allow a

dynamic equilibrium between a low concentration of active propagating chains and a large mole fraction of dormant chains, which are unable to propagate or self-terminate. CRP techniques enable a wide range of well-defined polymer synthesis, including the ability to prepare bioconjugates, organic/inorganic composites, and surface-tethered copolymers as illustrated on the figure II.3.

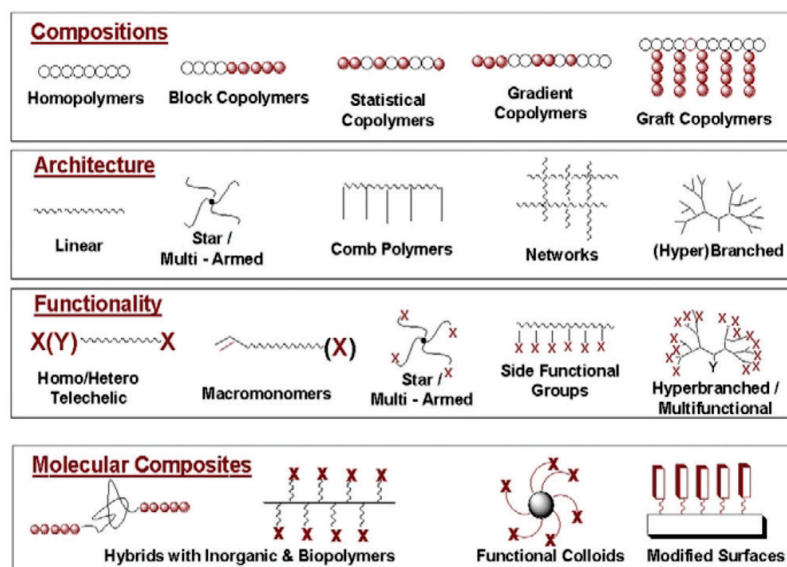


Figure II.3 – Examples of the molecular structures attained through Controlled Radical Polymerization from [Matyjaszewski and Spanswick, 2005]

CRP processes were widely developed depending on the mechanism and chemistry, exchange process as well as on the structure of the dormant species. Some of these processes requires a catalyst while others exhibit the persistent radical effect. Currently, three major methods appear to be the most efficient and may lead to commercial applications: the nitroxide-mediated polymerization (NMP), the reversible addition fragmentation chain transfer polymerization (RAFT) [Destarac, 2010] and the atom transfer radical polymerization (ATRP). For each strategy, extensive efforts have been devoted to design control agents for polymerizing an increasing number of monomers while keeping optimized control over the molecular weights and dispersity ($\bar{M}_w/\bar{M}_n$) and targeting rates of polymerization approaching those of conventional FRP. Special interest was taken in developing CRP under environmentally friendly conditions, e.g, the use of water as polymerization medium, ambient temperature polymerization and for ATRP method, the key-challenge of reduction of metal catalyst content. ATRP was specifically selected to synthesize the desired polymers in this chapter and is described in the section below.

2.2 Atom Transfer Radical Polymerization (ATRP): basics

Atom Transfer Radical Polymerization was devised by Matyjaszewski in 1995 and has imposed itself as one of the most robust controlled radical polymerization method which present the advantage of being shut down and restarted at will [Wang and Matyjaszewski, 1995]. It also allows a wide range of polymers synthesis in a reasonable range of temperatures.

ATRP consists in introducing in the reactional medium a specie able to interact with radicals by

reversible termination to reach an equilibrium between a dormant specie, unable to propagate, and a radical active specie. This equilibrium is strongly displaced in favor of the dormant specie and allows to add monomer in a very controlled way, hence chains grow linearly with less probable recombination or termination during polymerization process. The general scheme depicting the mechanism of ATRP is represented in figure II.4:

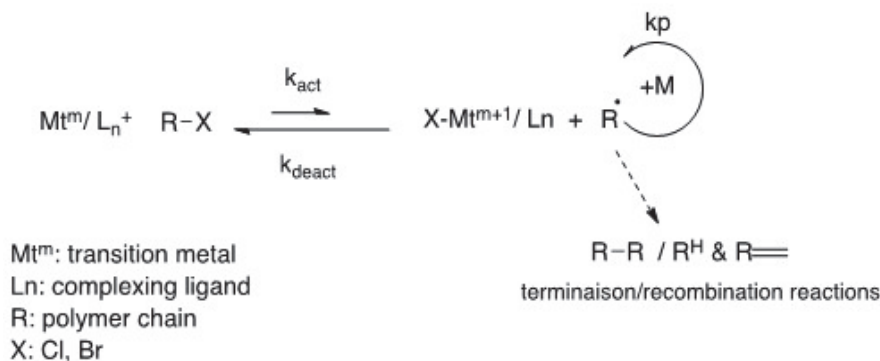


Figure II.4 – General scheme of metal complex-mediated ATRP, from [Wang and Matyjaszewski, 1995].

The number average degree of polymerization, DP_n is one of the main feature of controlled radical polymerization [Matyjaszewski, 1996; Coleman and Fox, 1963]. The 'living' aspect (or control) of this polymerization process can be ascertained from a linear first-order kinetic plot, accompanied by a linear increase in polymer molecular weight with the conversion p . The value of DP_n is determined by the ratio of reacted monomer $[M]$, to initially introduced initiator $[RX]$, giving:

$$DP_n = \frac{[M]}{[RX]} \times p \quad (\text{II.1})$$

with p , probability of growing chain. If exchanges between dormant and active form are even, chains grow in the same range of time.

ATRP involves a reversible homolytic halogen transfer between dormant species, an added initiator or dormant specie (RX or $R-P_n-X$) and a transition metal complex in the lower oxidation state (Mt^m/L_n) resulting in the formation of propagating radicals ($R\cdot$) and the metal complex in the higher oxidation state with a coordinated halide ligand ($X-Mt^{m+1}/L_n$). The reaction is reversible, meaning that the oxidized complex is reduced while the chain carrying the radical is oxidized and the propagation of polymerization stopped. The equilibrium between dormant polymer chains (halogenated, RX) and the active form (radical, $R\cdot$) is strongly displaced in favor of the dormant species ($K_{act} \lll K_{deact}$) throughout the whole reaction, allowing good control over the polymer growth. Control over created radical rate lies on the reduction of the halogenated compound by the metallic complex. The reaction is usually catalyzed by organometallic complex, mainly of copper or ruthenium. Ideal growth of molecular weight with conversion is shown in figure II.5.

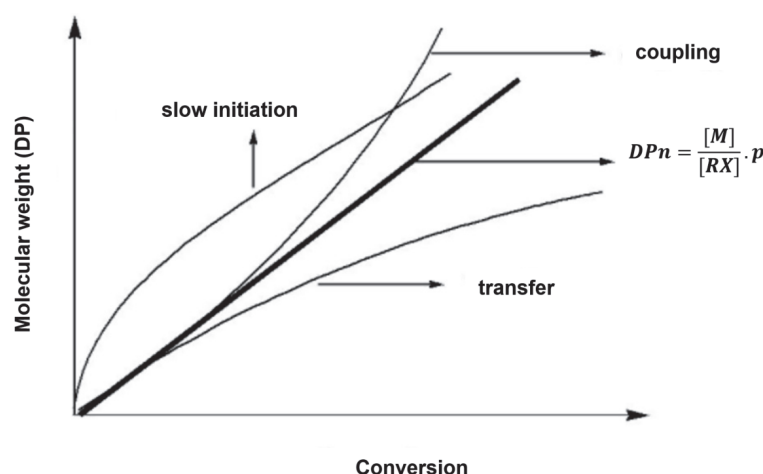


Figure II.5 – Ideal growth of molecular weight with conversion and effects of slow initiation and chain transfer on the molecular weight distribution, from [Wang and Matyjaszewski, 1995].

Under those conditions, it is possible to reach targeted M_n as well as narrow dispersity $\bar{D}$ (or molecular weight distribution), preferably inferior to 1.5. The design of a narrow molecular weight distribution is highly desirable but requires the suppression of chain transfer or termination processes, which is the result of a well-controlled polymerization. The sharpness of the molecular weight distribution has been attributed to:

- fast initiation rate compared to the propagation rate, so that all chains grow at the same time.
- exchange between species of different reactivity is fast compared to the propagation rate, all the active sites of growing chains can equally react with a monomer
- negligible chain transfer (that would increase the total number of chain) or termination
- depropagation rate is significantly lower than propagation, polymerization must be irreversible.

This technique was specifically used to obtain polymers based on acrylamides monomers, acrylamide (AAm), *N,N*-dimethylacrylamide (DMA) and *N*-isopropylacrylamide (NIPAm). The protocol used in this work is adapted from the one designed by Wever *et al.* for the synthesis of PAAm/PNIPAm block copolymers using methyl-2-chloropropionate (MeClCr) as the initiator and CuCl (I)/tri[2-(dimethyl)ethyl]amine (Me₆TREN) as the catalytic system, according to the following reaction depicted in figure II.6. We propose here a new method for ATRP synthesis of PAAm, PDMA and statistic copolymers.

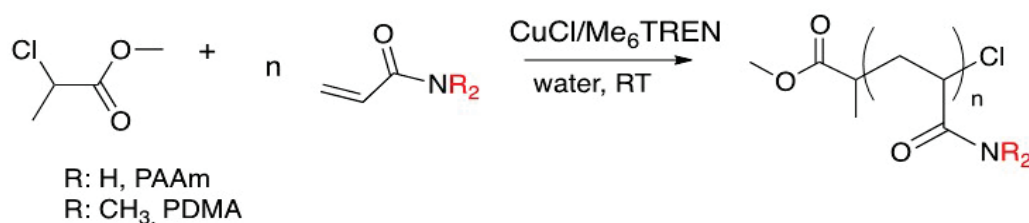


Figure II.6 – Chosen system for ATRP synthesis of PAAm and PDMA.

The monomers, initiators and the ligand of the catalytic system are represented in figure II.7.

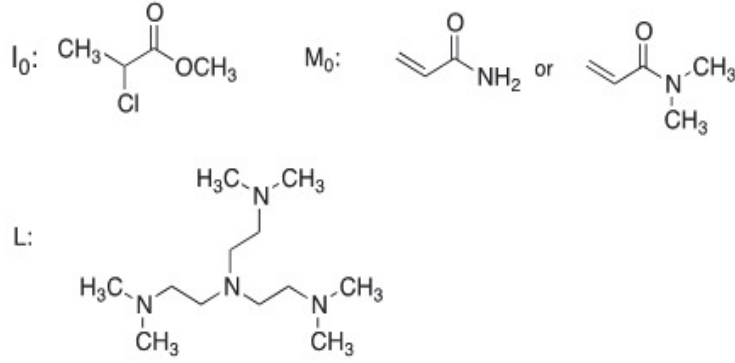


Figure II.7 – Schematics of methyl-2-chloropropionate (I_0), monomer (DMA or AAm), tri[2-(dimethyl)ethyl]amine, Me_6TREN (L).

The catalyst system remains the same as in Wever's work, the difference lies in the monomers used and the purification process developed to obtain the desired polymers. The details are explained in the Results and Discussion section.

2.3 1H Nuclear Magnetic Resonance relaxation time analysis of the solvent

2.3.1 Effect of interfaces on the solvent relaxation time

In NMR, the so-called transverse magnetic signal, excited after a single pulse, relaxes to zero under the effect of various interactions imposed on spins. The corresponding NMR transverse relaxation time (also called spin-spin relaxation time, as it depends on dipolar interactions between spins), denoted T_2 is directly related to molecular mobility. Therefore, measuring relaxation times (so-called time-domain NMR) gives dynamic information on a system. We consider here proton (1H) NMR. 1H NMR solvent relaxation has been used in the literature to get insight on the dynamics of an adsorbed polymer close to a particle surface [Cooper et al., 2013; Van der beek and Cohen-Stuart, 1991]. Protons belonging to mobile (liquid-like behavior) and immobile (solid-like) molecules have very different relaxation processes with vastly different time scales. The relaxation time is proportional to the inverse of the correlation time τ_c , of molecule reorientation. Solvent (water) molecules diffusing freely within the liquid phase show exponential relaxation with a long relaxation time T_2^{free} of a few seconds typically, while solvent molecules bound to an interface have strongly constrained molecular motions and relax within a time scale T_2^{bond} typically lower than 1 ms. If water molecules exchange very fast between these two populations, then a single average T_2 relaxation time, or equivalently relaxation rate $R_2=1/T_2$, is measured, given by:

$$R_2(p) = p_b R_2^{bond} + (1 - p_b) R_2^{free} \quad (II.2)$$

where p_b is the fraction of protons attached to or constrained by the interfaces. As T_2^{bond} is very short compared to T_2^{free} , the measurement of T_2 (Φ_i) is very sensitive to the presence of even a small quantity of interfaces in the system. For complex systems, the specific relaxation rate R_{2sp} may be used to describe solvent relaxation and is defined as:

$$R_{2sp} = p_b \left(\frac{R_2}{R_2^0} - 1 \right) \quad (II.3)$$

$$p_b = k \frac{[particles]}{[solvent]} \quad (\text{II.4})$$

where R_2^0 is the relaxation rate constant of a reference system for example of pure water. p , the bound fraction can be defined as the bound fraction of solvent divided by the total amount of solvent giving:

$$R_{2sp} = k \frac{[particles]}{[solvent]} \left(\frac{R_2}{R_2^0} - 1 \right) \quad (\text{II.5})$$

For fast exchanges, plotting R_{2sp} against particles concentration will give a linear curve and an increase or decrease in the specific relaxation rate constant will change the slope of this curve. This method is therefore particularly fit for measurements involving changes at the particles surface such as adsorption [Piculell and Halle, 1986].

2.3.2 Principle of the measurements

In practice, the T_2 relaxation time cannot be measured directly because the observed relaxation is dominated by inhomogeneities of the static magnetic field. A classical spin echo technique must be used. The principle is the following one: a single 90° pulse applied at time $t = 0$ gives the observed relaxation signal

$$M(t) = M_0 \exp\left(-\frac{t}{T_2}\right) \langle \exp(-i\delta\omega_0 t) \rangle \quad (\text{II.6})$$

in which, in addition to the T_2 relaxation term (which is intrinsic to the studied sample and reflects the molecular mobility), there is a contribution to relaxation from magnetic field inhomogeneities. This contribution may be written as due to a distribution of small shifts $\delta\omega_0$ of the Larmor frequency, depending on the local value of the magnetic field. At a time τ , a 180° pulse is applied. Its effect is to revert the phase factor due to field inhomogeneities $-i\delta\omega_0\tau \rightarrow +i\delta\omega_0\tau$ (see figure II.8). The signal then continue to relax as before (starting from $t = \tau$, which gives:

$$M(t) = M_0 \exp\left(-\frac{t}{T_2}\right) \langle \exp(i\delta\omega_0\tau) \exp(-i\delta\omega_0(t - \tau)) \rangle \quad (\text{II.7})$$

$$= M_0 \exp\left(-\frac{t}{T_2}\right) \langle \exp(-i\delta\omega_0(t - 2\tau)) \rangle \quad (\text{II.8})$$

So that at time $t = 2\tau$ (the top of the spin echo) the effect of magnetic field inhomogeneities cancels out and:

$$M(t = 2\tau) = M_0 \exp\left(-\frac{t}{T_2}\right) \quad (\text{II.9})$$

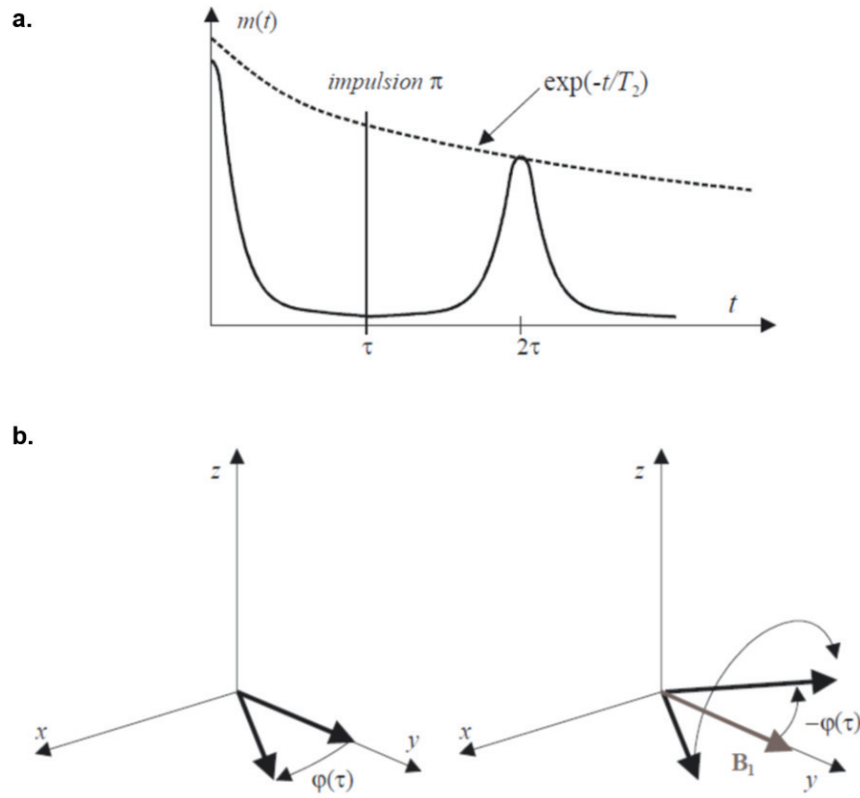


Figure II.8 – **a.** Schematics of the evolution of the magnetic component of the relaxation $m(t)$, as a function of time with the associated pulse sequence at $t = 0$ and $t = \tau_i$. **b.** Shift of the transverse magnetic field B_1 over the time and the pulse sequence applied to cancel the field inhomogeneities, represented in Cartesian coordinates.

A train of successive 180° pulses separated by $2\tau_i$ can then be applied and the true relaxation curve, $\exp(-t/T_2)$ is obtained by recording the amplitudes of all successive spin echos. This is the so-called Carr-Purcell-Meiboom-Gill (CPMG) sequence

2.4 Total Organic Carbon Analysis

Depletion techniques allow a quantitative description of adsorption behavior. A concentration change in bulk solution prior to and after adsorption is measured. These techniques are particularly adequate for high surface area material [Hlady et al., 1999] and are widely used to assess adsorption behavior of linear polymer chain on solid surface. Measurement of the remaining quantity of materials after adsorption can be performed using phosphomolibdic acid coupled with UV spectroscopy [Chaplain et al., 1995; Wisniewska, 2012] or FT-IR spectroscopy [Frantz and Granick, 1994; Liu and Xiao, 2008], precipitation and turbidimetry [Malmsten et al., 1992], drying, thermogravimetric analysis [Liu and Xiao, 2008] and TOC measurements [Hourdet and Petit, 2010; Mathur and Moudgil, 1997].

The adsorbate (the polymer, at initial concentration C_0) is put in contact with the adsorbent, here the silica nanoparticles at fixed concentration C_{Si} until adsorption equilibrium. Then silica particles and adsorbed polymer are removed from the solution using separative method such as centrifugation then the concentration remaining in the solution is tested and the adsorbed amount is retraced as

shown in figure II.9.

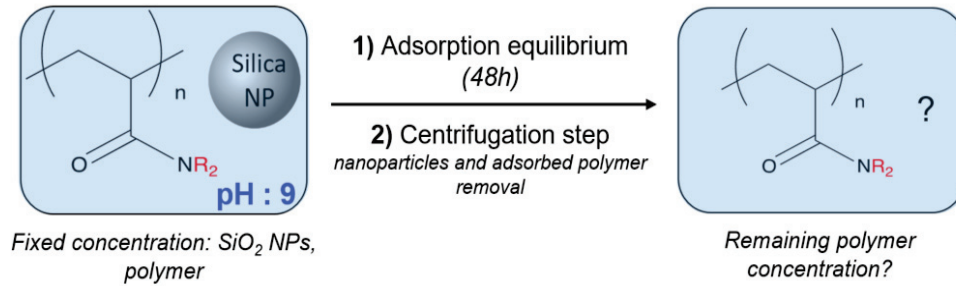


Figure II.9 – General scheme of depletion method for adsorption. First the silica nanoparticles and the polymer are put together for 48h until adsorption equilibrium is reached. Centrifugation is then applied to the suspension to remove the nanoparticles and the adsorbed polymer. The supernatant contains the non adsorbed polymer which quantity can be assessed.

TOC analysing consists in measuring the total quantity of carbon contained in a solution after complete combustion of the sample and detection of the corresponding CO_2 (g). The carbon detected is called Total Carbon TC . It is the result of two contributions, the organic and inorganic.

$$Total\ Carbon\ (TC) = Organic\ Carbon\ (OC) + Inorganic\ Carbon\ (IC) \quad (II.10)$$

Phosphoric acid and an oxidant (persulfate) can be added to the sample, which is heated at 680 °C under UV illumination to convert the carbon in the sample to carbon dioxide. This carbon dioxide flows with the carrier gas into a non-dispersive Infra-Red sample cell. The area of the carbon dioxide peak signal is measured and converted to TC concentration using a pre-prepared calibration curve. The intensity follows the Beer Lambert Law: $A_{abs} = \epsilon_i \times C_i \times l$ with A_{abs} the absorbance or optic density for a given wavelength λ_l (without dimension) with ϵ_i the molar extinction coefficient (in $L.mol^{-1}.cm^{-1}$), depending on the wave length, the chemical properties of the compound and the temperature, l , the length of the optic course (in cm) and C_i the molar concentration (in $mol.L^{-1}$).

2.5 Zeta potential measurements

Silica nanoparticles in solution with solubilized polymer chains can be depicted as a solid/liquid interface with a slipping surface between a charged surface and liquid layer. The figure II.10 represents the hydrodynamic shear plane (or slipping plane) between solid surface and electrolyte solution at the interface. Slipping occurs due to adsorbed ions in the Outer Helmutz Plane (OHP) and mobile ions in the diffuse layer.

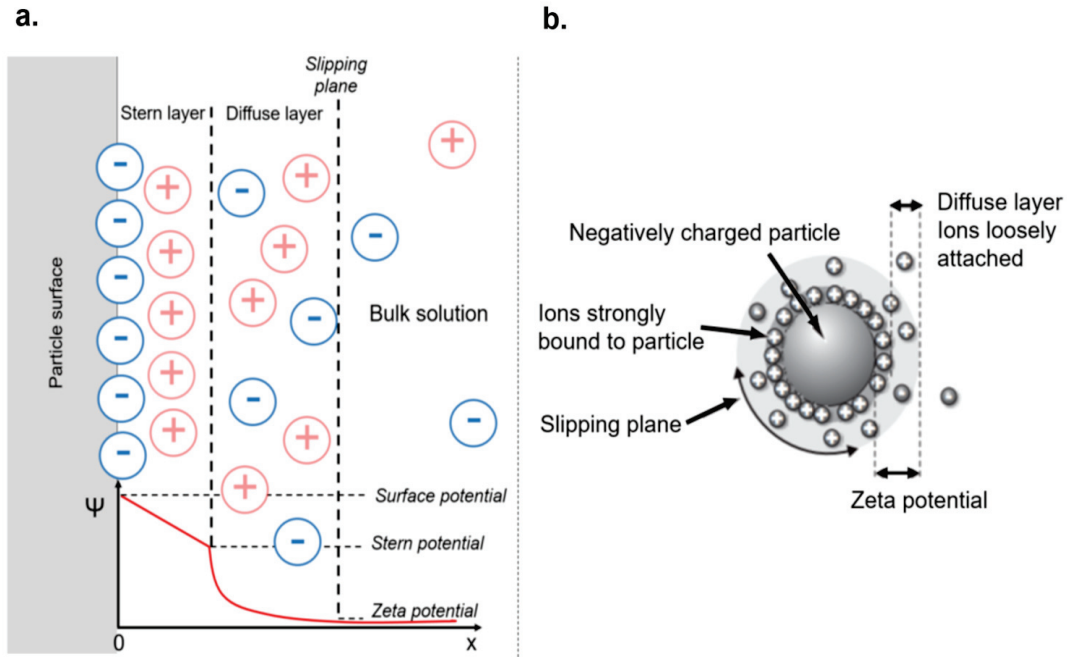


Figure II.10 – **a.** Conceptual representation of the electrical double layer at the interface of charged solid surface and a weak electrolyte solution. Potential and is shown (red curve) and the slipping plane is where hydrodynamic motions take place and ζ is the potential at that plane. **b.** Schematics of zeta potential for a negatively charged nanoparticle, from [Kirby and Hasselbrink Jr, 2004]

The zeta potential is determined by measuring the electrophoretic mobility of the particle, μ_e , which is the velocity of the particle, ν_p in an electric field E_f which gives:

$$\mu_e = \frac{\nu_p}{E_f} \quad (\text{II.11})$$

The mobility is a function of the zeta potential, ζ , the viscosity η of the suspending medium the ratio of the particle radius to the electrical double layer thickness κR and the dielectric constant ϵ_r

$$\mu_e = \frac{4\pi\epsilon_0\epsilon_r\zeta}{\eta} f(\kappa R) \quad (\text{II.12})$$

For small κR like for small particles in dilute electrolyte, $f(\kappa R)=1$. As might be expected, the zeta potential is the most significant measurable property that can be used to characterize the stability of a colloid and generally a surface potential in excess of 25 mV is required to produce a stable dispersion.

Description of colloidal solutions like zirconia or silica using zeta measurements is well described in the literature [Kirby and Hasselbrink Jr, 2004; Fengqiu et al., 2000]. The charge of a colloid is generally pH dependent, as depicted in figure II.11.

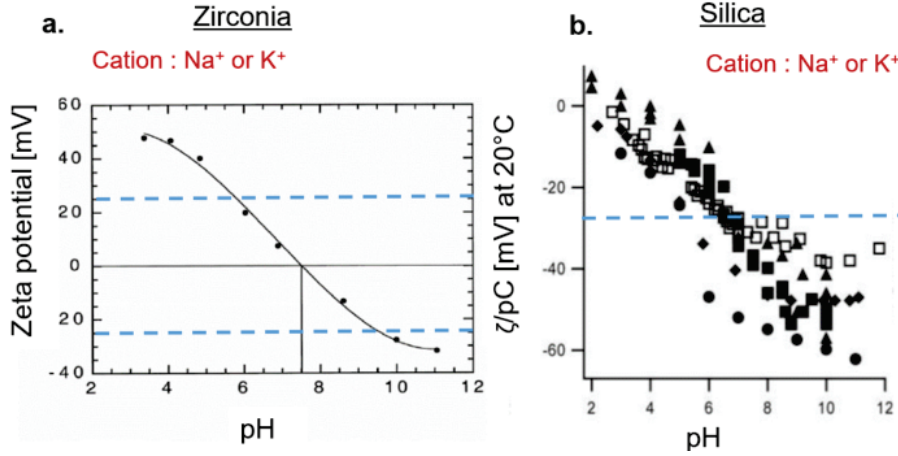


Figure II.11 – **a.** Zeta potential of zirconia as a function of the pH, from [Fengqiu et al., 2000]. **b.** pH dependence of temperature-corrected normalized zeta potential (20). Filled symbols: electro-osmotic or electrophoretic mobility. Open symbols: streaming potential, from [Cohen-Stuart and Mulder, 1985]. The stability domain of the colloidal suspension (surface excess of 25 mV is illustrated on both curves by the dashed blue lines)

Adsorbed neutral polymer in aqueous media are known to reduce strongly the zeta potential of charged surface as it has already been well described in the literature [Hunter, 1985]. While zeta potential cannot be used to provide exact amount about the adsorbed quantity, it can provides useful information on the thickness of the adsorbed layer and on its conformation. The main observable is the outward shift of the plane shear, since it can be related to the thickness of the adsorbed layer and the zeta potential through the following equation:

$$\tanh \frac{ze\zeta}{4k_B T} = \tanh \frac{ze\zeta_0}{4k_B T} e^{-\lambda_D \delta_E} \quad (\text{II.13})$$

Where ζ and ζ_0 are the zeta potentials measured in and without adsorbed polymer, z is the valency of the electrolyte, e the electronic charge, λ_D is the Debye length and δ_E the position of the plane shear. This technique can be used to assess in a very simple and non-invasive way the impact of an adsorbed polymer on a well-defined surface such as the one of charged silica nanoparticles.

3 Materials and methods

3.1 Chemicals

Nanoparticles Silica nanoparticles used for all experiments are Ludox-TM 50 produced by Grace and bought from Sigma-Aldrich, used without further purification. The neat silica suspension contains 52 wt% silica (33 vol%) and is diluted with deionized water. The spherical shape of the nanoparticles as well as their radii ($r_{Si} \approx 14$ nm) nanoparticles were characterized by Scanning Electronic Microscopy (SEM) and Small Angle X-Ray scattering (SAXS) using a fitting procedure for experimental data that considers polydisperse spherical particles with a Gaussian distribution of size. This model gave a mean radius of 13.5 nm with a standard deviation $\sigma = 0.13$. The specific surface S_{spe} (m²/g) was then calculated from the measured radius according to:

$$S_{spe} = \frac{3000}{\rho_{Si} r_{Si}} \quad (\text{II.14})$$

where r_{Si} is the silica particles radius (in nm) and ρ_{Si} is the specific weight of 2.3 g/cm³. The corresponding specific surface area determined in this way is 100 m²/g.

Monomers and reactants Acrylamide (AAM, 99% electrophoresis grade, Aldrich), *N,N*-dimethylacrylamide (DMA, 99%, Aldrich), copper chloride (CuCl, 99.999% trace metals basis, Aldrich), tris[2-(dimethylamino)ethyl]amine (Me₆TREN, 97%, Aldrich), methyl-2-chloro propionate (MeClCr) and *N,N,N',N'*-tetramethylethylenediamine (TEMED, 99% bio reagent, Aldrich) were used as received without further purification.

Other chemicals Anhydrous sodium sulfate (Na₂SO₄, 99% ACS reagent, Aldrich) and sodium chloride (NaCl, 99.5%, BioXtra, Aldrich) were used as received.

Polymers Poly(acrylamide) (PAAm-c, average M_n 100 000 g/mol, $\bar{D}$: 2.05 Aldrich) and poly(*N,N*-dimethylacrylamide) (PDMA-c, average M_n 45 000 g/mol, $\bar{D}$: 1.6, Polymer Source) are used as such without further purification.

Milli-Q water was used for all experiments.

3.2 Polymer synthesis

Polymer synthesis by ATRP the molar ratios between each reactant (monomer [M], initiator [MeClCr], and catalyst metal and ligand [CuCl] and [Me₆TREN]) were fixed to fit the aimed DP_n as depicted in table II.1.

Aimed DP_n	[M] ₀ : [MeClCr] ₀ : [CuCl] ₀ : [Me ₆ TREN] ₀	monomer (wt)/water (v) ratio
500	470 : 1 : 1.5 : 1.5	1:6
2 000	2 000 : 1 : 1.5 : 1.5	1:6
5 000	5 000 : 1 : 1.5 : 1.5	1:6

Table II.1 – Molar ratios between each reactant (monomer [M], initiator [MeClCr], and catalyst metal and ligand [CuCl] and [Me₆TREN]).

The overall polymerization reaction was performed under nitrogen atmosphere to prevent termination reactions due to oxygen pollution. The monomer was solubilized in water and left under stirring overnight to ensure complete dissolution. Copper chloride was placed in two-necked flask and was submitted to three successive vacuum/nitrogen cycles and is placed in an oil bath at 25 °C. If the monomer was DMA the flask was placed in an ice bath as the reaction involving dimethylacrylamide is exothermic. Solubilized acrylamide, methyl-chloropropionate and Me₆-TREN were placed in a two-necked flask and left under N₂ bubbling for 30 minutes. The solution was then transferred into the two-necked flask containing copper chloride through over pressure using canula transfer. The solution was dark green and left under vigorous stirring. The polymerization was left running for 60 minutes. At the end the solution was viscous and had turned to blue. Polymerization was stopped by exposition to ambient air.

The mixture was then transferred into a dialysis membrane with 6-8 kDa cut off. The solution was dialyzed for 5 days against a solution of water and TEMED to remove all residual copper and then the solution was dialyzed for two more days against pure water. Solvent evaporation was obtained by freeze drying overnight to yield a white solid.

Free Radical Polymerization of PDMA In a three-necked flask 100 mmol of monomer (DMA) were dissolved in 100 mL of water and the solution was deoxygenated for 1h with nitrogen bubbling. The redox initiators, KPS and TEMED were separately dissolved in 10 mL of water and deoxy-

generated under nitrogen bubbling for 30 min before adding to the monomer solution. The reaction was allowed to proceed in an ice bath and the polymerization was left running for 4 hours. The reaction was stopped by exposure to ambient air. Due to its high viscosity, the polymer could not be analyzed by SEC analysis, probably due to polymer branching.

3.2.1 Polymer characterization

Polymers molecular masses are analyzed using Viscotek TDA302 triple detection Size Exclusion Chromatography, SEC max VE2001, using aqueous solution of NaNO_3 0.2M and structural characterization was conducted using high resolution ^1H and ^{13}C NMR measurements, performed on Bruker 400 MHz, in D_2O .

3.3 Adsorption measurements

A series of polymer/silica mixtures (pH set at 9, using HCl or NaOH) were prepared in centrifuge vials by introducing increasing amounts of polymer in silica suspension with a fixed concentration 0.25vol% (i.e., 5 g/L equivalent to an available silica area of 46 m^2), carefully chosen to avoid gelation of the solutions. The samples were left under gentle stirring for 48 hours and the silica material settled via centrifugation over the course of 12 hours at 25 000 g. The supernatant was recovered and submitted to the same procedure. The presence of remaining particles was checked using Dynamic Light Scattering analysis performed on Malvern Zetasizer Nano SZ90 with a 632 nm laser and a 90° detection angle. The pH was then readjusted between 5 and 6 as the measuring device was sensitive to basic pH. The concentration of free polymer chains was determined by titration of the total organic carbon (TOC) using Shimadzu VCSH COT carbon analyzer using a relation $area \times constant = concentration$. A calibration trend line using polymer solutions of increasing concentrations was established for each polymer. The same procedure was applied for each polymer concentration and two measurements were made each time. The amount of adsorbed polymer per surface unit Γ , in mg/m^2 was calculated from the equilibrium polymer concentration (C_p , in g/L), and the initial polymer concentration (C_0 , in g/L) using the following relation:

$$\Gamma = \frac{C_0 - C_p}{1000 \times C_{Si} \times S_{spe}} \quad (\text{II.15})$$

Where C_{Si} is the silica concentration in g/L, S_{spe} the specific surface of silica in m^2/g .

3.4 Zeta potential measurements

Before measurements, suspensions of 0.25 vol% (5 g/L) and 1vol% (23 g /L) of silica were made, with and without polymer. The pH of all solutions was set at 9 using HCl or NaOH and ionic force is adjusted with Na_2SO_4 (divalent) or NaCl (monovalent). For samples containing adsorbed polymers, a known quantity of the polymer was added to the silica suspension then the mixtures were left under mechanical stirring for 48 hours to reach adsorption equilibrium.

1 mL of the solutions were then filtered using cellulose acetate filter-syringes with cut off $45 \mu\text{m}$ to remove residual dusts are then transferred into zeta tanks and sealed with appropriate plugs. Measurements are conducted on a Zetasizer Nanoseries SZ90 device equipped with 633 nm laser and a detection angle of 90° , using Laser Doppler Velocimetry in disposable DTS 1070 cells.

The thickness of the adsorbed layer is evaluated through the shift of the plane of shear δ_e using an approximate equation of the well-known equation:

$$\tanh \frac{ze\zeta}{4k_B T} = \tanh \frac{ze\zeta_0}{4k_B T} e^{-\lambda_D \delta_E} \quad (\text{II.16})$$

Where ζ and ζ_0 are the zeta potentials measured with and without adsorbed polymer, z is the valency of the electrolyte, e the electronic charge, λ_D is the Debye length and δ_E the position of the shear plane, which gives, for low potential approximation (zeta potentials not exceeding 50 mV) :

$$\delta_E = -\lambda_D \ln(\zeta/\zeta_0) \quad (\text{II.17})$$

3.5 ^1H NMR relaxation times

Silica samples of various concentrations (from 5 vol% to 25 vol%) were prepared by diluting dispersions of Ludox in water (pH settled at 9, using HCl or NaOH). Polymers solution were prepared in water and left under stirring for two days to ensure full dissolution. Samples containing polymers at several concentration (from 0.05 wt% to 0.5 wt%) were made by adding a known quantity of silica to a polymer solution with an equilibration time of 48 hours. The suspensions were transferred in conventionnal NMR tubes of 0.8 cm diameter.

All measurements were performed on a low-field, low resolution apparatus Bruker Minispec mq20 at 20 MHz proton resonance frequency. The Minispec has typical $\pi/2$ pulse lengths of down to 2 μs (125 kHz nutation frequency), with switching times in the 2 μs range. The sample temperature was controlled with a BVT 3000 heater working with air and all measurements were done at $35 \pm 0.05^\circ \text{C}$. The Carr-Purcell-Meiboom-Gill (CPMG) sequence was used with a τ spacing of 1 ms and recording every second echo which gives a dwell time of 4 ms between data points. 2000 data points were collected. A 90° pulse time of 4.36 μs was used and recycle delay of 20 s between two scans was set to ensure full recovery of magnetization between acquisitions. 32 scans were collected by acquisition. T_2 relaxation times were determined from the decay curves using the following fitting equation:

$$M(t) = M_0 e^{-\frac{t}{T_2}} \quad (\text{II.18})$$

With M_0 , the transverse magnetization following the 90° pulse. Assuming rapid exchanges between bulk solvent (isotropic motions) and the surface (anisotropic motions), the relaxation processes are described with an average single relaxation rate R_2 where $R_2 = \frac{1}{T_2}$, which is equal to $R_2 = (1 - p_b) \times R_{2f} + p_b R_{2b}$ where R_{2f} is the relaxation rate in the bulk (free) solvent, R_{2b} the relaxation rate of solvent molecules adsorbed or constrained by the interfaces and p_b the (small) fraction of bonded solvent molecules. The specific relaxation rate R_{2sp} used to describe solvent relaxation is defined as:

$$R_{2sp} = \left(\frac{R_2}{R_2^0} - 1 \right) \quad (\text{II.19})$$

where R_2^0 is the relaxation rate constant of a reference system, here the one of pure water. Assuming that the relaxation rate R_{2f} in the bulk (free) solvent is the same as that of pure water R^0 (which may be justified in a relatively diluted system), Eq. (I.19) can be rewritten:

$$R_{2sp} = p_b \left(\frac{R_{2f}}{R_2^0} - 1 \right) \quad (\text{II.20})$$

The bound fraction in the system can be calculated as:

$$p_b = k \frac{[particles]}{[solvent]} \quad (\text{II.21})$$

Where k is the concentration of solvent bonded on the surface of the particles per unit concentration of particles. Thus, if there is fast exchange, the relaxation of the solvent should be described by a single exponential in all cases and the specific relaxation rate R_{2sp} should be linear with the ratio $[particles]/[solvent]$.

4 Results and Discussions

4.1 PDMA, PAAm and P(AAm-co-DMA) ATRP synthesis

These experiments were conducted thanks to the help and expertise of N. Pantoustier (SIMM, ESPCI).

To get better insight on polymer adsorption in PDMA and PAAm hybrid gels, the aim was to first synthesize linear polymer chain targeting the average length of polymer segments between two cross-linking points in hybrid gels cross-linked at 0.1 mol% ($\approx 50\,000$ g/mol for PDMA gels). Higher chain lengths were then targeted to assess the impact of the polymer size on adsorption. Linear polymer chains of homopolymers and copolymers of poly(acrylamide) and poly(N,N -dimethylacrylamide) of controlled size (targeted M_n of 50 000, 200 000 and 500 000 g/mol) using Atom Transfer Radical Polymerization were synthesized. The nomenclature used throughout this study is PAAm- c or PDMA- c for commercial polymers and PAAm- x , x being the targeted M_n in kg/mol. The copolymers P(AAm-co-DMA) are named PAD $y/z-x$ with y and z respectively the molar content of AAm and DMA. For example, a copolymer containing 20 mol% of acrylamide and 80 mol% of N,N -dimethylacrylamide with a targeted M_n of 50 000 g/mol will be named: PAD20/80-50. PDMA synthesized by Free Radical Polymerization will be named PDMA-FRP.

Tables II.2 and II.3 present the results of the synthesized homopolymers and copolymers with different targeted M_n .

Polymer	Exp M_n (g/mol)	Targeted M_n (g/mol)	$\bar{D}$	R_H (nm)	Conversion rate (60 min, %)	a Mark- Houwink	
PDMA-50	63 000	50 000	1.5	10.6	34	0.727	0.71
PAAm-50	68 000	50 000	1.3	10.0	57	0.758	0.52
PAD80/20-50	74 000	50 000	1.6	10.3	49	0.748	0.54
PAD50/50-50	150 000*	50 000	2.10	17.0	63	0.750	1.15
PAD20/80-50	78 000	50 000	1.7	9.9	51	0.746	0.54

Table II.2 – Summary table of synthesized polymers. The experimental molecular weight (exp M_n), the hydrodynamic radius (determined in NaNO_3 0.2M solution), the dispersity $\bar{D}$, the Mark-Houwink parameter a , the intrinsic viscosity η_{int} (in dl/g) are obtained from the SEC analysis. (*) indicates synthesis where reached M_n is superior to the targeted one and points to a loss of control of the polymerization.

Polymer	Exp M_n (g/mol)	Targeted M_n (g/mol)	$\bar{D}$	R_H (nm)	Conversion rate (60 min, %)	a Mark Houwink	
PAAm-200	230 000	200 000	1.7	18	54	0.747	1.51
PDMA-200	155 000	200 000	1.4	17	68	0.784	1.62
PDMA-500	740 000*	500 000	1.5	36	42	0.758	2.99
PAD80/20-200	160 000	200 000	1.5	18	56	0.728	1.81
PAD50/50-500	650 000	500 000	1.4	38	60	0.632	4.35
PAD20/80-200	190 000	200 000	1.7	18	49	0.770	1.30

Table II.3 – Summary table of synthesized polymers with higher targeted M_n . The experimental molecular weight (exp M_n), the hydrodynamic radius (determined in NaNO_3 0.2M solution), the dispersity $\bar{D}$, the Mark-Houwink parameter a , the intrinsic viscosity (in dl/g) are obtained from the SEC analysis. (*) indicates synthesis where reached M_n is superior to the targeted one and points to a loss of control of the polymerization.

It is important to underline here that controlled radical polymerization of acrylamide and derivatives is usually performed by Reversible Addition Fragmentation Chain Transfer (RAFT) [Donovan et al., 2002; Baum and Brittain, 2002; Lutz and Matyjaszewski, 2003] since difficulties to maintain high and constant ATRP equilibrium with acrylamides were reported [Xia and Matyjaszewski, 2002]. However, ATRP synthesis method was specifically selected for the stake of simplicity. It allows the synthesis of homopolymers and statistic copolymers using only one initiator for the two monomers contrary to RAFT where each monomer would usually require one initiator. This last statement has to be moderated since RAFT synthesis of acrylamides using only one initiator for several monomers was recently reported with very good results concerning both the polymer chain size and the molecular weight distribution ($\bar{D} < 1.2$) [Read et al., 2014]. This path involves the synthesis of RAFT/MADIX agents which adds a supplementary synthesis step for the polymerization. For this reason, ATRP route was chosen to use commercially available initiators only and because of previously reported success of ATRP on poly(*N*-alkyl)acrylamides [Ding et al., 2004] with good control over M_n and relatively low dispersity. Furthermore, Wever and *al.* reported ATRP synthesis of *N*-isopropylacrylamide (PNIPAm) and block copolymers of poly(NIPAm-co-AAm) in aqueous solvent at RT which is preferable for practical, safety and environmental reasons [Wever and Broekhuis, 2012].

For homopolymers the targets were reached with an experimental M_n of 63 000 g/mol and of 68 000 g/mol, for PDMA and PAAm respectively, for a targeted M_n of 50 000 g/mol. $\bar{D}$ of homopolymers remains of the order of 1.5 which confirms the control of the polymerization process. For copolymers, it is obvious that even though the obtained M_n remains close to the targeted one (50 000g/mol), however slightly higher, the dispersity is higher than that of homopolymers. Reactions involving PDMA are more difficult to control due to exothermicity of the reaction. PAD-50/50-50 synthesis shows that control has certainly been lost since both dispersity and molar mass are higher than expected.

It must therefore be stated that the obtained dispersities stay beyond what could be expected for a perfectly successful ATRP synthesis, with $\bar{D}$ within the 1.05-1.1 range [Destarac, 2010]. However, as previously indicated, ATRP synthesis is not the best way to conduct Controlled Radical Polymerization on acrylamides. Indeed, the control of the polymerization process relies on the

equilibrium between dormant and active species and is catalyzed by the ligand/metal complex, here the Cu/ Me₆-TREN couple. Me₆-TREN is an hindered tetradentate ligand as illustrated in figure II.7, bearing four nitrogen group dedicated to complex the copper atom. Poly(N-alkylacrylamides) and poly(acrylamide) are substituted with amide functional group thus also composed of a large amount of nitrogen atoms. A valid hypothesis consists in the deactivation of the catalyzer by the growing polymer chains, leading to a loss of control of the equilibrium between dormant and active species, which leads to a Free Radical Polymerization process.

To check whether it was really possible to control targeted M_n , other trials were made to synthesize polymers and copolymers of different M_n . Results are close to those obtained for polymers of smaller size, with a good control over polymer size and still a dispersity reaching higher value than those expected for ATRP on adequate monomers. Higher M_n than targeted could indicate a slow initiation leading to increasing DP_n as it is the case for PAD50/50-50 and PDMA-50, while a lower M_n could indicate transfer reaction leading to polymer with inferior M_n like PAD80/20-200 and PDMA-200. For PDMA-500 and PAD-50/50-500 of high targeted M_n , experimental M_n are slightly higher than expected but looking closely to figure II.5, maybe a slow initiation can be the cause of the higher value. The others synthesis are very close to the expected M_n . High conversion rate (>70%) remains hard to obtain and aside from PAAm, higher conversion led to an increase of dispersity. As a matter of a comparison, Free radical Polymerization of PDMA was run and yielded a highly branched polymer. This experiment confirmed the choice of controlled polymerization to synthesize the polymers needed for adsorption experiments.

No data are available concerning the dispersity or the M_n of PDMA-FRP synthesized by Free Radical Polymerization because it was unfit for SEC analysis, due to its high viscosity leading to the hypothesis of a high dispersity and branched polymer [Needles and Whitfield, 1964]. ¹H and ¹³C structural characterization of polymers: PDMA-1 NMR ¹H: (400 MHz, D₂O, δ , ppm): 2.88 (s, 6 H), 2.59 (m, 1 H), 1.60 (m, 2 H), 1.34 (m, 1 H)

PDMA-1 NMR ¹³C: (400 MHz, D₂O, δ , ppm): 179.49, 175.97, 37.90, 37.39, 35.91, 34.94

PAAm-1 NMR ¹H:(400 MHz, D₂O, δ , ppm): 7.61 (t, 2 H), 6.91 (m, 2 H), 3.76 (s, 4 H), 2.87 (t, 4 H), 2.67 (s, 4 H), 2.50 (t, 4 H), 1.58 (m, 4 H), 1.32 (m, 12 H), 0.91 (m, 6 H)

PAAm-1 NMR ¹³C: (400 MHz, D₂O, δ , ppm): 175.92, 37.07, 35.92

4.2 Surface chemistry of silica suspensions

Silica colloidal suspensions are complex systems which stability and reactivity are driven by their chemical environment, as seen in Chapter 1. The goal here is to better understand how silica nanoparticles respond to a change of their environment, to get insight of the silica surface state when it is used in hybrid hydrogels gels or with linear polymer chains in solution i.e, in diluted conditions. The impact of pH and ionic force were investigated using pH, conductivity and dynamic light scattering measurements and silica content was assessed using gravimetric analysis. In table II.4 are reported the physico-chemical properties of Ludox TM-50[®] silica sol, provided by the supplier and those tested at the lab.

Data	pH	[Na ₂ SO ₄] (wt%)	Radius (nm)	Specific surface (m ² /g)	Conductivity (mS/cm)	Silica fraction (wt%)
Furnisher values	8.5-9.5	0.135	13.5	110-150	-	50
Tested values	8.8-9.2	0.2	13 (SAXS) 14 (SEM)	100	4.9-5.2	52

Table II.4 – *Physico-chemical properties of Ludox TM-50[®]. Density value for silica is fixed at 2.3 for all calculations and density reported for Ludox TM-50[®] is 1.4*

In figure II.12 is displayed a SEM picture of crude suspension of Ludox TM-50 nanoparticles, showing monodispersed spherical silica nanoparticles.

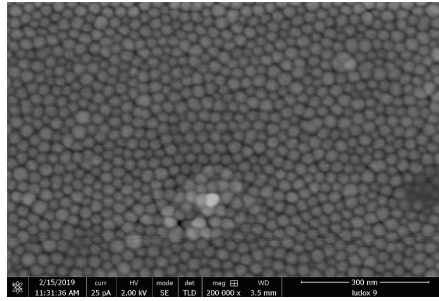


Figure II.12 – *SEM picture of Ludox TM-50.*

Conductivity and pH were approximately the same for all tested batches. pH was always found ranging from 8.8 to 9.2 which correspond to the stability domain of silica nanoparticles [Iler, 1979]. These values are used for concentrated sol to ensure stability especially to prevent particles agglomeration since 1) basic pH favor the formation of silanolates at the particle surface, 2) negative charges prevent agglomeration by electrostatic repulsion and 3) the weak salts concentration contribute to the overall stability by decreasing the Debye length λ_D allowing an increase of particles concentration. The silica content was found to be around 52 wt% for all tested batch.

4.2.1 pH effect on dilution behavior of Ludox TM-50[®]

Dilution in pure water

For all conducted work, special attention was paid to the control of silica surface chemistry. In hybrid gels or dilute solutions, Ludox TM-50[®] is always used in dilute conditions. So, the study of pH evolution during dilution was investigated in pure water and in presence of salts (mono- and divalent). pH variation from the crude silica suspension was defined as $\Delta\text{pH} = \text{pH}_{\text{diluted}} - \text{pH}_{\text{Ludox}}$. Contrary to the usual expectation, the pH values do not decrease monotonically when the neat Ludox suspension (pH 8.8-9.5) is diluted, as illustrated in figure II.13.

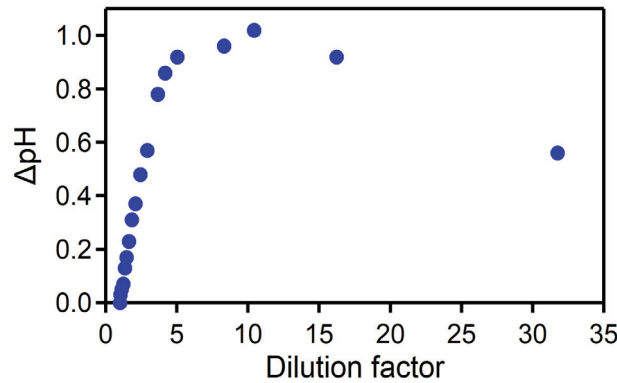
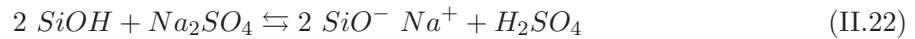


Figure II.13 – ΔpH defined as $(pH_{diluted} - pH_{Ludox})$ of Ludox TM-50[®] upon dilution with pure water.
Dilution factor is calculated as $(V_{Ludox} + V_{H_2O})/V_{Ludox}$

The increase of pH during dilution is surprising since the addition of deionized water (with a lower pH) is expected to lead to a lowering of pH values. One explanation for this unexpected behavior would be the presence of Na_2SO_4 salts in the suspension leading to the following equilibrium:



Silanolates protonation provoked by the addition of water leads to an increase of pH until it reaches a maximum observed for a concentration of 45g/L in silica (2 vol%/4.5 wt%).

The pH can increase by almost one unit value during dilution and this must be taken into account for two reasons:

- the silica surface chemistry strongly depends on pH, such an increase impacts the proportion of silanols and silanolates at the surface which could tune the adsorption ability of the polymers onto the particles.
- The purchased Ludox TM-50[®] has a pH within the 8.5-9.5 range. For batches with a pH around 9.5, dilution by a factor 10 could bring pH values around 10.5 which is close to dissolution threshold of silica [Iler, 1979].

Dilution in the presence of monovalent and divalent salts

As ionic force is also of main importance in the silica surface chemistry the same experiments are conducted on suspensions containing 50 mmol of monovalent salts (NaCl) and divalent salts (Na_2SO_4), which corresponds to an ionic force closed to the one of pure Ludox TM-50[®] of 5 mS/cm.

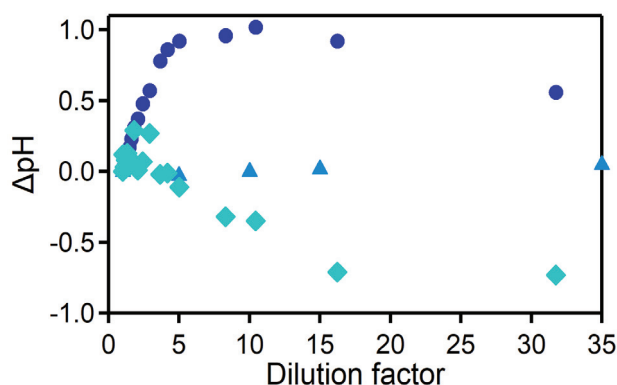


Figure II.14 – ΔpH of Ludox TM-50[®] during dilution with 50 mmol NaCl (blue triangles) and with 50 mmol Na₂SO₄ (turquoise diamonds). Dilution of Ludox in pure water is also displayed as a reference (dark blue dots). Dilution factor is expressed as $(V_{Ludox} + V_{H_2O})/V_{Ludox}$

Contrary to the dilution in pure water, dilution with a 50 mmol solution of NaCl does not lead to an increase of pH as shown in figure II.14. The pH is slightly decreasing before stabilizing. It is in good accordance with the previous results of dilution in pure water since the increase of pH is believed to be due to the equilibrium taking place between dissociated salt and silica nanoparticles in suspension in water.



Adding NaCl in the solution displaces the equilibrium towards the association of the Na^+ cation with the silanolate group (right hand side) thus lowering the pH. As the salt concentration is constant, the pH value does not change during dilution. In the presence of Na₂SO₄ (divalent ions), after a small increase at weak dilution factors, pH values start to decrease. This behavior is still in good agreement with the hypothesis made previously, the impact seems only stronger with divalent ions.

Experiments led on silica have allowed to characterize more precisely the Ludox TM-50[®] behavior, especially under dilution. **pH will be the key parameter for all synthesis to control surface chemistry and/or to tune the aggregation state of the sol.** The ionic force value can change significantly during dilution but this factor will not be tuned as silica is usually used in diluted conditions so that experiments are all conducted at weak ionic force. At these high dilutions, pH is the driving parameter for the silica surface chemistry thus the one kept constant throughout this study.

4.3 Adsorption isotherms of PAAm, PDMA and P(AAm-co-DMA) on silica nanoparticles using TOC depletion method

Here are presented the results for several analysis conducted to assess the adsorption behavior of previously synthesized polymers or commercial polymers of PAAm and PDMA. The goal is to characterize adsorption of both PAAm and PDMA onto silica nanoparticles with a constant surface chemistry. A specific interest is given to PAAm since contradictory data are found in the literature.

4.3.1 Adsorption isotherms on homopolymers of PAAm and PDMA

As previously mentioned, the same procedure has been applied for the adsorption experiments of PDMA, PAAm and copolymers on silica beads. Increased concentrations of polymer were added in silica suspension with a fixed concentration of 0.25vol% (i.e., 5 g/L equivalent to an available silica area of 46 m²). The samples were provided with sufficient time for adsorption and reorganization of the chains at the silica surface before the nanoparticles were removed. The amount of adsorbed polymer is tested by dosing the remaining quantity of polymer in the supernatant. The amount of adsorbed polymer on silica nanoparticles, Γ (in mg.m⁻²) is plotted against the polymer concentration (in g/L) in figure II.15. In the case of PDMA, a strong adsorption regime is observed at low coverage with a sharp increase of the adsorbed amount up to $\Gamma \approx 0.5$ mg.m⁻². This regime corresponds to the adsorption onto silica surface with nearly all polymer segments interacting with silanols groups (meaning a higher proportion of polymer chains in trains conformation compared to loops and tails) with amounts in good agreement with the ones previously reported in the literature [Hourdet and Petit, 2010]. This regime is followed by a weaker interaction domain (starting from $\Gamma > 0.5$ mg.m⁻²) before reaching a plateau value with a $\Gamma_{max} \approx 1.04$ mg.m⁻². As expected, PDMA adsorption isotherm displays two regimes. First, the adsorbed polymer amount increases rapidly with polymer concentration then it reaches a plateau value which does not change with further increase of polymer concentration [Frantz and Granick, 1994; Chaplain et al., 1995]. Using the Langmuir isotherm model, the equilibrium constant K is evaluated at ≈ 30 L.g⁻¹, confirming strong interactions between PDMA and silica surface.

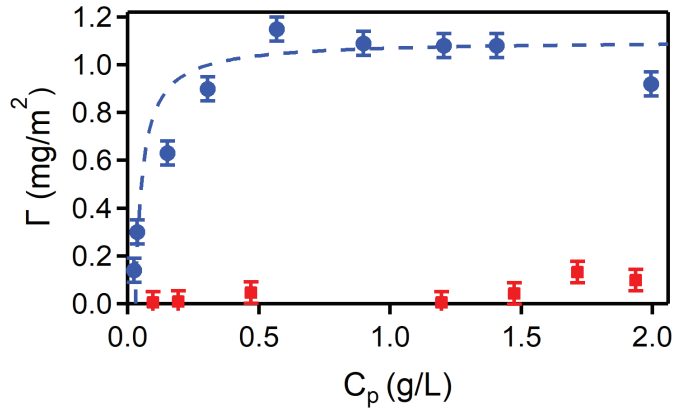


Figure II.15 – Adsorption isotherms of PAAm-200 (red squares) and PDMA-200 (blue dots) as a function of the remaining concentration of polymer C_p for SiO₂ 0.25 vol% concentration. The adsorbed amount Γ is expressed in mg of polymer per m² of silica surface. The blue dashed line is obtained from the Langmuir isotherm $\Gamma^{-1} = \Gamma_{max}^{-1}(1 + K^{-1}C_p^{-1})$, with Γ_{max} , the maximum adsorbed amount and K , the Langmuir equilibrium constant (in L.g⁻¹).

Conversely, PAAm adsorption isotherm displays no strong adsorption regime and a much lower plateau value with $\Gamma_{max} \approx 0.07$ mg.m⁻² and the fit using Langmuir isotherm does not give relevant results. As theoretically described by Scheutjens and Fleer [Scheutjens and Fleer, 1979] the amount of non ionic polymers adsorbed at liquid/solid interfaces mainly depends on their affinity for the surface. In the present case, the lower amount of adsorbed PAAm clearly shows a lack of affinity for silica surface under the given chemical conditions. This difference of behavior remains puzzling

since the two polymers are structurally quite close. The larger binding energy of adsorption for PDMA compared to PAAm can be correlated to the higher strength of proton acceptor (or higher polarizability) of the carbonyl group in the disubstituted amide compared to the primary one, as illustrated in figure II.16.

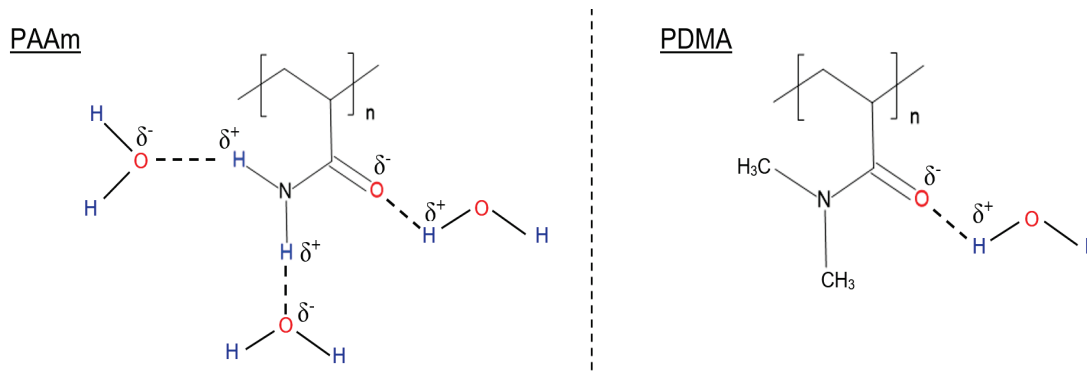


Figure II.16 – On the left, schematics of hydrogen bonding sites of PAAm (donnor and acceptor). On the right, hydrogen bonding sites of PDMA (donnor site on the carbonyl group).

Furthermore, as PAAm amide group is both proton acceptor and donnor, it could lead to a stronger affinity with its solvent that prevents adsorption between PAAm and the silica surface. This hypothesis is supported by the theoretical work conducted by Molinari *et al.* on the role of polymer solvation for the adsorption of the polymer on the silica surface [Molinari and Angioletti-Uberti, 2018].

4.3.2 Impact of molecular weight and molecular weight distribution on adsorption of PDMA and PAAm

Impact of molecular weight, M_n

It has been demonstrated that adsorption abilities are sensitive to increasing M_n and polydispersity of samples [Liu and Xiao, 2008; Mathur and Moudgil, 1997]. Adsorption isotherms of PDMA of different size (PDMA-50, 63 000 g/mol and PDMA-200, 150 000 g/mol) are depicted in figure II.17 and demonstrate the marked influence of the polymer molecular weight on the extent of adsorption. This arises from the bonding of the macromolecules with the solid surface via a limited number of segments. The total amount of the adsorbed polymer is increased for higher molecular weight due to the greater participation of loop and tail segments at the interface. PAAm of different size (PAAm-50, 68 000 g/mol and PAAm-200, 230 000 g/mol) show few affinity towards silica surface with no marked effect of the polymer chains length.

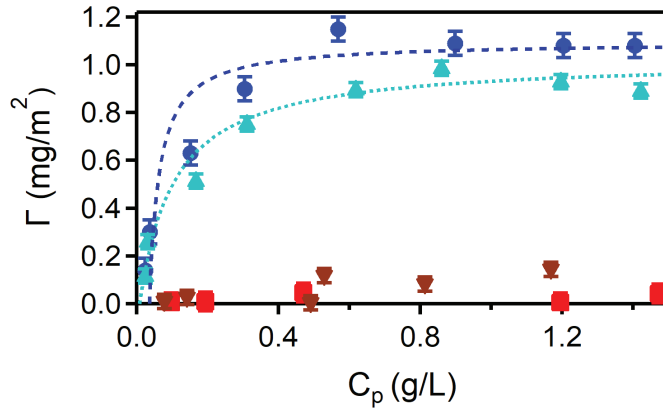


Figure II.17 – Adsorption isotherms of PDMA-200, 155 kg/mol (dark blue dots) and PDMA-50, 68 kg/mol (light blue triangles) and PAAm-200, 230 kg/mol (dark red triangles) and PAAm-50, 63 kg/mol (red squares). Silica concentration is fixed at 0.25vol% and measurements are performed at pH 9.

Impact of polymer architecture

The adsorption isotherms of linear (PDMA-200) and branched PDMA (PDMA-FRP) are displayed in figure II.18 and reveal the impact of the dispersity and polymer architecture on the adsorbed amount. PDMA-FRP does not show feature of strong interactions with silica nanoparticles and reach a lower plateau value with $\Gamma_{max} < 0.8 \text{ mg/m}^2$. It indicates that dispersity and topology may have an important impact on the adsorbed amount, underlying the importance of using linear polymer chains to assess adsorption ability.

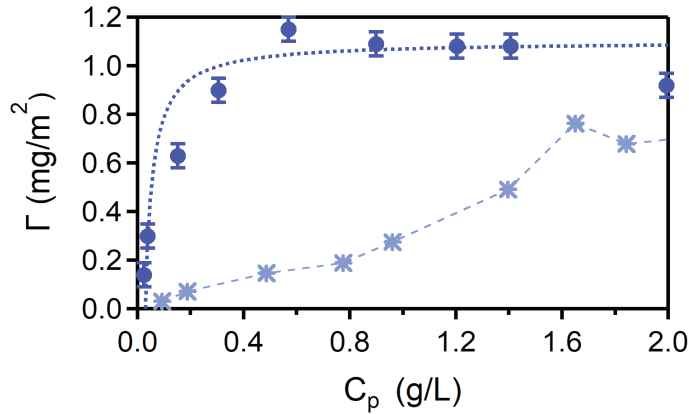


Figure II.18 – Adsorption isotherm of PDMA-200 (blue dots) and PDMA synthesized by Free Radical Polymerization, PDMA-FRC (purple stars) as a function of the remaining concentration of polymer C_p for 0.25 vol% silica concentration.

Questions remain concerning the accuracy of the measurement since the branched polymer that can be assimilated to a microgel may be partly removed along with the silica particles during the centrifugation process used to separate the particles from the non-adsorbed polymer.

4.3.3 Adsorption isotherms of P(AAm-co-DMA) at various AAm content

Adsorption isotherms of copolymers are displayed in figure II.19 for two copolymers and homopolymers of PDMA and PAAm as a reference of non-adsorbing/adsorbing behavior. The ratio of acrylamide and *N,N*-dimethylacrylamide in the obtained copolymers were checked using ^1H NMR which allowed to conclude that reactivities of both monomers are quite close, indicating statistic copolymerization. Compared to adsorption isotherms of pure PDMA or PAAm, the copolymers adsorption behavior significantly differs depending on their acrylamide content, reflecting the adsorption abilities of the two monomers composing them.

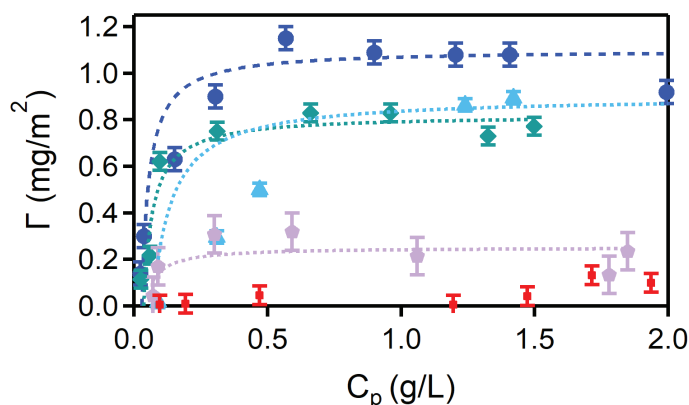


Figure II.19 – Adsorption isotherms of PAD 50/50-50 (blue-green diamonds), PAD 20/80-200 (light blue triangles), PAD 80/20-200 (light purple starred-shapes), PAAm-200 (red dots) and PDMA-200 (blue dots) as a function of the remaining concentration of polymer C_p for 0.25 vol% silica concentration, at pH 9.

Still, some discrepancies appear concerning the adsorbed amount relative to the acrylamide content. PAD-50/50-50 composed of half acrylamide and half *N,N*-dimethyl acrylamide possesses Γ_{max} close to the one of PAD-80/20-200, mainly composed of the adsorbing monomer. Furthermore it seems to possess a higher affinity with the silica surface with a constant K evaluated at 26 L.g^{-1} which is very close to the one obtained for PDMA homopolymer. The other copolymers show adsorbed amounts in good correlation with their acrylamide content but remain difficult to fit with Langmuir isotherms maybe due to the random repartition of the monomers.

The maximum adsorbed amounts (Γ_{max}) of the homopolymers and of copolymers are summarized in figure II.20.

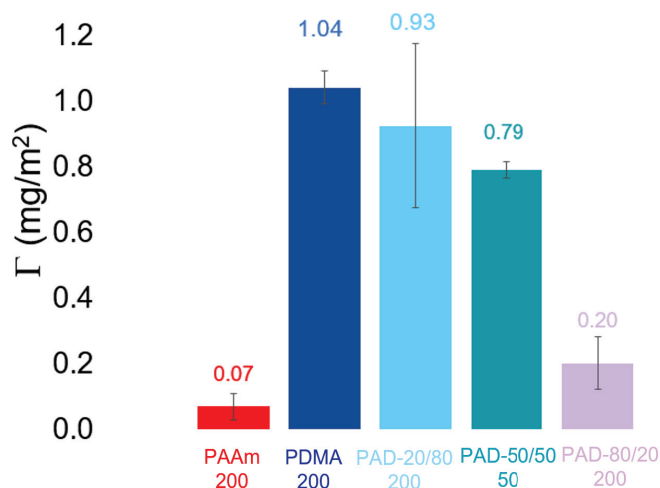


Figure II.20 – Adsorbed amounts Γ_{max} of PAAm-200 (red), PDMA-200 (dark blue) and of PAD 20/80-200 (light blue), PAD 50/50-50 (blue-green) and PAD 20/80-200 (light purple), in mg/m² for 0.25 vol% silica concentration at pH 9.

To summarize, adsorption isotherms of the homopolymers and copolymers were established using TOC technique. PDMA and PAAm displayed two distinct behaviors with a plateau value around $\Gamma_{max} \approx 1$ mg/m² increasing with increasing M_n for PDMA and $\Gamma_{max} \approx 0.1$ mg/m² for PAAm, independently of the polymer chain length tested.

For the considered chemical conditions (pH 9, silica concentration 0.25 vol% and weak ionic force in pure water), PAAm is not displaying strong affinity for the silica surface. This hypothesis is supported by the adsorption isotherms of the copolymers that show lowered Γ values for increasing PAAm content. Dispersity has also an impact on adsorbed amount with lowered Γ for highly dispersed polymer, lowering the adsorbed amount close to the one recorded for copolymers with high molar content of PAAm. Beside the chemical environment and the chemical nature of the monomers, the polymer architecture and dispersity have a very significant impact on the adsorption ability onto a given solid surface. This method allows quantitative measurement of the adsorption capabilities of the different polymers. Still others techniques were used, first to confirm the obtained results and secondly to provide other information such as the polymer conformation at the solid interface.

4.4 Zeta potential analysis

In order to obtain a more detailed description of the adsorption and the properties of the electrical double layer at the solid-solution interface, zeta potential measurement were performed.

4.4.1 Silica and polymers measurements

Experiments were first conducted on silica suspensions at various pH as illustrated in figure II.21.

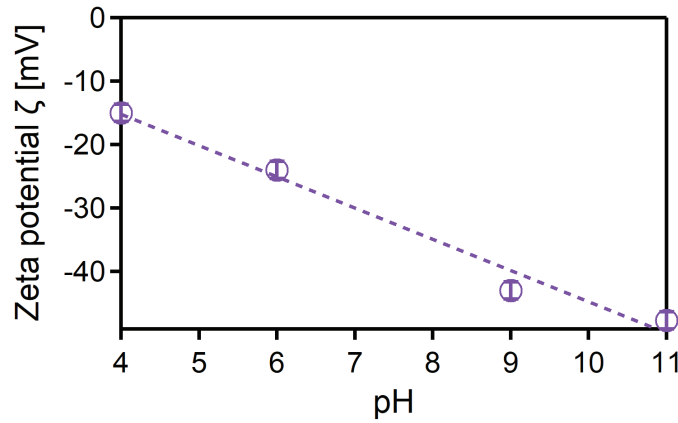


Figure II.21 – Zeta potential values (ζ , mV) of silica suspensions at 0.25 vol% concentration at several pH for conductivity of 0.1 mS/cm.

As expected, ζ values decrease for increasing pH, with recorded values in good accordance with the ones found in the literature [Hunter, 1985]. As the pH increases the density of silanol groups is enhanced which causes a change of the ionic double layer around silica nanoparticles, thus the plane of shear.

Polymer solutions are also tested at pH 9 to have the zeta potential reference values of PAAm and PDMA. The results are presented in the table II.5.

Polymer	Concentration (g/L)	ζ (mV)
PDMA-200	2	-2.49 ± 0.17
PAAm-c	2	-7.60 ± 0.39
SiO ₂	730	-43 ± 1.35

Table II.5 – Zeta potentials values ζ of PAAm-c (100 kg/mol) and PDMA-200 (155 kg/mol) at pH 9 and conductivity of 0.1 mS/cm and bare silica at pH 9 and conductivity of 5.2 mS/cm.

Recorded zeta potential values are inferior to that of silica nanoparticles which is expected for well-solvated neutral polymers. As they do not possess well-defined solid/liquid interface, the zeta potential of the solution does not seem perturbed by the presence of the polymers.

4.4.2 Zeta potential of adsorbing and non adsorbing polymer onto silica

Zeta potential measurements of PDMA-200 and PAAm-c with increasing concentrations in presence of silica nanoparticles at low ionic force ($I = 10^{-4}$ mol.L⁻¹, $\lambda_D = 15.5$ nm) are displayed in figure II.22.

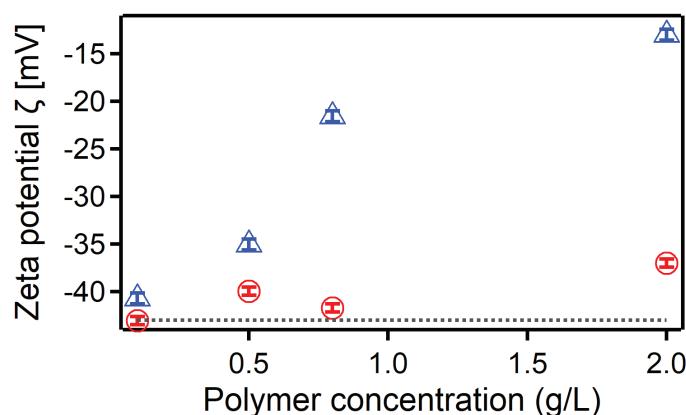


Figure II.22 – Zeta potentials of PAAm-c, 100 kg/mol (red circles) and PDMA-200, 155 kg/mol (blue triangles) conducted at fixed pH value ($pH=9$), conductivity ($\sigma=0.1$ mS/cm) and silica concentration of 0.25 vol%, as a function of polymer concentration (in g/L). Zeta potential of bare silica at 0.25 vol% at pH 9 is displayed as a reference (grey dashed line)

Polymer adsorption influences the distribution of charge in the diffuse part of the electrical double layer through modification of the shearing plane leading to the observed decrease of $|\zeta|$ values. For low concentrations of polymers (< 0.5 g/L) recorded zeta potential values are of the same order as bare silica, around -40 mV. For increasing concentrations of PDMA, the behavior starts to change with a decrease of $|\zeta|$ probably due to considerable covering of the active sites on the silica surface by adsorbing PDMA macromolecules. Hence the decrease of $|\zeta|$ for increasing concentration of PDMA is considered to be the result of the increased amount of adsorbed polymer. PAAm in contact with silica displays a completely different behavior with ζ values remaining within the range of those of bare silica for the whole range of tested concentrations, never exceeding -36 mV (against -13 mV for PDMA at the highest concentration of 2mg/mL). This indicates that PAAm in contact with silica particles impacts only weakly the silica/electrolytes solution electrical double layer, which implies a lack of surface interactions between the two compounds, reinforcing the idea of a non-adsorbing polymer.

4.4.3 Impact of molecular weight, M_n on PDMA adsorption

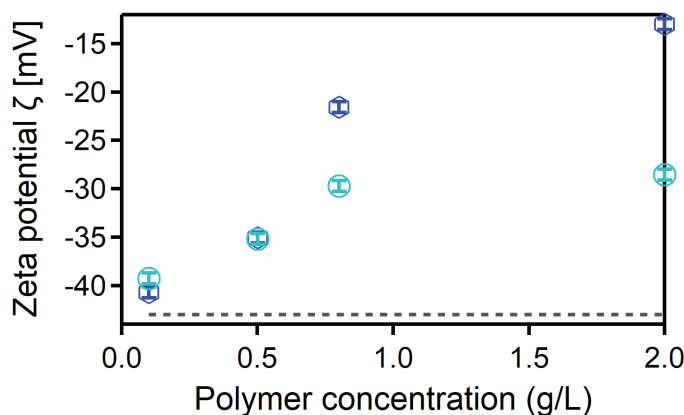


Figure II.23 – Zeta potential values of PDMA-c (40 kg/mol) (light blue dots) and PDMA-200 (155 kg/mol) (dark blue symbols) conducted at 0.1 mS/cm and at pH 9 as a function of polymer concentration.

Zeta potential of bare silica at 0.25 vol% at pH 9 is displayed as a reference (grey dashed line)

The shift of the plane of shear δ_e observed through the decrease of the zeta potential can be identified with the thickness layer and is thus sensitive to polymer molecular weight. In figure II.23, zeta potential values of PDMA of different sizes are displayed. They remain negative in all cases and both show a decrease of $|\zeta|$ with increasing polymer concentrations.

However, the increase is less pronounced for PDMA-c, of smaller M_n . This phenomenon has already been observed [Liu and Xiao, 2008] and could be due to a change of configuration of the adsorbed segments. The main conformation adopted by the polymer chains of smaller size (PDMA-c) at the particle surface is train conformation, leading to a thin adsorbed layer, with a slighter decrease of $|\zeta|$. For higher M_n , like PDMA-200, the conformations of adsorbed chains include loops and tails with larger size, increasing the thickness of adsorbed layer which leads to a greater shift of the slipping plane, thus larger $|\zeta|$ reductions. TOC analysis conducted on PAAm and PDMA already showed a clear influence of the molecular weight on polymer adsorption. Zeta potential measurements allow concluding that this behavior is correlated to a larger thickness of the adsorption layer, very likely due to longer loops and tails for chains with higher molecular weights [Santore and Fu, 1997].

4.5 ^1H NMR solvent relaxation times to quantify adsorption

4.5.1 Silica and polymers measurements

Measurements of silica suspensions

Measurements were performed first on pure water and bare silica suspensions and on polymer solutions with increasing polymer content. The typical magnetization decay curves of silica suspension are illustrated in figure II.24.a. They extend over 8 sec and the relaxation time T_2 is measured over almost three decades in signal amplitude. One single T_2 value is observed in all cases, confirming the fast exchanges assumption. The reference factor R_{2sp}^0 is the relaxation rate of pure water (see equation II.19).

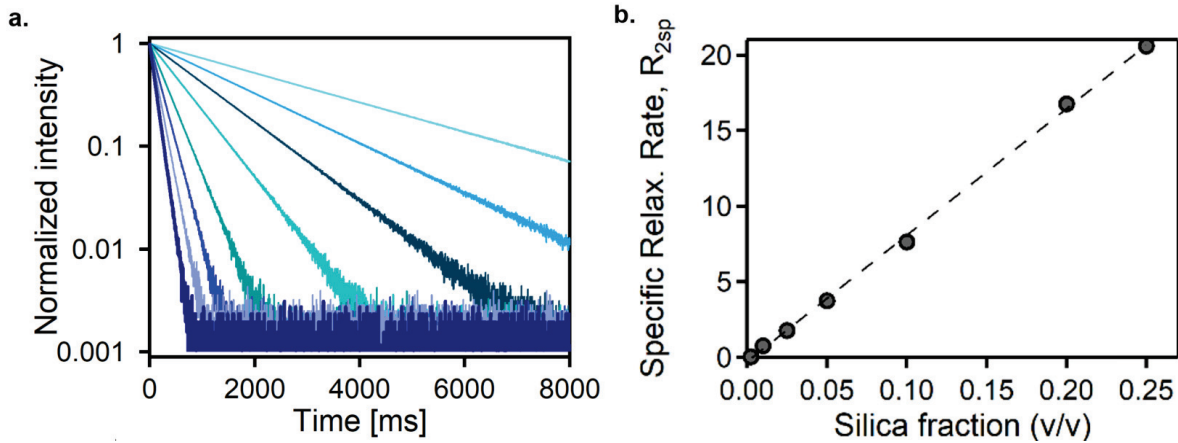


Figure II.24 – **a.** Typical magnetization decay curves for silica dispersions of various concentration: 0.0025 (light turquoise) , 0.01 (sky blue), 0.025 (dark green), 0.05 (turquoise), 0.10 (blue-green), 0.15 (blue), 0.20 (violet), 0.25 (dark blue) v/v. All curves were fitted with an exponential function. **b.** Specific relaxation rate constant R_{2sp} of bare silica suspension (grey dots) plotted against the silica volume fraction (0.0025, 0.01, 0.025, 0.05, 0.10, 0.15, 0.20, 0.25 v/v), fitted linearly (dashed black line).

Figure II.24.b shows the evolution of R_{2sp} of silica for suspensions of increasing concentration. The specific relaxation rate R_{2sp} increases linearly with increasing silica fractions.

Measurements of polymer solutions

R_{2sp} of pure water and PDMA-2 of several concentrations were tested to assess polymer impact on R_{2sp} . the corresponding results are displayed in table II.6.

Sample	Polymer wt%	T_2 [ms]	R_{2sp}
Pure water	-	3187	-
PDMA-0.05_SP0	0.05	2685	0.19
PDMA-0.1_SP0	0.1	2414	0.32
PDMA-0.2_SP0	0.2	2758	0.16
PDMA-0.5_SP0	0.5	2591	0.23
PDMA-1_SP0	1	3074	0.03
PDMA-1.5_SP0	1.5	2548	0.25

Table II.6 – Summary table of T_2 measurements and corresponding R_{2sp} of pure water and PDMA in pure water for increasing polymer concentrations

Adding polymer in the solution does not seem to disturb much the solvent average dynamics compared to the effect of silica. T_2 values are slightly decreased compared to that of pure water but increasing the polymer concentration does not lead to large R_{2sp} enhancement as seen for silica measurements, (see figure II.26). This is related to the fact that the dynamics of the polymer in solution remains fast from the NMR point of view.

4.5.2 Solvent relaxation times of PDMA/silica dispersions

Several PDMA concentrations have been tested (0.05, 0.1, 0.2, 0.5 wt %) for increasing silica content from 0 to 10 vol%. The specific relaxation rates were calculated taking as the reference R_2^0 , the relaxation rate of pure water. Results are displayed in figure II.25.

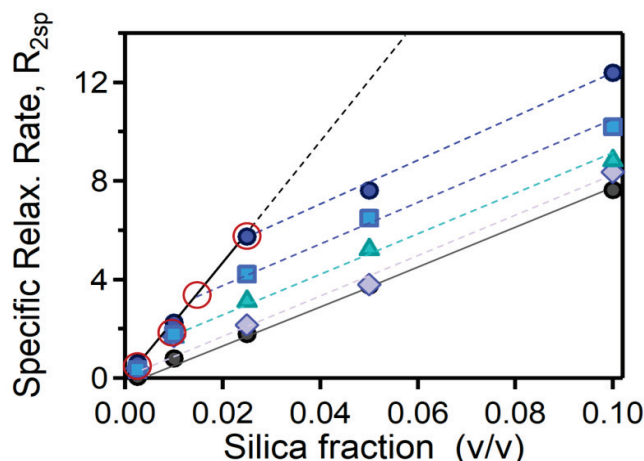


Figure II.25 – R_{2sp} of PDMA at several concentrations: 0.05 (purple diamonds), 0.1 (blue-green triangles), 0.2 (blue squares), 0.5 wt% (blue dots) for increasing silica volume fraction, from 0 to 0.1 v/v. R_{2sp} of aqueous silica dispersions is also displayed (grey dots). Transition points are highlighted (red circles).

Two linear domains are clearly identified with “transition” points, emphasized by red circles, which occur at different silica concentrations depending on the polymer concentration. The first regime (low silica concentration) is characterized by a strong enhancement of R_{2sp} for increasing silica concentration with a slope much larger than for the bare silica R_{2sp} (grey circles). This slope seems to be independent of the PDMA concentration. Then, a clear break in the slope is observed and obtained at lower silica concentration for PDMA solution of lower concentrations (0.05 wt% and 0.1 wt%). Since the polymer in solution alone has only negligible effects on the solvent mobility (see Table II.6), this enhancement can be reasonably attributed to adsorption of PDMA. Comparing the amounts of polymer and silica in the various solutions, it appears that in the first regime silica particles are fully covered by PDMA (adsorption plateau in Figure II.17). The bound fraction of solvent at the solid/liquid interface is increased as compared to bare silica since water coordinating adsorbed segments has reduced mobility. As previously reported [Nelson et al., 2002], neither loops nor tails polymer conformations are able to slow down the solvent enough to strongly impact the R_{2sp} . Only the train conformation can impact significantly R_{2sp} values, providing thus insight on the adsorbed polymer structure.

The second regime has a lower slope, comparable to that of bare silica. Beyond the break in the slope, all the available polymer is adsorbed and when free silica is added, the overall solvent dynamics is governed by solvent interacting with bare silica. Figure II.26 shows the proportionality between polymer concentration at the transition point and the silica concentration.

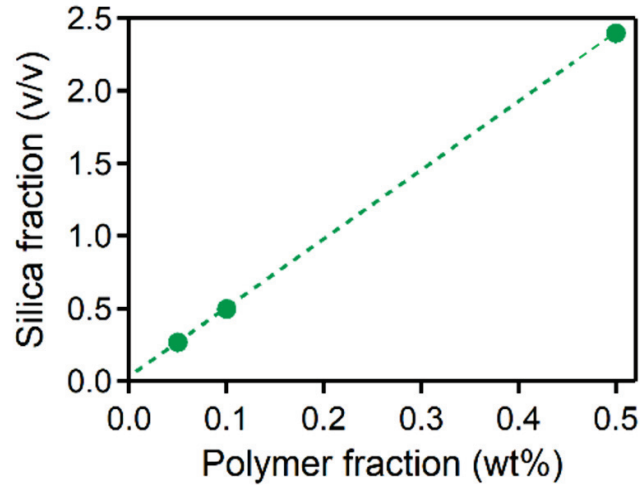


Figure II.26 – *Proportionality between silica volume fraction and initial polymer content (in wt %) at the ‘transition’ points between the two domains. (Preliminary data).*

Besides the information on the adsorbed polymer conformation, quantitative results can be calculated from these data. The adsorbed polymer amount Γ_{PDMA} (mg/m²) can be determined, assuming that the silica density is equal to 2.3, and the specific surface is equal to 100 m²/g, which gives the adsorbed amount $\Gamma_{PDMA} = 0.8$ mg/m². This value is consistent but slightly lower than the values obtained through TOC measurements with $\Gamma_{PDMA} = 1.04$ mg/m².

The difference in both values may be related to the fact that loops and tails do not contribute significantly to the reduction in polymer mobility while they contribute to TOC measurements. Based on the measured figures, it could be concluded that about 75 to 80% of the adsorbed polymer segments have a strongly reduced mobility, i.e. belong to trains or to very short loops. This conclusion however should be further confirmed by more extensive measurements.

4.5.3 Impact of non-interacting monomer

The same experiments were carried out on PAAm-silica dispersions and PAD50/50-50-silica dispersion. Results for a polymer concentration of 0.5 wt% are shown in figure II.27, the different polymers display distinct behavior.

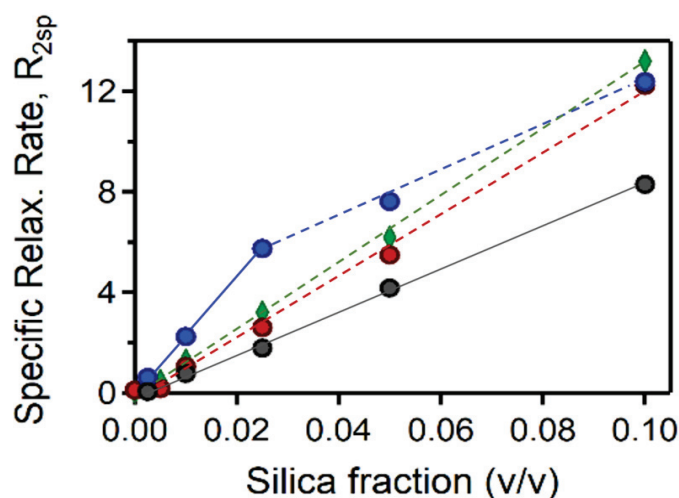


Figure II.27 – R_{2sp} of PAAm-200 (red dots), PDMA-200 (blue dots) and PAD50/50-50 (green diamonds) at 0.5 wt% for increasing silica volume fraction, from 0 to 0.1 v/v. R_{2sp} of aqueous silica dispersions is also displayed (grey circles)

PDMA 0.5 wt%-silica is represented as a reference of the adsorbing polymer. R_{2sp} of PAAm shows an enhancement compared to the one of the bare silica R_{2sp} , but the slope still remains inferior to PDMA R_{2sp} over the same range of silica concentrations. Furthermore, in contrast with PDMA results, no transition point is observed, meaning that plateau value of adsorption is not reached. As a very small amount of polymer is adsorbed per unit surface (of order 0.1 mg/m²), the transition point should be located around 0.25 v/v silica, well beyond the range shown in figure II.27. Attempts to realize measurements at higher silica content were realized but all led to gelation of the samples beyond 0.15 v/v silica. Altogether, this result is consistent with a polymer displaying few affinity towards silica surface. This is in good accordance with the PAAm-silica interactions values provided by TOC experiments where the adsorbed amount Γ is evaluated around 0.1 mg/m². Hypothesis about the conformation of PAAm at the interface can also be made given the fact that spin-spin relaxation measurements are specifically sensitive to train adsorbed segment. The lower slope of the curve can indicate that only a tiny fraction of polymer is adsorbed through train segments.

For the copolymer PAD50/50-50, the behavior is similar to that of PAAm, with an increased slope compared to bare silica and PAAm specific relaxation rates but still lower than PDMA values. The enhanced slope compared to PAAm is expected to be due to presence of PDMA segments able to strongly adsorb onto silica particles. Like PAAm, no transition point is observed which is surprising given the PDMA content. With an adsorbed amount of order 0.8 mg/m², the transition point should actually be located close to that of PDMA. A possible interpretation is that the adsorbed PAD50/50-50 copolymer has a significantly lower train fraction, i.e. a smaller fraction of the adsorbed polymer has a strongly reduced mobility. An hypothesis to explain this phenomenon could be that PAAm segments statistically distributed along the chain prevent the copolymer to form trains. Once again, this hypothesis should be confirmed by further measurements.

5 Conclusion

In this chapter, several techniques were used or developed to assess quantitatively the adsorption of linear polymer chains onto non-modified silica particles of defined diameter and controlled surface chemistry (fixed pH and low ionic force) using PDMA, PAAm and statistic P(AAm-co-DMA) with several molar ratio of the two monomers.

The first step consisted in finding a way to synthesize the homopolymers and statistic copolymers of PAAm and PDMA prior to evaluating their adsorption abilities. While ATRP remains a challenging way to synthesize these polymers in a controlled manner, its simplicity compared to others polymerization routes and the relatively good control obtained over M_n and dispersity allowed to produce the desired compounds. Several parameters of the reaction could be optimized such as a change of ligand or initiator to get full control of the reaction and significantly lower the dispersity index along with higher conversion rate. This kind of synthesis is very time consuming to master but could be an interesting lead to follow in the future.

Depletion method using TOC measurements, ^1H NMR solvent relaxation times and zeta potential measurements of solutions of PAAm, PDMA and silica indicated a good affinity of PDMA for silica surface with experimental plateau value Γ (mg/m^2) ranging between 0.8 (NMR) and 1.04 (TOC). The lower value obtained using NMR measurement can be due to the low sensibility of the technique for polymer adsorbed in loops and tails conformations. The ratio between both results may thus be related to the fraction of trains in adsorbed chains. Zeta potential measurements also showed a significant modification of silica surface when PDMA is present with an enhancement of the $|\zeta|$ which is attributed to the polymer adsorption. The same experiments conducted on PAAm revealed low affinity of the polymer for silica surface with experimental plateau value Γ (mg/m^2) close to 0.1 which is way lower than PDMA. Both NMR and zeta potential experiments showed that even though PAAm is interacting with silica, its adsorption abilities in the chosen conditions are weak. Copolymers displayed an adsorption behavior impacted by PAAm segments leading to intermediate behavior with higher experimental Γ values than PAAm but ranging between 0.2 and 0.8 mg/m^2 depending on the molar ratio of PAAm. NMR measurements confirm the absence of strong adsorption. For the copolymer the discrepancy between adsorption and NMR results may be related to a quite different (lower) fraction of trains. It would be interesting to continue the experiments on other copolymers to precisely assess the amount of PDMA necessary to obtain adsorption behavior close to pure PDMA which would be the ratio for which PAAm does not disrupt adsorption. These experiments allowed to define the adsorption behavior of polyacrylamide in its pure, non-modified, neutral form onto non-modified silica particles surface which remained lightly described in the literature. These experiments confirmed the non-adsorbing behavior of PAAm solubilized in water towards pure silica nanoparticles and the copolymers adsorption data validate the strategy to use PAAm to tune PDMA affinity for silica surface.

The strongly different adsorption behavior of PDMA and PAAm may seem difficult to explain as both polymers have relatively similar structure. However, their affinity towards the solvent (water) is quite different. While water is a theta solvent for PDMA, it is a good solvent for PAAm. This may be the predominant factor explaining the difference in adsorption behavior in the presence of water.

The next step is now to synthesize hybrid gels of PDMA and PAAm with special care taken to the control of the silica nanoparticles dispersion state to assess the impact of non-adsorbing monomer on the gel structure and the mechanical behavior.

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Chapter III

Tuning polymer/particles interactions in hybrid hydrogels

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1 Introduction

The introduction of solid particles in a polymer matrix to form hybrid gels may provide remarkable mechanical properties, as described in the first chapter. However, the understanding of the relative contributions of the various physical mechanisms that can explain mechanical reinforcement remains an interesting point to issue. The reported studies on PDMA/silica hybrid gels clearly indicate the importance of polymer adsorption for gel toughening or adhesion properties, knowing to which extent remains an open question though.

The idea here is to assess the impact of polymer adsorption in hydrogel toughening by tuning the reversible polymer/silica interactions. While poly(*N*-alkylacrylamides) are known to be able to form hydrogen-bonds with silica surfaces [Petit, 2007], the study conducted in Chapter II demonstrated and quantified the adsorption of linear polymer chains of poly(acrylamide) onto silica, showing lower interactions.

First attempts were made to synthesize PAAm/silica nanocomposites hydrogels, with some of them showing a decrease of mechanical properties using PAAm, supposedly non-interacting with non-modified silica nanoparticles, instead of poly(*N*-alkylacrylamides) [Lin et al., 2011; Rose et al., 2013a]. Still, some authors argue on the presence of strong interactions between PAAm and silica [Jang and Park, 2002]. Furthermore, those studies did not assess the dispersion state of the nanoparticles within the polymer matrix which could be affected by the presence of a non-interacting polymer and so far the reported mechanical properties were performed on swollen samples only.

Experimental evidences point out that polymer adsorption happens within a certain range of parameters in term of polymer/solvent, polymer/substrate affinities, nanoparticles nature and chemical environment (pH, ionic force) [Griot and Kitchener, 1965a; Bessaies-Bey et al., 2018]. This was also supported by theoretical work [Molinari and Angioletti-Uberti, 2018]. Adsorption is thus very sensitive to experimental conditions. Therefore it is important to investigate thoroughly the structure and behavior of PDMA and PAAm hybrid gels of similar composition while keeping control over the chemical environment of the nanoparticles (pH, ionic, force, dispersion state) so as to truly identify the reinforcement mechanisms at stake.

Two strategies were followed. First, by changing the nature of monomer from interacting *N,N*-dimethylacrylamide (DMA) to non-interacting acrylamide (AAm) while keeping constant the silica surface chemistry and the dispersion state. Using SANS experiments, it was confirmed in a previous paper that in our systems, silica nanoparticles embedded in PDMA matrix are well-dispersed [Rose et al., 2013b]. This has not been checked yet for PAAm/silica nanocomposites, so that the study of the impact of reversible interactions alone can be evaluated. Secondly, the polymer/nanoparticles associative interactions were disturbed by tuning the surface chemistry of the nanoparticles. The time-dependence, fracture energy and conditions for modulus recovery of hybrid hydrogels where adsorption is purposely inhibited will be probed, specifically at large strain.

More generally, understanding the role played by adsorption could be relevant for other materials, including other types of nanocomposite gels and for filled elastomers. In the case of elastomers, tuning adsorption could play a role to control the dispersion state during the mixing process, as solid particles are known to be very difficult to disperse in a rubber matrix. [Mujtaba et al., 2012; Perez-Aparicio et al., 2013].

The hybrid gels composition was fixed to reach the compromise between stretchability and stiffness. The general architecture is schematically represented in figure III.1.

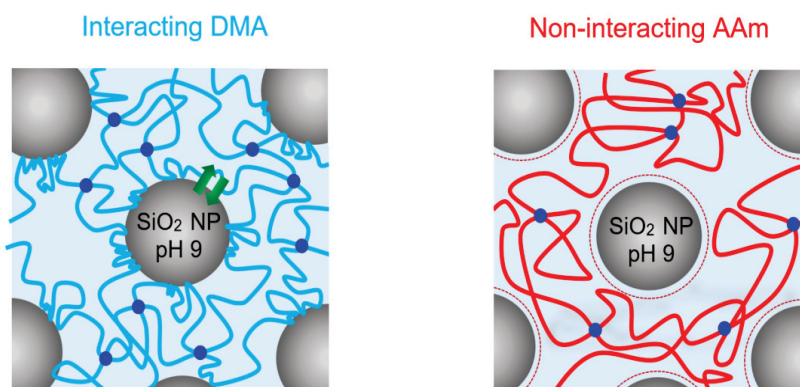


Figure III.1 – On the left, schematic representation of PDMA hybrid hydrogels combining covalent cross-links (dark blue dots) and physical interactions (adsorbed polymer chains at the surface of silica nanoparticles, sketched in blue). Arrows symbolize the exchange processes between adsorbed and unadsorbed polymer segments at the silica surface. On the right, PAAm hybrid gels. The lack of interactions between the polymer chains (red) and the nanoparticles (NP) leads to depletion zones around the silica NPs (dashed circles).

Three important points should be underlined: (1) a small amount of chemical cross-linker (0.1mol%) was added to fix the network topology. This small value is a compromise to overcome the ill-controlled self cross-linking that takes place during polymerization process [Carlsson et al., 2010] and to avoid a dramatic reduction of the cross-linking extensibility. (2) To be able to compare the samples quantitatively, the hybrid gels structure and mechanical behavior were characterized at the gel preparation conditions. Thus the gel matrix hydration is well-controlled and the silica volume fraction is fixed at 20 vol%, which correspond to the maximum amount using the commercial suspension Ludox-TM 50. (3) Synthesis of PAAm/silica hybrid gels was developed to keep good control over the dispersion state of silica particles in the polymer network. After a short description of the synthesis procedure, we first present the structural results of the silica dispersion state within the polymer matrices then the mechanical characterization at small and large strain. We will specifically focus on the modification of the mechanical properties and on the time-dependence of the mechanical response when the monomer is substituted or when the silica surface chemistry is modified.

2 Principles and techniques

In the following section, the principles of the synthesis route developed and some of the analysis techniques used are presented for the reader's convenience only. A skilled reader can skip this section and go directly to the 3rd section, Materials and Methods.

2.1 Titration of extractibles

Hybrid gels were synthesized via *in situ* radical polymerization, with chain growth and cross-linking occurring at the same time. This synthesis method is known to lead to heterogeneous structures with a broad size distribution of chains [Norisuye, 2002] and unbounded elements, such as unreacted

MBA cross-linker or uncrosslinked oligomers and unreacted monomers referred to as extractibles. In order to quantitatively determine extractibles molecules, a rectangular piece of gel was immersed in excess solvent. The gel swelled in this medium and the uncross-linked material could be extracted from the gel. The swollen sample was then analyzed using Thermal Gravimetric Analysis (TGA) to estimate the remaining quantity of organic and inorganic material within the sample. Another technique used to determine extractibles was to dry the gel sample in an oven (at 100 °C). After it reached its swollen equilibrium state it was then weighted it to calculate the weight loss during the swelling that corresponds to the extractible content.

2.2 Mechanical properties

Mechanical tests were performed using an uniaxial tensile device to investigate the mechanical properties of hydrogels (tensile behavior, dissipative process, relaxation, fracture energy) in relation with their macromolecular architecture, as illustrated in figure III.2.

The device is equipped with home-made clamps suited for soft samples and a video extensometer which can precisely follow the local displacement of markers to rule out slipping of the sample during the test. Experiments conducted at low strain rate are performed in an immersion cell to avoid any drift in the sample composition.

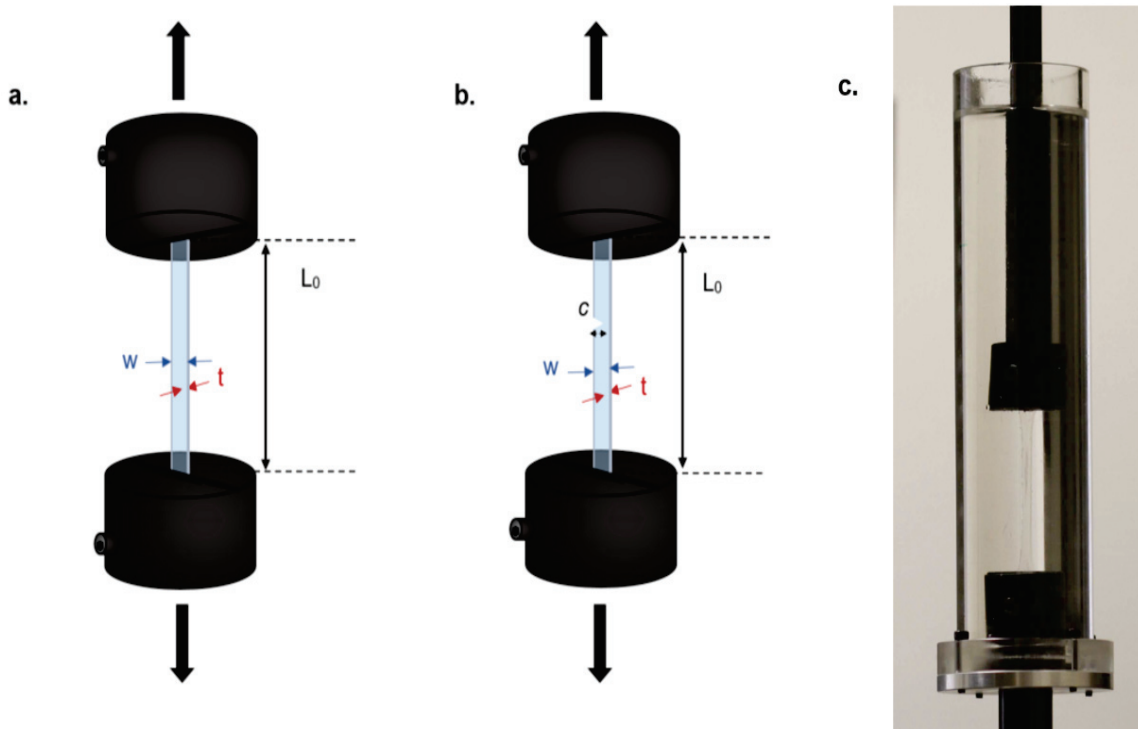


Figure III.2 – *a. Uniaxial tensile geometry. b. Fracture experiments geometry. Sample is notched on a defined length (c) prior to uniaxial deformation. c. Immersion cell*

During the test, the force F and displacement L were recorded while the nominal (engineering) stress σ_N and the strain ϵ were calculated. The nominal (engineering) stress σ_N was defined as the tensile force per unit of non deformed area and the true stress σ_T was calculated assuming

iso-volume deformation, thanks to the following relation:

$$\sigma_T = \sigma_N \times \lambda \quad (\text{III.1})$$

$$\lambda = \frac{L}{L_0} \quad (\text{III.2})$$

with λ , the strain ratio. The true strain ϵ_T is calculated according to:

$$\epsilon_T = \ln(1 + \epsilon_N) \quad (\text{III.3})$$

The definition of true strain is usually used for the characterization of materials exhibiting plastic deformation and studied here because of the viscoelastic behavior displayed by the samples.

From these data, the classic representation used is the nominal stress σ_N as a function of the strain, as shown in figure III.3. Tests were conducted on samples of defined dimensions (length, $L_0=25$ mm, thickness $t=2$ mm, width $w=5$ mm).

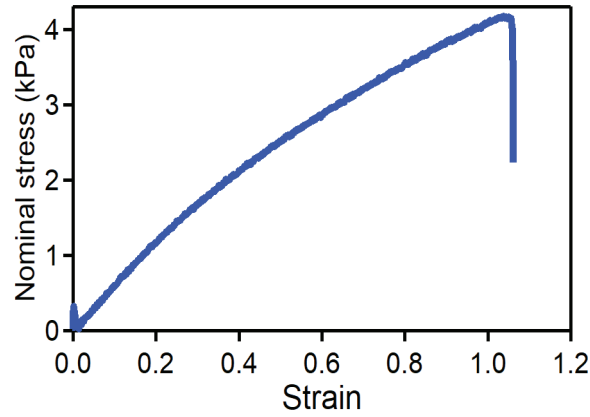


Figure III.3 – Stress-strain curve of PDMA chemical hydrogel weakly cross-linked (0.1 mol%).

Several strain rates were applied, from $3 \cdot 10^{-4} \text{ s}^{-1}$ to 0.6 s^{-1} corresponding to a velocity of 0.4 to 900 mm.min⁻¹. Measurements are performed at room temperature and the reproducibility is checked, performing at least three tests per sample formulation.

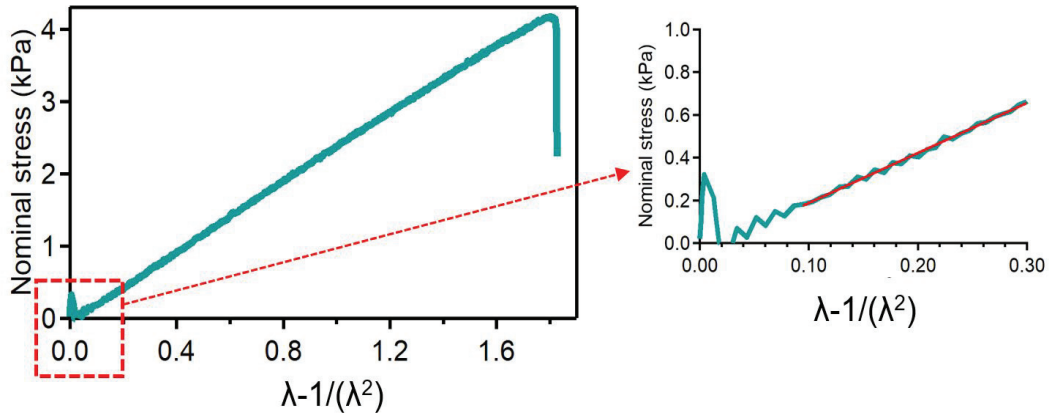


Figure III.4 – Representation of the experimental method used to define the initial modulus E : plot of the nominal stress versus $\lambda - 1/\lambda^2$ for a PDMA chemical hydrogel weakly cross-linked at 0.1 mol% (i.e., covalently cross-linked). The insert on the right shows a zoom of the curve at low strain and in red, the fitting curve (linear) that allows to determine the shear modulus G . Young's modulus is then calculated as $E = G \times 3$.

The Young's modulus is the relevant parameter for the evaluation of hydrogel stiffness. For that purpose, the interval of strain where the shear modulus G is determined, is represented in the insert of the figure III.4. The classical rubberlike elasticity model gives a linear relationship between the nominal stress σ_N and the function $\lambda - 1/\lambda^2$ of the strain ratio λ . Actually this relation simply expresses the incompressibility of the system:

$$\sigma_N = G(\lambda - 1/\lambda^2) \quad (\text{III.4})$$

with G the shear modulus. The linear tensile modulus E is then calculated as follow:

$$E = 3G \quad (\text{III.5})$$

The stress-strain curves displayed in figure III.5. evidence that the strain coming from the video extensometer and from the global displacement of the cross-bar are fully comparable. This agreement, which has been observed for all the samples, clearly emphasizes the absence of slippage during hydrogel extension and validates the determination of the Young's modulus.

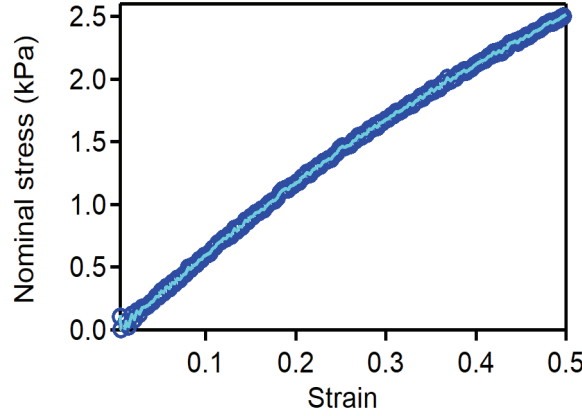


Figure III.5 – Comparison of the standard stress-strain representations for PDMA chemical hydrogel weakly cross-linked (0.1 mol%): nominal stress (in kPa) versus strain sample. In dark blue: cross-head strain and in light blue: video extensometer strain.

Experimentally, a strain-softening is often observed, which is represented by the empirical Mooney-Rivlin equation, still following the classical rubberlike elasticity model:

$$\sigma_N = (2C_1 + \frac{2C_2}{\lambda})(\lambda - 1/\lambda^2) \quad (\text{III.6})$$

With $2C_1 = G$ and $2C_2 = 0$ for classic models. Thus the deviations from the model are often read in a Mooney plot, using the Mooney stress (reduced stress) defined as:

$$\sigma_{\text{Mooney}} = \frac{\sigma_N}{(\lambda - 1/\lambda^2)} \quad (\text{III.7})$$

This reduced stress normalizes the measured stress by the predicted rubberlike behaviour in uniaxial extension and is usually plotted as a function of $1/\lambda$. At very large strain ratios, stress hardening can also be observed, due to finite extensibility of network chains.

Fracture

Fracture tests were performed using the classical single edge notch geometry, which is known as Single Edge Notch Tensile (SENT) geometry. For that purpose, a notch of length c was made in the centre of the rectangular samples using a rasor blade as illustrated in figure III.2.

Fracture mechanics approach has been based on the energy necessary to propagate a crack. Greensmith [Greensmith, 1963] addressed a rather simple method for determination of the strain energy release rate or fracture energy, G_{1c} in the case of a single edge notched specimen:

$$G_{1c} = 2KW_c c \quad (\text{III.8})$$

with W_c the strain energy density, λ_c the extension ratio at break, c the initial length of the crack and K a strain-dependent correction associated to the lateral contraction of the sample in extension. The strain dependence of K has been studied by Greensmith and is approximated by:

$$K = \frac{3}{\sqrt{\lambda_c}} \quad (\text{III.9})$$

Hence, the fracture energy at the onset of crack propagation can be calculated as:

$$G_{1c} = \frac{6cW_c}{\sqrt{\lambda_c}} \quad (\text{III.10})$$

2.3 Small Angle X-ray scattering

X-rays are used to investigate the structural properties of gels. Photons interact with electrons, and provide information about the fluctuations of electronic densities in heterogeneous matter. A typical experimental set-up is shown in figure III.6.

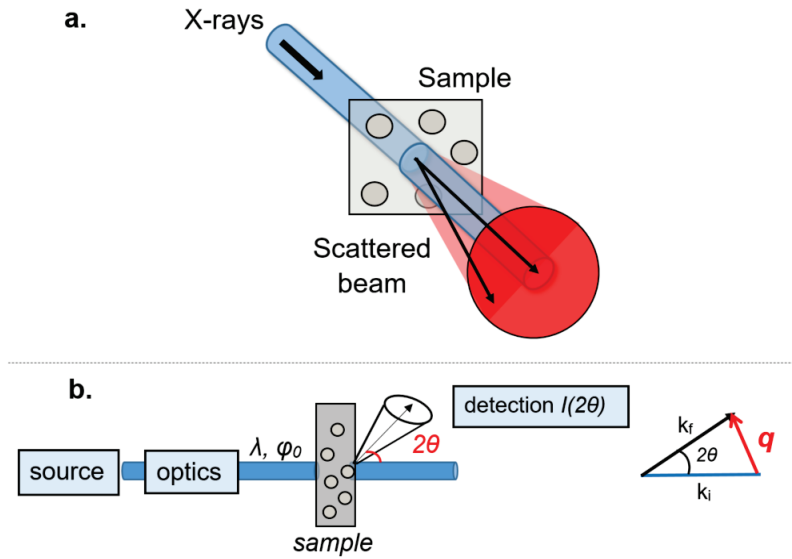


Figure III.6 – **a.** A typical experimental set-up. **b.** Monochromatic beam of incident wave vector k_i is selected and falls on the sample. The scattered intensity is collected as a function of the so-called scattering angle 2θ . Elastic interactions are characterised by zero energy transfers, meaning that the final wave vector k_f is equal in modulus to k_i . The relevant parameter to analyse the interaction is the momentum transfer or scattering vector $q = k_i - k_f$

The small angle scattering experiments can be described as follows: an incident radiation of wave vector k_i (with a wavelength λ) is sent through a gel sample, inducing a scattered radiation. The incident wave vector k_i and the scattered wave vector k_f have the same modulus. The angle between these two wave vectors is named the scattering angle q . The scattering vector is then defined as $q = k_i - k_f$ and the modulus is:

$$q = \frac{4\pi \sin \theta}{\lambda} \quad (\text{III.11})$$

The scattered intensity $I(q)$ is the Fourier Transform of the correlation function of the electronic density. For small scattering angles the scattering vector is in the plane of the detector and no further geometric correction is needed.

Small angle scattering experiments are designed to measure $I(q)$ at very small scattering vectors in order to investigate systems with characteristic sizes ranging from crystallographic distances (few Å) to colloidal sizes (up to few microns) [Glatter and Kratky, 1982].

3 Materials and methods

3.1 Chemicals

Nanoparticles Silica nanoparticles used for all experiments are Ludox-TM 50 produced by Grace and bought from Sigma-Aldrich, used as such without further purification. The nanoparticles were characterized by SEM and Small Angle X-Ray scattering. The experimental data were fit using a procedure that considers polydisperse spherical particles with a Gaussian distribution of size. This model gave a mean radius of 13.5 nm with a standard deviation $\sigma = 0.13$. The corresponding surface area was evaluated at 100 m²/g, considering a specific weight of 2.3 g/cm³.

Monomers and reactants Acrylamide (AAM, 99% electrophoresis grade, Aldrich), *N,N*-dimethylacrylamide (DMA, 99%, Aldrich), *N,N'*-methylenebis(acrylamide) (MBA, 99%, Aldrich) and *N,N,N',N'*-tetramethylethylenediamine (TEMED, 99% bio reagent, Aldrich) and potassium persulfate (KPS, >99%, ACS reagent, Aldrich) were used as received without further purification.

Others (3-Aminopropyl)triethoxysilane (APTES, 99%, Aldrich)

3.2 Experimental part

Gel preparation and composition

Poly(*N,N*-dimethylacrylamide) and poly(acrylamide)-based hybrid hydrogels were prepared in a nitrogen-filled overpressured glove box ($O_2 < 5$ ppm) by *in situ* free radical polymerization, using *N,N'*-methylenebisacrylamide (MBA) as the cross-linker and KPS/TEMED couple as the redox initiators. All the reactants were initially deoxygenated and introduced in the glove box in order to prevent any oxygen contamination. Solid reagents were initially dissolved in water prior to synthesis: KPS, 4.1 wt% solution and MBA, 1.5 wt% solution. After dilution of the silica suspension Ludox-TM50 in water, the pH is readjusted to 9 using either HCl or NaOH, or at pH 11 using NaOH. The MBA in solution and the monomer were then added. The resulting solution was left under stirring and cooled down with ice-patches. A solution of KPS (at room temperature) and of pre-cooled (below 5 °C) *N,N,N',N'*-tetramethylethylenediamine (TEMED) were added under stirring. The mixture was then rapidly transferred into moulds initially placed under the nitrogen atmosphere of the glove box. The geometry of moulds depended on the characterization techniques subsequently used.

Experimentally we observed that the redox initiation starts rapidly (as shown by Orakdogan [Orakdogan et al., 2005]) and the polymerization was let to proceed during 24 hours in the moulds. After demoulding, hydrogels were immediately characterized or stored in paraffin oil to avoid drying before analysis.

For all synthesis, the monomer/KPS and monomer/TEMED molar ratio were fixed at 100. The cross linking density of hybrid gels was also kept constant using a MBA/monomer molar ratio of 0.1 mol%. The cross-linking density of chemical gels was varied between 0 mol% and 1.5 mol%. The following study was mainly based on hydrogels at the preparation state with a fixed molar ratio between polymer and water equals to 0.025 (with $M_{AAM} = 71.08$ g/mol and $M_{DMA} = 99.13$ g/mol). This corresponds to a polymer molar fraction, $\phi_{mol} = 0.026$. Silica volume fraction was fixed at 0.2 for all nanocomposite samples.

The nomenclature used in this study is *M* for chemical gels (pure polymer matrix covalently cross-linked), *NC* for nano composite samples (containing 0.2 v/v silica nanoparticles), *A_x* for acrylamide based gel and *D_y* for *N,N*-dimethylacrylamide-based gel, *x* and *y* being the molar content of each

monomer. For chemical gels, the molar ratio of cross-linker is referred as R_z with z , the molar ratio to the monomer. As an example, a PDMA chemical gel cross-linked at 0.1mol% of MBA will be named:

MD_R01

A hybrid gel sample composed of both PAAm and PDMA containing 20 mol% of AAm and 80 mol% of DMA, at 20vol% of silica nanoparticles will be named:

NC_A₂₀-D₈₀

A PDMA gel with modified silica surface chemistry (at pH 11) will be labeled:

NC_D_pH11

The formulations of hybrid hydrogels used in this chapter are given in Table III.1 and those of chemical gels in Table III.2. In the following, we will mainly focus on the characterization of NC_D and NC_A, the other ones being mainly used for comparison purposes.

Nomenclature	m_{Si}/g	m_{water}/g	m_{AAm}/g	m_{DMA}/g	Q_0	SR ($\frac{Q_{eq}}{Q_0}$)	extractibles (wt%)
NC_D	7.063	10.621	0	1.487	8.45	3.4 ± 0.4	1.81
NC_A	7.063	10.621	1.069	0	11.34	17 ± 3	1.96
NC_A ₉₉ -D ₁	7.063	10.621	1.056	0.015	11.34	16.8 ± 0.4	1.51
NC_A ₉₀ -D ₁₀	7.063	10.621	0.960	0.149	11.13	7.2 ± 0.1	1.78
NC_A ₈₀ -D ₂₀	7.063	10.621	0.853	0.297	10.59	5.3 ± 0.4	1.03
NC_A ₅₀ -D ₅₀	7.063	10.621	0.533	0.743	9.65	4.1 ± 0.2	0.94
NC_A ₂₀ -D ₈₀	7.063	10.621	0.213	0.189	8.88	3.9 ± 0.3	0.87

Table III.1 – *Nomenclature and composition of hybrid hydrogels. For all compositions, the amounts of co-initiators were fixed at $m_{KPS} = 0.041$ g and $v_{TEMED} = 22.5$ μ L, and the amount of chemical cross-linker was fixed at $m_{MBA} = 2.3$ mg. SR is the swelling ratio of the gel calculated as Q_e/Q_0 , Q_e and Q_0 are respectively the measured equilibrium swelling and the theoretical initial swelling, corresponding to the preparation state and calculated according to Eq. (III.12). Silica volume fraction was defined as the volume ratio of silica nanoparticles to the total volume of hybrid hydrogels, fixed at 0.2 for all hybrid compositions (using $\rho_{Si} = 2.3 \times 10^6$ g.cm⁻³).*

Nomenclature	m _{water} /g	m _{monomer} /g	m _{MBA} (mg)	Q ₀	SR ($\frac{Q_{eq}}{Q_0}$)	extractibles (wt%)
MA_R01	10.621	1.069	2.3	11.34	6.5 ± 0.3	1.12
MD_R0	10.621	1.487	0	8.45	12.3 ± 0.3	1.65
MD_R01	10.621	1.487	2.3	8.45	5.5 ± 0.3	0.74
MD_R05	10.621	1.487	11.6	8.45	2.8 ± 0.1	0.51
MD_R1	10.621	1.487	23.1	8.45	2.1 ± 0.2	1.15
MD_R1.5	10.621	1.487	34.7	8.45	1.8 ± 0.1	0.87
MD_R01_pH11	10.621	1.487	0	8.45	5.7 ± 0.3	1.1

Table III.2 – *Nomenclature and composition of chemical hydrogels. For all compositions, the co-initiators amounts were fixed at $m_{KPS} = 0.041$ g and $v_{TEMED} = 22.5$ μ L. Q_e and Q_0 are respectively the measured swelling equilibrium and the theoretical initial swelling that corresponds to the preparation state. Q_e and Q_0 were calculated according to Eq. (III.12)*

3.3 Analytical methods

3.3.1 Swelling experiments

Equilibrium swelling experiments were conducted in deionized water at pH 9. The samples were weighed in their preparation state and put in a large solvent excess for 15 days. The solvent was changed every day and after 15 days, the swollen gels were weighed again. The swelling ratio SR defined as the ratio of the volume of the gel in its fully swollen state (Q_e) and the volume in its initial swelling state (Q_0), was calculated assuming negligible extractible content and additivity of volumes as follow :

$$Q_0 = 1 + \frac{\nu_{spe}^w}{\nu_{spe}^{pol}} \left(\frac{m_{p,w}^0}{m_p^0} - 1 \right) \quad (\text{III.12})$$

$$Q_e = 1 + \frac{\nu_{spe}^w}{\nu_{spe}^{pol}} \left(\frac{m_{p,w}^0 + m_{p,w}^{abs}}{m_p^0} - 1 \right) \quad (\text{III.13})$$

$$SR = \frac{Q_e}{Q_0} \quad (\text{III.14})$$

where ν_{spe}^p is the specific volume of the dry polymer network ($\nu_{spe}^p\text{-DMA} = 0.95$ mL.g⁻¹; $\nu_{spe}^p\text{-AAm} = 0.709$, mL.g⁻¹), ν_{spe}^w is the specific volume of the solvent ($\nu_{spe}^w\text{-water} = 1$, mL.g⁻¹), $m_{p,w}^0$, $m_{w,p}^0$ and $m_{w,p}^{abs}$ are the mass of the dry polymer network, the mass of the water in the preparation state and the mass of the absorbed water, respectively.

The analysis of the organic and inorganic content was systematically carried out after swelling. The swollen sample was either analyzed using thermal gravimetric analysis (TGA) or placed in an oven at 80C for 72 hours and weighted once fully dried. For all samples, the yield was above 98%. Similarly, the solvent washed-out after swelling experiments of hybrid gels was controlled by dynamic light scattering (DLS) and did not reveal the presence of silica nanoparticles after swelling equilibrium, showing that the silica particles do not diffuse out of the gel matrix.

3.3.2 Mechanical tests

Tensile tests were performed on a standard tensile Instron device, model 5565, using a 10 N load cell (with a relative uncertainty of 0.16% in the range of 0 to 0.1 N) and a video extensometer,

model SVE, able to precisely follow the local displacement of markers up to 120 mm, with a relative uncertainty of 0.11% at full scale. The strain can be measured using both the video extensometer and the displacement of the crosshead. The force (F) and displacement (L) were recorded.

The nominal strain rate was varied from $3 \times 10^{-4} \text{ s}^{-1}$ to 0.6 s^{-1} corresponding to a displacement speed comprised between 0.4 and 900 mm.min⁻¹. To avoid any drift in the gel composition during the experiments, tests conducted at $3 \times 10^{-4} \text{ s}^{-1}$ were carried out under immersion in paraffin oil. For that purpose, we designed a specific cell and to correct the buoyancy, blank tests were systematically carried out for each experimental condition.

Samples preparation.

The gel samples used for the mechanical tests were synthesized in home-made moulds consisting of two covered glass plates spaced by a stainless steel spacer of 2 mm thick. The gels were cut with a punch and their final dimensions were $L_0 = 25 \text{ mm}$, $w_0 = 5 \text{ mm}$ and $t_0 = 2 \text{ mm}$. The sample geometry has been chosen in order to reduce the volume of material. All gel samples were placed in home-made screw side action grips and marked by two white dots.

Uniaxial tensile tests.

The nominal stress σ_N defined as engineering stress was calculated from the tensile force and the initial cross section area ($5 \times 2 \text{ mm}^2$) as follow:

$$\sigma_N = \frac{F}{w_0 \times t_0} \quad (\text{III.15})$$

and the strain ϵ was obtained from the optical extensometer and defined as the ratio:

$$\epsilon = \frac{\Delta L}{L_0} \quad (\text{III.16})$$

The reduced (Mooney) stress was calculated according to:

$$\sigma_{Mooney} = \frac{\sigma_N}{(\lambda - 1/\lambda^2)} \quad (\text{III.17})$$

The true stress σ_T was calculated assuming iso-volume deformation, thanks to the following relation:

$$\sigma_T = \sigma_N \times \lambda \quad (\text{III.18})$$

$$\lambda = \frac{L}{L_0} \quad (\text{III.19})$$

with λ , the strain ratio. L and L_0 were respectively the length during stretching and the initial length. The true strain was calculated according to:

$$\epsilon_T = \ln(1 + \epsilon_N) \quad (\text{III.20})$$

Fracture experiments

Fracture data were obtained using single edge notch geometry and the fracture energy G_{1c} (in J.m⁻²) at the onset of crack propagation was calculated as:

$$G_{1c} = \frac{6cW_c}{\sqrt{\lambda_c}} \quad (\text{III.21})$$

with λ_c the extension ratio at break, W_c the strain energy density at break, calculated by the integration of the nominal stress versus strain up to break $\epsilon_c = \lambda_c - 1$ and c the initial length of the crack. Each notch was measured by optical microscopy in order to determine its exact length c of approximately 1 mm. The same procedure as the one used for tensile tests was performed: the strain rates were varied from $3 \times 10^{-4} \text{ s}^{-1}$ to 0.6 s^{-1} , the force and the displacement data were recorded. The previous formula supposes that the material has a perfectly elastic behavior, meaning that all the elastically stocked energy is used to propagate the crack. However, hybrid gels possess dissipative mechanisms so that the relevance of this model can be discussed. However, it allows to compare the behavior of the pure polymer matrix, covalently cross-linked (chemical gels) with the one of the hybrid gels. For each measurements, three samples were tested for reproducibility.

Loading-unloading cycles

Loading-unloading cycles were performed in order to investigate the self-recovery process of the gels and the characteristic times of the viscoelastic processes. Cycles at constant strain rate were applied from 0 to a maximal strain ϵ_0 and then the sample was unloaded. For each measurement, three cycles were performed.

3.3.3 Rheological measurements

The viscoelastic properties of hydrogels discs (22 mm diameter, 2mm thickness) were studied at the preparation state using a stress-controlled rheometer (DHR-3 from TA Instruments) equipped with a plate/plate geometry. Particular care was taken to avoid the drying of the samples by immersing them into paraffin oil during the experiment. Frequency sweep measurements were performed at 25°C . The angular frequency was varied from 1 to 100 rad.s^{-1} (from 0.159 to 15.9 Hz) while the strain amplitude was fixed at 0.1%. The storage modulus $G'(\omega)$ and the loss modulus $G''(\omega)$ were recorded and plotted against the angular frequency ω in a double logarithmic scale as all these parameters varied over several order of magnitude.

Samples preparation.

The setup was designed at the SIMM lab jointly with L. Olanier, A. Lantheaume and G. Ducouret (SIMM, ESPCI). As illustrated in figure III.7, the geometry consists of two covered glass plates spaced by a removable stainless steel spacer of 2 mm thick. The gel samples used for the rheology tests were directly synthesized in the moulds.

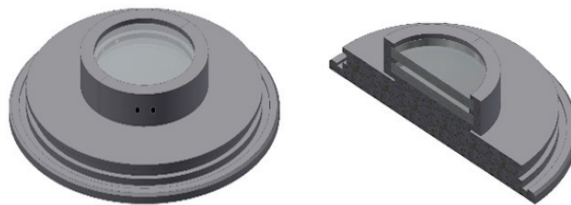


Figure III.7 – Schematics of the rheology cell developed for LAOS experiments. Samples were injected between the covalently grafted glass plates and left to polymerize until gelation.

The gels were covalently grafted to the glass using (3-aminopropyl)triethoxysilane (APTES) as a coupling agent. Prior to the grafting, the glass plates were cleaned using cerium oxide suspension

(20 wt% in water) and RBS detergent (10 wt% in water). After drying, they were treated with a solution of APTES at 2 wt% in absolute ethanol in presence of hydrochloric acid then heated at 100 °C in an oven for 10 minutes. Glass plates were directly glued on the rheometer using bi-component epoxy glue, their final dimensions being $d_0 = 22$ mm in diameter and $t_0 = 2$ mm in thickness.

3.3.4 Small Angle X-Ray Scattering

Small angle X-ray scattering experiments were carried out at Laboratoire Léon Brillouin (CEA, Saclay), in collaboration with A. Brulet, with a high resolution X-ray spectrometer Xeuss 2.0 from Xenoxs company equipped with PILATUS3 1M detector 168.7 x 179.4mm active detection dimensions. In order to compare with hydrogels, solutions of silica nanoparticles were also prepared at volume fraction varying from 0.01 to 0.33 (pure Ludox suspension). Gel samples were prepared according to the synthesis protocole described at the beginning of this chapter then injected directly in poly(imide) capillars purchased from MicroLumen of dimensions 0.75 x 60 mm under nitrogen atmosphere, then welded to prevent drying.

After treatment, the absolute intensity $I(q)$ (in cm^{-1}) was plotted versus the wave vector modulus q . The corresponding values of the scattering vector modulus ranged between 0.0038 and 0.01 $\text{\AA}^{-1}$. Data were treated and fitted using the SASView software v3.2.1.

4 Results and discussion

4.1 Characterization of pure PAAm and PDMA networks

First of all, it is important to characterize the chemical hydrogels composed of PDMA and PAAm matrix. The mechanical properties and the swelling behavior were assessed both for PDMA at several cross-linking ratio, from 0 to 1.5 mol% (MD_R_z) and for PAAm at a constant cross-linking ratio of 0.1 mol% (MA_R01), the same as the one of hybrid gels. The molar concentration of polymer ($\phi_{mol} = 0.026$) was kept constant in order to keep the same density of elastically active chains within the network.

4.1.1 Tensile behavior of chemical gels

The stress-strain curves in figure III.8.a. show the tensile behavior of PDMA chemical gels at various cross-linker content. It is clear that increasing the amount of chemical cross-linker leads to an increase of the gel's stiffness along with a decrease of the strain at break. Indeed, MD_R0 shows elastic deformation with a high strain at break ($\epsilon = 600\%$ against $\epsilon = 30\%$ for MD_R1.5) but remains very soft, contrary to chemical gels with higher cross-linking content.

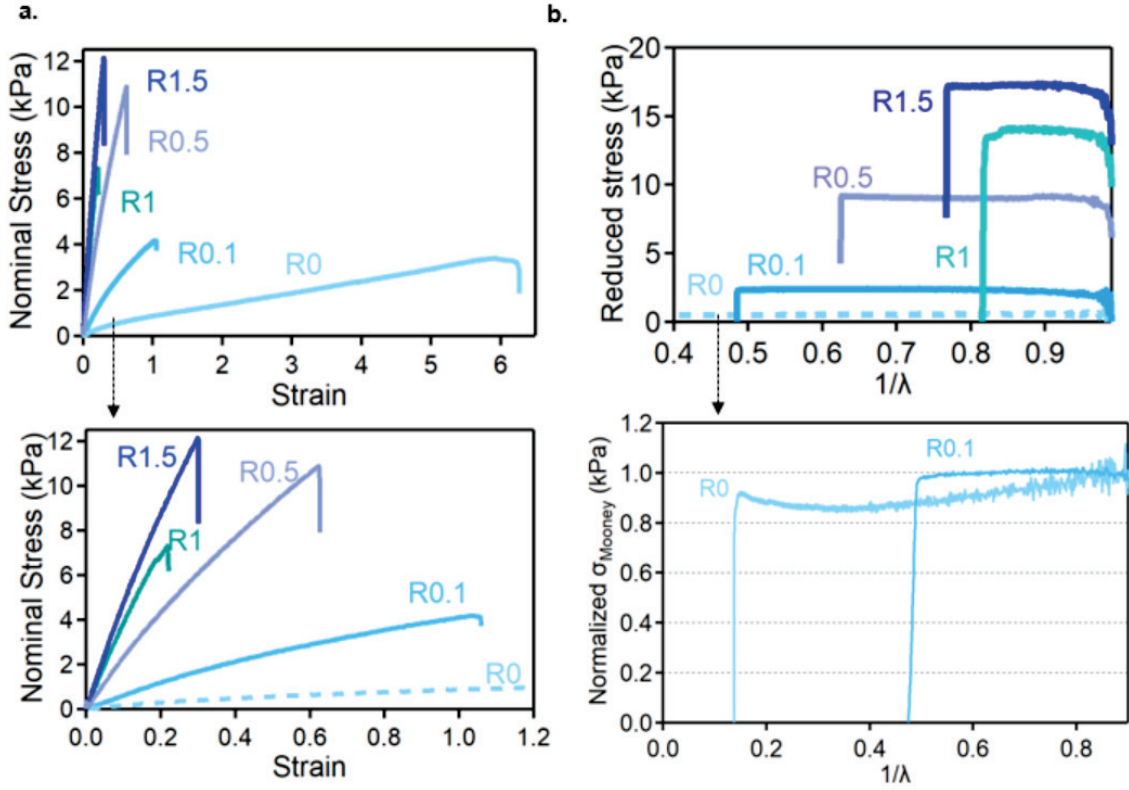


Figure III.8 – **a.** Stress-strain curves of MD_ R_z gels at various MBA content (0, 0.1, 0.5, 1 and 1.5 mol%), conducted at 0.06 s^{-1} in their preparation state. Below, zoom on the chemical gels, with MBA content of 0.1, 0.5, 1 and 1.5 mol%, at strain ranging from $\epsilon = 0$ to 1.2 **b.** Reduced (Mooney) stress plotted as a function of $1/\lambda$ of MD_ R_z chemical gels. Normalized reduced (Mooney) stress plotted as a function of $1/\lambda$ of MD_ R_0 , with MD_ R_{01} curve displayed as a reference of chemically cross-linked PDMA gel.

This behavior is perfectly consistent with a tighter mesh size of the polymer network that reduces the maximal extensibility of the polymer chains between cross-links since in all classical models, the contribution to the shear modulus G coming from covalent bonds G_x varies as:

$$G_x \propto \nu_e \propto \frac{1}{M_{CL}} \quad (\text{III.22})$$

with ν_e , the number of cross-linked chains per unit volume, M_{CL} , the average strand molar mass between cross-links.

The *a priori* uncrosslinked gel MD_ R_0 evidences the self cross-linking process that can take place during the polymerization process [Carlsson et al., 2010], since without any chemical cross-linker added in the system, the gel does not display flowing phenomenon (at the time scale of the experiment). This result is supported by the work conducted by Needles et al. on self cross-linking of PAAm and PDMA polymer chains in aqueous media in presence of KPS. Peroxydisulfate is known to yield sulfate- and hydroxyl-free radicals on decomposition in aqueous solutions that can react on the *N*-methyl moieties, leading to cross-linking reactions [Needles and Whitfield, 1965]. This feature is of importance when polymerizing AAm and DMA in the presence of silica nanoparticles, since side reactions could lead to the covalent grafting of polymer chains onto the surface of silica nanoparticles as suggested by Haraguchi in PNIPAm/clay nanocomposites, with polymerization

initiated by KPS [Haraguchi, 2002].

Reduced stress curves of the chemical samples display nearly horizontal straight lines, in good accordance with the theoretical predictions of the rubberlike elasticity ($\sigma_N = (2C_1 + C_2/\lambda)(\lambda - 1/\lambda^2)$ with $C_2=0$ and $2C_1 = G$ for classical models). The reduced (Mooney) stress curve of MD_R0 displayed in figure III.8.b differs from the the ones of the others samples. It displays a softening at intermediate strains that is absent from the other chemical hydrogels. This softening corresponds to a ratio $C_2/C_1 \approx 0.45$, which is typical for trapped entanglements in elastomers for instance [Perez-Aparicio et al., 2013]. This could point to the presence of trapped entanglements that cannot be seen in the chemically cross-linked samples. For the first time, the signature of entanglements is identified in PDMA chemical gels.

At small strain levels, a downfall of the Mooney stress is observed for all samples which remains complex to analyze and will not be discussed further.

Classical tensile tests are not appropriate to the study of failure but these results can provide a general idea of the behavior of hydrogels with different cross-linker content.

4.1.2 Young's modulus

The evolution of the Young's modulus with increasing cross-linker content, assuming incompressibility of the hydrogels, is shown in table III.3. It confirms the increase of stiffness along with higher MBA content.

Nomenclature	E (kPa)	M_c theor.(g/mol)	M_c calc. (g/mol)
MD_R0	$1.8 \pm$	0	-
MD_R01	7.8 ± 1	50 000	113 000
MD_R05	27.9 ± 1.4	10 000	22 000
MD_R1	42.7 ± 2.4	5 000	11 300
MD_R1.5	54.5 ± 2.2	3 500	8 000
MA_R01	6.9 ± 0.3	35000	70 000

Table III.3 – E modulus of MD_ R_z samples and of MA_R01 and theoretical and experimental values of M_c , the average strand molar mass between covalent cross-links. The theoretical M_c is calculated according to $M_c = (2 \times N_m / f) \times M_0$ with f , the functionality of the cross-linker ($f_{MBA} = 4$) and N_m the number of monomer units between cross-links calculated as: $N_m = \text{molar content of cross-linker} / \text{cross-linker molar ratio}$, and M_0 , the molecular weight of the monomer ($M_0\text{-DMA} = 99.13 \text{ g/mol}$, $M_0\text{-AAm} = 71.08 \text{ g/mol}$).

The PAAm-based gels (MA_R01) displays slightly smaller E modulus value than the one of the corresponding PDMA chemical gel at the same MBA molar ratio (MD_R01) along with higher strain at break, as displayed in figure III.9 which is in good agreement with previous work reported on chemical PAAm and PDMA concerning a higher network inhomogeneity for PAAm gel when the polymerization is initiated by a redox couple such as KPS and TEMED [Orakdogan and Okay, 2007].

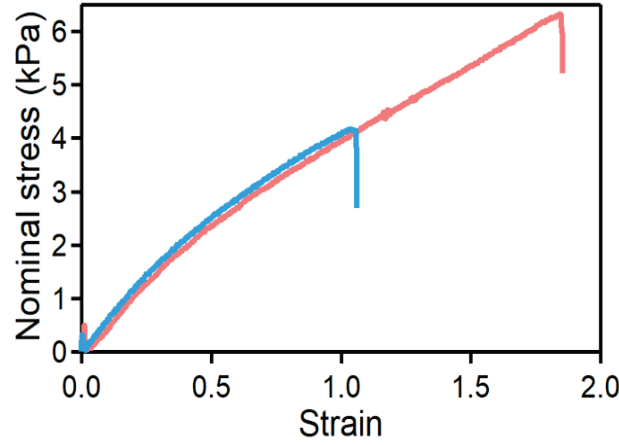


Figure III.9 – Stress-strain curves of MD_R01 (blue) and MA_R01 (pink) at 0.06 s^{-1} .

In figure III.10, the shear modulus G ($G = 1/3 E$) with E , the Young's modulus is represented as a function of the cross-linker content. The representation of the shear modulus vs the molar amount of chemical cross-linker can be fitted linearly according to $G = 1.75 + 11.57 R_z$, (G in kPa) which emphasizes the contributions of both entanglements ($G_e = 1.75 \text{ kPa}$) and covalent cross-links (G_x) with $G = G_e + G_x$. As reported by Obukhov et al. [Obukhov et al., 1994], the elastic modulus value is linked to the contributions of trapped entanglements and chemical cross-links that mainly depends on the polymer concentration and the cross-linker content. For the weakly cross-linked MD_ R_z , trapped entanglements seem to be the major contribution to the modulus while their contribution reaches only about 10% for the higher cross-linking densities ($R = 1.5 \text{ mol\%}$).

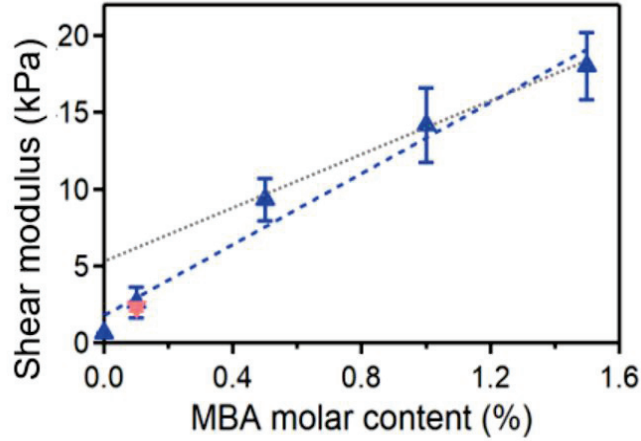


Figure III.10 – Shear modulus of MD_ R_z gels (blue triangles). MA_R01 (pink reversed triangle) is displayed as a reference. The MD_ R_z samples are fitted linearly to extract the relative contributions of entanglements (G_e) and of covalent cross-linking (G_x). The linear fit of the high cross-linking content ($>0.5 \text{ mol\%}$, grey dashed line) allows to evaluate the contributions of trapped entanglements in those samples.

The dominant contribution of entanglements in lowly cross-linked gels could confirm the hypothesis of trapped entanglements in MD_R0 sample that were observed in the reduced (Mooney) stress curves. Nevertheless, stress-strain curves do not show any clear evidence of softening for

covalently cross-linked chemical gels. Note that the contribution from trapped entanglements may vary according to the cross-link density and decrease as the chemical cross-link density itself goes to zero. This is suggested by the alternative dotted fitting line chemical gels covalently cross-linked in figure III.10. In this case the contribution of trapped entanglements to the modulus at high cross-link densities (0.5 to 1.5 mol%) would be higher.

Assuming that all cross-linking molecules used in the gel synthesis participate in forming effective crosslinks, a theoretical modulus G_{theo} of the hydrogels can be calculated as [Orakdogan and Okay, 2007]:

$$G_{theo} = A \times \frac{2\rho_{pol}}{M_0} RT\phi_0 \quad (\text{III.23})$$

where the front factor A equals 1 for an affine network and $1 - 2/f$ for a phantom network, f being the functionality of the cross-links, ρ_{pol} is the polymer density (1.35 and 1.15 for PAAm and PDMA gels, respectively), M_0 is the molecular weight of repeat unit (71.08 and 99.13 g/mol for AAm and DMA, respectively), ϕ_0 is the polymer concentration in the gels at the preparation state (in wt). The cross-linking efficiency ξ_{eff} can be calculated as:

$$\xi_{eff} = \frac{G_{exp}}{G_{theo}} \quad (\text{III.24})$$

Considering a phantom network, the average cross-linking efficiency that is the fraction of MBA forming effective cross-links, is estimated at $\approx 44\%$ for PDMA network and 51% for PAAm network cross-linked at 0.1 mol%. The difference between G_{exp} and G_{theo} is attributed to the polymerization process that involves a broad distribution of molar masses between cross-links due to the concomitant polymerization of monomers and cross-linker units [Norisuye, 2002]. Since extractibles contents displayed in table III.1 do not reveal significant fraction of unreacted material the most likely hypothesis is the presence of non elastically active chains (loops and dangling chains carrying one free unreacted double bond).

4.1.3 Swelling behavior

These defects can significantly impact the mechanical properties of the networks but also the swelling behavior. In figure III.11, swelling equilibrium ratios of PDMA chemical gels at varying MBA content are plotted. The swelling ratios decrease as the cross-linker content increases which is still consistent with a decrease of average number of monomer units between cross-links. MD_R0 gel swells a lot more than the other ones which seem in good accordance with a gel presenting only few covalent cross-linking points but also with entanglements. Since entanglements are not trapped into the matrix, meaning that disentanglement can occur during the swelling process, allowing a larger swelling.

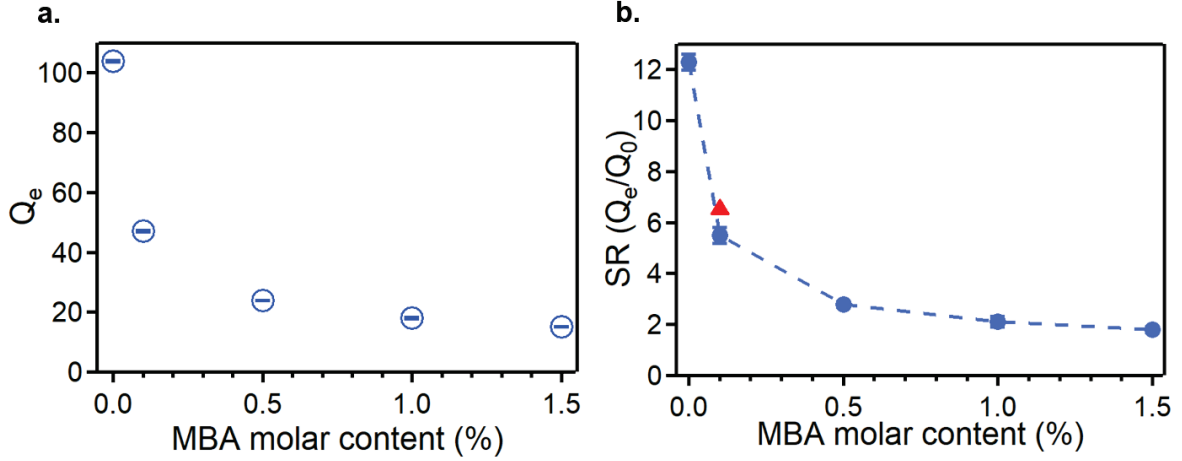


Figure III.11 – **a.** Swelling equilibrium Q_e of MD_R_z hydrogels as a function of the cross-linker content (MBA, in mol%). **b.** SR of MD_R_z (blue dots) and of MA_R01 (red triangle).

For MA_R01, the swelling ability slightly increases compared to that of corresponding PDMA, as depicted in figure III.11.b, which could originate either from a greater homogeneity of chemical PDMA network compared to PAAm ones but also to the fact that the polymer volume fraction is slightly lower for PAAm gel than that of PDMA. As shown by Gundogan *et al.*, a higher polymer concentration improves the cross-linking efficiency, thus decreasing the presence of cross-linking defects such as cyclization and multiple cross-linking-reactions (for $\phi_0 < 0.3$ in PDMA networks) [Gundogan *et al.*, 2003]. Furthermore PAAm better solvated by water than PDMA, leading to the slight increase of absorbed solvent.

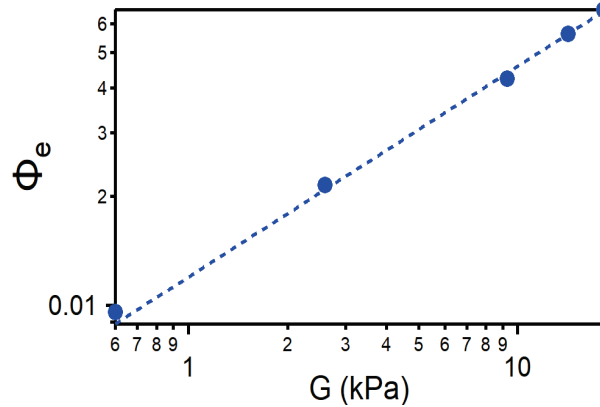


Figure III.12 – Polymer volume fraction of PDMA chemical gels ϕ_e at several cross-linker ratio (0, 0.1, 0.5, 1 and 1.5 mol%) at swelling equilibrium plotted vs the shear modulus G (in kPa) obtained in the preparation state (blue dots). Polymer volume fraction at swelling equilibrium is calculated as $\phi_e = 1/Q_e$ for each cross-linking content. The curve is fitted by a power law (blue dashed line).

PDMA chains swollen in water are considered to be in theta conditions, meaning that the attraction between monomers cancels the steric repulsion. According to the Flory theory, a polymer chain swollen in theta solvent, constituted of N monomers of Kuhn length a , uniformly distributed within the volume R^3 without any correlation between them will have a mean radius R following

$R = aN^\nu$ with the scaling parameter $\nu = 1/2$. The volume occupied by a swollen chain is described by $R^3 = a^3 N^{3/2}$ and the polymer volume fraction at swelling equilibrium ($1/Q_e$) will be equal to:

$$\phi_e = \frac{a^3 N}{(a^3 N^{1/2})^3} \approx N^{-1/2} \quad (\text{III.25})$$

With the polymer volume fraction at swelling equilibrium is defined as $\phi_e = 1/Q_e$. In figure III.12 is represented the polymer volume fraction ϕ_e of PDMA gels cross-linked at several MBA ratio (from 0 to 1.5 mol%) swollen at equilibrium as a function of the shear modulus G in the preparation state. The shear modulus varies as $G \approx (k_B T \phi_0)/N$, with ϕ_0 the polymer volume fraction in the preparation state. The fitting of the obtained values by a power law gives $\nu = 0.5$, confirming experimentally that PDMA chains swollen in water are in theta conditions.

4.1.4 PAAm and PDMA hydrogels dynamics studied by Linear Rheology

The mechanical behavior of chemical gels MA_R01 and MD_R01 was investigated by scanning the shear frequency over two orders of magnitude, from 1 to 100 rad.s^{-1} as shown in picture III.13. As expected for a chemical gel the storage modulus $G' \gg G''$ and G' does not vary with the frequency. The amplitude of the loss modulus G'' is mostly related to the amounts of defects in the network (dangling chains and loops) [Curro and Pincus, 1983] and to their relative length with respect to the network mesh size. If no slow relaxation process would occur within the investigated frequency range, G'' would vary as $G'' \approx \omega$, corresponding to a constant viscosity. For pure chemical PDMA and PAAm networks the frequency dependence of $G'' \approx \omega^m$ with $m=0.26$ for MA_R01 and $m=0.50$ for MD_R01 clearly indicates the formation of such defects. The power-law relaxation process reveals the (slow) relaxation process of dangling chains in presence of topological constraints within the network. The value of the exponent m is expected to scale with the reciprocal of the number of constraints per dangling chains suggesting heterogeneities in the case of MA_R01, as shown in table III.5, with longer dangling chains but with less constraints than PDMA. This result highlights the random feature of the polymerization that generates a broad dispersion of chains, especially for MA_R01. PAAm networks synthesized under the same conditions as PDMA chemical gels were already reported as more heterogeneous which seems to be confirmed by these results.

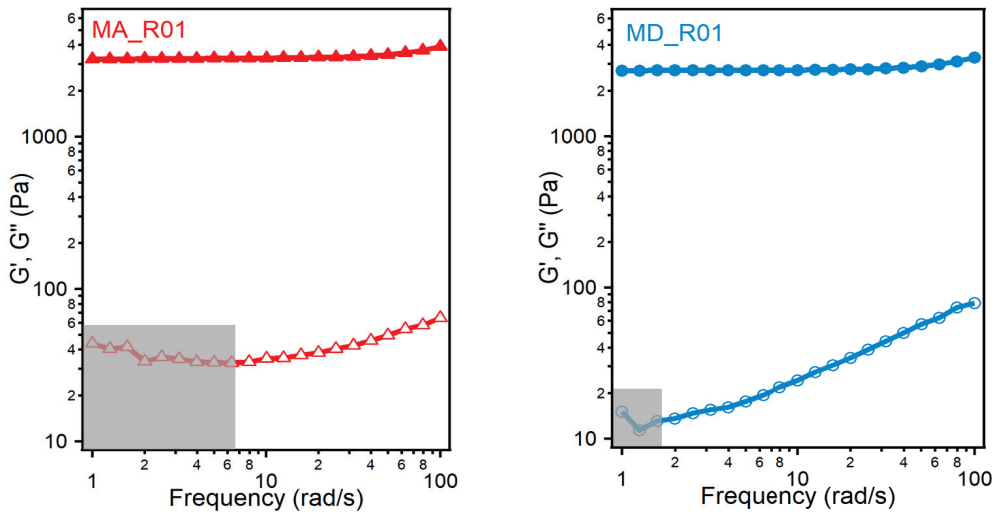


Figure III.13 – Frequency dependence of the storage (filled symbols, G') and the loss (open symbols, G'') moduli of PDMA (MD_R01, blue circles) and PAAm (MA_R01, red triangles) chemical gels, cross-linked at 0.1 mol% at oscillation strain = 0.1%. Note that the fluctuations of G'' at low frequency are attributed to the low values recorded, reaching the detection limits of the device.

4.2 Introducing silica nanoparticles in PAAm and PDMA polymer networks

In the following section, the mechanical behavior of hybrid gels based on both PDMA and PAAm will be investigated. The idea here was to assess the impact of non-interacting monomer on hybrid hydrogels while keeping every chemical aspects (pH, silica surface chemistry, ionic force, monomer/water molar ratio, cross-linker content) identical to those of hybrid gels based on PDMA. Then the swelling behavior and the mechanical properties were assessed with a special interest in the non linear behavior.

The synthesis process of silica nanoparticles and PDMA was shown to be simple, robust and highly reproducible [Rose et al., 2013b]. On the contrary, the first synthesis of hybrid gels with PAAm matrix led to opaque and stiff gels, indicating aggregation of the silica nanoparticles within the network. Since PAAm does not adsorb onto silica, it is very likely that the polymerization process led to a destabilization of the nanoparticles dispersion since they are not protected by an interacting polymer. Several attempts were made to prevent nanoparticles aggregation, the first one being to thermally initiate the polymerization (with KPS heated at 80 °C). This method provided transparent and soft samples but the drying of the gels remained hard to prevent, and mechanical tests were not consistent with a good dispersion of the nanoparticles. Another way was to introduce a small amount of DMA (≈ 1 mol%) to prevent the flocculation during the polymerization. This strategy revealed hardly relevant since adding DMA was efficient to prevent aggregation but in amounts too high to study the impact of pure PAAm matrix. The chosen path to address this issue was to run the polymerization with a thorough control of the temperature for all reactants (inferior to 5 °C, TEMED included). This procedure yielded translucent and soft gels in a reproducible way, still the aggregation state of the fillers needed to be assessed to make sure that both PAAm and PDMA hybrid gels were obtained with a similar dispersion state of the nanoparticles.

4.2.1 Hybrid gel structure: uniform dispersion of nanoparticles in the gel

SAXS experiments were carried out to probe the dispersion state of the silica nanoparticles within the polymer matrix. For binary systems such as a suspension of monodispersed spherical silica particles (denoted by f , the filler) in a homogeneous solvent or gel matrix (denoted by s , the solvent) the intensity scattered by the particles per unit volume can be described as:

$$I_0(q) = N_f(\Delta\rho)^2 P(q)S(q) \quad (\text{III.26})$$

with q the scattering vector, N_f the number of fillers per unit volume, $\Delta\rho = \rho_f - \rho_s$ the difference of scattering length densities between the matrix and the fillers and $P(q)$ and $S(q)$, respectively the form and the structure factors of the particles.

This is the signal obtained after subtracting the scattering by the pure matrix. The form factor $P(q)$ is of the form $P(q) = (v_f)^2 P_0(q)$ where $v_f = 4\pi r_f^3/3$ is the volume of a particle of radius r_f and the function $P_0(q)$ is normalized to one in the limit $q \rightarrow 0$. To compare scattering curves with different formulations, $I(q)$ can be divided by $\phi_f(\Delta\rho)^2$ where $\phi_f = Nv_f$ is the volume fraction of particles or by the experimental value of the invariant (the so-called Porod's invariant, which gives the total scattering power of the sample) given by:

$$Q_{exp} = \frac{1}{2\pi^2} \int_0^\infty q^2 I_0(q) dq \quad (\text{III.27})$$

For an incompressible two-phase system with sharp interfaces, as in the case of particles in suspension, the invariant depends only on the volume fraction and the contrasts between the two phases so that $Q_{th} = (\Delta\rho)^2 \phi_f(1 - \phi_f)$. The scattering intensity as well as $q^2 I(q)$ decreases rapidly at high q values following the Porod's law $I(q) \approx q^{-4}$. The form factor $P(q)$ represents the scattering by isolated (non-interacting) particles and is directly related to their size. The structure factor $S(q)$ describes the interactions between fillers and provides insight on their correlation. $S(q)$ is the Fourier transform of the pair correlation function of the centers of mass of the particles. Note that, in the general case, dissociating the signal $I(q)$ as the product of two separate factors $P(q)$ and $S(q)$ is an approximation, which is exact only for a collection of centrosymmetric identical (in our case, monodisperse spherical) particles [Baldon et al., 2015]. For polydisperse suspensions such as Ludox-TM 50 nanoparticles, a size distribution function, here Gaussian distribution function $w(r)$, with σ the standard deviation is included:

$$w(r) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{(r - R)^2}{2\sigma^2}\right)$$

In this case the average form factor is calculated as:

$$P(q) = \int_{-5\sigma}^{+5\sigma} \left(\frac{4\pi r^3}{3}\right)^2 3 \left(\frac{\sin(qr) - qr \cos(qr)}{(qr)^3}\right)^2 w(r) dr$$

In very diluted concentrations, the interparticle interactions are negligible and $S_q = 1$ over the whole range of q and the scattering intensity is thus equal to the form factor as illustrated in figure III.14 with a dilute silica suspension at 1 vol%. The best fit is obtained here for a particle radius of 13.4 nm and a standard deviation $\sigma = 0.13$ nm.

At higher silica concentrations of the order of those used in hybrid hydrogels, particles interactions take place and $S(q)$ is no longer negligible which is the case for all tested samples.

The scattering behaviour of the concentrated silica suspension is illustrated in figure III.14 (pure and diluted at 20 vol%) and was analyzed using the hard sphere form factor described just above. The used interparticle structure factor takes into account the interactions between charged particles using an implementation of the Rescaled Mean Spherical Approximation which calculates the structure factor for a system of charged, spheroidal objects in a dielectric medium that corresponds well to silica suspension with a negative pH at low ionic force [Hayter and Penfold, 1981; Hansen and Hayter, 1982]. Coupled with the hard sphere form factor, this model allows for inclusion of the interparticle interference effects due to screened coulomb repulsion between charged particles.

From previous work conducted by S. Rose using SANS measurements [Rose, 2013], it appeared that silica beads interact in these experimental conditions (pH of 9 and weak ionic strength) mostly through short-range repulsive inter-particle forces, justifying the use of this specific model that takes into account the effective radius of the fillers (r_f , in nm), the distribution of radius (σ), the volume fraction of the fillers (ϕ_f), the temperature (in K), the salts concentration (in mol/L) and the dielectric constant (ϵ_r). The salt concentration is used to compute the ionic strength of the solution which in turn is used to obtain the Debye screening length, assuming that the salts (counterions included) are monovalent.

The application of this previous model, taking into account polydisperse spheres interacting with a hard sphere potential, is given in Figure III.14 for the Ludox-TM50 suspensions at several concentrations ($C = 33$ vol% and 20 vol%).

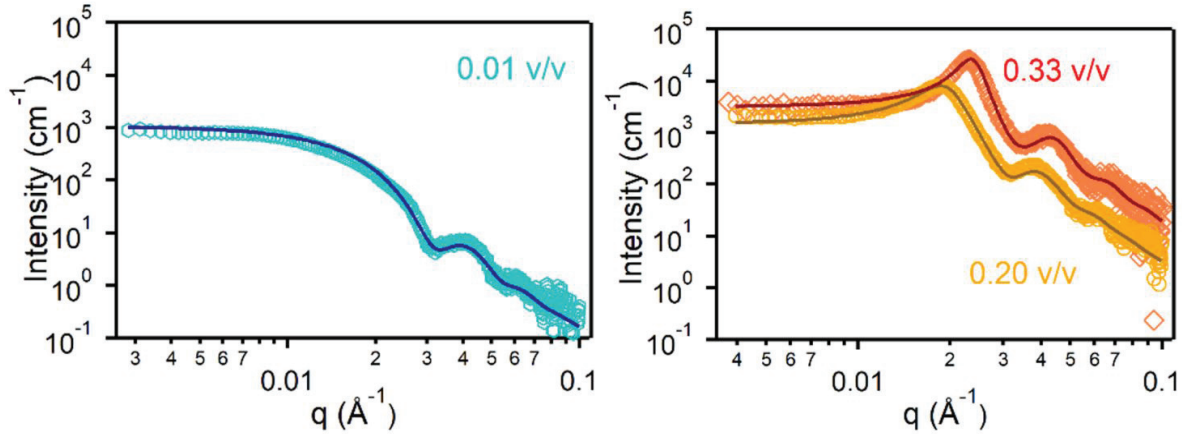


Figure III.14 – On the left, double logarithmic plots of the scattering intensity obtained from diluted dispersion of silica particles of $\phi_{Si} = 0.01$ (blue circles), fitted with hard sphere form factor. On the right, scattering intensities of concentrated dispersions of silica particles of $\phi_{Si} = 0.33$ (red diamonds), $\phi_{Si} = 0.20$ (yellow circles). The corresponding fit based on a sphere model with charged hard sphere repulsions is indicated in solid lines.

In that case, the fitting procedure gives a radius of 13.4 nm for the radius of the particles that is similar to the one extrapolated in previous experiments and an average polydispersity of about 13% in good agreement with the literature data. The salts concentration are calculated from conductivity measurements and gives $C_{salts} = 0.02$ M for $\phi_{Si} = 0.33$ and $C_{salts} = 0.008$ M for $\phi_{Si} = 0.20$ which is also consistent with value provided by the furnisher.

The fits also give an estimated volume fraction of $\phi_{Si} = 0.34$ for the pure Ludox suspension which stays in good agreement with the values provided by the furnisher (50 wt%, 33vol%) and the one

found in previous experiments (52 wt%, cf Chapter 2) and $\phi_{Si} = 0.213$ for the suspension at 20 vol %.

Figure III.15.a shows the scattering intensities of NC_D and of concentrated Ludox suspension at $\phi_{Si}=0.2$. The main difference between the hybrid hydrogel and the concentrated silica suspension arises in the reached intensities of the correlation peak at q_{max} that slightly decreases when silica beads are embedded into the PDMA network (I_{max} -Ludox 0.2 v/v = 8090 cm⁻¹ at $q_{max}=0.0188$ Å⁻¹ against I_{max} -NC_D = 4870 cm⁻¹ at $q_{max}=0.0185$ Å⁻¹). The polymerization of DMA slightly increases the osmotic compressibility of the system but at this low cross-linking content, the interactions remain repulsive in nature. Another feature that appears in figure III.15.b is that all the hybrid gels at the same particle concentration (≈ 0.2 volume fraction) are fully superimposed on the high- q regime. This behavior as well as the q^{-4} dependence obtained in this regime show that particles are of the same size and morphologies (monodispersed spheres) between the three samples. The general morphology of the curves are very similar to the one of the silica suspension at $\phi_{Si}=0.20$. For PAAm-based hybrid gels (NC_A and NC_A₉₀-D₁₀) a slight increase in the intensity is noticed at low q pointing to slightly lower repulsion between silica beads that could be linked to closer interparticular distance, confirming the fact that for PAAm-based hydrogels, silica is more prone to aggregate than in PDMA gels.

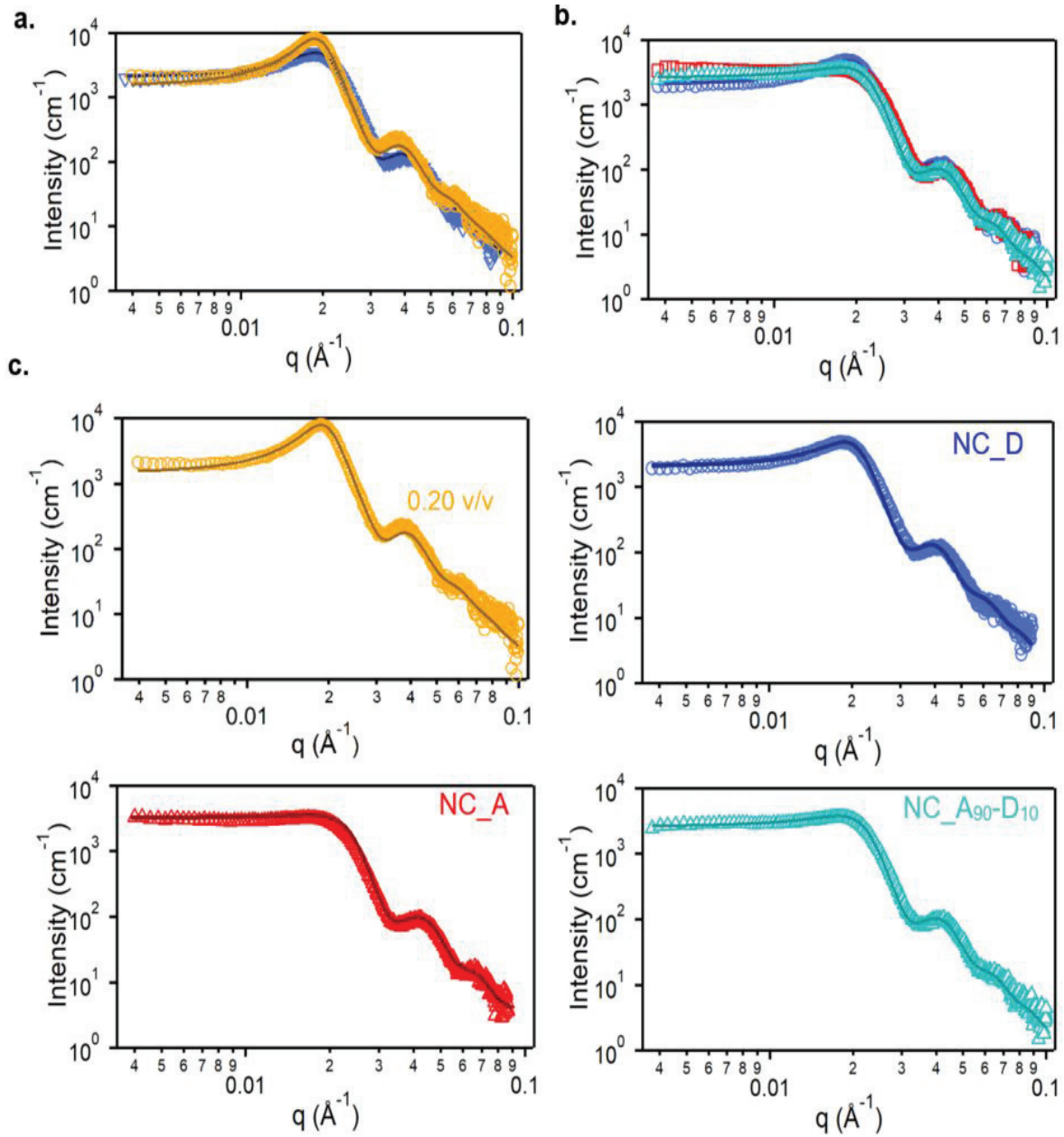


Figure III.15 – **a.** Double logarithmic plots of the scattering intensity obtained from concentrated dispersion of silica particles of at $\phi_{Si} = 0.20$ (yellow circles) and from NC_D sample at 0.2 v/v silica fraction (blue circles). The corresponding fit based on a sphere model with charged hard sphere repulsions for the silica suspension and on the sticky hard sphere model for NC_D are indicated in solid lines. **b.** Double logarithmic plots of the scattering intensity obtained from PAAm and PDMA hybrid gels at 0.2 v/v silica fraction (NC_D, blue circles, NC_A, red shapes, NC_A₉₀-D₁₀, turquoise triangles). The corresponding fit based on the sticky hard sphere model is indicated in solid lines. **c.** Scattering curves of concentrated dispersion of silica particles of at $\phi_{Si} = 0.20$ (yellow circles), NC_D sample (blue circles), NC_A samples (red triangles) and NC_A₉₀-D₁₀ (turquoise triangles). The corresponding fit based on a sphere model with charged hard sphere repulsions for the silica suspension and on the sticky hard sphere model for NC_D, NC_A and NC_A₉₀-D₁₀ are indicated in solid lines.

The destabilization of silica particles in the presence of polymers can be understood on the basis of enthalpic or entropic contributions. An enthalpic contribution can govern the general behavior when a strong attractive potential between polymer and particles is present, like between silica and cationic polymers, or as it was observed by Shibayama and co-workers during the polymerization of N-isopropylacrylamide at low pH (between 3 and 6) in the presence of silica particles [Suzuki et al., 2009]. Entropic effects are generally described by the existence of a depletion layer of polymer chains near hard particles. Indeed, weak flocculation of colloidal particles induced by non-adsorbing polymers has been widely reported in the literature [Gast and Leibler, 1985, 1986] and this phenomenon could be responsible for the slight increase of intensity at low q for NC_A gels and the aggregation observed during the first synthesis. Indeed the depletion effect (attraction induced by polymer depletion in between close-by particles) may be observed in PAAm, which does not adsorb on silica particles. Conversely, in the case of PDMA, the depletion effect would be inhibited due to adsorption of the polymer on silica. Thus, the SAXS observation is perfectly coherent with the strong differences in adsorption properties of the polymers as illustrated in figure III.16. However, this impact remains weak and none of these curve indicate significant aggregation patterns.

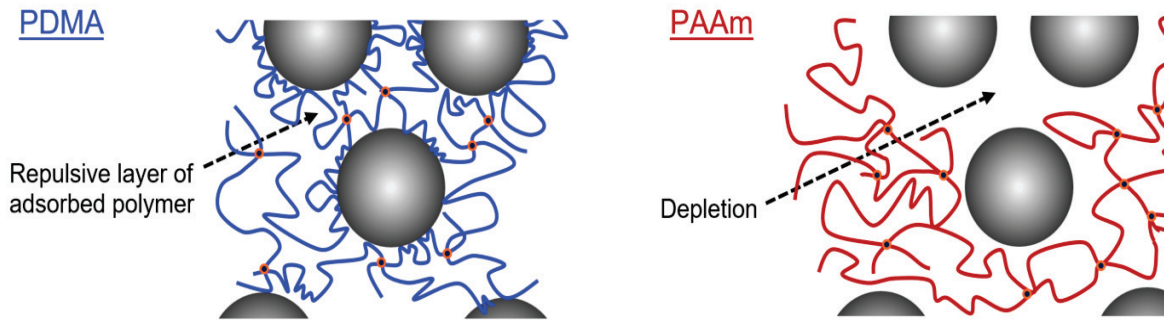


Figure III.16 – On the left, schematics of adsorbed polymer layer (blue lines) onto silica nanoparticles in PDMA hybrid gels (NC_D). On the right, schematics of the depletion layer around the nanoparticles when a non-interacting monomer, like AAm (in red), is introduced in the network. The cross-linking points are represented by the orange dots.

The scattering curves of hydrogels were analyzed using SASView software. A hard sphere form factor and the interparticle structure factor was calculated for a hard sphere fluid with a narrow attractive well, using a perturbative solution of the Percus-Yevick closure which is adequate for attractive interparticle potential the so-called sticky hard sphere model) [Percus and Yevick, 1958]. The returned value is a dimensionless structure factor, $S(q)$. The experimental data are then fit using as adjustable parameter the strength of the attractive well, described in terms of “stickiness” as described below [Menon et al., 1991]. The interaction potential $U(r)$ is defined as :

$$U(r) = \begin{cases} \infty, & r < \sigma_{int} \\ U_0, & \sigma_{int} \leq r \leq \sigma_{int} + \Delta \\ 0, & r \geq \sigma_{int} + \Delta \end{cases} \quad (\text{III.28})$$

with Δ , the width of the square well, U_0 the depth of the well (in $k_B T$ units) and σ_{int} the hard sphere diameter $\sigma_{int} = 2R$. The stickiness τ_{int} is defined as:

$$\tau_{int} = \frac{1}{12\epsilon_p} \exp(U_0/k_bT) \quad (\text{III.29})$$

$$\epsilon_p = \frac{\Delta}{\sigma_{int} + \Delta} \quad (\text{III.30})$$

with ϵ_p , the perturbation factor. U_0 is negative for an attractive potential, positive for a repulsive potential. From this definition, it is clear that smaller values of τ_{int} will mean stronger attraction. In figure III.17.b is illustrated the effect of aggregation (stickiness) on the structure factor.

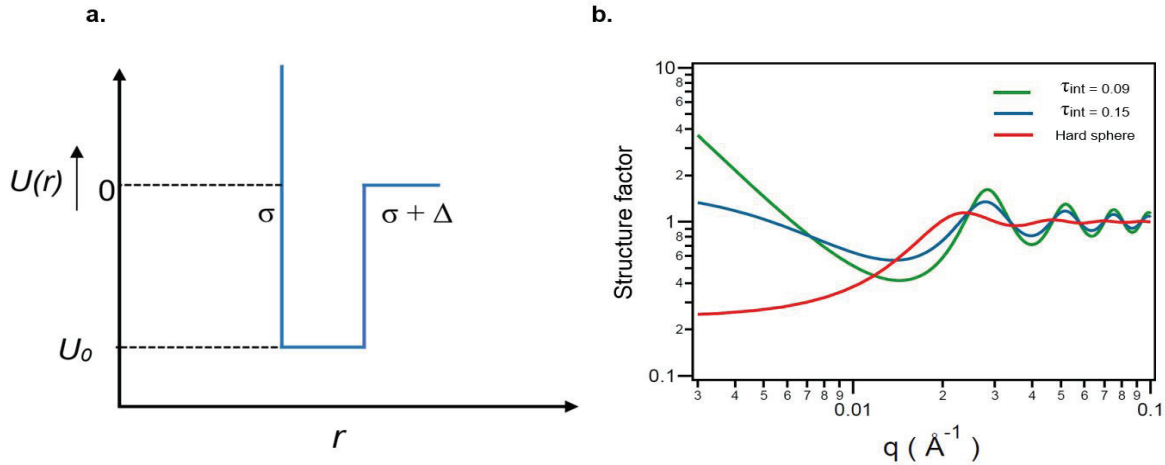


Figure III.17 – **a.** Scheme of the well of interaction potential $U(r)$ (in blue line) of the Sticky Hard Sphere model as a function of the interparticle distance r **b.** Impact of the stickiness factor on the form factor $S(q)$. Hard sphere form factor (in red) and sticky hard sphere model for $\tau_{int} = 0.09$ (in green, weak repulsion) and 0.15 (in blue, weak repulsion) are plotted vs q (in $\text{\AA}^{-1}$)

Fitting results using Sticky Hard Sphere model are gathered in table III.4. Value of particles radius is the one found by the fitting of the silica suspension ($r_{Si} = 13.4$ nm). All parameters but the perturbation factor ϵ_p and the stickiness τ_{int} are fixed.

Parameter	NC_D	NC_A	NC_A _{90-D10}
Radius (nm)	13.4	13.4	13.4
Volume fraction	0.23	0.22	0.23
ϵ_p	0.1 ± 0.001	0.095 ± 0.01	0.090 ± 4.10^{-12}
τ_{int}	5680 ± 0.06	2.1 ± 0.08	2.52 ± 0.001
$I_{\max}$ (cm^{-1})	4870	3 650	3 620
$q_{\max}$ ($\text{\AA}^{-1}$)	0.0185	0.0168	0.0185
$U_0/k_B T$	8.83	0.873	1
	repulsion	weak repulsion	weak repulsion

Table III.4 – Fitting parameters obtained for NC_D, NC_A and NC_A_{90-D10} hybrid gels.

The stickiness factor describing the strength of interactions between particles shows that in the case of PDMA, there is few interactions meaning that the silica particles are well-dispersed in the polymer matrix. For increasing acrylamide content in the network, τ_{int} is decreasing, showing closer

interparticular distance as illustrated for NC_A₉₀-D₁₀. It confirms the fact that silica tends to be destabilized by a non-interacting polymer which could explain the difficulties encountered at first to synthesize these materials without aggregation of the fillers.

4.3 Impact of polymer adsorption on mechanical properties at small strain and swelling behavior

4.3.1 Swelling behavior and extractibles content: impact of non-interacting monomer

Measurements of extractibles content run on NC_D and NC_A gels allowed us to conclude whether or not the presence of nanoparticles in the network disturb the polymerization process as illustrated in table III.1. Similarly to what was found for chemicals gels, the extractibles content remain low (< 2 wt%) for both PAAm and PDMA. Furthermore, DLS analyses conducted on the supernatant of the swelling experiments led to the conclusion that the silica stayed embedded in the polymer matrix since no measurable content of nanoparticles was found in the surrounding solvent, even for NC_A gels. From these results, one can state that the difference in the swelling behavior is due to a difference in polymer/filler interactions and not to a perturbation of the polymerization due to the presence of silica nanoparticles.

As shown in table III.1, the swelling ratios at equilibrium determined for PDMA gels and PAAm gels greatly differ. For PDMA gels, the presence of silica particles leads to a decrease of the swelling ratio, attributed to the attractive interactions between PDMA and silica that adds a constraint, exerted by the adsorbed polymer layer on the gel, limiting the absorption of solvent [Rose et al., 2013b]. On the contrary, the presence of silica in PAAm hybrid gels (NC_A) leads to an increase of the swelling at equilibrium by comparison with the corresponding chemical hydrogels, as displayed in figure III.18, which is consistent with the presence of non-interacting fillers in the matrix.

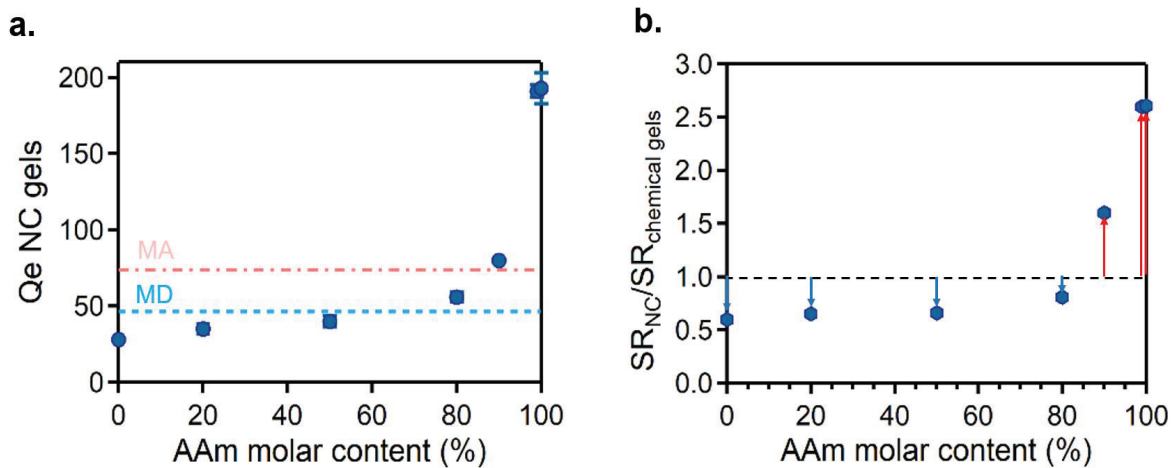


Figure III.18 – **a.** Swelling equilibrium Q_e of hybrid gels a ϕ_{Si} : 0.2, as a function of the AAm molar content (%), in water at pH 9. The dashed line represents Q_e of MD_R01 (blue dashed line) and of MA_R01 (pink dashed line). **b.** Variation of the normalized swelling ratio SR (normalized by the swelling ratio SR of the corresponding chemical gels) at equilibrium as a function of the molar fraction of AAm for hybrid hydrogels, in water at pH 9. The dashed line represents a normalized $SR = 1$, meaning that in that case the nanocomposite would possess the same swelling behavior as the pure organic corresponding gel.

The swelling behavior of polymer networks (hydrogels and elastomers) in the presence of solid fillers has been widely studied and represents a useful tool to investigate the polymer/filler interactions. In the case of attractive interactions, the swelling equilibrium of the network will be reduced in comparison to the one of the unfilled system ($SR_NC_D = 3.4$ against 5.5 for MD_R01), while an absence of interactions will provoke a increase of the swollen quantity ($SR_NC_A = 17$ against 6.5 for MA_R01) because of the formation of solvent cavities near the solid interface as illustrated in figure III.19. These situations have been described by Berriot et al. [Berriot et al., 2002] using a continuum media mechanics approach. The uptake of solvent for increasing acrylamide content is in good qualitative agreement with the model developed by Berriot et al., linking the high increase of swelling to a depletion zone between the filler and the matrix and consequently, to the formation of solvent cavities around the particles which can be roughly estimated to be approximately of the same order of size that the silica nanoparticles, assuming that the created cavities are spherical (≈ 12 nm).

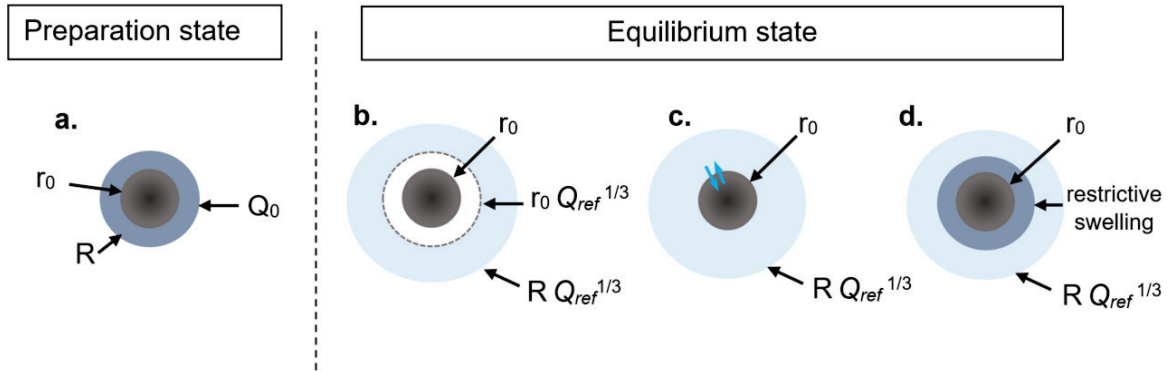


Figure III.19 – **a.** Schematics of a polymer layer (blue-grey) near a solid particle (dark grey), unswollen case **b.** Swelling non-interacting polymer (formation of solvent cavity, in white) **c.** Swelling with interacting polymer without the presence of an unswollen polymer layer. The attractive interactions are symbolized by the blue arrows **d.** Swelling with interacting polymer, with unswollen polymer layer (blue-grey layer).

Another interesting feature is that acrylamide content needs to be high (around 90 mol%) for noticing a larger amount of absorbed solvent compared to the corresponding PDMA hybrid gels. The swelling properties of the PAAm-based hybrid hydrogels compared to the ones of PDMA hybrid hydrogels is an experimental confirmation of the absence of interaction with silica nanoparticles.

4.3.2 Small strain behavior within the viscoelastic regime

The mechanical properties of hybrid gels were first studied at small deformations within the viscoelastic linear regime to specifically investigate the impact of the presence of the nanoparticles on the dynamic moduli. Results are shown in figure III.20.

The frequency-dependence was measured from 0.1 to 100 rad.s^{-1} . For NC_D gels, the introduction of silica nanoparticles leads to an increase of G' but also of the frequency dependence. Moreover, G'' strongly increases as compared to the one of the corresponding chemical gels, from less than 100 Pa at 100 rad.s^{-1} for MD_R01, up to several thousands Pascals at similar frequencies for NC_D. Both G' and G'' follow a power-law frequency response, similar to the one reported for physical gels [Kong et al., 2003; Ng and McKinley, 2008, 2011] or hydrophobically-modified systems [Hao and

Weiss, 2011]. These measurements do not give the possibility to define a characteristic time that would correspond to a maximum in the loss modulus, indicating that there is a large distribution of PDMA segments more or less adsorbed to the silica surface by one or more sites, giving a wide range of characteristics relaxation times.

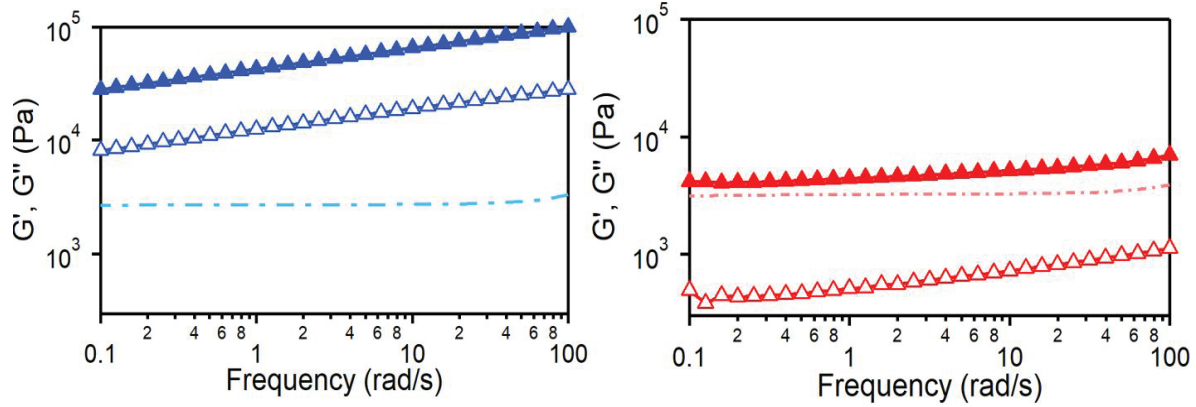


Figure III.20 – Frequency dependence of the storage (filled symbols, G') and of the loss (open symbols, G'') moduli of hybrid PDMA (blue triangles) and hybrid PAAm (red triangles) at oscillation strain = 0.1%. Chemical MD_R01 (light blue dashed line) and MA_R01 (pink dashed line) storage modulus are displayed as a guide line.

The NC_A gels display a slightly different behavior, with an increase of the dynamic moduli but with a lower frequency-dependence, especially of G' . This indicates that the polymer/filler interactions do not contribute to the modulus to the same extent as in the NC_D gel. The corresponding data values are reported in table III.5. The values of calculated Young's modulus from the rheology experiments and the experimentally determined ones from the uniaxial tensile tests at low strain are in good accordance both for chemical and hybrid samples. It is worth noticing that large discrepancies between moduli obtained from tensile measurements and from shear experiments have already been observed [Okomura and Ito, 2001; Sudre, 2011]. The fact that the samples are covalently grafted to the rheology cell may prevent the shift of values observed between rheology measurements and uniaxial tensile tests.

	NC_A	NC_D	MA_R01	MD_R01
n ($G' \approx \omega^n$)	0.07 ± 0.001	0.18 ± 0.0001	0.018 ± 0.003	0.01 ± 0.002
m ($G'' \approx \omega^m$)	0.17 ± 0.002	0.17 ± 0.001	0.26 ± 0.01	0.50 ± 0.011
$\tan \delta$ at 0.37 rad/s	0.14	0.25	0.02	0.01
$E_{calc} 3(G'^2 + G''^2)^{1/2}$ (kPa) at 0.37 rad/s	19	85	9	8
$E_{tensile}$ (kPa)	23 ± 1	92 ± 5	7 ± 1	8 ± 1

Table III.5 – Experimental values of power laws of storage and loss moduli, corresponding value of modulus E and experimental values of linear tensile modulus obtained in tensile tests at 0.06 s^{-1} for NC_D, NC_A and the corresponding chemical gels MD_R01 and MA_R01 so as to compare the relevance of the obtained values.

4.4 Impact of the chemical nature of the monomer at a given strain rate

4.4.1 Linear tensile modulus

The linear tensile modulus can be obtained from tensile experiments at low strain and the values are reported in table III.5 for NC_D and NC_A and the corresponding chemical gels. The impact of filler in a rubbery matrix was addressed by Guth and Gold and Simha [Guth and Simha, 1936; Guth, 1945], from purely elastic considerations (i.e, an incompressible polymer matrix and fillers treated as cohesive hard spherical particles. They predicted an evolution of the linear tensile modulus at low strain for low volume fractions of filler ($\phi_{Si} < 0.2$) according to the following equation:

$$E = E_0(1 + 2.5\phi_{filler} + 14.1\phi_{filler}^2) \quad (\text{III.31})$$

with E , the initial modulus, E_0 , the unfilled matrix modulus and ϕ_{filler} , the volume fraction of the particles. It was already shown that this model clearly underestimates the value of E in the case of strong interactions between the matrix and the fillers, that serve as multiple anchor points for the polymer chains providing an increase of the elastically active chains per unit of volume. Here, the acrylamide content in hybrid hydrogel leads to a significant decrease of the gel's stiffness from one hundred of kPa to 23 kPa for a constant silica volume fraction of 0.203 as depicted in figure III.21.

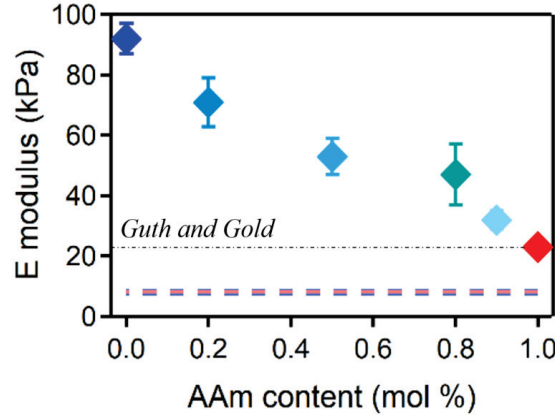


Figure III.21 – Initial modulus of hybrid gels containing various contents of DMA and AAm at 0.203 v/v silica, conducted at $0.06s^{-1}$. Dashed lines represent the linear tensile modulus of the chemical gels, MA_R01 (pink) and MD_R01 (blue). The dashed black line represents the Guth and Gold theoretical prediction for the Young modulus for a silica volume fraction $\phi_{Si} = 0.203$

The experimental modulus values of NC_A and hybrid gels containing increasing content of acrylamide is in good accordance with the Guth and Gold prediction (≈ 22.5 kPa for a silica volume fraction of 0.203), confirming once more the lack of interactions between PAAm and silica nanoparticles and their strong impact on the gel stiffness as shown in table III.6.

Sample	w_{AAm} (mol. fraction)	E (kPa) at $\dot{\epsilon} = 0.06 \text{ s}^{-1}$	E_{calc} (Guth and Gold)
NC_D	0	92 ± 5	22.5
NC_A	1	23 ± 1	22.5
NC_A ₉₀ -D ₁₀	0.9	32 ± 3	22.5
NC_A ₈₀ -D ₂₀	0.8	47 ± 10	22.5
NC_A ₅₀ -D ₅₀	0.5	62 ± 7	22.5
NC_A ₂₀ -D ₈₀	0.2	71 ± 8	22.5

Table III.6 – *Experimental values of initial modulus E , compared to the predicted value calculated from the Guth and Gold model for a silica volume fraction of 0.203. Silica volume fraction was defined as the volume ratio of silica nanoparticles to the total volume of hybrid hydrogels, fixed at 0.203 for all compositions (using $\rho_{Si} = 2.3 \times 10^6 \text{ g.cm}^{-3}$).*

We consider first the mechanical behavior at a standard strain rate of 0.06 s^{-1} (3 mm/min) and we explore the effect of the monomer nature.

4.4.2 Tensile behavior

Typical stress-strain curves are given figure III.22 for a strain rate $\dot{\epsilon} = 0.06 \text{ s}^{-1}$. Monotonic uniaxial tensile tests to final failure allow the investigation of the behavior of the hybrid gels at large strain and the role of physical bonds on the reported hyperelasticity.

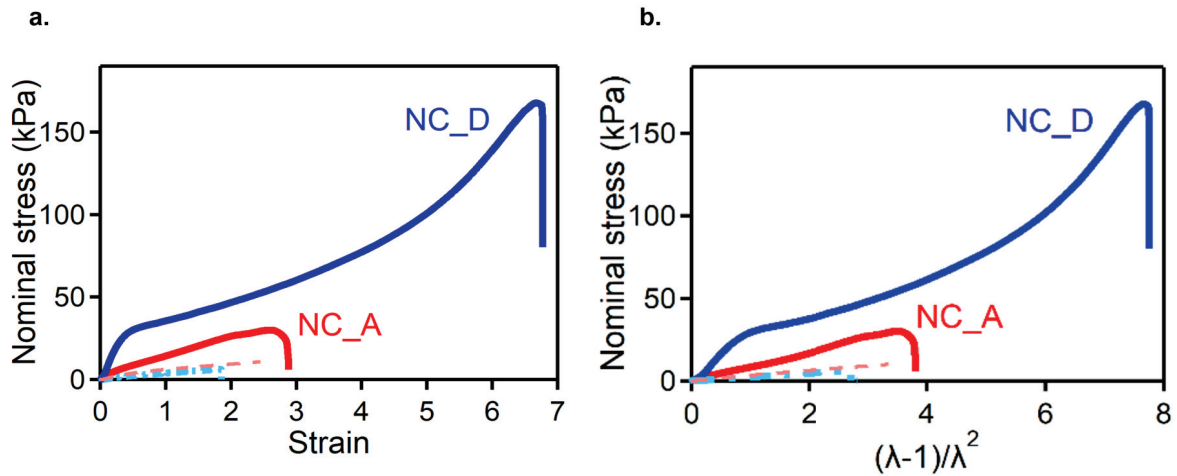


Figure III.22 – **a.** Stress-strain curves of PAAm and PDMA hybrid gels at 0.203 v/v silica (NC_D, in dark blue and NC_A, in red), conducted at 0.06 s^{-1} . Chemical PDMA and PAAm gels curves are displayed as a reference (MD, light blue dashed line and MA, in pink dashed line.) **b.** Stress of NC_D (dark blue) and NC_A (red) plotted vs $\lambda - 1/\lambda^2$. MD_R01 (light blue dashed line) and MA_R01 (pink dashed line) are displayed as a reference. All samples are cross-linked with 0.1% MBA molar ratio.

Both NC_A and NC_D exhibit homogeneous deformation without necking phenomenon. NC_D displays highly non-linear behavior with marked "S-shaped" curve indicating strong deviation from the classical model of rubber elasticity, with a softening at intermediate strain (around $\epsilon = 0.5$) and a strain hardening at higher strain indicating finite extensibility of the polymer chains. As previously reported, the stretchability is highly improved ($\epsilon \approx 700\%$) compared to the one of chemical

PDMA gel. The nominal strain at break determined from the stress-strain curves largely underestimates the nominal strain undergone by the gel matrix itself [Mullins and Tobin, 1957]. In order to appreciate this increase in strain at failure, it is crucial to note that the local average strain in the polymer matrix is necessarily amplified over that of the macroscopic sample. The high contrast in modulus between the soft polymer matrix and the hard silica filler implies strain amplification effects, associated with the volume occupied by the non-deformed particles. A strain amplification factor, X , can be calculated for any type of matrix (viscous, elastic, viscoelastic) [Domurath et al., 2012] as:

$$X = \frac{1}{1 - \phi_{Si}} \quad (\text{III.32})$$

With ϕ_{Si} , the silica volume fraction. For PDMA hybrid gel (NC_D), the previous equation gives an amplification factor of 1.26 (for $\phi_{Si} = 0.203$) meaning that the strain at failure within the gel would reach approximatively 1000% compared to the mean nominal strain at failure. This effect can be explained by the synergy between the silica nanoparticles and the matrix, allowing exchanges of polymer segments with the surrounding nanoparticles.

On the other side, NC_A gels shows quasi linear deformation with drastically reduced strain and stress at break, of the order of the corresponding chemical gels. Reinforcement is clearly decreased by the introduction of a non-interacting monomer underlying the key-role of polymer adsorption for hydrogel reinforcement. The calculated strain at failure within the gel using the strain amplification factor for NC_A is estimated at 380 % only for a nominal strain at break of $\approx 300\%$.

The ability of the hybrid networks to relax stress concentration by dynamic exchanges between adsorbed and unadsorbed polymer segments is permanently disabled when the interacting monomer is substituted with one displaying lower affinity. However, single stress-strain curves are not sufficient to describe the mechanical behavior since in most applications, materials undergo repeated loading at various strain rates, therefore the investigation of the behavior at several strain rates through cyclic and fracture experiments becomes necessary to fully assess the mechanical response. The evolution of the modulus on successive loading cycles is also a relevant parameter of the permanent damage or the self-healing ability.

4.4.3 Impact of non-interacting monomer on dissipation processes and recovery

Strain-controlled tensile loading-unloading cycles were conducted from $\epsilon_0=0$ to $\epsilon_0=0.2$ to stay away from the particle/particle compression in the transverse direction upon deformation. This critical deformation (ϵ_c) can be roughly estimated according to the following formula, assuming that the nanoparticles are arranged in a cubic conformation:

$$\epsilon_c \approx \left(\frac{\pi}{6\phi_{Si}} \right)^{2/3} - 1 \quad (\text{III.33})$$

In the case of NC_D cross-linked at 0.1 mol% the critical strain is estimated to 0.88 for silica volume fraction of 0.203.

Indeed, above the critical strain of particle/particle interaction, recovery and dissipative processes are more complex to analyze. As shown in figure III.23, the dissipated strain energy is clearly induced by the polymer/particle interactions for NC_D while NC_A displays reduced dissipated energy (evaluated from the area under the loop). Still, compared to the chemical gels that behave like purely elastic systems (without any dissipative processes), here some small but measurable dissipation is noticed.

This dissipation can be attributed to the presence of the high concentration of fillers and/or to the fact that PAAm possesses indeed few affinity toward silica surface but is still able to interact ($\Gamma=0.07\text{mg/m}^2$, from previous work on adsorption of linear polymer chains of PAAm and PDMA onto silica surface in the same chemical conditions, as described in Chapter 2.)

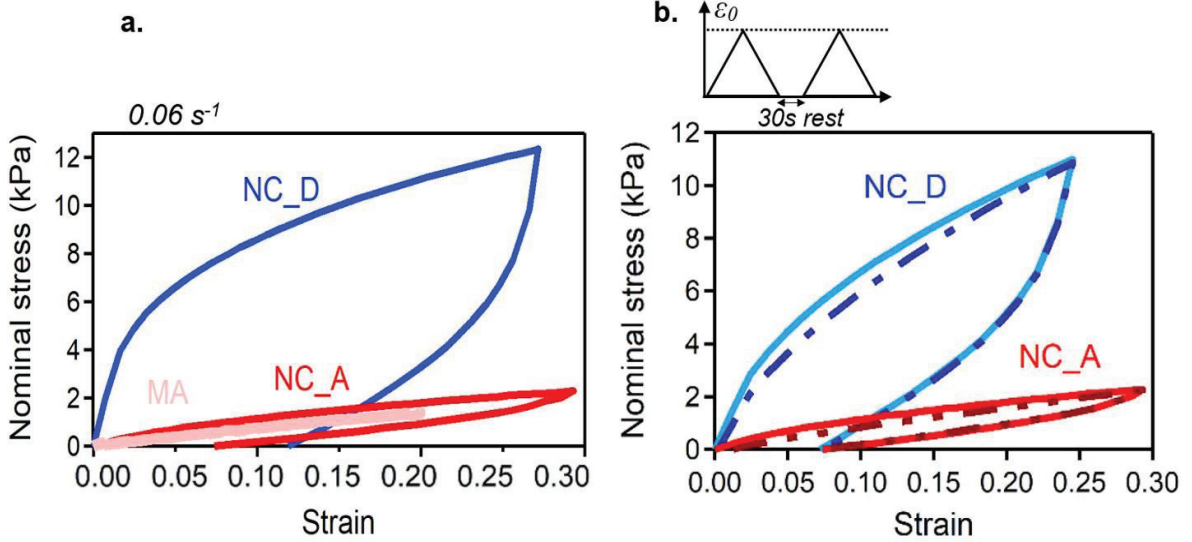


Figure III.23 – **a.** Impact of interacting and non-interacting monomer on the first loading-unloading cycle ($\epsilon_0=0.2$ at $\dot{\epsilon} = 0.06\text{s}^{-1}$ for NC_D (blue), NC_A (red). Chemical MA_R01 (pink) is displayed as reference. **b.** Successive loading cycles on NC_D (blue) and NC_A (red). Residual strain and mechanical behavior were fully restored after 30s. of rest (dashed lines).

The linear tensile modulus is related to the density of elastically active polymer chains, thus it can be regarded as a good indicator of the connectivity of the transient network than can be evaluated through the recovery parameter defined as:

$$R = \frac{E_i^{2nd}}{E_i^{1st}} \quad (\text{III.34})$$

With E_i^{1st} and E_i^{2nd} respectively the linear tensile moduli during the first and the second cycle. Results are reported in table III.8. As shown in figure III.23.b, NC_D hydrogels achieve a full recovery of the modulus and of the residual strain after 30 seconds of rest. The duration the experiment, $t_{exp} \approx \tau_c$, the characteristic time needed for the breaking and reforming of the reversible interactions, allowing the full recovery since $\tau_c \approx 10$ seconds. The stress relaxation here is ensured by a release of strained polymer chains. More surprisingly, at low strain, NC_A also shows good recovery after the same time of rest and no residual deformation. However, these tests are conducted at low strain and constant strain rate which does not allow to probe the time-dependence of the mechanical response.

4.4.4 Mechanical behavior of hybrid gels at swelling equilibrium

The mechanical properties of gels were previously characterized in the preparation state which is far from the thermodynamic equilibrium. As presented in figure III.24, the tensile behavior of both NC_A and NC_D is strongly impacted at swelling equilibrium.

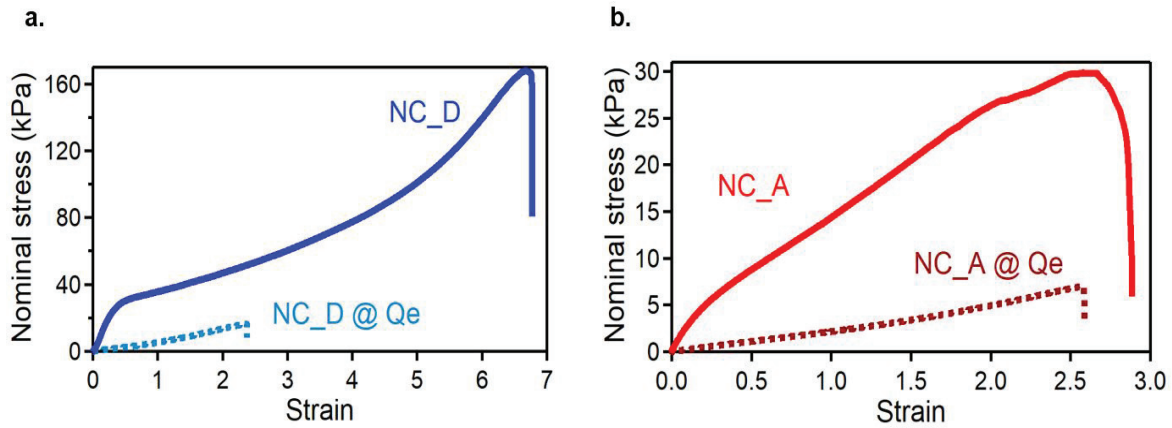


Figure III.24 – **a.** Comparison of the stress-strain curves of NC_D (dark blue line) at Q_0 (preparation state, dark blue line) and at Q_e (swelling equilibrium, light blue dashed line) **b.** Same comparison for NC_A at Q_0 (red line) and at Q_e (dark red dashed line). Tests were conducted at 0.06 s^{-1} .

The impact of the swelling state is obvious, with a large decrease of the linear tensile moduli and the strain at break for both PDMA and PAAM hydrogels. The decrease of the stiffness and the strain at break go together with a loss of the dissipative processes for NC_D at Q_e , as presented in figure III.25.

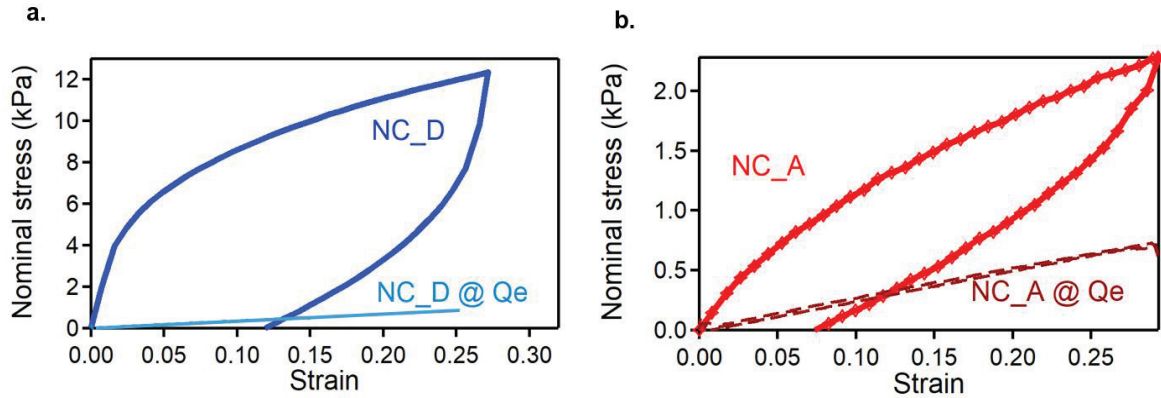


Figure III.25 – **a.** Effect of swelling conditions on the dissipation under loading cycle: at preparation state Q_0 (blue line) and at swelling equilibrium Q_e (light blue dashed line). **b.** Same comparison for NC_A at Q_0 (red line) and at Q_e (dark red line). Tests were conducted at 0.06 s^{-1} .

The swelling state decreases drastically the mechanical properties of the hybrid gels: linear tensile modulus, strain at break and dissipative properties, as reported in table III.7. However, the linear tensile modulus of NC_D as well as the strain at break remain higher than the ones of NC_A as reported in table III. This could mean that the reversible interactions are still at play in the swollen state.

	NC_D @	NC_D @	NC_A @	NC_A @
	Q_0	Q_e	Q_0	Q_e
Swelling	8.45	29	11.34	193
SR (Q_e/Q_0)		3.43		17
E_d (kJ.m ⁻³)	1.87	-	0.196	-
E_d/E_a (kJ.m ⁻³)	0.64	-	-	0.45
E (kPa)	92 ±8	5.6±0.6	23 ±4	2.9±0.4

Table III.7 – Swelling state effect on linear tensile modulus (E), dissipated strain energy (E_d , calculated as the area under the loading cycle curve) and the normalized E_d/E_a with E_d the dissipated strain energy and E_a the strain energy of the loading of NC_A and NC_D in the preparation state (Q_0) and at swelling equilibrium (Q_e).

4.5 Time-dependence and behavior at large strain

4.5.1 Impact of strain rate on the mechanical behavior at large strain

The PDMA hybrid gels containing a high content of silica nanoparticles display a significant time-dependence of the mechanical response, with an increase of the gel stiffness for higher strain rates as shown in table III.8. This result reveals an important viscoelastic contribution which is correlated to the content of nano-filler. This is consistent with the frequency variation of the modulus G' measured in rheology. Nominal and true stress-strain curves are given in figure III.26, for strain rates varying by several decades. As previously stated for monotonic tensile tests at $\dot{\epsilon}$: 0.06 s⁻¹, the deformation of NC_D gels remains homogeneous and the stress-strain curves present an highly non-linear general shape. The reinforcing impact of silica nano particles in presence of interacting polymer is clearly visible on the true stress-strain curve of NC_D at $\dot{\epsilon}$: 0.6 s⁻¹ reaching a maximal stress of 2 MPa. Since the duration of experiments $t_{exp} \ll \tau_c$, the contributions of the frozen physical network and of the chemical one are probed. Conversely the stiffness, strain and stress at break of PAAm hybrid gels do not vary much with increasing strain rate, with a maximum true stress that does not exceed 200 kPa.

For NC_A hybrid hydrogels, deviations from the classical model of rubber elasticity (large strain softening at intermediate strains and strain hardening at large strains) are strongly weakened with almost no hardening at the early stages of deformation and less pronounced stress softening at intermediate strain whatever the applied strain rate. In this case, since the nano particles content is the same as NC_D gels the softening effect can be attributed to the lack of reversible polymer/silica associations leading to a drastic decrease of the failure properties.

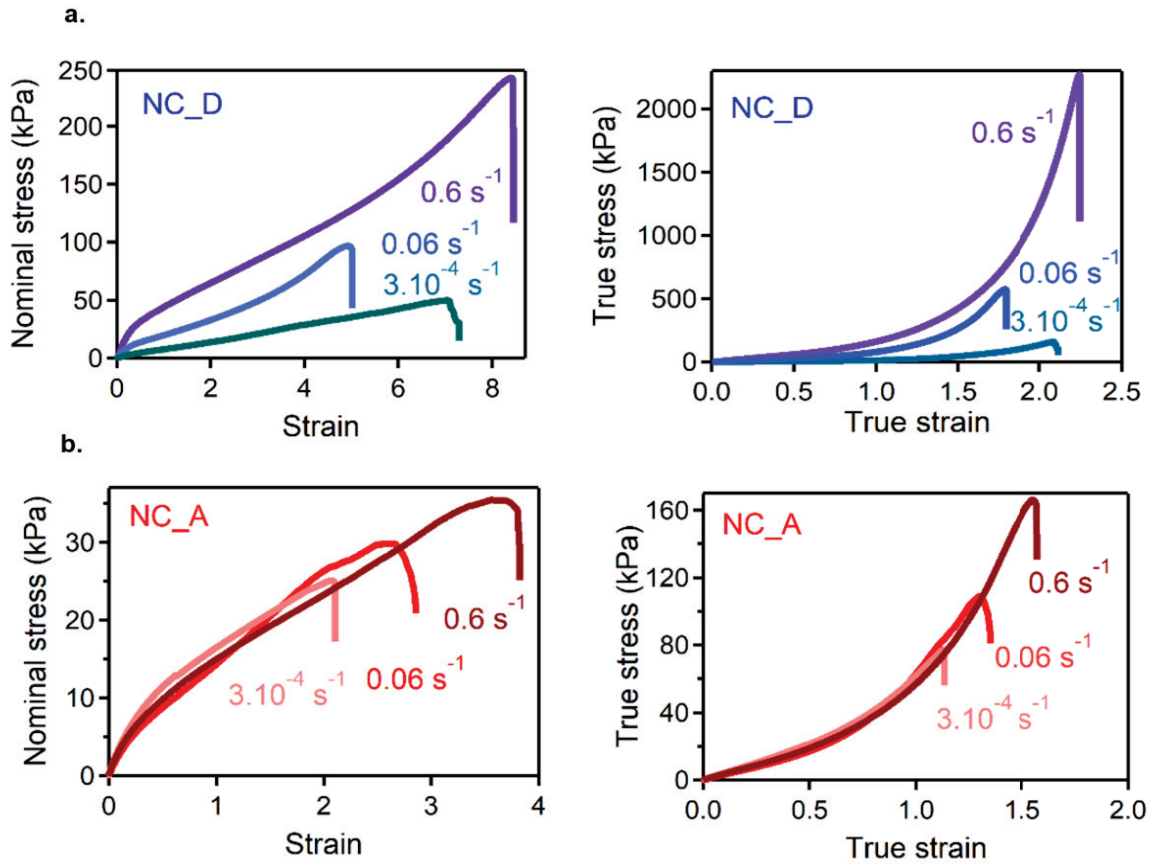


Figure III.26 – **a.** Stress-strain curves of NC_D at various $\dot{\epsilon} = 3.10^{-4}$ (grey), 0.06 (blue) and 0.6 (purple) s^{-1} . On the left, nominal stress is plotted against the strain, on the right true stress-strain curves are displayed **b.** Stress-strain curves (nominal stress, left and true stress-strain curves on the right) of NC_A at various $\dot{\epsilon} = 3.10^{-4}$ (pink), 0.06 (res) and 0.6 s^{-1} (dark red). Silica volume fraction is fixed at 0.203 for all compositions.

Tensile tests conducted at low strain rate reveal similar behavior of NC_D and NC_A in term of stiffness and dissipation. Note that differences in the strain at break are observed with higher stretchability for NC_D than for NC_A, as shown in figure III.27. At this strain rate, the duration of the experiments $t_{exp} \gg \tau_c$, the PDMA/silica system is fully relaxed and the contribution of the nanoparticle/polymer interactions seems to be screened.

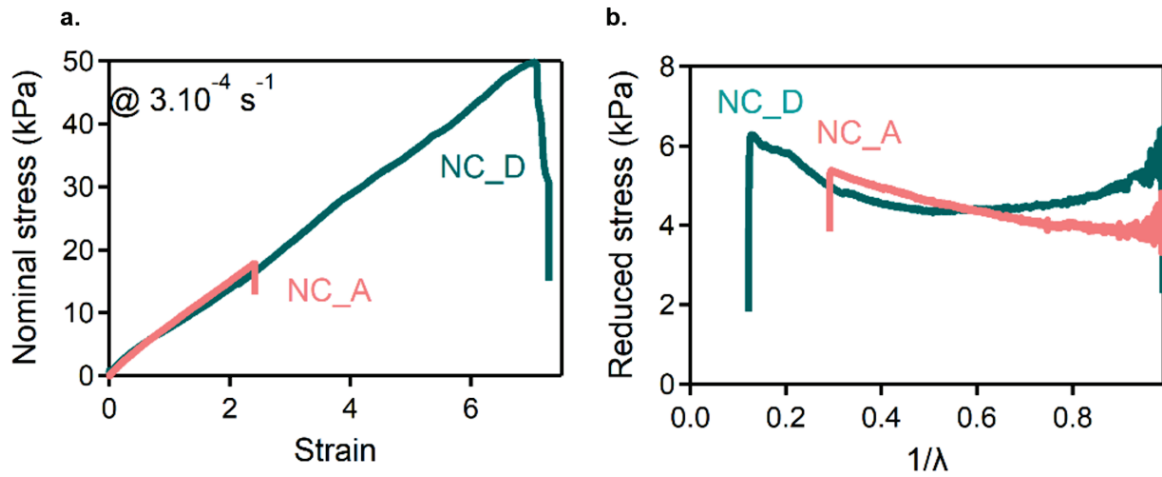


Figure III.27 – **a.** Stress-strain curves of NC_D (blue-green) and of NC_A (pink) at $\dot{\epsilon} = 3.10^{-4}$. **b.** Reduced (Mooney) stress plotted as a function of $1/\lambda$ of NC_D (blue-green) and of NC_A (pink) at $\dot{\epsilon} = 3.10^{-4}$

But more interestingly, the obtained Young's modulus of NC_A gels remain almost independent of the applied strain rate and is in good agreement with the Guth and Gold's model, nearly the same as the fully relaxed NC_D at low strain rate (i.e. $3 \times 10^{-4} \text{ s}^{-1}$) as illustrated in figure III.28.

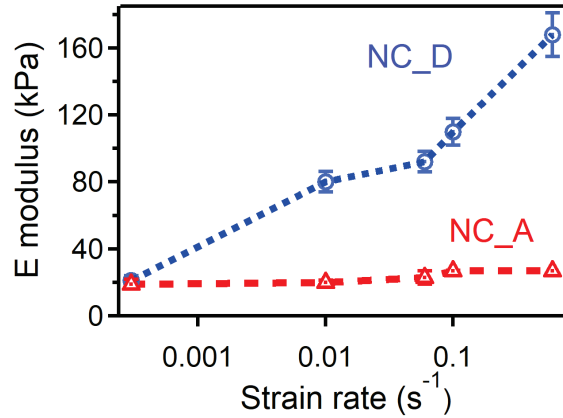


Figure III.28 – Evolution of E modulus of NC_A (red triangles) and NC_D (blue circles) at various strain rates ($\dot{\epsilon} = 3.10^{-4}, 0.01, 0.06, 0.1$ and 0.6 s^{-1})

4.5.2 Impact of strain rate on dissipation processes

The impact of strain rate on loading-unloading cycles is illustrated in figure III.29 and clearly indicates the weaker time-dependence of the mechanical response of NC_A gels. The calculated dissipated energy does not vary much with increasing strain rate, excepted for very low strain rate, contrary to NC_D gels that show increased dissipated energies with increasing strain rate (E_d of NC_D = 5.234 against E_d of NC_A = 0.226 at 0.6 s^{-1} , in kJ.m^{-3}).

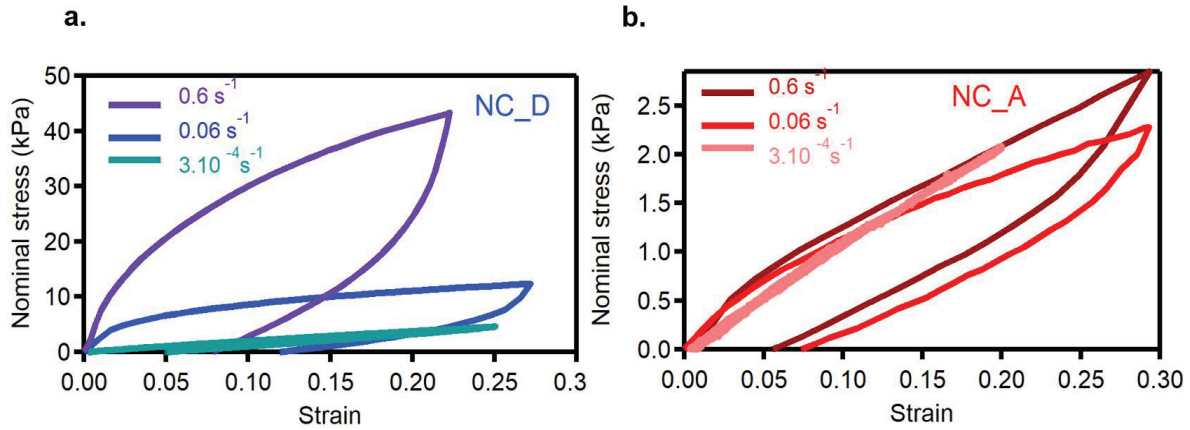


Figure III.29 – **a.** Impact of strain rate on NC_D gels by varying the strain rate of several decades ($\dot{\epsilon} = 3.10^{-4}$, 0.06 , and 0.6 s^{-1}). **b.** Impact of strain rate on NC_A gels ($\dot{\epsilon} = 3.10^{-4}$, 0.06 , and 0.6 s^{-1})

The dissipative capabilities as well as the time dependence are much weaker for NC_A confirming the role played by labile sacrificial bonds for gel toughening. Two interesting features appeared: at low strain, the modulus value is barely affected by the strain rate underlying the lack of connection between the silica and the polymer network, as shown in table III.8, but no dissipation is noticed, which might indicate that the dissipation observed at higher strain rate might be due to the weak interactions between PAAm and silica.

Sample		NC_D	NC_A	MD	MA
ϕ_{Si}		0.203	0.203	0	0
$\dot{\epsilon} = 3 \times 10^{-4} \text{ s}^{-1}$	$E(\text{kPa})$	21 ± 3	19 ± 3	-	-
	$E_d(\text{kJ.m}^{-3})$	0.045	0.01	-	-
	$E_d/E_a(\text{kJ.m}^{-3})$	0.09	0.045	-	-
	R	0.96 ± 0.02	0.87 ± 0.01	-	-
$\dot{\epsilon} = 0.06 \text{ s}^{-1}$	$E(\text{kPa})$	92 ± 8	23 ± 4	8 ± 1	7 ± 1
	$E_d(\text{kJ.m}^{-3})$	1.87	0.176	0	0
	$E_d/E_a(\text{kJ.m}^{-3})$	0.64	0.45	-	-
	R	0.97 ± 0.02	0.86 ± 0.01	1	1
$\dot{\epsilon} = 0.6 \text{ s}^{-1}$	$E(\text{kPa})$	168 ± 12	27 ± 1	8 ± 1	-
	$E_d(\text{kJ.m}^{-3})$	5.234	0.226	0	0
	$E_d/E_a(\text{kJ.m}^{-3})$	0.71	0.54	-	-
	R	0.97 ± 0.02	0.88 ± 0.02	1	1

Table III.8 – Strain rate effect on linear tensile modulus (E), dissipated strain energy (E_d), the normalized E_d/E_a with E_d the dissipated strain energy and E_a the strain energy of the loading and initial stiffness recovery (ratio R , Eq (III.35)) for NC_A and NC_D. Corresponding chemical gels (MA_R01 and MD_R01) are displayed as a reference for unfilled hydrogels materials. Recovery parameter R is calculated after 30 s of rest for each sample.

4.5.3 Fracture properties at large strain

Fracture energies (or equivalently energy release rates) calculated from single-edge notch tensile tests for NC_A and NC_D for various strain rates ($\dot{\epsilon} = 3.10^{-4}$, 0.01, 0.06, 0.1 and 0.6 s^{-1}) are represented in figure III.30 and values are reported in Table III.9.

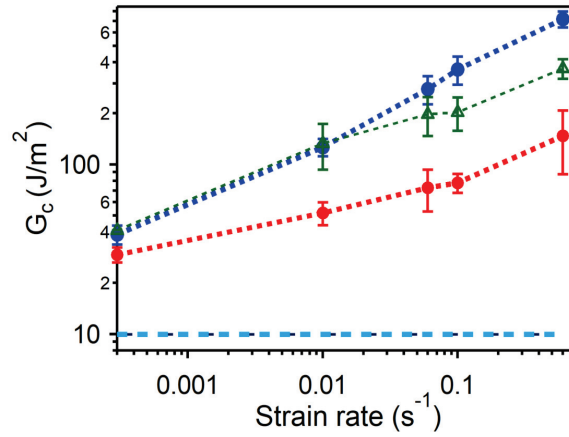


Figure III.30 – Calculated fracture energies for NC_A (red dots) and NC_D (blue dots) for various strain rate ($\dot{\epsilon} = 3.10^{-4}$, 0.01, 0.06, 0.1 and 0.6 s^{-1}). Fracture energies of NC_D at pH11 are also displayed (green). Fracture energies of chemical gels (MD_R01, $G_{1c} = 9.92$ J/m^2) are displayed as a reference (blue dashed line)

The addition of silica nanoparticles in presence of an interacting polymer matrix (NC_D) significantly increases the energy release rate, in all the range of strain rate investigated. As the polymeric matrix has a low cross-link density, the effect of the silica nanoparticles is very important. However, polyacrylamide hybrid gels with the same cross-linker molar content lead to weaker fracture energies, highlighting the lack of dissipative processes of these materials. A comparison can be done with the Lake and Thomas's prediction [Lake and Thomas, 1967] developed for elastomers to estimate the threshold energy G_{LT} necessary to propagate a crack in unfilled rubbers according to:

$$G_{LT} = \Sigma J N_c$$

with Σ the surface density of chains crossing the fracture plane, N_c is the number of monomer units between cross-links and J is the required energy to break one covalent bond. This model is based on the assumption that the transmitted load brings each bond in a polymer strand crossing the interface close to its maximal free energy which gives a calculated value of 1.2 J/m^2 , for a number of monomer units of 500 between two cross-linking points (0.1 mol %). The model proposed by Lake and Thomas propose a quite good estimation estimation of the fracture energy for chemically cross-linked samples. Clearly, this model is not appropriate to describe the fracture experiments proposed which involve large deformations, crack blunting and presumably large dissipative volume contributing to the overall measured fracture energy. Furthermore, the experiments are conducted without control of the crack propagation rate, so that an apparent G_{1c} is calculated.

strain rate (s^{-1})	G_{1c} NC_D (J/m^2)	G_{1c} NC_A (J/m^2)	G_{1c} MD_R01 (J/m^2)
3.10^{-4}	39 ± 5	29 ± 3	-
0.01	126 ± 15	52 ± 8	-
0.06	278 ± 52	73 ± 20	10 ± 2
0.1	363 ± 68	78 ± 10	-
0.6	717 ± 77	142 ± 60	-

Table III.9 – *Experimental values of fractures energies at various strain rate for NC_D, NC_A and MD_R01 (chemical gel displayed as a reference) compared to the Lake and Thomas calculation estimated at 1.2 J/m^2 .*

The increase of fracture energy with the strain rate noticed for NC_D hybrid gels is also observed for unfilled elastomers [Gent, 2000]. This variation parallels closely the variation of viscoelastic properties with rate: as the strain rate increases, a larger fraction of the energy is dissipated, which means that a higher overall mechanical energy must be provided to break the sample. The fracture energy increases with viscoelastic energy dissipation. These experiments gives an insight on the role played by the polymer adsorption in dissipative processes and by the dynamic exchanges between adsorbed and unadsorbed polymer segments for gel toughening as the hybrid gels based on non-interacting monomer display lowered fracture energies.

5 Identifying the nature of interactions

Poly(*N*-alkylacrylamides) are supposed to interact through hydrogen-bonding between the carbonyl group of their amid moieties and the silanol group at the silica surface.

The aim here is to identify more precisely the nature of the PDMA/silica interactions by changing the surface chemistry of silica with an increase of the surrounding pH (around the dissolution threshold of silica nanoparticles, close to 11 [Iler, 1979] while keeping the same (interacting) monomer (DMA) in the polymer matrix. The shift towards an higher pH value should change the proportion of silanol/silanolate groups available at the silica surface. It was demonstrated that for poly(acrylamide) the presence of silanols (Si-OH) was crucial for interactions [Griot and Kitchener, 1965a,b] so tuning the silanols density should modulate the strength of interactions between PDMA and silica and thus the mechanical response.

Similarly to the control experiments conducted on PDMA and PAAm chemical gels synthesized at pH 9, the stability of the polymer matrix of chemical PDMA gels at pH 11 was investigated. Indeed, as amide groups present in the acrylamide skeleton are sensitive to basic conditions that can lead to their degradation, their stability needs to be investigated first. PDMA at pH 9 and 11 show similar swelling and tensile behavior with similar Young moduli (8kPa for MD_R01 against 6 kPa for MD_R01_pH11) and swelling ratios ($\text{SR} = 5.92 \pm 0.39$ for pH 11 and 5.65 ± 0.32 for PDMA at pH 9). Therefore, the network seems to keep its integrity at higher pH values and the polymerization process does not seem to be affected either. In addition, the titration of extractibles contents realized on the chemical samples at pH 11 do not show more extractibles content than their counterparts synthesized at pH 9. On the other hand, DLS conducted on silica nanoparticles over two weeks at pH 9 and 11 did not show any significant change in their average size.

5.1 Tensile behavior and swelling properties

Stress-strain curves of the chemical and the hybrid PDMA gels at pH 9 and 11 are represented in figure III.31. Hybrid gels synthesized at pH 11 display decreased stiffness and strain at break, with nearly no strain softening at intermediate strain and strain hardening at large strain.

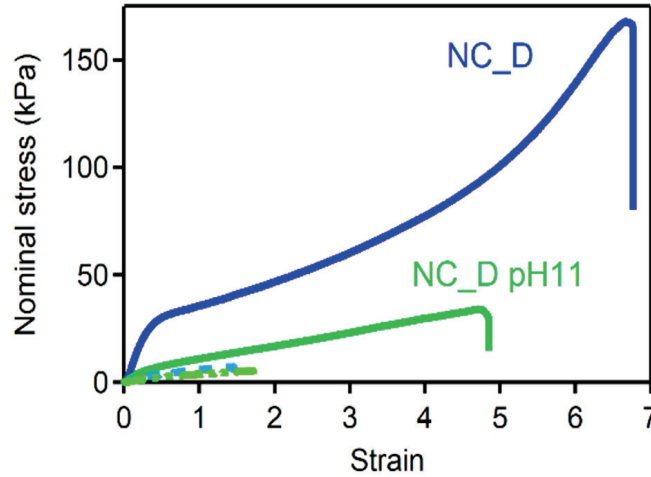


Figure III.31 – Large strain behaviour of chemical and hybrid PDMA hybrid gels at pH 9 (dark blue) and 11 (green). The curve of MD_R01 (dashed light blue line) and of MD_R01_pH11 (dashed light green line) are given as a comparison. All tensile experiments were conducted at $\dot{\epsilon} = 0.06 \text{ s}^{-1}$

The Young's modulus values obtained for these hydrogels (19 kPa at pH 11 as compared to 88 kPa for PDMA hybrid gel at pH 9). These results highlight the fact that reinforcement in PDMA hybrid gels strongly decreases at high pH, which is consistent with other reported work conducted on the pH dependence of polymer adsorption [Van der beek and Cohen-Stuart, 1991; Van der Boomgaard et al., 1987]. The phenomenon can be explained by the increase of negative charges at silica surface at high pH, inhibiting the hydrogen bonding between the carbonyl group of PDMA and the surface groups of silica.

Sample	Q_0	Q_{eq}	$SR = \frac{Q_{eq}}{Q_0}$	$E \text{ (kPa)}$
MD_R01	8.45	50 ± 5	5.92 ± 0.39	8 ± 1
MD_R01_pH 11	8.45	48 ± 3	5.65 ± 0.32	6 ± 1
NC_D	8.45	34 ± 1	3.97 ± 0.11	88 ± 1
NC_D_pH 11	8.45	39 ± 6	4.63 ± 0.5	19 ± 5

Table III.10 – Swelling of hybrid and chemical hydrogels, at pH9 and pH 11, $E \text{ (kPa)}$ determined at 0.06 s^{-1} . All samples are synthesized with a molar cross-linker ratio of $0.1 \text{ mol}\%$

The swelling behavior of the PDMA hybrid gels synthesized at pH 9 and 11 is displayed in table III.10. The gels synthesized at higher pH display slightly higher swelling ratio than that of NC_D. Still the uptake of absorbed water remains way smaller than the one obtained for acrylamide-based gels with the same silica content. Since the basic pH does not seem to have a great impact on either the polymer matrix or the stability of the silica nanoparticles, the difference of behavior points

to lack of affinity of the polymer for the silica surface. Still, the obtained swelling ratio are not consistent with the presence of non-interacting fillers as it is the case for PAAm-based hybrid gels but rather with an interacting polymer with fewer adsorption sites available.

5.2 Dissipative properties

Tensile cycles carried on at small strain show the decrease of dissipative properties for NC_D at higher pH as illustrated in figure III.32, with reduced hysteresis and a deformation behavior close to the ones of the chemical gels. However, at small strain, full recovery after the first cycle is reached, independently of the time of rest allocated between two cycles. The lack of dissipative processes ($E_d = 1.171$ for NC_D and $E_d = 0.174$ for NC_D pH 11, in kJ.m^{-3}) associated with the absence of characteristic time needed to reform the polymer/silica interactions that characterizes PDMA/silica hybrid gels as previously reported [Rose et al., 2013b] point to the fact that polymer adsorption is almost completely impaired at higher pH.

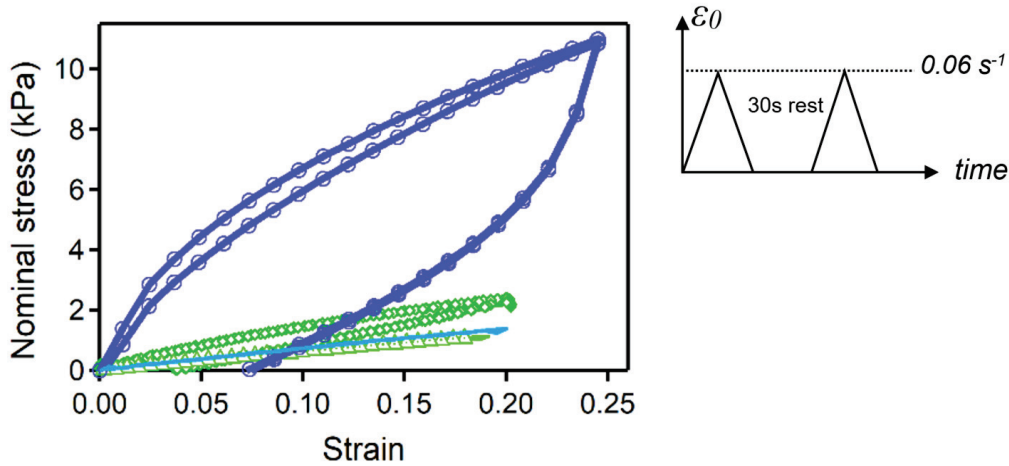


Figure III.32 – Effect of 30 sec. of rest on the cycling behavior at small strains at 0.06 s^{-1} for NC_D_pH11 (green diamonds) and NC_D (dark blue circles) and the corresponding chemical gels. Dissipated energies (in kJ.m^{-3}) are calculated from the area under the loop and give 0.174 kJ.m^{-3} for NC_D_pH11 and 0.254 kJ.m^{-3} for NC_D.

5.3 Strain rate impact and fracture properties

The behavior of PDMA hybrid gels at pH 11 follows the same trend as hybrid gels synthesized with non-interacting monomer (AAm), meaning that fracture experiments and tensile tests conducted at various strain rates show weakened time-dependence of the mechanical response as depicted in figure III.33. The values of linear tensile modulus for various strain rate are reported in table III.11. Hybrid gels synthesized at higher pH show significantly decreased stiffness.

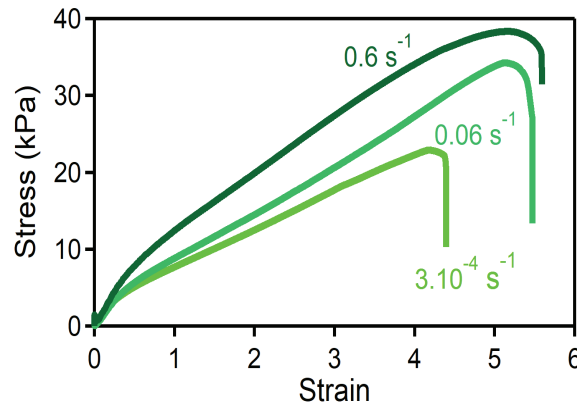


Figure III.33 – Strain rate effect on tensile mechanical behavior of NC_D pH 11 at various $\dot{\epsilon} = 3.10^{-4}$ (light green), 0.06 (green) and 0.6 s^{-1} (dark green).

strain rate (s^{-1})	G_{1c} D_SP20_pH9 (J/m^2)	G_{1c} D_SP20_pH11 (J/m^2)	E (kPa) D_SP20_pH11
3.10^{-4}	38.7 ± 5	41 ± 3	15.8 ± 5.5
0.01	126 ± 15	133 ± 8	-
0.06	278 ± 52	198 ± 51	18 ± 6
0.1	363 ± 68	203 ± 45	-
0.6	620 ± 187	368 ± 48	22 ± 5

Table III.11 – Experimental values of fractures energies and initial modulus E at various strain rate for D_SP20_pH11 and D_SP20_pH9 A_SP20.

Still, fracture energies display a slightly higher time-dependence than the ones obtained for PAAm-based hybrid gels at pH 9. One can wonder if a small fraction of PDMA-silica interactions are still effective at these high pH values since these values remain much higher than the one obtained for similar chemical hydrogels and for PAAm-based hydrogels.

6 Conclusion

In this chapter, the use of acrylamide monomer (AAM) as the main component of the polymer matrix has allowed to probe its impact on the structure and mechanical properties of chemical and hybrid gels. In pure chemical gels, both PAAm and PDMA possess similar mechanical and swelling behavior, to the difference of a slightly more inhomogeneous network for PAAm gels, as evidenced with the increased swelling at equilibrium and the rheology measurements.

In hybrid gels, the use of PAAm induces a significant weakening of the mechanical behavior with a strong decrease of the dissipative properties and of the obtained stiffness compared to those of PDMA networks. The large strain elasticity usually reported for these systems seems to be lowered as well. The structure analysis conducted using SAXS experiments points to lower repulsion between silica beads in PAAm hybrid networks that could be linked to closer interparticular distance, confirming the fact that silica is more prone to aggregate than in PDMA gels. This last result

emphasizes the importance of the polymer/filler affinity for the reinforcement but also for the dispersion of the fillers within the matrix.

The experiments carried on PDMA hybrid gels synthesized at pH 11 revealed decreased mechanical properties compared to the ones of PDMA hybrid gels at pH 9, probably induced by the change of silica surface chemistry. These results underline the crucial role of the surface chemistry of the adsorbate, here the availability of the possible adsorption sites at the filler surface to create the transient physical network necessary to reach an efficient reinforcement.

As PAAm and PDMA are structurally very close, one can wonder why the resulting hybrid gels display such a different mechanical response in the same experimental conditions (composition, matrix hydration, pH, silica content and nanoparticles size). Under our specific conditions (pH, size of nanoparticles, weak ionic force) studies of adsorption of linear polymer chains of PAAm have displayed few affinity towards silica surface compared to PDMA. As adsorption between silica and poly(*N*-alkylacrylamides) proceeds through hydrogen-bonding, a possible explanation could be that, as PAAm is better solvated by water than poly(*N*-alkylacrylamides), solvent-polymer interactions prevail on the polymer- NPs ones, leading to the experimentally observed decreased adsorption of PAAm. This was suggested by Perrin *et al.* who used molecular dynamics simulations to propose the possible role of the solvent and also by the theoretical work conducted by Molinari *et al* [Molinari and Angioletti-Uberti, 2018; Appel and Scherman, 2014].

To go further into the understanding of those materials, the next chapter is dedicated to the use of ^1H NMR spectroscopy of PAAm and PDMA hybrid gels, to get more insight on their networks structure and dynamics.

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Chapter IV

^1H NMR structural study of PDMA and PAAm hybrid hydrogels

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1 Introduction

The last Chapter investigated the impact of the chemical nature of the monomer and of the surface chemistry of the silica nanoparticles on the mechanical behavior of hybrid gels with well-dispersed silica within the matrix.

It evidenced that tuning the reversible polymer/filler interactions leads to a drastic decrease of the mechanical properties (stiffness, dissipation and recovery processes, fracture resistance, swelling behavior, strain at break). The role of hydrogen bonding between PDMA and silica was more specifically identified with hybrid gels synthesized at higher pH displaying lowered mechanical response due to a change of the silica surface chemistry disturbing the interactions between PDMA and silica nanoparticles.

The main purpose of this chapter is to investigate the structure of these hybrid gels using ^1H NMR as a probing tool to provide useful insight on the structure of both PAAm and PDMA hybrid gels that could be linked to the different mechanical responses.

The use of NMR spectroscopy for the characterization of polymer hydrogels and organogels is a growing field [Shapiro, 2011], involving magic angle spinning (MAS) in the solid-state NMR, spin relaxation times, nuclear Overhauser enhancements (NOE), or multiple-quantum (MQ) spectroscopy, the pulse field gradient (PFG) technique and magnetic resonance imaging (MRI) allow obtaining the detailed information on morphology, molecular organization, specific interactions and internal mobility of constituents.

Time-domain proton NMR is used here, in two distinct perspectives. First, measurement of the proton relaxation function enables the study of the polymer mobility and allows the determination of the immobilized (adsorbed) polymer fraction at the interface with the silica nanoparticles. Secondly, multiple-quantum (MQ) proton NMR gives insight into the structure of the gel network, namely the cross-linking and/or the entanglement density, homogeneity of the gel network and the fraction of ‘defects’, i.e. the sol fraction and/or unreacted chains, oligomers, dangling chain ends etc. Specific pulse sequences have to be applied to obtain selective observation.

When dealing with proton relaxation function, two problems emerge. The first problem is related to a technical limitation of NMR observation. After applied an excitation pulse or pulse sequence, there is a so-called dead time, of order $15\ \mu\text{s}$ during which the signal cannot be observed. As a rigid material has a relaxation time of order $20\text{--}40\ \mu\text{s}$, this dead-time problem completely impair the proper observation of the signal. This is why so-called spin-echo method must be used to effectively observe the full signal starting from the very beginning of the relaxation. The NMR sequences generally applied for the study of the polymer mobility in filled rubbers are the solid-echo pulse sequence, used to observe the presence of an immobilized polymer fraction in the vicinity of the fillers (seen at short time scales) and the Hahn echo, applied to analyze the mobile fraction (at longer time scales) [Papon et al., 2011]. Here the magic-sandwich echo (MSE) sequence is used to study the polymer relaxation at short time scales (less than $0.2\ \text{ms}$).

The second problem is related to the intrinsic structure of the relaxation signal in a complex fluid system like a gel, in which motions are fast on the NMR time scale (because the material is locally fluid) but motions of chain segments are constraint on a larger scale, because of the permanent network structure. The relaxation signal contains contributions from both the dynamics and the network structure, and these contributions must be discriminated to obtain selective information on the network structure. This is why the so-called double-quantum (MQ) method is used, as it

has been shown that it allows this discrimination in a quantitative way [Saalwachter, 2007]. Thus the combination of these two methods provides a broad view on the polymer dynamics in hybrid hydrogels: the MSE enables the determination of the immobilized (adsorbed) polymer fraction at the interface with the silica nanoparticles and MQ NMR give insight into the cross-link density and homogeneity of the network in the filled samples. To quantify the adsorbed polymer fraction, it is then crucial to control the quantity of silica surface accessible to the polymer and thus the dispersion state of the fillers. The SAXS analysis conducted on PAAm and PDMA hybrid gels (as seen in the last Chapter) have evidenced the good dispersion of fillers in both PDMA and PAAm polymer matrices.

2 Materials and methods

All gels studied in this Chapter are prepared in D_2O to observe selectively the signal of the polymer by ^1H NMR. However, the presence of residual water in the polymer must be considered, as described below.

2.1 Chemicals

Nanoparticles Silica nanoparticles used for all experiments are Ludox-TM 50 produced by Grace and bought from Sigma-Aldrich, used as such without further purification. The nanoparticles were characterized by SEM and Small Angle X-Ray scattering using a fitting procedure for experimental data that considers polydisperse spherical particles with a Gaussian distribution of size. This model gave a mean radius of 13.5 nm with a standard deviation $\sigma = 0.13$. The corresponding surface area is $100 \text{ m}^2/\text{g}$ considering a specific weight of $2.3 \text{ g}/\text{cm}^3$. Silica was deuterated for NMR measurements. Pure Ludox TM-50 was dialyzed against D_2O using dialysis membrane with cut-off 6-8 kDa purchased from Sigma-Aldrich and used after 30 minutes rinse in D_2O . Dialysis solvent was changed every 5 days, this step was repeated three times to ensure proper deuteration of silica. Dialyzed silica maximum concentration was evaluated at 24.85 wt%. Possible agglomeration of particles was ruled out using DLS measurements which did not revealed signs of aggregation.

Monomers and reactants Acrylamide (AAm, 99% electrophoresis grade, Aldrich), *N,N*-dimethylacrylamide (DMA, 99%, Aldrich), *N,N'*-methylenebis(acrylamide) (MBA, 99%, Aldrich) and *N,N,N',N'*-tetramethylethylenediamine (TEMED, 99% bio reagent, Aldrich) and potassium persulfate (KPS, >99%, ACS reagent, Aldrich) were used as received without further purification. Deuterium oxide 99.9 atom % D is purchased from Sigma-Aldrich (verified using ^1H NMR measurements) and used as such.

Polymers Linear polymer chains of poly(acrylamide) (PAAm-2, 230 000 g/mol) and poly(*N,N*-dimethylacrylamide) (PDMA-2, 155 000 g/mol) were synthesized at the lab using ATRP polymerization, as described in Chapter II.

2.2 Gel preparation and composition

Poly(*N,N*-dimethylacrylamide) and poly(acrylamide)-based hybrid hydrogels were prepared at room temperature in a nitrogen-filled overpressured glove box ($\text{O}_2 < 5 \text{ ppm}$) by *in situ* free radical polymerization, using *N,N'*-methylenebisacrylamide (MBA) as the cross-linker and KPS/TEMED

couple as the redox initiators. All the reactants were initially deoxygenated and introduced in the glove box in order to prevent any oxygen contamination. Solid reagents were initially dissolved in deuterated water prior to synthesis: 4,1 wt% for KPS and 1,5 wt% for MBA. After dilution of the silica suspension Ludox-TM50 in deuterated water, the pH was readjusted to 9 or 11 using either HCl or NaOD. The MBA (solution) and the monomer were added. The resulting solution was left under stirring and cooled down with ice-patches. A solution of KPS (at room temperature) and pre-cooled (below 5°C) N, N, N', N' -tetramethylethylenediamine (TEMED) were added under stirring. The mixture was then rapidly transferred into the NMR tubes initially placed under the nitrogen atmosphere of the glove box.

Experimentally we observed that the redox initiation starts rapidly (as shown by Orakdogan [Orakdogan et al., 2005]) and the polymerization was let to proceed during 24 hours in the NMR tubes. The tubes were then sealed using parafilm, Teflon tape and proper plugs in the glovebox.

For all synthesis, the monomer/KPS and monomer/TEMED molar ratio were fixed at 100. The cross linking density (MBA/monomer molar ratio) was varied from 0 mol% to 1 mol% and the silica volume fraction was varied from 0 to 10 vol%. The measurements were performed on the hydrogels in their preparation state, with a fixed molar ratio between polymer and D_2O equal to 0.28. The nomenclature used in this study is A for acrylamide based gel and D for N, N -dimethylacrylamide-based gel. Cross-linking is referred to as R_z with z , the molar ratio of cross-linker to monomer. The silica content is referred as SP_x , with x , the silica volume fraction. As an example, a PDMA chemical gel cross-linked at 0.1 mol% of MBA will be named,:

D_SP0_R01

A PDMA gel, cross-linked at 0.1 mol% with a silica volume fraction of 0.1 and with modified silica surface chemistry (at pH 11) will be labeled:

D_SP10_R01_pH11

The formulations of hybrid hydrogels used in this chapter are given in Table IV.1.

Nomenclature	m _{DMA} /g	m _{D₂O} /g	m _{MBA} /mg	m _{Si} /g	m _{KPS} /mg	m _{TEMED} /μL
D_SP10_R1	0.495	3.536	7.7	0.941	13.5	7.53
D_SP10_R05	0.495	3.536	3.8	0.941	13.5	7.53
D_SP10_R01	0.495	3.536	0.77	0.941	13.5	7.53
D_SP10_R0	0.495	3.536	0	0.941	13.5	7.53
D_SP5_R1	0.495	3.536	7.7	0.470	13.5	7.53
D_SP5_R05	0.495	3.536	3.8	0.470	13.5	7.53
D_SP5_R01	0.495	3.536	0.77	0.470	13.5	7.53
D_SP5_R0	0.495	3.536	0	0.470	13.5	7.53
D_SP2_R1	0.495	3.536	7.7	0.208	13.5	7.53
D_SP2_R05	0.495	3.536	3.8	0.208	13.5	7.53
D_SP2_R01	0.495	3.536	0.77	0.208	13.5	7.53
D_SP2_R0	0.495	3.536	0	0.208	13.5	7.53
D_SP0_R1	0.495	3.536	7.7	0	13.5	7.53
D_SP0_R05	0.495	3.536	3.8	0	13.5	7.53
D_SP0_R01	0.495	3.536	0.8	0	13.5	7.53
D_SP0_R0	0.495	3.536	0	0	13.5	7.53
A_SP10_R1	0.356	3.536	7.7	0.677	13.5	7.53
A_SP10_R05	0.356	3.536	3.8	0.677	13.5	7.53
A_SP10_R0	0.356	3.536	0	0.677	13.5	7.53

Table IV.1 – *Nomenclature and composition of hybrid hydrogels. The matrix hydration is fixed at 87.7wt%. The amount of chemical cross-linker was varied from 0 mol% to 1 mol%. The silica volume fraction is defined as the volume ratio of silica nanoparticles to the total volume of hybrid hydrogels, varied from 0 to 0.1 for all hybrid compositions (using $\rho_{\text{Si}} = 2.3 \times 10^6 \text{ g.cm}^{-3}$).*

2.3 Analytical methods

All time-domain ^1H NMR measurements were performed on a Bruker Minispec mq-20 at 20 MHz proton resonance frequency. The Minispec has typical $\pi/2$ pulse lengths of down to 2 μs (125 kHz nutation frequency), with switching times in the 2 μs range. Each FID and MSE signal was recorded with 128 scans with 4 seconds recycle delay (PDMA) or 2 seconds recycle delay (PAAm and PDMA pH11 samples) and 128 or 256 scans for each DQ points. All measurements were done at $35 \pm 0.05^\circ \text{C}$.

2.3.1 ^1H NMR MSE measurements

The polymer mobility can in principle be investigated by simply studying the standard transverse relaxation, (so-called free-induction decay, FID). As the response of a mobile polymer has a long relaxation time, whereas a rigid or less mobile polymer has a very rapid decay, this technique allows identifying the dynamics of the studied materials. However in our case the FID could not be directly measured at short time due to the rather long dead time of the receiver: the first 15 μs of the FID are missing and this part of the signal is very important since it contains the initial fast decay part corresponding to the immobilized polymer, if any. To obtain the shape of the entire signal decay, a solid-echo technique, so-called Magic-sandwich echo (MSE) is then used. The MSE refocuses the

initial part of the free-induction decay (FID) and thus avoids the dead time issue. Compared with solid echo, it enables a better refocusing of multispin dipolar interactions and has been shown to be a robust method to investigate polymer mobility [Mauri et al., 2008]. The pulse sequence used is sketched in Figure IV.1.

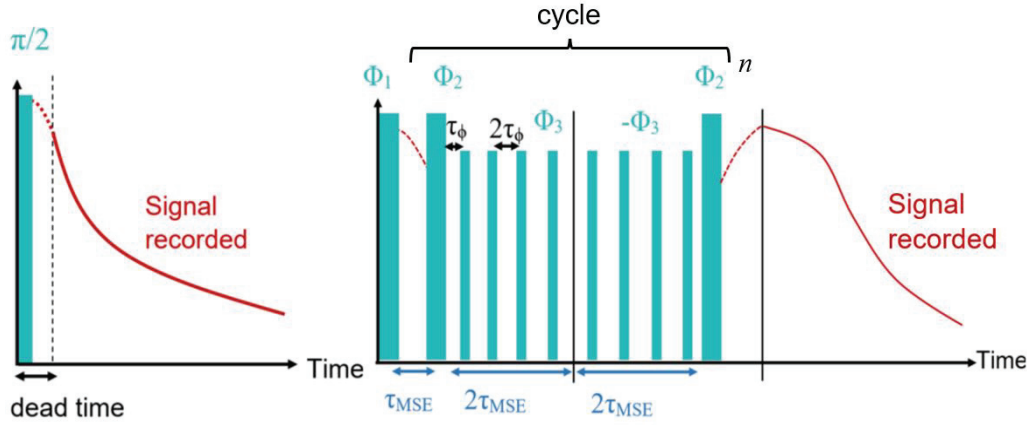


Figure IV.1 – On the left, the initial part of the free-induction decay (FID) is missing due to the dead time of the receiver. On the right, magic-sandwich echo (sequence used to refocus the signal and thus measure the entire shape of the decay. The phase cycle is composed of 12 pulses with varying interpulse time δt :

$$\phi_1 = x\bar{x}x\bar{x} \quad \phi_2 = \bar{y}y\bar{y}y, \quad \phi_3 = x, \quad \text{and } t_\phi \text{ is the finite switching time. From [Papon et al., 2011]}$$

Measurements on dry polymers

MSE sequences were performed with varying interpulse delays ($4 \mu\text{s}$ to $8 \mu\text{s}$) to reconstitute the whole shape of the decay of the rigid fraction. The efficiency of the sequence can be varied by either increasing the number of cycles or increasing τ . The shorter the delay τ , the more complete is the refocusing of the dipolar interactions. The initial part of the signal ($< 0.15 \text{ ms}$) is generally well described by Gaussian function $\exp-(t/\tau)^2$ and is characteristic of the rigid polymer.

Measurements on hybrid gels

The initial part of the signal ($< 0.15 \text{ ms}$) is fitted with Gaussian function $\exp-(t/\tau)^2$. Adsorbed amount is evaluated by the fitting of the decay at longer times with a simple modified exponential $\exp-(t/T_2)^b$ with b ranging between 1 and 2, or double exponential function.

2.3.2 ^1H NMR DQ measurements

The response of polymeric networks or melts in proton NMR experiments is commonly analyzed in terms of residual dipolar interactions [Cohen-Addad, 1974; Sotta et al., 1996] which originate from imperfect motional averaging of chain segments fluctuating rapidly between topological constraints. The orientation of the polymer segments in a network can be described by the time average of the second Legendre polynomial P_2 .

$$\langle P_2(\cos\theta) \rangle = \int_0^t \frac{3\cos^2\theta(t') - 1}{2} dt' \quad (\text{IV.1})$$

where θ is the time-dependent angle between the local chain direction (segmental orientation) and a reference direction (the magnetic field). At high enough temperature (with respect to T_g), reorientational motions are fast and the above time average stabilizes rapidly at short times. Topological constraints, such as entanglements in a melt or cross-links in elastomers and gels lead to a nonzero permanent time average, which gives a dynamic average orientation of the polymer backbone, related to the length R and orientation α of the end-to-end vector for a polymer chain in the network as illustrated in figure IV.2.

$$\langle P_2(\cos\theta) \rangle = \frac{3\cos^2\psi - 1}{2} \frac{3\cos^2\alpha - 1}{2} = S_b \frac{3\cos^2\alpha - 1}{2} \quad (\text{IV.2})$$

where the dynamic order parameter of the polymer backbone S_b is directly related to the chain length, or equivalently to the cross-link density, and is thus characteristic of the network structure:

$$S_b \approx \frac{3}{5} \frac{r^2}{N^2 b^2} \approx \frac{1}{N_{CL}} \approx \frac{1}{M_{CL}} \approx \nu_e \quad (\text{IV.3})$$

N_c is the number of statistical segments (freely jointed rigid rods) between constraints and b the statistical segment length. The overall NMR signal is then the sum of contributions from all chains.

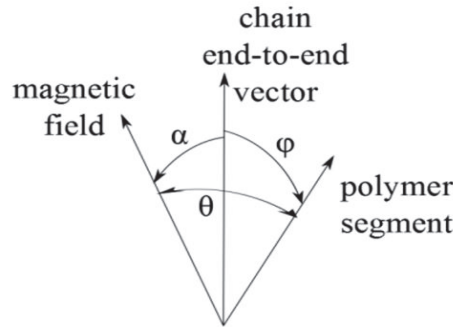


Figure IV.2 – Scheme of the orientation of a polymer segment in a network during MQ ^1H NMR measurement.

What is measured in NMR is the proton dipolar coupling. Since it depends on the molecular orientation, the nonzero dynamic orientation of the polymer backbone S_b is detected in NMR because it gives a nonzero residual dipolar coupling. It is calculated from the experimentally measured average residual dipolar coupling constant D_{res} , by comparison with its static counterpart, D_{stat}

$$S_b = k \frac{D_{res}}{D_{stat}} \quad (\text{IV.4})$$

where k is a correction factor <1 accounting for the spin arrangement and motions within a statistical segment. Therefore, from Eq (IV.3) D_{res} is inversely proportional to the average molecular weight of network chains between cross-links M_c or, equivalently, proportional to the cross-link density μ_e . As entanglements also contribute to the NMR signal, $D_{res} = 1/M_c + 1/M_e$, with M_e the entanglement molecular weight, assuming a constant entanglement density and additivity of

signal, the quantity D_{res} can be extracted in a simple way by taking the slope of the normalized signal at $t = 0$.

3 Results and discussion

The idea here is to assess the structure of the PDMA and PAAm hybrid hydrogels at various cross-linker and silica contents using DQ and MSE ^1H NMR sequences to get better insight on the polymer mobility within the gel (adsorption at the solid/liquid interface) and to get information on the cross-linking density, especially the role played by silica. Special attention is paid to the surface chemistry of silica nanoparticles by controlling the pH (at 9) of the gels during the synthesis step except for PDMA hybrid hydrogels synthesized at pH 11. Comparison with the mechanical behavior of those compounds based on the results described in the Chapter III of this manuscript will be made.

3.1 Adsorbed polymer

A better understanding of the polymer mobility around the fillers is thus of great importance since the presence of an immobilized polymer layer around the silica particles (i. e, adsorbed polymer), is supposed to have a drastic impact on the mechanical behavior of the filled samples. Low-field proton NMR is a well-established method for this purpose in filled rubbers [Papon et al., 2011; Berriot et al., 2002]. Recently, the use of NMR spectroscopy for the characterization of polymer hydrogels and organogels has seen enormous growth [Shapiro, 2011]. As presented in Chapter 2, T_2 relaxometry has already permitted to distinguish between different polymer mobilities and to distinguish the presence of a layer of immobilized polymer around the fillers for linear polymer chains in solution in presence of silica nanoparticles, though in an indirect way. Here the polymer relaxation was studied in hybrid gels containing various amounts of silica nanoparticles and several chemical cross-linker ratios.

3.1.1 Measurements on dry polymers

The polymer mobility can in principle be investigated by studying the free-induction decay (FID) signal of the samples. A slow decay of the FID corresponds to the response of mobile polymer whereas a rapid decay shows the presence of less mobile polymer. Still, direct and quantitative observation of the rigid part is not possible since a significant part of the rigid-part signal, which usually decays within $20\ \mu\text{s}$, vanishes during the dead time. Here MSE-refocused FID was used to recover the missing part of the FID signal. The whole shape of the decay can be reconstructed and allows the study of polymer relaxation at short times. We first characterized the signal of the rigid polymer by performing FID and MSE measurements on the dry PDMA at 308 K. This experiment temperature is far below the glass transition of PDMA. As shown in figure IV.4, in FID measurement, most of the signal has already decayed after $15\ \mu\text{s}$ while MSE allows to recover the missing part. However, the efficiency of the MSE sequence is not 100% and the MSE signal has to be renormalized to get the short time signal quantitatively which can be done using several methods of signal renormalization. As illustrated in figure IV.4.a, the efficiency of the MSE sequences (i.e the overall amplitude of the signal) decreases as the interpulse delay increases. The first way is to perform MSE with varying interpulse delays τ_{MSE} ($4\ \mu\text{s}$ to $8\ \mu\text{s}$) and extrapolate to $\tau_{MSE} = 0$.

Another way is to multiply the MSE signal by a factor to superpose it to the FID in the common time interval.

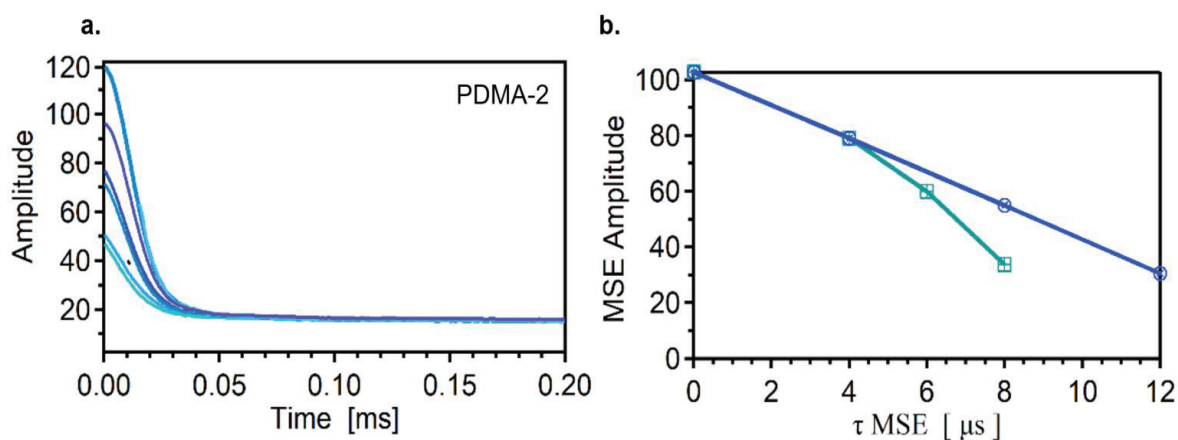


Figure IV.4 – **a.** MSE-refocused FID at various interpulse delay τ_{MSE} and FID measurements of PDMA-2 at room temperature (FID: light blue) and MSE curves with interpulse delay τ_{MSE} of 12, 8, 6 and 4 μs **b.** MSE amplitude of PDMA-2 for varying τ of 12, 8, 6 and 4 μs . The extrapolation at $\tau_{\text{MSE}} = 0$ allows to recover the whole shape of the curve.

The PDMA-2 relaxation signal is composed of two components, one liquid-like, relaxing slowly, and a rigid one, relaxing fast. The liquid part keeps the same amplitude whatever the interpulse delay since the MSE sequence does not impact the liquid-like part of the signal, while the rigid one is very sensitive to the interpulse delay τ_{MSE} . Applying a shorter delay τ_{MSE} enables to better refocus the dipolar interactions as illustrated in figure IV.4.b. The renormalization of the rigid part of the MSE signal allows to reconstitute the whole shape of the curve as depicted in figure IV.5 with the superposition of the FID and of the normalized MSE curve.

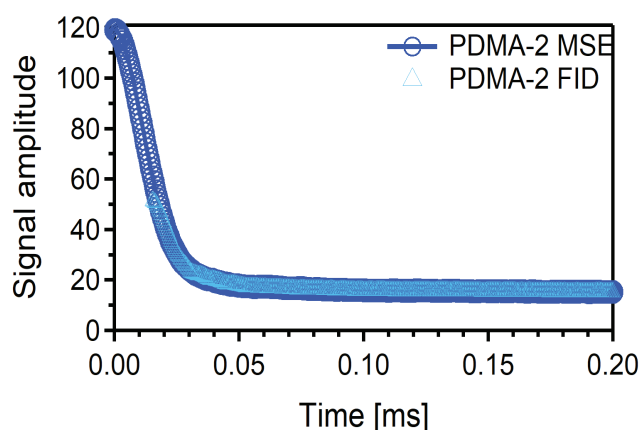


Figure IV.5 – MSE-refocused FID (blue circles) and FID measurements of PDMA-2 (light blue circles) conducted at room temperature of PDMA-2. MSE sequence allows to access missing part of the signal due to dead time receiver (around 15 μs). The second part of the curve indicates a fraction with a long relaxation time, indicating that water is present in the sample.

The same measurements conducted on dry PAAm polymer (PAAm-2) showed significant dif-

ferences in the relaxation behavior as illustrated in figure IV.6. MSE sequences with different durations were applied still in the idea of separating the long time relaxation of the sample (linked to the presence of mobile protons that are attributed to the presence of water) from the fraction relaxing very fastly (dry polymer signal). Contrary to what was observed in PDMA, in PAAm the amplitudes of both the rigid and more mobile contributions are affected when τ_{MSE} is changed. The liquid-like contributions could easily be differentiated from the solid-like component for PDMA while for PAAm both contributions are affected.

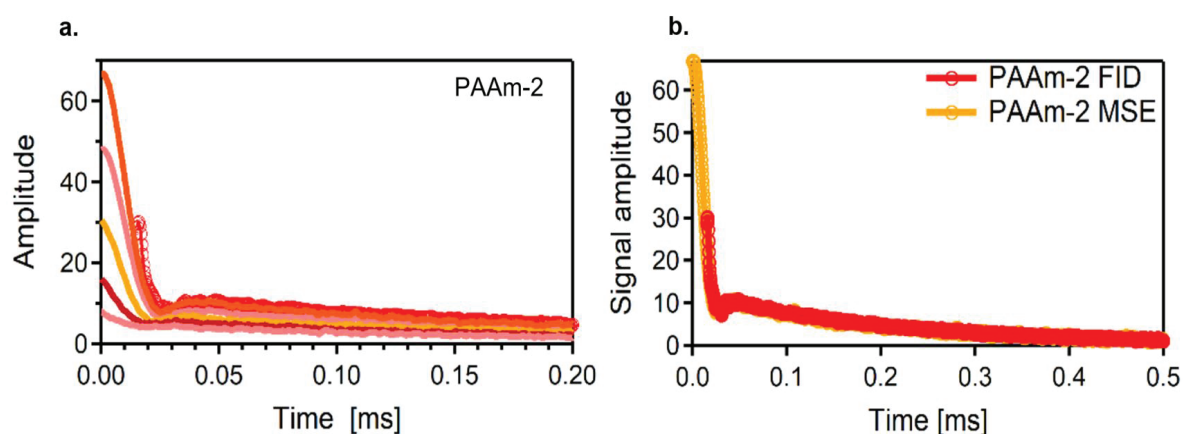


Figure IV.6 – **a.** FID (red circles) and MSE-refocused FID at various interpulse delay $\tau = 12$ (in pink), 9 (in dark red), 6 (yellow), 3 (light pink) and extrapolation at $0 \mu\text{s}$ (orange) of PAAm-2 at room temperature **b.** Superposition of FID and MSE extrapolated at $\tau = 0$ amplitudes of PAAm-2 showing the reconstitution of the whole shape of the curve.

This phenomenon is probably due to the fact that PAAm possesses labile protons that complexify the signal as illustrated in figure IV.7.

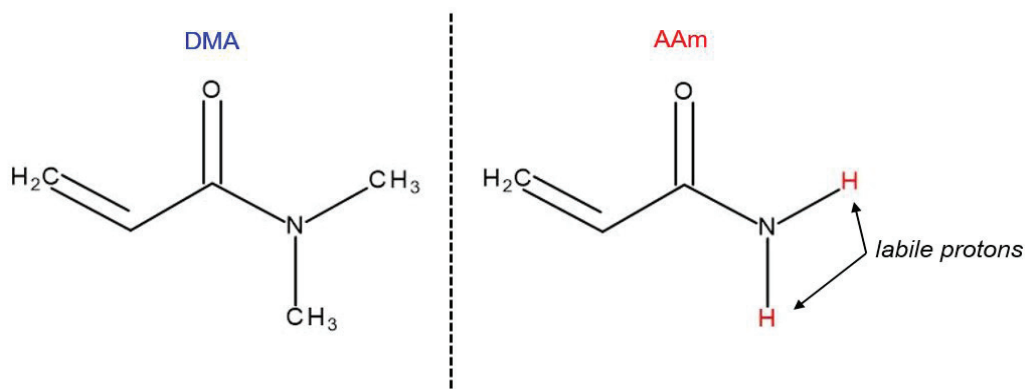


Figure IV.7 – Schematics of DMA and AAm monomers. Labile protons of AAm, able to exchange with deuterated water are highlighted in red.

Labile protons can exchange with water and thus have an average mobility intermediate between that of water molecules and that of the polymers. The measurements revealed a significant water fraction contained in the "dry" polymers. For PDMA, the weight fraction of water x_{water} is calculated

by identifying Φ_{rigid} with the intensity of the 'rigid' protons (born by the polymer) and $[1 - \Phi_{rigid}]$ the protons of the liquid fraction (water).

$$x_{water} = \frac{[H_{H_2O}]}{[H_{PDMA}]} \quad (\text{IV.7})$$

with $[H_{H_2O}] = 2(1 - \Phi_{rigid})$ and $[H_{PDMA}] = 9(\Phi_{rigid})$, as the PDMA monomer contains 9 protons. The weight fraction is obtained by multiplying by the molar masses with $M_{PDMA} = 99.13$ g/mol and $M_{H_2O} = 18$ g/mol, which give a water content of 12.3 wt%. The same reasoning is applied to PAAm to the difference that since it possesses exchangeable protons, the rigid part Φ_{rigid} corresponds only to the protons born by the skeleton (3 protons) and the exchangeable ones (2 protons) contribute to the mobile fraction $[1 - \Phi_{rigid}]$, which gives a water content of 15 wt%. This result was also confirmed through measurement of the mass variation of the polymers that were weighted after exposure to ambient air and after drying in an oven at 80°C for several hours. Both results are in reasonably good agreement and are gathered in table IV.2, indicating strong hygroscopic behavior of both PAAm and PDMA.

Sample	Water content (NMR, wt%)	Water content (scale measurements, wt%)
PDMA-2	12.3	13
PAAm-2	15	12

Table IV.2 – *Water fraction of PAAm-2 and PDMA-2 linear polymer chains, assessed through NMR measurements and scaling after drying under temperature (80°C for 48 hours.)*

3.1.2 Measurements on PDMA hybrid gels: impact of interacting monomer

Measurements conducted on PDMA-based hybrid gels indicated that, similarly to the ones conducted on the pure polymers at $\tau = 4$ ms, MSE sequence allows to recover a signal relaxing very fast at short time scale (< 0.15 ms) as illustrated in figure IV.8. The chemical gels do not show this fast relaxing contribution. This indicates that there is indeed a fraction of little mobile polymer in the sample. This immobilized fraction of polymer is believed to be due to polymer adsorption onto nanoparticles. Based on observations made on the dry PDMA polymer (PDMA-2) we can assume that the amplitude of the mobile part is not affected by the MSE sequence, while the rigid part signal should be multiplied by ≈ 1.2 .

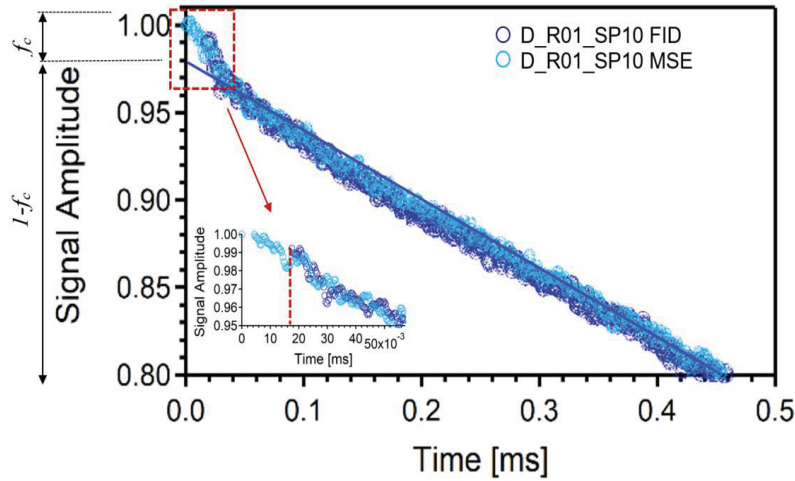


Figure IV.8 – FID (dark blue) and MSE-refocused FID (light blue) measurements of $D_R0.1_SP10$. Zoom at short times shows the missing part of the FID around $15\ \mu\text{s}$ reconstituted by MSE sequence. The increase in intensity reveals immobilized polymer fraction, relaxing very fast (of the order of the microseconds)

To quantify the rigid polymer fraction, the components of the signal were fitted. Usually, the fitting of MSE/FID data is up to 0.25 ms since the decay at longer times is dominated by field inhomogeneities and is not representative of the actual intrinsic relaxation time of the polymer. The analysis of the curves was performed on the initial part of the signal using the following function:

$$\frac{MSE(t)}{MSE(0)} = f_c \exp \left[-(t/T_{2c})^2 \right] + (1 - f_c) \exp \left[-(t/T_{2a})^b \right] \quad (\text{IV.8})$$

The first part of the signal decaying very quickly associated with the rigid adsorbed fraction f_c has the same shape as the one measured in the dry polymer. It is fitted with a Gaussian-type function. The more mobile part of the signal ($1-f_c$) is decaying more slowly and can be fitted with different functions, here with a combination of stretched or compressed exponential (Weibullian) functions $\exp \left[-(t/T_{2a})^b \right]$. With $b = 2$, the function corresponds to a Gaussian decay which describes the behavior of a rigid polymer, whereas a simple or slightly stretched or compressed exponential ($b \approx 1$) will describe a more mobile elastomer. The weight of each fit component gives the amount of mobile/less mobile polymer in each (usually weak) signal decay during the echo time (true relaxation or imperfection effects), that needs to be accounted for. However, residual H_2O contained in the monomer also contributes to the overall ^1H NMR signal and must be taken into account to get a quantitative estimate of the amount of adsorbed polymer.

3.1.3 Impact of chemical cross-linker content

Each tested samples at 10 vol% silica presented an immobilized polymer fraction as shown in figure IV.9. For the second (mobile) contribution, the relaxation strongly depends on the cross-linker content. This is due to the fact that the relaxation function of a network contains a contribution from the residual dipolar coupling, related to the cross-link density (as explained in Section IV.4 above). The relaxation increases altogether with the cross-linker content. Thus the FID curves of PDMA hybrid gels at high cross-linker amount show a sharper decrease of mobile part of the signal. In all cases the signal could be reasonably fitted with two distinct components as in Eq (IV.10),

with an exponential fitting for the longer (mobile) component. The adsorbed amount in the samples seemed to vary along with increasing chemical cross-linker content. We infer that the adsorbed amount determined for each chemical cross-linking molar ratio (from 0 to 1 mol% relative to the monomer) agree within the error limit.

Below the silica content of 0.1 v/v, the immobilized polymer fraction could not be detected which could be consistent with the mechanical properties reported for those systems with a significant reinforcement observed for a silica volume fraction of 0.1 v/v or higher.

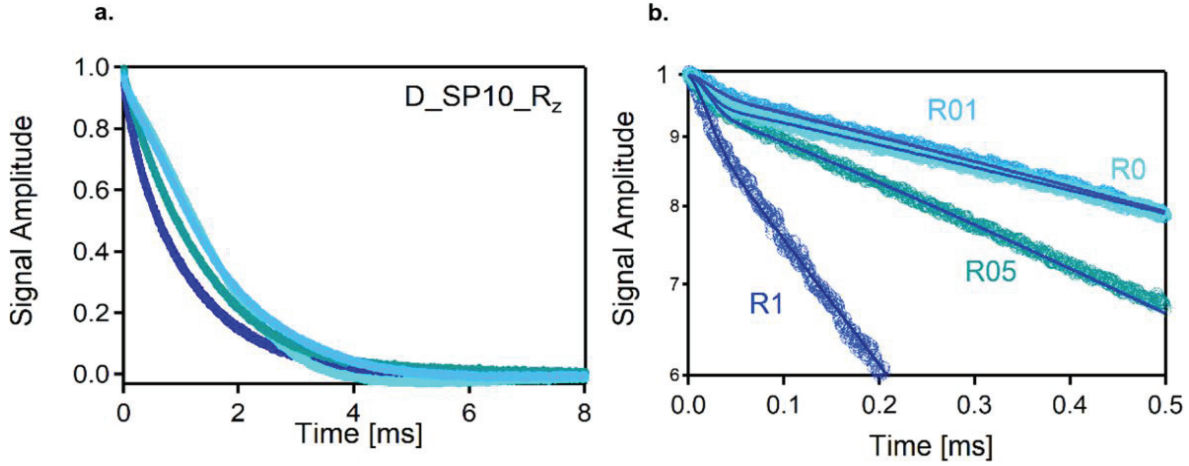


Figure IV.9 – **a.** FID curves of $D_SP10_R_z$ with $z = 0$ (turquoise), 0.1 (light blue), 0.5 (blue-green) and 1 (dark blue) mol% **b.** MSE curves (logarithmic representation) of $D_SP10_R_z$ with $z = 0$ (turquoise), 0.1 (light blue), 0.5 (blue-green) and 1 (dark blue) mol% . Increased intensities at short times is more marked for D_SP10_R0 than that of D_SP10_R1 indicating greater adsorbed polymer fraction onto silica nanoparticles. Fit of the curves are made using $f_c \exp[-(t/T_{2c})^2] + (1 - f_c) \exp[-(t/T_{2a})^b]$

The adsorbed polymer fraction seems to decrease with increasing chemical cross-linker content, which is consistent with a higher cross-linking density of the network yielding additional constraint on the network, decreasing thus the adsorbed fraction of polymer. Indeed, physical gel D_R0_SP10 is only cross-linked with silica nanoparticles hence the polymer chain length between two cross-linking points is longer than that of chemically and physically cross-linked gels, leading to facilitated adsorption of the polymer chains onto silica.

The approximated adsorbed amounts are calculated given the following data: specific surface of silica nanoparticles $S_{spe} = 100 \text{ m}^2/\text{g}$, $\Gamma_{PDMA} = 1 \text{ mg}/\text{m}^2$ (as determined in Chapter II) and are gathered in Table IV.3.

Sample	Calculated adsorbed amount (wt%)	Experimental adsorbed amount (wt%)	Relaxation time T_{2c} [ms]
D_R0_SP10	2.87	3.72 ± 0.4	0.027
D_R0.1_SP10	2.87	2.25 ± 0.3	0.024
D_R0.5_SP10	2.87	2.4 ± 0.5	0.026
D_R1_SP10	2.87	2.4 ± 0.7	0.028

Table IV.3 – *Theoretical and experimental calculated adsorbed amounts of adsorbed polymer in PDMA hybrid gels at constant silica volume fraction ϕ_{Si} of 0.1 for varying chemical cross-linker content R (0, 0.1, 0.5 and 1 mol%). The theoretical adsorbed amount is calculated using $\Gamma_{PDMA} = 1 \text{ mg/m}^2$ of silica, and silica specific surface of $100 \text{ m}^2/\text{g}$.*

Relaxation times are in good accordance with polymer chains with very slow rearrangement processes i.e, that is strongly immobilized. Adsorbed amounts are quite close from the calculated ones that do not take into account the cross-linking density of the polymer network. A molar cross-linking ratio of 0.1 corresponds to a mesh size of the order of the silica nanoparticles diameter, with theoretically 500 monomers between two cross-linking points, assuming the polymerization is complete and the defects are negligible. A tighter mesh size will obviously impact the adsorbed amount since the polymer chain mobility is reduced. These quantities seem to decrease for increasing cross-linking content at the exception of D_SP10_R0.5 that displays higher adsorbed amount than PDMA hybrid gels at 0.1 mol%.

For all the samples, similar parameters were found with $T_{2c} \approx 0.03$, $b = 1$ or 1.05 . The adsorbed amounts, as stated before remained difficult to determine precisely since it strongly depends on the fitting of the signal contribution relaxing at longer times. PDMA hybrid hydrogels (at pH 9) seem to be governed by a gradient of polymer mobility. A small fraction is relaxing very fastly, that is attributed to adsorbed polymer segments at the silica nanoparticles surface. Another polymer fraction is relaxing at long time, that could be attributed to either water contained in the monomer prior to synthesis (as the measurements on the dry polymer evidenced) or to the networks defects (pending chains). An intermediate region could be corresponding to polymer chains not strongly adsorbed but still possessing slower dynamics than polymer chains simply chemically cross-linked.

3.1.4 Disturbing polymer-filler interactions

The same experiments conducted on poly(acrylamide) hybrid gels containing the same silica content and on PDMA hybrid gels synthesized at pH11 led to different behavior as illustrated in figure IV.10.

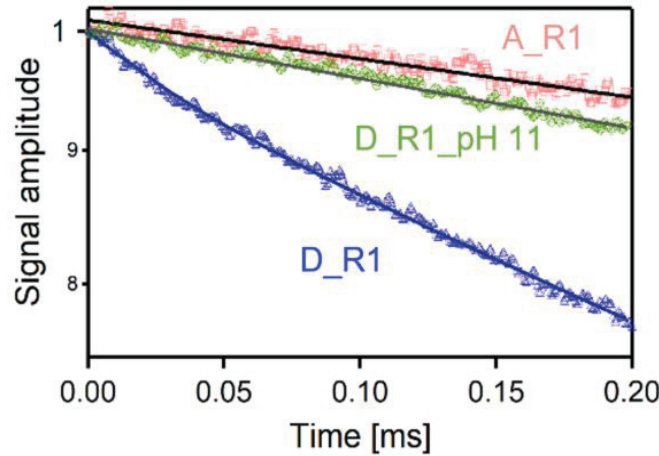


Figure IV.10 – Log of the amplitude of MSE curves of A_R1_SP10 (red squares), D_SP10_R1 (blue triangles) and $D_SP10_R1_pH11$ (green circles) plotted as a function of the time (in ms). Both the amplitudes of A_SP10_R1 and $D_SP10_R1_pH11$ show no increase at short times, pointing to the absence of an immobilized polymer layer at the nanoparticles interface. Fit of the curve of D_SP10_R1 is made using $f_c \exp[-(t/T_{2c})^2] + (1 - f_c) \exp[-(t/T_{2a})^b]$, the others are fitted linearly, displaying no immobilized polymer fraction.

Contrary to PDMA-based hybrid gels synthesized at pH 9, no rigid signal is revealed at short times by the MSE measurements conducted on PAAm hybrid gels and PDMA hybrid gels synthesized at pH 11. As shown in Chapter III, the introduction of a non-interacting acrylamide monomer or the tuning of the silica surface chemistry lead to a significant decrease of the mechanical properties of the hybrid gels compared to the one of PDMA hybrid gels (synthesized at pH 9). These results point to the fact that the reinforcement is strongly linked to the interactions taking place between polymer and nanoparticles. Thus NMR measurements provide here a way to confirm both the non-adsorbing behavior of polyacrylamide and the change of affinity towards silica surface of PDMA synthesized at pH 11. The last Chapter evidenced the impact of the non-interacting monomer on the mechanical response (decreased stiffness, strain at break, dissipative capabilities and fracture toughness) and the importance of the silica surface chemistry when the hybrid gels are synthesized with the interacting polymer. MSE measurements allow to nicely confirm the polymer adsorption as the main reinforcement mechanism for hybrid gels with well-dispersed silica within the matrix.

3.2 DQ measurements on PDMA and PAAm hydrogels

The idea is to characterize the gel network structure through the presence of non-zero residual dipolar interactions. The measured residual tensorial interactions originate from incomplete motional averaging of chain segments fluctuating rapidly between topological constraints, such as cross-links or chain entanglements. Let us recall that samples were prepared here in deuterated water to selectively observe the polymer signal.

3.2.1 Normalization of the DQ signal

In chemical networks where large scale slow dynamics is mostly absent, a normalized DQ signal can be obtained that depends on the network structure only, by properly normalizing the DQ build-up signal with the so-called reference signal, as shown in figure IV.11.

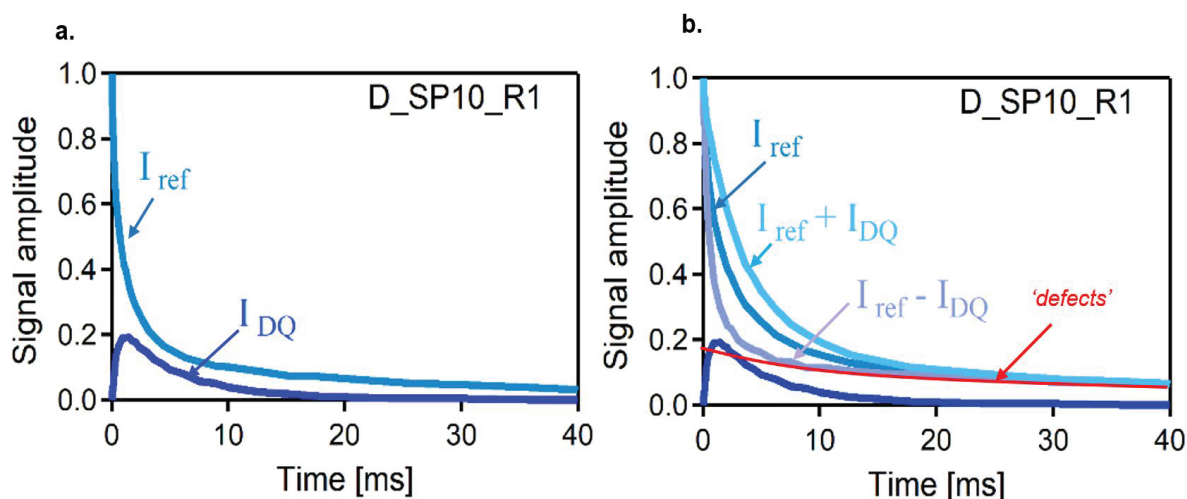


Figure IV.11 – **a.** Obtained FID curve, I_{ref} (blue) and DQ build-up signal, I_{DQ} (dark blue) for D_SP10_R1 . **b.** Curves $I_{ref} + I_{DQ}$ (light blue) and $I_{ref} - I_{DQ}$ (purple), used to subtract the fraction of defects and of water in the network to to normalize the DQ build-up signal.

To normalize the DQ curve, the fraction of the reference signal with a long relaxation time needs first to be subtracted first as it does not contribute to the DQ intensity. This fraction (denoted as 'defects') contains the non-elastically active polymer chains (pending chains and loops). It includes also the un-reacted compounds during the polymerization (oligomers, un-reacted monomers and cross-linkers, referred to as extractibles and evaluated at less than 2 wt% of the synthesized hydrogels, as seen in the previous Chapter), the water contained in the silica after deuteration (less than 2% of the signal) and the residual water contains in the monomers.

As seen in figure IV.11, it is not easy to subtract the signal from the defects in a unambiguous way, as the relaxation rates of both contributions in the reference signal are not strongly different. One heuristic way to emphasize this difference is to plot $I_{ref} - I_{DQ}$, as shown in Figure IV.11.b. The fraction of the signal possessing a long relaxation time is generally quite high in PDMA hybrid gels (around 20 %). This high fraction is mainly due to the residual (protonated) water present in the samples. Indeed, the tests conducted on the dried polymers revealed that both PDMA and PAAm are hygroscopic. The water content of the monomers (AAm and DMA) was then assessed using ^1H NMR for DMA and thermogravimetric analysis (TGA) for AAm. The monomers are also highly hygroscopic with an estimated water content of 40 wt% for AAm and of 30 wt% for DMA. 30 wt% water in DMA corresponds to about 34% in terms of number of protons. It follows that, due to this significant amount of residual water, the 'true' fraction of elastic defects in the network (sol fraction, dangling chains, etc) cannot be measured quantitatively. In any case, the mechanical and swelling properties described in the previous Chapter clearly indicate that the networks possess a quite homogeneous structure, and probably contain a relatively low amount of defects. The contributions with a long relaxation time was fitted with a single or double exponential function. The normalized

DQ curves I_{DQ}^{norm} are then obtained as follow:

$$I_{DQ}^{norm} = \frac{I_{DQ}}{(I_{ref} + I_{DQ} - I_{def})} \quad (\text{IV.9})$$

3.2.2 Impact of chemical cross-linking

In figure IV.12 are displayed the reference curves and the DQ curves of PAAm and PDMA hybrid gels at constant silica volume fraction (0.1 v/v) for various cross-linking content. For PDMA, the cross-linking content impacts the shape of the obtained reference curve due to the contribution to the FID signal of the residual dipolar interactions. This is perfectly consistent with an increasing cross-linking density, thus the importance of the contribution of the residual dipolar interactions in the overall relaxation signal increases. The shape and intensity of the DQ curves are also greatly influenced by the cross-linking amount, with almost no signal for the physical gel D_SP10_R0. Assuming that the extractibles content of the PDMA gels does not exceed 2 % as shown by the swelling experiments conducted in the Chapter III, the proportion of defects in the network was evaluated between 5 and 8% for PDMA hybrid gels and at 16 % for the physical gel, which seem in good accordance with a gel only weakly and reversibly cross-linked by the silica nanoparticles.

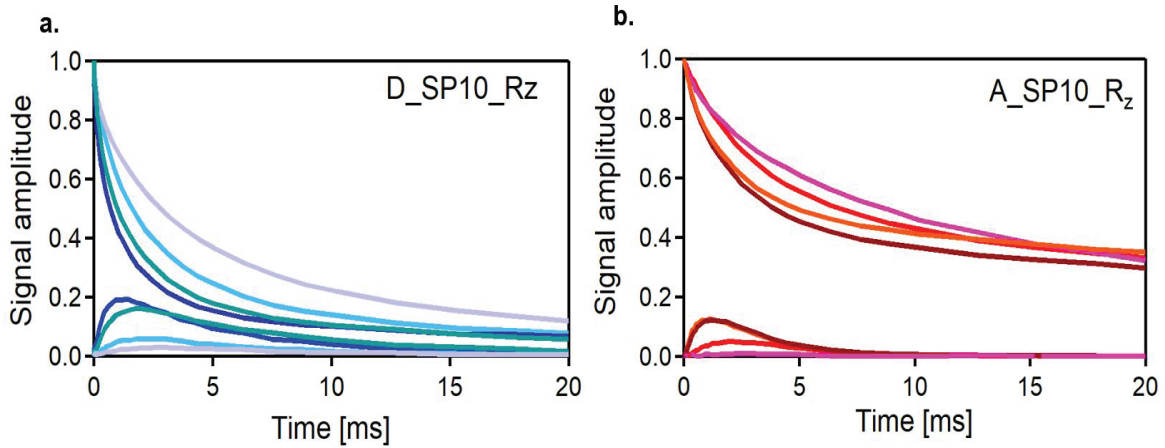


Figure IV.12 – **a.** Reference (so-called FID, plain lines) and DQ curves (dashed lines) of $D_SP10_R_z$ with $z = 0$ (purple), 0.1 (light blue), 0.5 (blue-green) and 1 mol% (dark blue). **b.** Reference (so-called FID) and DQ curves of $A_SP10_R_z$, with $z = 0$ (pink), 0.1 (red), 0.5 (orange) and 1 mol% (dark red).

PAAm hybrid gels follow the same trend to the difference that the reached intensities of the DQ curves seem to be lower than those of PDMA at the same silica and cross-linking contents. Another important feature lies in the fact that almost 50% of the signal seems to possess a long relaxation time, which renders the evaluation of the network defects hard to perform. As mentioned above, the TGA analysis conducted on the monomer revealed the presence of bounded water (around 40 wt% for AAm) but another explanation lies in the fact that the amide moiety of PAAm is a primary one, meaning that it can exchange its protons with the deuterium atoms of the surrounding solvent. Assuming complete exchange of these protons with the excess water in the gels, the only protons contributing to the signal are the three ones linked to the skeleton (that cannot exchange) which could explain the difference between the PDMA and PAAm curves. The normalized DQ curves of PDMA and PAAm are displayed in figure IV.13 and clearly show the strong impact of the chemical

cross-linker. As mentioned above, the quantity D_{res} , proportional to the cross-link density, can be extracted from the initial slopes of the normalized DQ curves. The initial slope clearly decreases as the cross-linker (MBA) content decreases for both PDMA and PAAm gels.

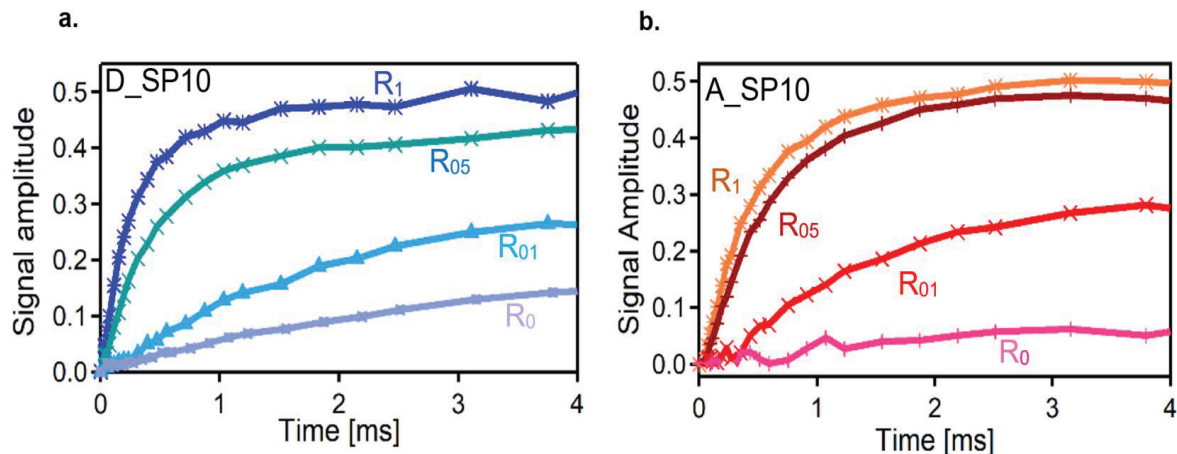


Figure IV.13 – **a.** Normalized DQ curves of $D_SP10_R_z$ with $z = 0$ (purple), 0.1 (light blue), 0.5 (blue-green) and 1 mol% (dark blue). **b.** Normalized DQ curves of $A_SP10_R_z$, with $z = 0$ (pink), 0.1 (red), 0.5 (orange) and 1 mol% (dark red).

These results are in good accordance with polymer networks possessing a lower density of cross-linking points. At the same MBA content, PDMA gels displays steeper slope at the origin compared to PAAm hybrid gels which could be attributed to the reversible interactions between PDMA and silica acting as supplementary cross-linking points. Conversely, the physical gels (no chemical cross-linker, $R = 0$ mol%) show drastically decreased signal amplitude, highlighting the predominant importance of chemical cross-linking on the gel structure. The PAAm physical gel displays nearly vanishing DQ signal which is perfectly consistent with a non-interacting polymer since aside from the self cross-linking process that can take place during the polymerization no further effective cross-linking (permanent or reversible) is expected. On the other hand, the physical PDMA gels shows decreased intensity but the obtained signal remains well-defined and could be attributed to the silica/polymer interactions acting as additionnal effective cross-links.

The obtained D_{res} quantity, extracted from the slope of the normalized DQ curves are plotted in figure IV.14 as a function of the cross-linker content for PDMA hybrid gels at constant silica volume fraction. Two features appear from this graph, the first being that D_{res} increases linearly with increasing chemical cross-linker content. The second is that for samples at 10 vol% silica, the obtained D_{res} is higher than that of gels with lower silica content, showing that silica nanoparticles play a part in the effective cross-linking of the network. This indicates that polymer/silica adsorption sites play the role of effective cross-link sites and contribute to the elasticity of the systems.

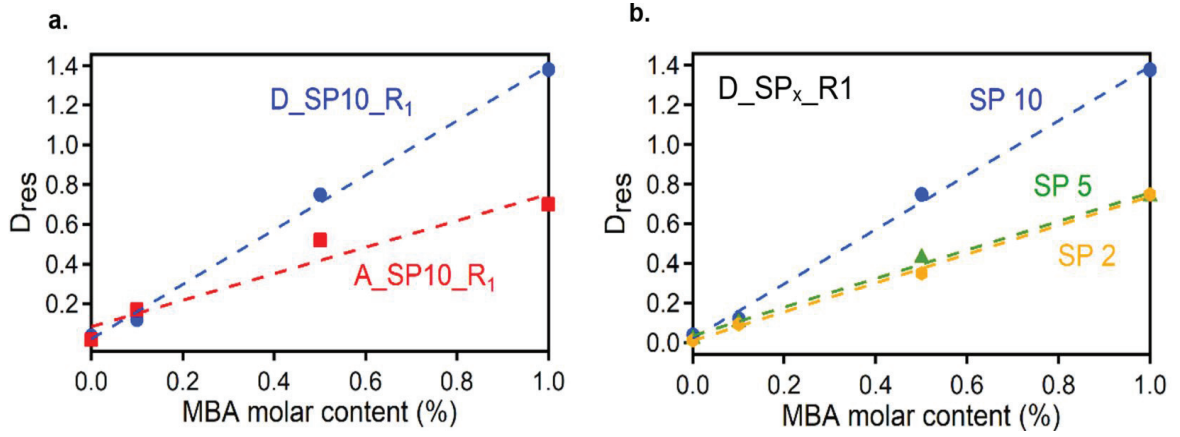


Figure IV.14 – **a.** Extracted D_{res} for PDMA (blue dots) and PAAm hybrid gels (red squares) at fixed silica content of 0.1 v/v and MBA molar ratio of 1 mol% **b.** Extracted D_{res} for PDMA hybrid gels at fixed silica content, D_{SP10_Rz} (blue dots), D_{SP5_Rz} (green triangles), D_{SP2_Rz} (yellow shapes) for various chemical cross-linker content (0, 0.1, 0.5 and 1mol%). Linear fit are indicated in dashed lines. The D_{res} quantities are obtained with linear fit at short times scales of the corresponding normalized DQ curves.

The obtained D_{res} values of PAAm hybrid gels are similar to the ones found for lower silica fraction in PDMA gels. This is coherent with the fact that PAAm gels do not contain the additional contribution to the measured effective cross-link density due to adsorption, as PAAm does not (or negligibly) adsorb onto silica nanoparticles.

3.2.3 Impact of silica on PDMA matrix

The impact of silica on PDMA hybrid gels on the normalized DQ signals remains weaker than that of chemical cross-linker as displayed in figure IV.15 with a significant impact noticed for a silica content of 0.1 v/v. The obtained D_{res} values are very close for PDMA gels with silica content ranging from 0 to 5 vol% as indicated in table IV.4.

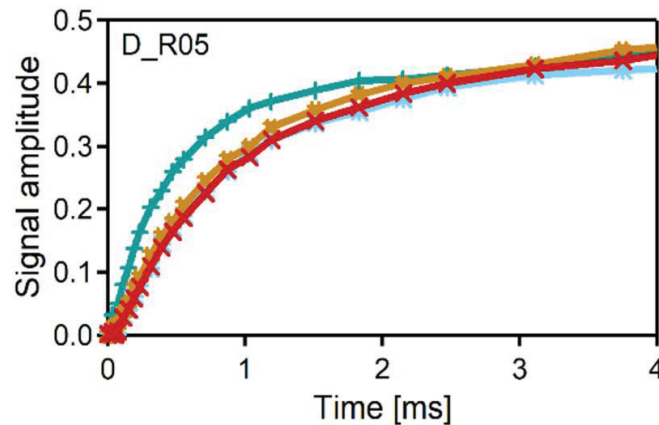


Figure IV.15 – DQ curves of hybrid PDMA at fixed cross-linker ratio 0.5 mol% D_{SP10_R05} (blue-green) and D_{SP5_R05} (yellow), D_{SP2_R05} (red) and D_{SP10_R05} (light blue). D_{res} is almost the same for silica content below 10 vol% indicating weak impact of silica on the global network cross-linking density for low silica amount.

These results are consistent with the mechanical behavior of PDMA hybrid gels with various silica content where significant reinforcement reached around silica content of 10 vol% both in modulus, with a marked deviation from the Guth and Gold model [Guth, 1945]) and strain at failure.[Rose et al., 2013].

Still, one can wonder if at these low silica contents (SP 2 and SP 5), the sensitivity of the experiment is enough to quantify the role played by silica nanoparticles in the cross-linking.

Sample	Extracted D_{res}
D_SP10_R05	0.73
D_SP5_R05	0.43
D_SP2_R05	0.41
D_SP0_R05	0.43

Table IV.4 – *Extracted D_{res} values from the curves displayed in figure IV.16 for PDMA hybrid gels at constant MBA molar ratio of 0.5 mol% and various silica content (0, 2, 5 and 10 vol%).*

3.2.4 Impact of the non-interacting monomer and the silica surface chemistry

The previous experiments conducted on PAAm and PDMA gels at fixed silica content allow to conclude that chemical cross-linkers have a major impact on the assessed D_{res} quantity, while the reversible interactions between polymer and silica are only detectable beyond a certain silica amount in PDMA hybrid gels. In figure IV.16 are shown the normalized DQ curves of PAAm chemical and hybrid gels (at $R = 1$ mol% and silica content 0 and 0.1 v/v). The comparison with the PDMA hybrid gel (D_R1_SP10) with the same molar ratio of chemical cross-linker and the same silica content shows that the extracted D_{res} quantity remains lower (0.75 for PAAm and 1.38 for PDMA), indicating that silica do not yield additional cross-linking point to the structure of PAAm gels. The results confirm the hypothesis of inert fillers embedded in the polymer matrix as evidenced by the MSE measurements conducted on those samples.

More surprisingly, the D_{res} of PAAm chemical gel, without silica (A_R1_SP0, $D_{res} = 0.80$) seems to be a little higher than that of (A_R1_SP10, $D_{res} = 0.75$). This could confirm that silica besides acting as an inert filler generates additional inhomogeneities in the network or partly inhibit cross-linking which could be a further reason for the observed decrease of the mechanical properties of these compounds [Lin et al., 2011]. This could result in the presence of a depletion zone formed around the silica nanoparticles. Observing this depletion zone, however, would require additional experiments providing some spatial resolution.

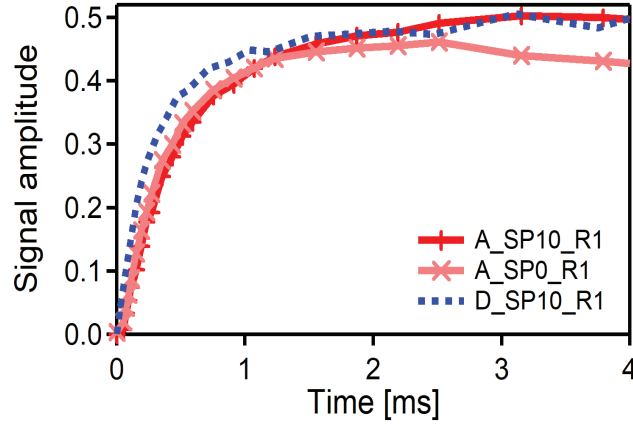


Figure IV.16 – DQ curves of A_SP10_R1 (red cross) and A_SP0_R1 (pink cross). D_SP10_R1 is displayed as a reference (blue dashed line)

The normalized DQ curves of PDMA synthesized at pH11 are shown in figure IV.17 and indicate a similar behavior than that of PAAm with decreased D_{res} values for equivalent chemical and physical cross-linker content as show in table IV.5, which is in good accordance with the decreased mechanical properties described in the Chapter III. The impact of chemical cross-linker is still clearly visible for those gels. Tuning the surface chemistry of silica nanoparticles has clearly a great impact on the cross-linking density of the PDMA network, underlying its crucial importance for mechanical reinforcement.

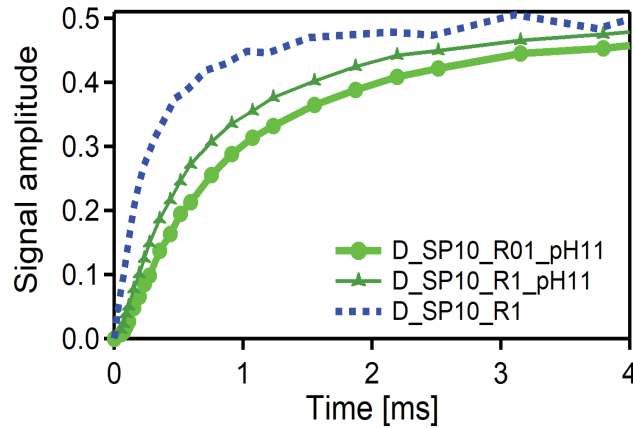


Figure IV.17 – DQ curves of $D_SP10_R1_pH11$ (green triangles) and $D_SP10_R01_pH11$ (green dots). D_SP10_R1 is displayed as a reference (blue dashed line).

The subtraction of the fraction relaxing slowly (i.e, pending chains, unreacted elements) point to the fact that synthesis at higher pH does not lead to a higher fraction of defects within the network, indicating that the difference of behavior is only due to the change in the silica surface chemistry. DLS experiments conducted on silica suspension at pH 11 during two weeks as well as the swelling behavior of chemical PDMA gels synthesized at higher pH (described in the third Chapter) seem to confirm this hypothesis.

Sample	Evaluated defects (%)	Extracted D_{res}
D_SP10_R1_pH11	4.5	0.73
D_SP10_R01_pH11	6	0.43

Table IV.5 – Extracted D_{res} values from the curves displayed in figure IV.17, for PDMA hybrid gels synthesized at pH 11 at MBA molar ratio of 1 and 0.1 mol% and constant silica content (10 vol%).

4 Conclusion

^1H NMR experiments were conducted on PAAm and PDMA hydrogels at various chemical cross-linker and silica nanoparticles content. MSE-refocused FID allowed identifying the presence of an adsorbed layer in PDMA gels synthesized at pH 9, but only for the highest silica volume fraction (0.1 v/v). Below this value, no significant signal was detected. The same measurements conducted on PAAm hybrid gels as well as on PDMA gels synthesized at higher pH show no sign of an adsorbed layer, whatever the silica volume fraction. These results are in good accordance with the reported mechanical behavior of those gels and allow concluding that mechanical reinforcement is indeed correlated to polymer adsorption. Polymer adsorption is thus a primary mechanism of reinforcement in PDMA gels. This also means that the surface chemistry of nanoparticles plays also a major part and needs to be controlled. The measurements conducted on the dry linear polymers chains revealed that both PDMA and PAAm are hygroscopic which was also confirmed for the monomers. The amount of adsorbed water was estimated. In particular, the ability for PAAm to exchange the protons with the surrounding water/solvent was evidenced. DQ measurements conducted on the samples showed that silica nanoparticles contribute to the overall effective cross-linking density of PDMA gels synthesized at pH 9. At 0.1 v/v silica, this contribution is comparable to that of the chemical cross-linker. DQ experiments conducted on PAAm and on PDMA synthesized at higher pH showed no contribution of the silica in the effective cross-linking density. These experiments even indicate or confirm a detrimental impact of the presence of silica on the network cross-linking density and/or homogeneity. It is worth noticing that the hygroscopic behavior of the monomer, that adds an additional contribution to the fraction relaxing slowly due to the presence of residual water, made the quantitative analysis quite difficult, especially in the case of PAAm that possesses labile protons. This water contribution decreases the contribution of the polymer network defects and is large compared to the contribution of the polymer network defects. A better analysis of the signals would deserve further research to quantify more precisely the cross-linking density and the quantity of defects within the networks. Still, this study has allowed us to get good insight on the structural differences of the PAAm and PDMA hybrid gels, that can be linked to their mechanical response.

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Chapter V

Double networks: hybrid gels with clustered silica

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1 Introduction

The third chapter was dedicated to the study of hybrid gels with well-dispersed silica within the polymer matrix in order to investigate specifically the consequences of substituting of the interacting monomer (DMA) by a non-interacting one (AAm), more specifically the impact on the mechanical properties. In chapter four, ^1H NMR study allowed evidencing of the presence of an adsorbed polymer layer, providing supplementary reversible cross-linking points within the network of PDMA hybrid gels and an additional dissipative mechanism. Since this feature was not observed in PAAm hybrid gels, the difference in the mechanical behavior of PAAm and PDMA hybrid gels is likely due to their respective ability to interact (or not) with silica nano-particles.

The introduction of solid particles in a polymer matrix has demonstrated to be a very efficient way to drastically improve the mechanical properties of polymeric materials such as hydrogels [Li et al., 2018; Carlsson et al., 2010] or elastomers with an increase of the elastic modulus, fracture toughness and abrasion resistance [Chazeau et al., 2000; Heinrich and Kluppel, 2002; Wang, 1998]. The enhancement of mechanical properties is not only due to the geometrical effect due to the presence of a solid fraction into the polymer matrix but a consequence of the polymer dynamics at the filler interface of which the well-known Payne effect is an example [Payne and Watson, 1963; Harwood et al., 1965; Lion et al., 2003; Hofer and Lion, 2009; Berriot et al., 2003].

The study presented in this chapter has two objectives. First, besides the impact of the chemical nature of the monomer, the effect of the dispersion state of the silica on the mechanical properties will be assessed, by synthesizing hybrid gels with aggregated silica in PAAm and PDMA polymer matrices. Secondly, the non linear behavior will be explored using an experimental methodology developed for the study of filled rubbers in the first place [Papon et al., 2011], namely Large Amplitude Oscillatory Shear (LAOS) rheological measurements performed on hybrid gels based on PAAm and PDMA with either well-dispersed or aggregated silica nanoparticles.

The aim is to analyze more precisely the non-linearity of the mechanical response of the hybrid gels and to assess the similarities or differences with filled elastomers and in a second time to explore the impact of the aggregation state of silica nanoparticles for the mechanical reinforcement.

2 Materials and methods

2.1 Chemicals

Nanoparticles Silica nanoparticles used for all experiments are Ludox-TM 50 produced by Grace and bought from Sigma-Aldrich, used as such without further purification. The nanoparticles were characterized by SEM and Small Angle X-Ray scattering using a fitting procedure for experimental data that considers polydisperse spherical particles with a Gaussian distribution of size. This model gave a mean radius of 13.5 nm with a standard deviation $\sigma = 0.13$. The corresponding surface area is $100 \text{ m}^2/\text{g}$ considering a specific weight of $2.3 \text{ g}/\text{cm}^3$.

Monomers and reactants Acrylamide (AAm, 99% electrophoresis grade, Aldrich), *N,N*-dimethylacrylamide (DMA, 99%, Aldrich), *N,N'*-methylenebis(acrylamide) (MBA, 99%, Aldrich) and *N,N,N',N'*-tetramethyl ethylenediamine (TEMED, 99% bio reagent, Aldrich) and potassium persulfate (KPS, >99%, ACS reagent, Aldrich) were used as received without further purification.

Others (3-Aminopropyl)triethoxysilane (APTES, 99%, Aldrich)

2.2 Experimental part

2.2.1 Gel preparation and composition

Hydrogels were prepared at room temperature in a nitrogen-filled overpressured glove box ($O_2 < 5$ ppm) by *in situ* free radical polymerization using N, N' -methylenebisacrylamide (MBA) as cross-linker and KPS/TEMED couple as redox initiators. All the reactants were initially deoxygenated and introduced in the glove box in order to prevent any oxygen contamination. Solid reagents were initially dissolved in water prior to synthesis: 4,5 wt% for KPS and 1,5 wt% for MBA. After dilution of the Ludox-TM50 silica suspension in water, the pH was readjusted to 9 using either HCl or NaOH, or at pH ranging from 5 to 6 using HCl. The MBA (solution) and the monomer were then added. The resulting solution was left under vigorous stirring and cooled down with ice-patches. A solution of KPS and of pre-cooled ($0^\circ C$) N, N, N', N' -tetramethylethylenediamine (TEMED) were added under stirring. The mixture was then rapidly transferred into moulds initially placed under the nitrogen atmosphere of the glove box. The geometry of moulds depended on the characterization techniques used. We observed that the redox initiation started rapidly (as shown by Orakdogan [Orakdogan et al., 2005]) and the polymerization was left to proceed during 24 hours. After demolding, hydrogels were immediately characterized or stored in paraffin oil to avoid drying before analysis.

For all synthesis, the monomer/KPS and monomer/TEMED molar ratio were fixed at 100. The cross linking density of all gels samples was also kept constant using a MBA/monomer molar ratio of 0.1 mol%. The following study was mainly based on hydrogels at the preparation state with a fixed molar ratio between polymer and water equals to 0.025, corresponding to a polymer molar fraction, $\phi_{mol} = 0.025$. Silica volume fraction was fixed at 0.2 for all nano-composite samples. In most cases, the gels were studied in this preparation state.

The nomenclature used in this study is M for chemical gels (polymer matrix), NC for nano composite samples (at 0.2 v/v silica nanoparticles), A for acrylamide based gel and D for N, N -dimethylacrylamide-based gel. For instance, a PDMA gel containing 20 vol% silica and cross-linked with a MBA molar ratio of 0.1 mol% will be named:

NC_D

And a chemical PAAm gel, cross-linked at 0.1 mol% will be named:

MA_R01

Hydrogels with aggregated silica (synthesized at pH 6) will be labeled *ag*, for example a PDMA gel containing 20vol% silica and cross-linked with a MBA molar ratio of 0.1 mol% will be named:

NC_D_ag

The formulation of hydrogels used in this chapter is given in Table V.1.

Nomenclature	m _{Si} /g	m _{water} /g	m _{monomer} /g	Q ₀	Q _e	SR ($\frac{Q_{eq}}{Q_0}$)	extractibles (wt%)
NC_D	7.063	10.621	1.487	8.45	29	3 ± 1	1.81
NC_A	7.063	10.621	1.069	11.34	193	17 ± 3	1.96
NC_D_ag	7.063	10.621	1.487	8.45	33	4 ± 1	1.51
NC_A_ag	7.063	10.621	1.069	11.34	301	27 ± 3	1.78
MD	0	10.621	1.487	8.45	50	6 ± 1	0.74
MA	0	10.621	1.069	11.34	74	7 ± 1	1.12

Table V.1 – Nomenclature and composition of hybrid hydrogels. For all compositions, the amounts of co-initiators were fixed at $m_{KPS} = 0.041$ g and $v_{TEMED} = 22.5$ μ L, and the amount of chemical cross-linker was fixed at $m_{MBA} = 2.3$ mg. SR is the swelling ratio of the gel calculate as Q_e/Q_0 , Q_e and Q_0 are respectively the measured equilibrium swelling and the theoretical initial swelling, corresponding to the preparation state and calculated from Eq. (V.2). Silica volume fraction was defined as the volume ratio of silica nanoparticles to the total volume of hybrid hydrogels, fixed at 0.2 for all hybrid compositions (using $\rho_{Si} = 2.3 \times 10^6$ g.cm⁻³).

2.2.2 Swelling experiments

Equilibrium swelling experiments were conducted in deionized water at pH 9 (hybrid gels with well-dispersed silica) or pH 6 (hybrid gels with aggregated silica). The samples, as prepared, were weighed and put in a large solvent excess for 15 days. The solvent was changed every day and after 15 days, the swollen gels were weighed again. The swelling equilibrium Q_e , and the swelling ratio SR defined as the ratio of the gel in its fully swollen state and in its initial swelling state were calculated assuming negligible extractible content and additivity of volumes as follow :

$$Q_0 = 1 + \frac{\nu_{spe}^w}{\nu_{spe}^{pol}} \left(\frac{m_{p,w}^0}{m_p^0} - 1 \right) \quad (V.1)$$

$$Q_e = 1 + \frac{\nu_{spe}^w}{\nu_{spe}^{pol}} \left(\frac{m_{p,w}^0 + m_{p,w}^{abs}}{m_p^0} - 1 \right) \quad (V.2)$$

$$SR = \frac{Q_e}{Q_0} \quad (V.3)$$

where ν_{spe}^p is the specific volume of the dry polymer network (ν_{spe}^p -DMA = 0.950 mL.g⁻¹; ν_{spe}^p -AAm = 0.709 mL.g⁻¹), ν_{spe}^w is the specific volume of the solvent (ν_{spe}^w -water = 1 mL.g⁻¹), $m_{p,w}^0$, $m_{w,p}^0$ and $m_{w,p}^{abs}$ are the mass of the dry polymer network, the mass of the water in the preparation state and the mass of the absorbed water, respectively.

The analysis of organic and inorganic content was systematically carried out after swelling by analyzing the swollen sample by thermal gravimetric analysis (TGA) and weighing after drying of the samples. For all samples, the yield was above 98%. Similarly, the solvent washed-out after swelling experiments of hybrid gels was controlled by dynamic light scattering (DLS) and did not reveal any presence of silica nanoparticles after swelling equilibrium showing that the silica particles do not diffuse out of the gel matrix.

2.2.3 Mechanical tests

Tensile tests were performed on a standard tensile Instron device, model 5565, using a 10 N load cell (with a relative uncertainty of 0.16% in the range of 0 to 0.1 N) and a video extensometer, model SVE, which can precisely follow the local displacement of markers up to 120 mm, with a relative uncertainty of 0.11% at full scale. The strain can be measured using both the video extensometer and the displacement of the crosshead. The force (F) and displacement (L) are recorded.

The nominal strain rate was varied from $3 \times 10^{-4} \text{ s}^{-1}$ to 0.6 s^{-1} corresponding to a displacement speed comprised between 0.4 and 900 mm.min⁻¹. To avoid any drift in the gel composition during the experiments, the tests conducted at $3 \times 10^{-4} \text{ s}^{-1}$ were carried out under immersion in paraffin oil. For that purpose, we designed a specific cell and to correct the buoyancy, blank tests were systematically carried out for each experimental condition.

Samples preparation.

The gel samples used for mechanical tests were synthesized in home-made moulds consisting of two covered glass plates spaced by a 2 mm thick stainless steel spacer. The gels were then cut with a punch and their final dimensions are $L_0 = 25 \text{ mm}$, $w_0 = 5 \text{ mm}$ and $t_0 = 2 \text{ mm}$. The sample geometry was chosen in order to reduce the volume of material. All gel samples were placed in home-made screw side action grips and marked by two white dots.

Uniaxial tensile tests.

The nominal or engineering stress σ_N was calculated from the tensile force and the initial cross section area ($5 \times 2 \text{ mm}^2$) and is calculated as follow:

$$\sigma_N = \frac{F}{w_0 \times t_0} \quad (\text{V.4})$$

and the strain ϵ was obtained from the optical extensometer and defined as the ratio:

$$\epsilon = \frac{\Delta L}{L_0} \quad (\text{V.5})$$

The true stress σ_T was calculated assuming iso-volume deformation, thanks to the following relation:

$$\sigma_T = \sigma_N \times \lambda \quad (\text{V.6})$$

$$\lambda = \frac{L}{L_0} \quad (\text{V.7})$$

with λ , the strain ratio and L and L_0 are respectively the length during stretching and the initial length. The true strain is calculated according to:

$$\epsilon_T = \ln(1 + \epsilon_N) \quad (\text{V.8})$$

True stress-strain curves are usually used for the characterization of materials exhibiting plastic deformation and studied here because of the viscoelastic behavior displayed by the samples.

Fracture experiments

Fracture data were obtained using single edge notch geometry and the fracture energy (in J.m⁻²) at the onset of crack propagation was calculated as:

$$G_{1c} = \frac{6cW_c}{\sqrt{\lambda_c}} \quad (\text{V.9})$$

with λ_c the extension ratio at break, W_c the strain energy density at break, calculated by the integration of the nominal stress versus strain up to break $\epsilon_c = \lambda_c - 1$ and c the initial length of the crack. Each notch was measured by optical microscopy in order to determine its exact length c of approximately 1 mm. The same procedure as the one used for tensile tests was performed: the strain rates were varied from $3 \times 10^{-4} \text{ s}^{-1}$ to 0.6 s^{-1} , the force and the displacement data were recorded. This formula supposes that the material has a perfectly elastic behavior meaning that all the elastically stocked energy is used to propagate the crack. However, hybrid gels possess dissipative mechanisms so that the relevance of this model can be discussed, especially for hybrid gels with aggregated silica. However, it allows to compare the chemical gels (elastics) with the ones with well-dispersed and aggregated silica. For each measurements, three samples were tested for reproducibility.

Loading-unloading cycles

Loading-unloading cycles were performed in order to investigate the self-recovery process of the gels and the characteristic times of the viscoelastic processes. Cycles at constant strain rate were applied from 0 to a maximum strain ϵ_0 and then the sample was unloaded.

2.2.4 Rheological measurements

These experiments were conducted with the help and knowledge of G. Ducouret (SIMM). The viscoelastic properties of hydrogels discs (22 mm diameter, 2 mm thickness) were studied at the preparation state using a stress-controlled rheometer (DHR-3 from TA Instruments) equipped with a plate/plate geometry. Particular care was taken to avoid the drying of the samples by immersing them into paraffin oil during the experiment.

Frequency sweeps Frequency sweep measurements were performed at 25° C . The angular frequency was varied from 1 to 100 rad.s^{-1} (from 0.159 to 15.9 Hz) while the strain amplitude was fixed at 0.1% (measured at the outer diameter of the cell). The storage modulus $G'(\omega)$ and the loss modulus $G''(\omega)$ were recorded and plotted against the angular frequency ω in a double logarithmic scale as all these parameters varied over several order of magnitude.

Large Amplitude Oscillation Shear Oscillatory shear strain was applied at a fixed frequency of 1 Hz. The strain amplitude was varied from 0.1 to a maximum amplitude, depending on the nature of the hydrogel (800% for NC_D, 150 % for MD_R01 and MA_R01, 250 % for NC_A gels, 450 % for NC_D_ag and NC_A_ag). The storage modulus $G'(\omega)$ and the loss modulus $G''(\omega)$ were recorded and plotted against the strain amplitude γ in a double logarithmic scale as all these parameters varied over several order of magnitude. The stress (σ , in Pa) and strain amplitude (γ , in %) are calculated from the raw data measured by the torque transducer as follow:

$$\sigma = \frac{2 \times T_M}{\pi(r_s)^3} \quad (\text{V.10})$$

where T_M is the measured torque (in N.m^{-1}) and r_s is the radius of the rheology cell (in m).

$$\gamma = \frac{r_{sa}d}{w_s} \times 100 \quad (\text{V.11})$$

where d is the displacement and w_s , the sample thickness (in m). The recorded stress is then decomposed into the viscous σ'' and elastic part σ' as explained in section 4 below.

Samples preparation.

Gel samples used for rheology tests were synthesized in home-made moulds as described in the third Chapter of this manuscript. The geometry consists of two covered glass plates spaced by a 2 mm thick removable stainless steel spacer.

The gels were covalently grafted to the glass using (3-aminopropyl)triethoxysilane (APTES) as a coupling agent. Prior to the grafting, the glass plates were cleaned using cerium oxide suspension (20wt% in water) and RBS detergent (10wt% in water). After drying, they were treated with a solution of APTES at 2wt% in absolute ethanol in presence of hydrochloric acid then heated at 100 °C in an oven for 10 minutes. Glass plates were directly glued on the rheometer using bi-component epoxy glue, their final dimensions being $d_0 = 22$ mm in diameter and $t_0 = 2$ mm in thickness.

2.2.5 Small Angle X-Ray Scattering

Small angle X-ray scattering experiments were carried out at Laboratoire Léon Brillouin (CEA, Saclay), in collaboration with A. Brulet, with a high resolution X-ray spectrometer Xeuss 2.0 from Xenoxs company equipped with PILATUS3 1M detector of dimension 168.7 x 179.4mm with q range from $2.2 \cdot 10^{-3}$ to $3 \text{ \AA}^{-1}$. In order to compare with hydrogels, solutions of silica nanoparticles were also prepared with volume fraction varying from 0.18 to 0.33 (pure Ludox suspension). Samples were prepared according to synthesis protocols described at the beginning of this chapter, then injected directly in poly(imide) capillars of dimensions 0.75 x 60 mm purchased from MicroLumen under nitrogen atmosphere then welded to prevent drying.

After treatment, the absolute intensity $I(q)$ (in cm^{-1}) was plotted versus the wave vector modulus q . The corresponding values of the scattering vector modulus are in the range 0.0038 and $0.01 \text{ \AA}^{-1}$. Data were analyzed using the SASView software v3.2.1.

3 Results and Discussion

In the following the mechanical behavior of hybrid gels synthesized at acidic pH will be investigated. The idea here is to assess the impact of lowering the pH on the silica dispersion state of PAAm and PDMA hybrid gels of the same composition (in terms of monomer/water molar ratio, cross-linker content, matrix hydration) as the ones synthesized at pH 9 where silica remains well-dispersed within the polymer matrix. Then the swelling behavior and the mechanical properties will be assessed with a special interest in the non linear behavior.

3.1 Aggregating silica within hybrid gels network

The surface chemistry of silica surface drives its ability to interact with polymer through adsorption but also its abilities to remain stable in an aqueous suspension [Iler, 1979]. Synthesizing PDMA hydrogels at lower pH (5 to 6) induces an increase of the density of the silanol groups at the silica surface and reduces the proportion of silanates thus decreasing the electrostatic repulsion between particles that ensures their stability. The synthesis at more acidic pH yielded opaque and stiff gels, indicating that the silica dispersion state was modified as illustrated in figure V.1.

It is worth noticing that the silica surface chemistry is here purposely tuned to favor aggregation of the nanoparticles within the network. Since the pH value is lowered, the strength of polymer/silica

interactions is also changed. Griot and Kitchener underlined the importance of silanol groups for PAAm/ silica interactions [Griot and Kitchener, 1965a,b], a shift of pH towards lower values will increase the silanol density at the nanoparticles surface [Iler, 1979] thus increasing the strength of PDMA and PAAm interactions.

Experiments conducted on silica suspensions of Ludox TM-50 showed that lowering the pH favored aggregation of the silica nanoparticles within a few days at room temperature. The polymerization of hybrid gels at pH 6 revealed that gelation proceeds fast, especially for PAAm hybrid gels synthesis, within seconds after adding the initiators (KPS and TEMED). Several ways were explored to delay the gelation, like thermal initiation of KPS at 80 °C. This method gave good results for PDMA gels but the resulting PAAm gels showed weak aggregation of the silica (soft and transparent samples) even at pH 6. Redox initiation was preferred but remained hard to perform and needed a strict and thorough control of the temperature and the stirring. However, under those conditions, keeping good control over aggregation turned out to be very difficult, with great disparities between the different synthesis.

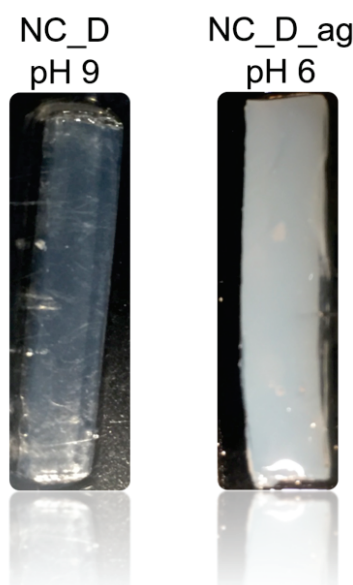


Figure V.1 – On the left, picture of *NC_D* (synthesized at pH 9) and on the right picture of *NC_D_ag* (synthesized at pH 6).

3.1.1 Structural characterization of hybrid gels

SAXS experiments were conducted to characterize the dispersion state of silica nanoparticles within the polymer matrix.

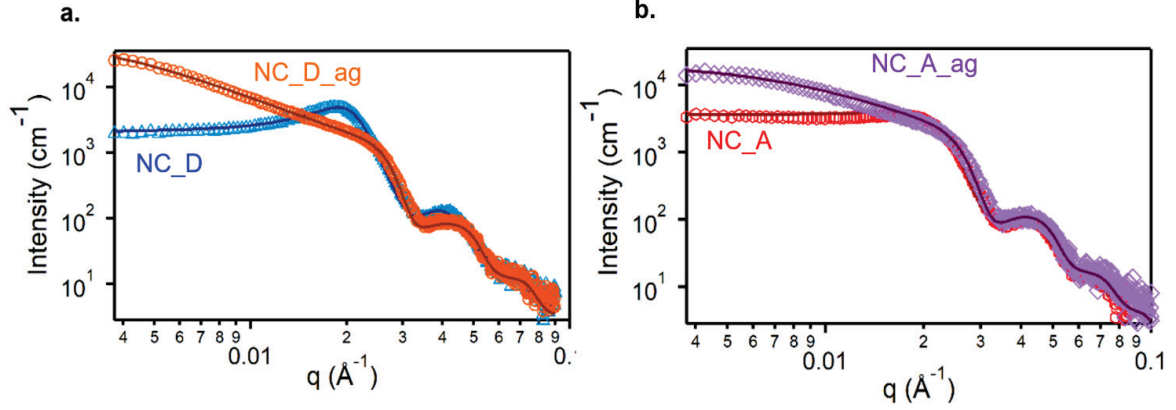


Figure V.2 – **a.** Double logarithmic plots of the scattering intensity obtained from NC_D (blue triangles) and NC_D_ag (orange circles) with ϕ_{Si} : 0.2. **b.** Scattering intensities of NC_A (red circles) and NC_A_ag, (purple diamonds). The corresponding fit based on the Sticky Hard Sphere model is indicated in solid lines.

As shown in figure V.2 the scattering curves of the samples synthesized at lower pH (NC_D_ag, NC_A_ag) and of hybrid gels with well-dispersed silica (NC_D and NC_A). The first feature that appears is that all the hybrid gels at the same particle concentration possess the same scattering pattern in the high q -range, in relation with the form factor of individual particles and the overall constant number of particles. However, the general morphology in the low- q regime differs greatly for NC_A_ag and NC_D_ag with a large increase of the intensity at low- q due to increasing interferences between particles. The disappearance of the peak at $I(q_{max})$ present in NC_D ($I(q_{max})$: $0.0188 \text{ \AA}^{-1}$) and NC_A ($I(q_{max})$: $0.0168 \text{ \AA}^{-1}$) curves also indicates a change in the dispersion state of the fillers. This peak corresponds to repulsive interactions with an average near-neighbor distance of order $2\pi/q_{max} = 33\text{-}34 \text{ nm}$, a little larger than the particle diameter. For NC_A_ag and NC_D_ag, the potential between particles becomes clearly attractive: the system becomes more compressible and tends towards aggregation.

The curves were fitted using a hard sphere form factor and the interparticle structure factor was calculated for a hard sphere fluid with a narrow attractive well, using a perturbative solution of the Percus-Yevick closure which is adequate for attractive interparticle potential (sticky hard sphere model) [Percus and Yevick, 1958]. The returned value is a dimensionless structure factor, $S(q)$. The strength of the attractive well is described in terms of “stickiness” as defined below [Menon et al., 1991]. The interaction potential $U(r)$ is defined as :

$$U(r) = \begin{cases} \infty, & r < \sigma_{int} \\ U_0, & \sigma_{int} \leq r \leq \sigma_{int} + \Delta \\ 0, & r \geq \sigma_{int} + \Delta \end{cases} \quad (\text{V.12})$$

with Δ , the width of the square well, U_0 the depth of the well (in $k_B T$ units) and σ_{int} the hard sphere diameter $\sigma_{int} = 2R$. The stickiness τ_{int} is defined as:

$$\tau_{int} = \frac{1}{12\epsilon_p} \exp(U_0/k_b T) \quad (\text{V.13})$$

$$\epsilon_p = \frac{\Delta}{\sigma_{int} + \Delta} \quad (\text{V.14})$$

with ϵ_p , the perturbation factor. U_0 is negative for an attractive potential, positive for a repulsive potential. From this definition, it is clear that smaller values of τ_{int} will mean stronger attraction, as illustrated in figure V.3.

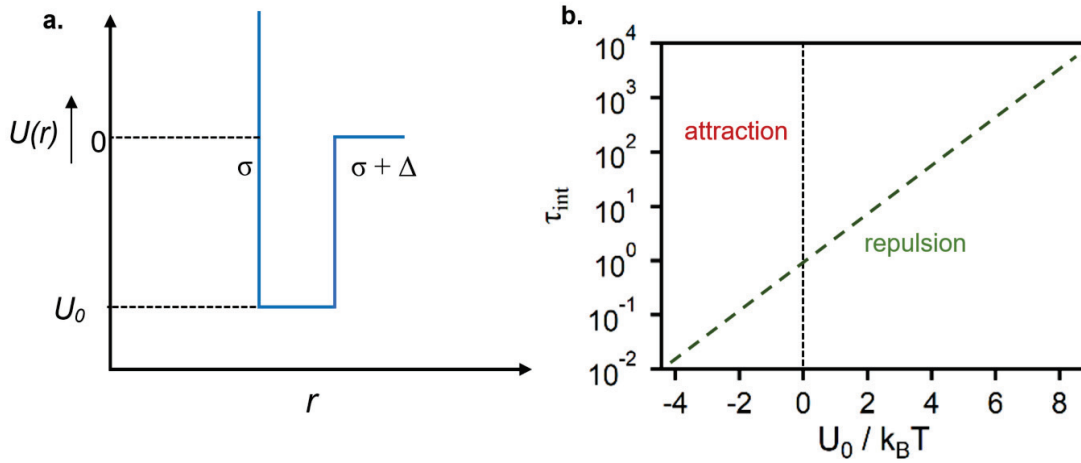


Figure V.3 – **a.** Scheme of the well of interaction potential $U(r)$ (in blue line) of the Sticky Hard Sphere model as a function of the interparticle distance r . **b.** Interaction parameter τ_{int} plotted as a function of $U_0/k_B T$. Attraction and repulsion domains can be clearly identified from the value of U_0

Fitting results using the Sticky Hard Sphere model are gathered in table V.2. The value of particles radius is the one found by the fitting of the silica suspension ($r_{Si}=13.4$ nm). All parameters but the perturbation factor ϵ_p and the stickiness τ_{int} are fixed.

Parameter	NC_D	NC_A	NC_D_ag	NC_A_ag
Radius (nm)	13.4	13.4	13.4	13.4
Volume fraction	0.23	0.22	0.23	0.22
ϵ_p	0.1 ± 0.001	0.095 ± 0.01	0.090 ± 4.10^{-12}	0.03 ± 0.006
τ_{int}	5680 ± 0.06	2.1 ± 0.08	0.011 ± 0.0003	0.164 ± 0.0007
$U_0/k_B T$	8.83	0.873	-4.43	-2.83
	repulsion	repulsion	strong attraction	moderate attraction

Table V.2 – Fitting parameters obtained for NC_D, NC_A and NC_A_ag and NC_D_ag hybrid gels.

The stickiness factor describing the strength of interactions between particles shows that in the case of PDMA, there is few interactions meaning that the silica particles are well-dispersed in the polymer matrix. For networks synthesized at lower pH, τ_{int} is drastically decreased, showing closer interparticle distance.

Measurements conducted on several samples showed great disparities in the aggregation state revealing the difficulties to control the dispersion state using redox-initiated Free Radical Polymerization. As polymerization starts almost instantaneously, at these low pH it is hard to proceed to injection before gelation occurs. In particular, the analyzed NC_A_ag samples showed weaker aggregation of nanoparticles compared to NC_D_ag whereas the other tests conducted revealed that silica tends to aggregate very easily and very strongly in PAAm matrix (see section V.3.2). This illustrates the

great disparities between several batches and the lack of control over the aggregation state.

3.1.2 Swelling behavior and extractible content

The extractibles content revealed that the change of silica surface does not impact the polymerization process and the DLS analysis conducted on the solvent washed out from samples at swelling equilibrium did not reveal leaching out of the silica nanoparticles, when the samples were able to withstand the osmotic pressure.

As reported in the table V.1, the swelling behavior of NC_D_ag (SR= 3.93) shows a different behavior at swelling equilibrium from the chemical (SR= 5.92) or hybrid gels (SR= 3.43) with well dispersed silica, with a slightly increased ability to absorb surrounding solvent. This result is quite unexpected since the silanol groups at the silica surface are supposed to favor the attractive interactions with PDMA. The difference can be attributed to a lowered specific surface available for polymer adsorption due to the aggregation state of the silica NPs which reduces the sensitivity of the swelling behaviour to the specific interactions between silica and PDMA.

PAAm with aggregated silica showed extremely high swelling at equilibrium, leading sometimes to their rupture (leading to lashing out of the nanoparticles and to a rise of the extractible content). The inability to withstand osmotic pressure can be related to the absence of interactions between PAAm and the filler as already reported by Berriot *et al.* [Berriot *et al.*, 2002a]. The presence of non interacting polymer has been linked to the presence of depletion zones near the fillers in the swollen state. In case of aggregated silica one may suspect that the cross-linking of the network might be more heterogeneous than their counterpart with well dispersed silica. These two combined factors could explain the large observed swelling and the fact that some samples were prone to disintegrate. It also demonstrates that the clusters of aggregated particles are able to dissociate under osmotic stress.

3.2 Mechanical properties

3.2.1 Mechanical properties: tensile behavior

The impact of the aggregation of silica nanoparticles on the mechanical properties of hybrid hydrogels has been investigated by tensile tests carried out at 0.06 s^{-1} as presented in figure V.4, for NC_A_ag and NC_D_ag. Interestingly, the behavior displayed by hybrid gels based either on PAAm or PDMA differs greatly.

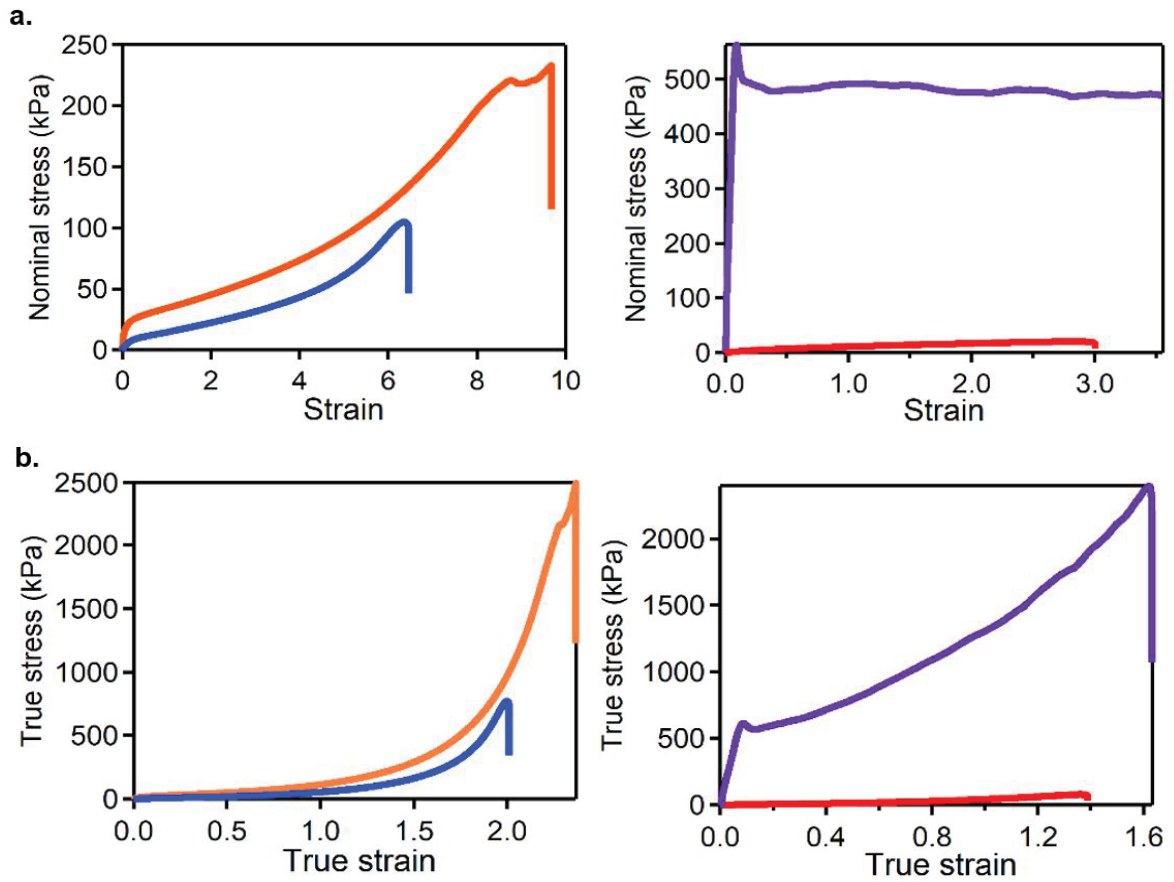


Figure V.4 – **a.** On the left, stress-strain curves of NC_D (blue) and NC_D_ag (orange). On the right, tensile curves of NC_A (red) and NC_A_ag (purple). The tests were conducted at 0.06 s^{-1} , all samples were synthesized at silica volume fraction of 0.2. **b.** True stress-strain curves of NC_D (blue) and NC_D_ag (orange), on the left and true stress-strain curves of NC_A (red) and NC_A_ag (purple) on the right.

The general shape of PDMA curves is identical to the one of the reference system NC_D, with a pronounced 'S' shape, to the difference that those gels seem much stiffer than their counterpart with well-dispersed silica. This phenomenon is attributed to the aggregation of the silica nanoparticles that breaks first under the load and prevents the polymer chains from stretching, providing higher linear tensile modulus values than the reference PDMA hybrid gel NC_D. At larger strain, once the hard silica network is broken, the PDMA chains are extended and provide high strains before break. The strain softening at intermediate strain and the strain hardening at large strain indicate that even though silica is aggregated, the dynamics of the reversible interactions are still at play in those systems. Similarly to what was observed in SAXS experiments, the aggregation state of the nanoparticles within the samples can vary greatly between tested samples, with large variations between experimental values of linear tensile modulus as indicated in table V.3 and of the strain at break (from 500% to 1000 %) revealing once more the difficulties to control the aggregation state. In PAAm-based samples, the tensile tests revealed an unusual mechanical behaviour, close to the one of semi-crystalline polymers with striction patterns for some samples. All samples exhibit inhomogeneous deformation and the strain at break differs greatly between several samples, indicating

also that the silica aggregation state is also not well controlled. Once the hard inorganic network is broken, the polymer chains extend until failure without any observed strain softening pattern, which remains consistent with a non-interacting polymer matrix. The obtained linear tensile modulus values are unusually high for hydrogels (of the order of MPa) but vary greatly, with great difficulties to get reproducibility from one batch to another. This result seems to be in contradiction with the SAXS results that indicated lower stage of aggregation of silica nanoparticles for NC_A_ag samples which underlines the inhomogeneity or poor reproducibility of the aggregation state of the silica within the samples. A good control of the aggregation state could not be reached in this study and would deserve further research.

3.2.2 Dissipation processes and recovery

The breakage of the silica network is also verified by cyclic experiments, with damage noticed for both NC_D_ag and NC_A_ag samples, considering the linear tensile modulus of the first loading cycle with respect to the second cycle. As noticed during the tensile experiments, the linear tensile modulus is much higher for hybrid gels synthesized at lower pH, inducing an important hysteresis. Furthermore, the full recovery previously reported for NC_D after a short time of rest (30 seconds) seems to be impeded when silica is aggregated within the network, as illustrated in figure V.5.a, with a recovery parameter R (defined as the ratio of the linear tensile modulus of the first cycle over the modulus of the second cycle) of 0.33 for NC_D_ag against 0.98 for NC_D. This observation is in good agreement with the swelling behavior of PDMA gels with clustered silica where the reversible interactions seem to be impacted by the aggregation state of silica.

Sample		NC_D_ag	NC_A_ag	NC_D	NC_A
$\dot{\epsilon} = 0.06 \text{ s}^{-1}$	$E(\text{kPa})$	732 ± 23	4966 ± 2495	92 ± 8	23 ± 4
	$E_d(\text{kJ.m}^{-3})$	6.53	7.68	1.87	0.196
	$R_{30\text{sec}}$	0.33	0.57	0.97	0.88
	R_{24h}	1.14	0.05	-	-

Table V.3 – Linear tensile modulus (E), dissipated strain energy (E_d) and recovery in initial stiffness for NC_A_ag and NC_D_ag. Recovery parameter R is calculated as the ratio of the modulus of the first cycle over the modulus of the second cycle.

The fact that the silica is clustered in NC_D_ag gels decreases the silica surface available for polymer adsorption. On the other hand, at this pH the density of silanols groups at the silica surface is high [Iler, 1979], which should favor the polymer/silica interactions. During the initial stage of the load, the silica network breaks and provides the high modulus and the high energy dissipation. Successive cycling at increasing strains (from 20 to 200%) showed instant damages with a drastic decrease of the initial modulus between each cycle ($\approx 90\%$ between the first and the last cycle) and an important residual strain. These cycling experiments were followed by tensile test until failure, with 24 hours of rest allocated between the tests. Full recovery was observed as shown in figure V.5.b with the curves fully superimposed showing that the reversible interactions between PDMA and silica still take place but at a larger time scale, probably due to slower rearrangement of the polymer chains. In figure V.5.c, the pictures at several stages of deformation indicate that deformation remains homogeneous. In the beginning, the samples are stiff and opaque while they become transparent during elongation, showing that the silica clusters break under elongation.

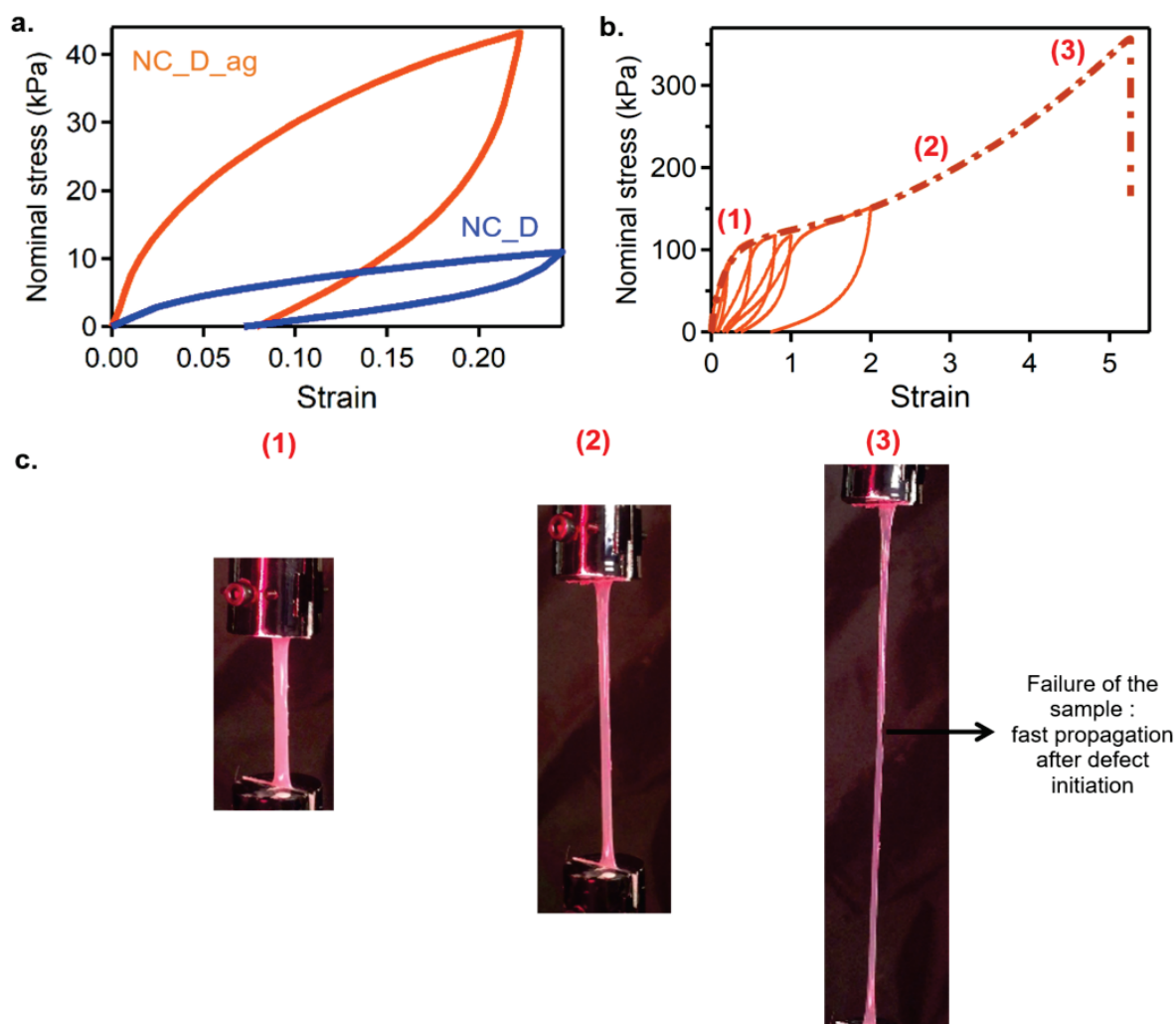


Figure V.5 – **a.** Loading cycles of NC_D_ag (orange) and NC_D (blue) at 20% of strain. **b.** Successive loading cycles of NC_D_ag at increasing strains (20, 50, 80, 100 and 200% of strain) and tensile test (dashed red line) performed 24 hours after the loading cycles. The tests were conducted at 0.06 s^{-1} . **c.** Pictures of the sample during the tensile test at several stages of elongation, showing homogeneous deformation.

NC_A_ag samples showed instant and permanent damages upon deformation as illustrated in figure V.6. The dissipated energy during the first load is even higher than that of NC_D_ag, which is in good accordance with a higher level of the nanoparticles aggregation. As PAAm does not interact with silica, the reinforcement here seems to originate from the break of the hard silica network only. The tensile test performed after 24 hours of rest shows residual plasticity and more important, no recovery of the mechanical behavior, as illustrated in figure V.6.b, underlying the absence of interactions and the irreversibility of the damages undergone by the sample. The pictures of the samples during the tensile tests in figure V.6.c show inhomogeneous deformation, with local zones that stay opaque while others are transparent, due to previous deformations during the loading cycles. Since these patterns are not observed in NC_D_ag hybrid gels after the same period of rest this behavior is attributed to the lack of reversible interactions.

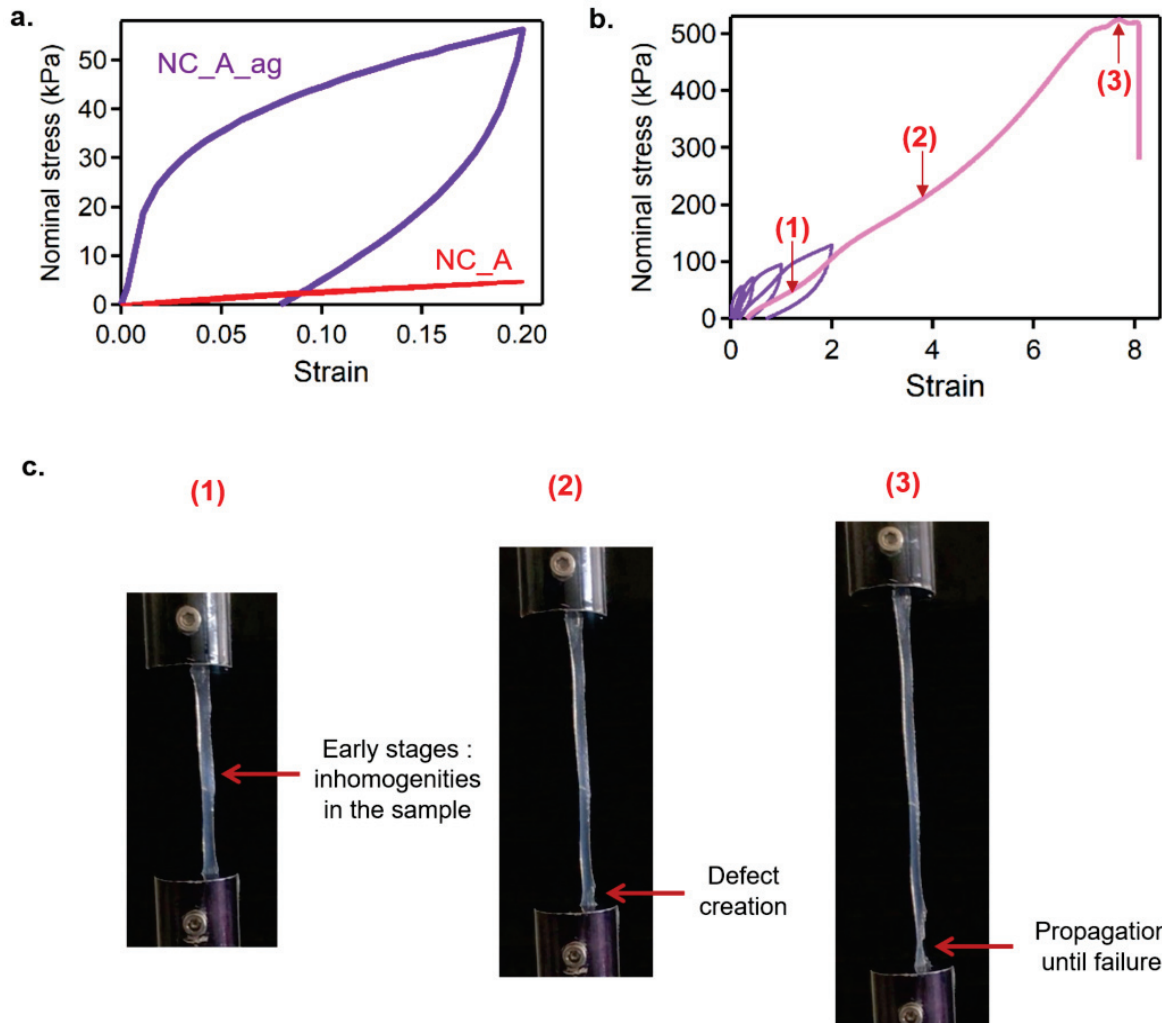


Figure V.6 – **a.** Loading cycles of NC_A_ag (purple) and NC_A (red) at 20% of strain. **b.** Successive loading cycles of NC_A_ag (purple) at increasing strains (20, 50, 80, 100 and 200% of strain) and tensile test (pink line). Time of rest of 24 hours is allocated between the two experiments and were conducted at 0.06 s^{-1} . **c.** Pictures of the sample during the tensile test after the loading cycles, showing inhomogeneous deformation of the sample.

3.2.3 Fracture properties

Calculated fracture energies of NC_D_ag at various strain rates ($\dot{\epsilon} = 3.10^{-4}$, 0.01, 0.06, 0.1 and 0.6 s^{-1}) are represented in figure V.7.

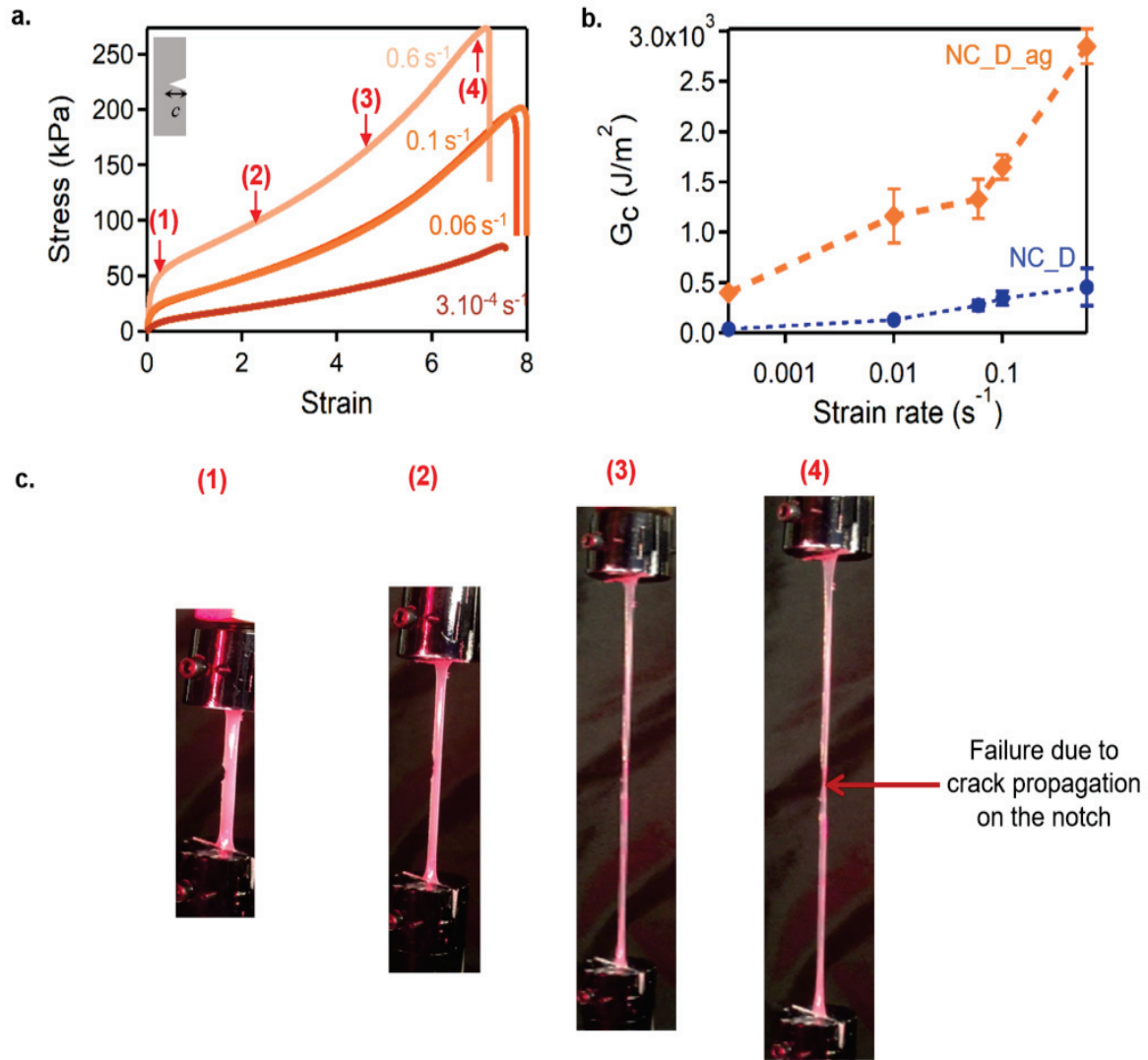


Figure V.7 – **a.** Tensile curves of NC_D_ag on pre-notched samples of length c at various strain rate, $\dot{\epsilon} = 3.10^{-4}$ (dark orange, $c = 1.04 \text{ mm}$), 0.06 (orange, $c = 0.82 \text{ mm}$), 0.1 (light orange, $c = 1.12 \text{ mm}$) and 0.6 (light pink, $c = 1.21 \text{ mm}$) s^{-1} . **b.** Calculated fracture energies for NC_D_ag (orange squares) and of NC_D (blue dots) plotted against the strain rate. **c.** Pictures of NC_D_ag samples at 0.6 s^{-1} at several stages of deformation.

Whatever the strain rate, the aggregation of silica nanoparticles significantly increases the energy release rate. The increase of dissipated energy along with the strain rate indicates that the time-dependence of the mechanical response observed for NC_D samples is still present when silica is aggregated, which tends to confirm the fact that the reversible polymer dynamics at the nanoparticles surface are still effective and play a part in the reinforcement even though the available specific surface is lowered. Moreover the calculated energies are higher than those of hybrid gels with well-dispersed silica as indicated in figure V.7.b. The hypothesis here is that the breakage of the hard silica clusters provide a supplementary mechanism to dissipate energy under the stress, and delay the propagation of the crack as illustrated in the picture (3) in figure V.7.c, where the notch is almost non-visible.

The fracture behavior of NC_A_ag appears to be completely different. While NC_A_ag samples exhibit very high tensile linear modulus and variable deformation abilities, tensile tests conducted on pre-notched samples revealed that those materials were quite fragile. Despite the stiffness the hard silica network provides, once a crack is present it propagates quite fast and critical failure happens at low deformation as illustrated in figure V.8. Furthermore, the stretching of the samples remain inhomogeneous as noticed during the tensile tests conducted on non-notched samples, which could be a cause for the lack of toughness of NC_A_ag. The strain rate does not seem to impact much the calculated fracture energies that remain inferior to the one calculated for PDMA gels with clustered silica (NC_D_ag), but it seems to impact on the crack propagation speed. The crack seems to propagate at lower strain for increasing strain rate, as illustrated in figure V.8.a where the sample stretched at $3 \cdot 10^{-4} \text{ s}^{-1}$ reaches higher strain at break but at the expense of the stress at break, contrary to sample stretched at 0.6 s^{-1} , where the failure happens at low strain but higher stress.

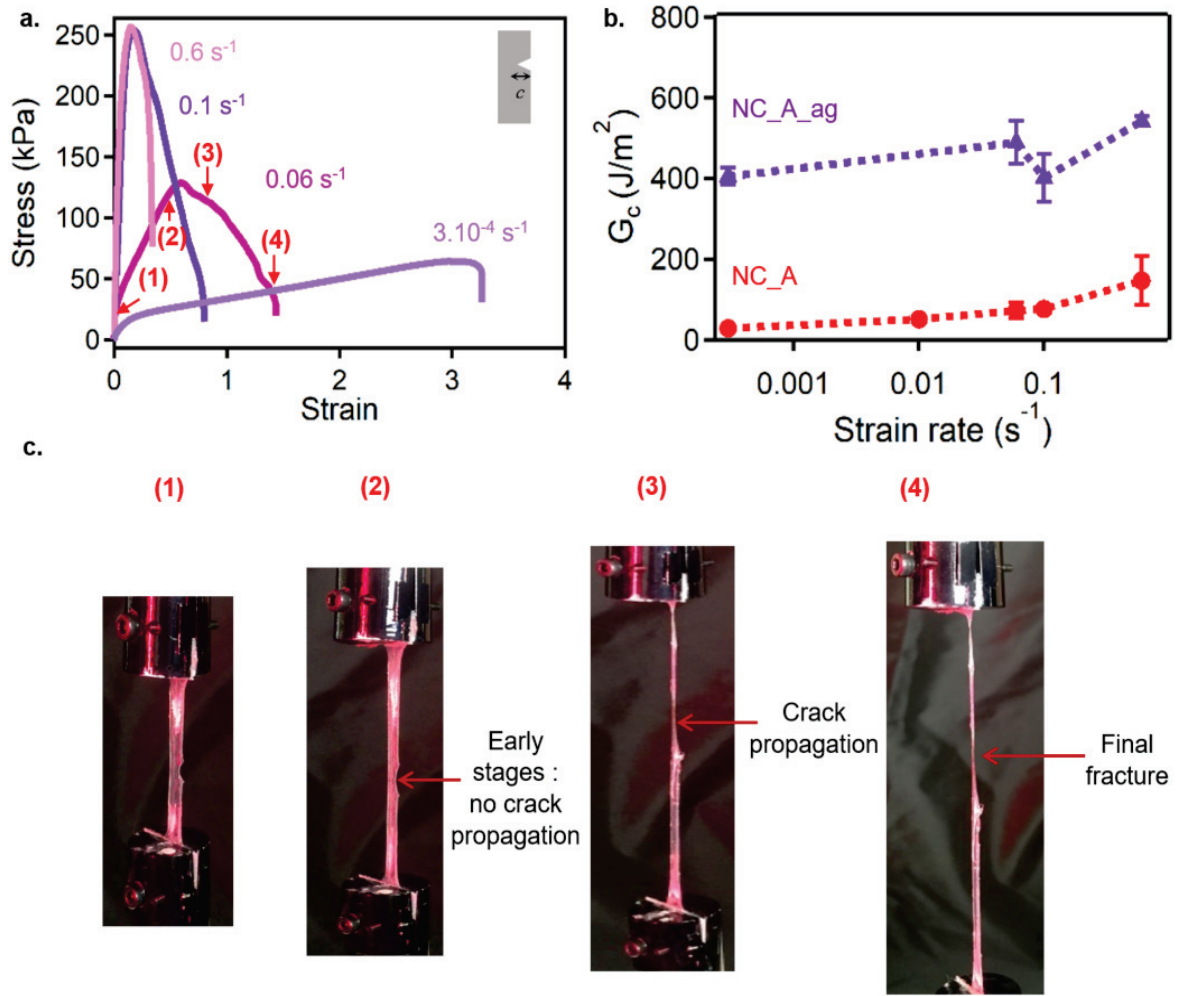


Figure V.8 – **a.** Tensile curves of NC_A_ag on pre-notched samples of length c at various strain rate, $\dot{\epsilon} = 3.10^{-4}$ (light purple, $c = 0.89 \text{ mm}$), 0.06 (violet, $c = 1.02 \text{ mm}$), 0.1 (dark purple, $c = 0.98 \text{ mm}$) and 0.6 (pink, $c = 0.92 \text{ mm}$) s^{-1} . **b.** Calculated fracture energies for NC_A_ag (purple triangles) and of NC_A (red dots) plotted against the strain rate. **c.** Pictures of NC_A_ag samples at 0.06 s^{-1} at several stages of deformation.

4 Exploring the non linear behavior: Large Amplitude Oscillatory Shear

Dynamic oscillatory shear tests are common in rheology and have been used to investigate a wide range of soft matter and complex fluids with a recent renewal of interest in exploiting large amplitude oscillatory shear (LAOS) tests to investigate and quantify their complex nonlinear viscoelastic behavior [Hyun et al., 2003; Hess and Aksel, 2011; Huyn et al., 2011].

Hybrid gels, composed of a dispersion of silica nanoparticles within a polymer matrix present obvious similarities with filled elastomers. Submitted to large sinusoidal strains, filled elastomers were demonstrated to show a decrease in their storage modulus (Payne effect) along with nonlinear behavior (strain stiffening), meaning that their response is no longer purely sinusoidal [Papon et al.,

2010]. The idea here is to assess the behavior of PDMA and PAAm hybrid gels where silica nanoparticles are either well-dispersed (NC_D and NC_A) or aggregated within the matrix (NC_D_ag and NC_A_ag). In Chapter four, the NMR study of hybrid gels showed the presence of a rigid polymer fraction around the fillers for NC_D gels that is attributed to polymer adsorption onto the silica nanoparticles, providing enhanced topological constraints and higher cross-linking density for significant silica content (10 vol%) within the network while none of these feature were observed for NC_A gels. These results highlight once more the similarities between hybrid hydrogels and filled elastomers, the main goal being now to explore the various contributions of reinforcement, following the study on mechanical properties described in Chapter III and in the first part of this chapter using LAOS experiments.

4.1 General background

The definitions of the linear viscoelastic moduli $G'(\omega)$ and $G''(\omega)$ are based on the assumption that the response to a sinusoidal strain is purely sinusoidal, with components in phase with $\gamma(t)$ and $\dot{\gamma}(t)$ respectively [Ferry, 1980]. However, a nonlinear stress response is not a perfect sine anymore and therefore the viscoelastic moduli are not uniquely defined; other methods are needed to quantify the nonlinear material response under LAOS deformation.

Several methods exist to describe the observed non-linearity. The first one is the Fourier transform analysis where non-linearity is described by the amplitude of the higher harmonics (which vanish in the small amplitude linear regime [Leblanc, 2003; Huyn and Wilhelm, 2009; Kallus et al., 2001]). Otherwise, a graphical approach consists in plotting parametrically the periodic stress response $\sigma(t, \omega, \gamma_0)$ against $\gamma(t)$ to obtain the commonly called Lissajous or Lissajous-Bowditch curves [Philippoff, 1966]. In both cases, the link between the observed behavior and the physical properties of the material remains hard to establish.

Another method proposed by Cho et al. [Cho et al., 2005] derives from a generalization of the linear regime where G' and G'' describe the elastic and viscous behavior of the material respectively, and depend only on the strain amplitude.

In the linear case, the stress is written as:

$$\sigma(t) = G'\gamma(t) + G''\dot{\gamma}(t)/\omega \quad (\text{V.15})$$

The total stress is the sum of an elastic stress $\sigma' = G'\gamma$ and of a viscous one $\sigma'' = G''\dot{\gamma}/\omega$. When the applied stress is a pure sine wave $\gamma = \gamma_0 \sin(\omega t)$, the elastic stress is the part of the signal in phase with the strain (odd part) and the viscous one is the one in phase with $\dot{\gamma}$ (even part). Within the linear domain, when the elastic stress is plotted as a function of γ and the viscous stress against $\dot{\gamma}/\omega$ during one shear cycle, straight lines are obtained with the slopes equal to G' and G'' , respectively.

This decomposition is then extrapolated to the non-linear case. At large amplitude oscillatory strains, the non-linear but still periodic stress $\sigma(t)$ can be decomposed into the sum of an odd (elastic) and even (viscous) contribution according to:

$$\sigma(t) = \sigma'(t) + \sigma''(t) \quad (\text{V.16})$$

with:

$$\sigma'(t) = (\sigma(t) - \sigma(-t))/2 \quad (\text{V.17})$$

$$\sigma''(t) = (\sigma(t) + \sigma(-t))/2 \quad (\text{V.18})$$

Similarly to the linear domain, the generalized moduli Γ' and Γ'' are introduced referring to the elastic and viscous response of the sample respectively:

$$\sigma'(t) = \Gamma' \gamma(t) \quad (\text{V.19})$$

$$\sigma''(t) = \Gamma'' \dot{\gamma}(t)/\omega \quad (\text{V.20})$$

In the linear case, the generalized moduli correspond exactly to the storage and loss moduli. In the nonlinear case the moduli also depend on the value of $\gamma(t)$ and $\dot{\gamma}(t)$ for each strain cycle, meaning that the plots of σ' versus γ and σ'' versus $\dot{\gamma}/\omega$ will not be straight lines anymore. It enables the analysis of the viscoelastic behavior of a sample inside each cycle. This method was already reported for the study of viscoelastic soft materials such as fibrin gels [Kang et al., 2009], amphiphilic polymer solution [Wang et al., 2010], PDMS [Fan and Liao, 2008] and filled elastomers [Papon et al., 2010].

LAOS experiments were conducted on hybrid gels based on PDMA and PAAm with aggregated and well dispersed silica to probe the non linearity of their mechanical response by analogy with previous studies conducted on filled elastomers [Papon et al., 2012]. The analysis is based on the method developed by Cho et al. to describe large amplitude oscillatory shear [Cho et al., 2005].

4.2 Performing LAOS experiments on hydrogels

While linear viscoelastic analysis has been extensively used to investigate physical or chemical sol/gel transitions in soft materials, this technique is more rarely used for characterizing stiff gels. Indeed, large discrepancies between moduli obtained from tensile measurements and those obtained from rheology have often been observed [Meyvis et al., 1999]. When it comes to investigate the rheological behavior of such materials at large strain (above $\gamma = 6\%$, with γ the deformation percentage) other difficulties arise, like slippage of the sample during the measurement [Gennissou et al., 2014]. Another problem to adress was the synthesis conditions, especially regarding the sensibility of the polymerization to ambient oxygen that stops the radicals propagation. To bypass these difficulties, a rheology cell was specifically designed to perform LAOS experiments on our hybrid gels. A schematic of the cell is illustrated in figure V.9 which allows to prevent the sample slippage and is fit to the polymerization under closed nitrogen atmosphere (overpressured glovebox).

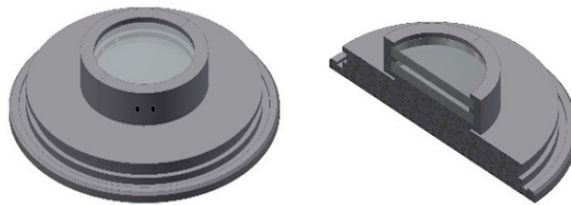


Figure V.9 – *Schematics of the rheology cell developed for LAOS experiments. Samples are injected between the covalently grafted glass plates and left to polymerize until gelation.*

Prior to gel synthesis, the glass plates were covalently grafted with aminosilane groups, here (3-aminopropyl)triethoxysilane (APTES), able to establish covalent bonds with both PAAm and

PDMA chains so that the gels were strongly attached to the glass. Then the glass plates were glued on a disposable plate-plate geometry, using bi-component epoxy glue as depicted in figure V.10.

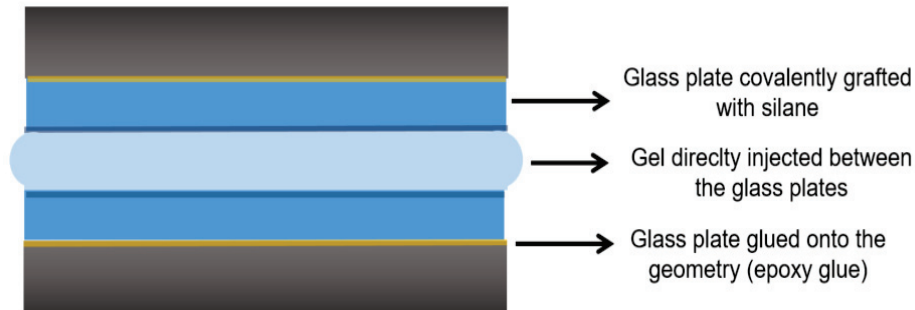


Figure V.10 – *Schematics of the gel grafting onto the rheology cell. The gels is polymerized in presence of silane groups grafted onto the glass (in dark blue) and the glass plates are glued onto the disposable rheology cell (yellow lines).*

That way, the samples were tested at high strain amplitude without slippage, allowing to explore the non-linear behavior through rheology measurements. A sinusoidal strain is applied to the samples and the amplitude is increased progressively, with a fixed frequency of 1 Hz. The full time-dependent stress and strain signals are recorded. For each strain amplitude, the analysis of the signal is made during 30 seconds (30 oscillation periods) and the acquisition is made on the last 20 seconds to get rid off the transient regime.

4.2.1 LAOS experiments on chemical gels

In figure V.11 are displayed the moduli from amplitude strain sweeps of chemical gels MD_R01 and MA_R01. They display an elastic behavior, with G' two orders of magnitude larger than G'' and without any variation of the dynamic loss and storage moduli over the applied range of strain. In particular no drop of the dynamic moduli (Payne effect) is noticed for increasing strain.

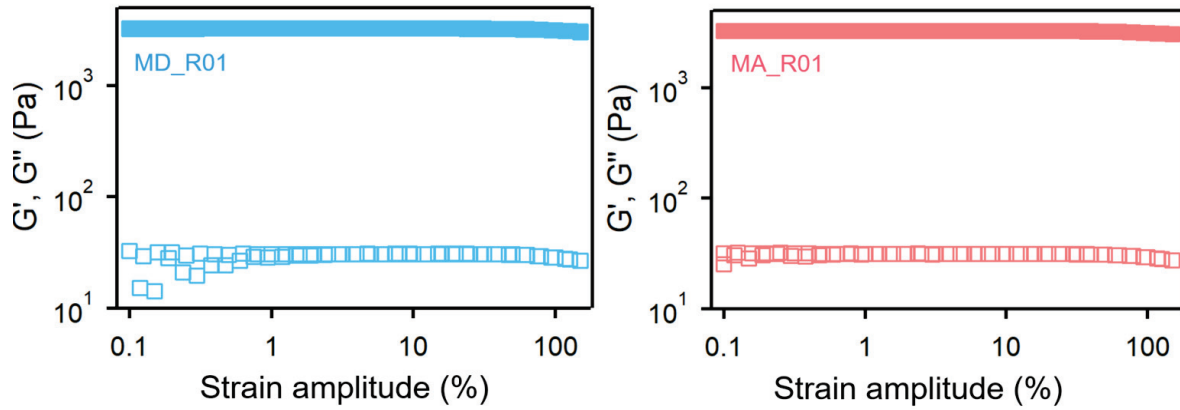


Figure V.11 – Storage (full squares) and loss (empty shapes) moduli of MD_R01 (blue) and MA_R01 plotted against the strain, varied from 0.1 to 150% back and forth. Frequency is fixed at 1Hz.

As shown in figure V.12, the typical linear viscoelastic response appears as an ellipse, which contains two mirror planes (major and minor axes of the ellipse, very narrow here). The Lissajous curves of MD_R01 do not show non-linear patterns, the stress remains well described with pure sine waves, with negligible dissipative component. The same behavior was also noticed for MA_R01, since as already described in the previous chapter, the chemical gels possess similar mechanical properties, independently of the chemical nature of the monomer.

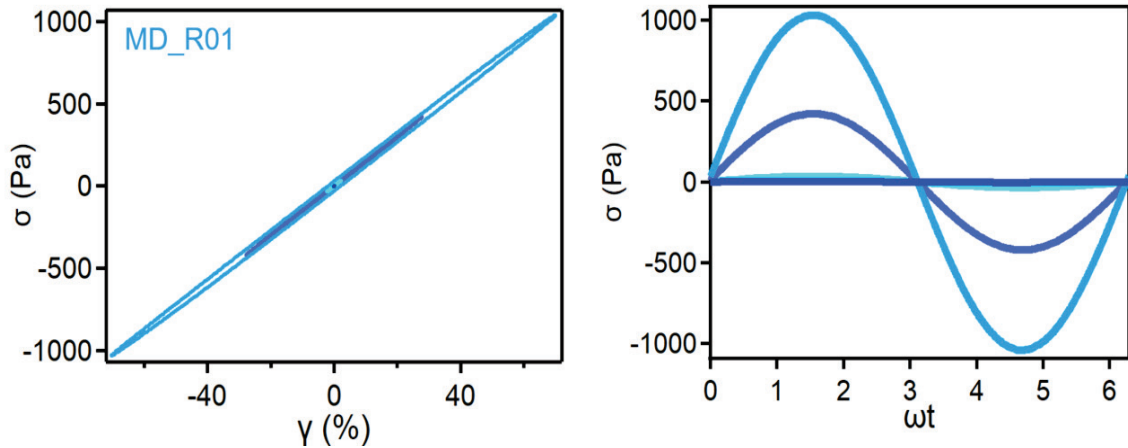


Figure V.12 – On the left, Lissajou curves of MD_R01 (blue) at 2 (dark blue), 3 (turquoise), 25 (blue) and 65 % (light blue) of strain. On the right, stress is plotted as a function of ωt , for MD_R01 as the same level of strain.

The stress of MD_R0 and MA_R01 is then decomposed into elastic and viscous part according to the method developed by Cho *et al.* Both elastic and viscous contributions of the stress give straight lines with slopes equal to the dynamic moduli, G' and G''/ω respectively, as displayed in figure V.13. This confirms the results of Chapter III that chemical gels have a linear behavior up to quite high strain amplitudes.

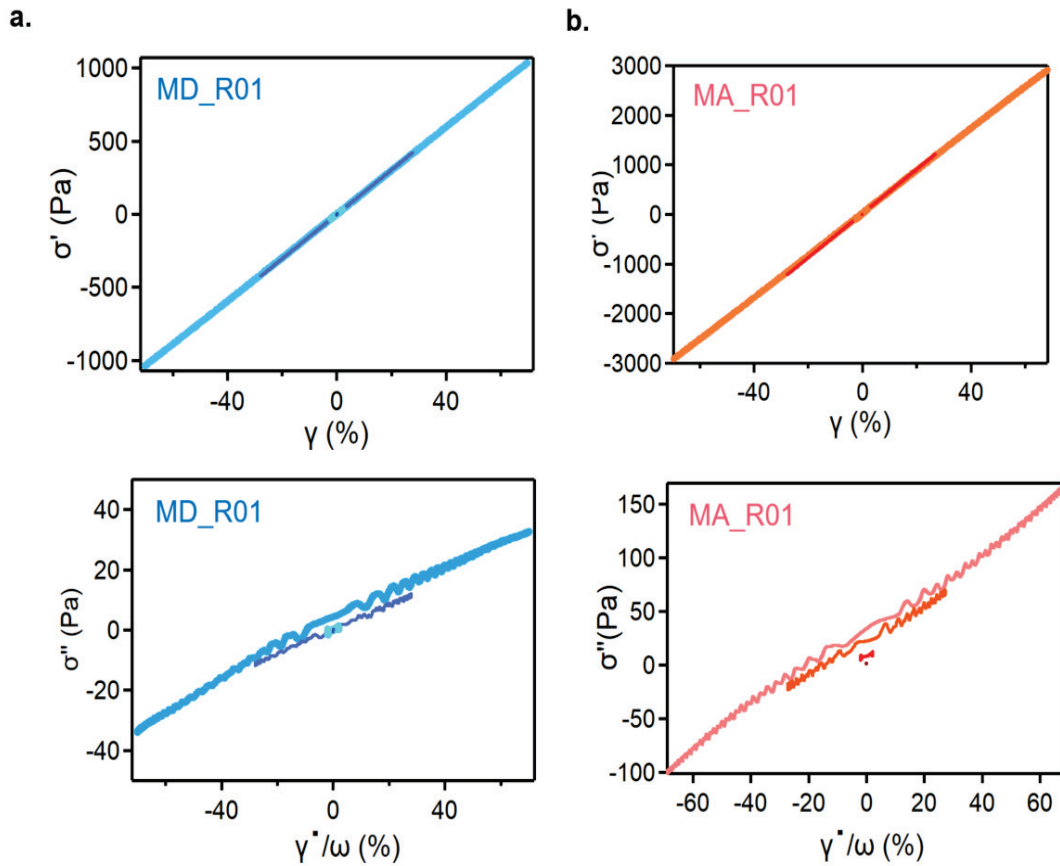


Figure V.13 – **a.** Decomposition of the stress into elastic σ' and viscous part σ'' for MD_R01 at 2 (dark blue), 3 (turquoise), 25 (blue) and 65 % (light blue) of strain as a function of γ (%) and $\dot{\gamma}/\omega$ (%), respectively. **b.** The same decomposition is applied for MA_R01 samples at the same levels of strain (2, in dark red, 3, in red, 25, in orange, and 65 % of strain, in pink, as a function of γ (%) and $\dot{\gamma}/\omega$ (%), respectively). Note the very different scales for σ' (top row) and σ'' (bottom row).

The viscous stress σ'' is very small, which explains the level of noise and the small artifact modulations in the σ'' curves (bottom row). This confirms that chemical gels have low dissipation, as they do not possess any efficient dissipation process. These results confirm the feasibility of LAOS measurements on hydrogels and the next section is dedicated to the analysis of LAOS measurements conducted on hybrid gels with well-dispersed silica.

4.2.2 Linear domain of PDMA hybrid gel

In figure V.14 are displayed the stress-strain curves at small strain of NC_D.

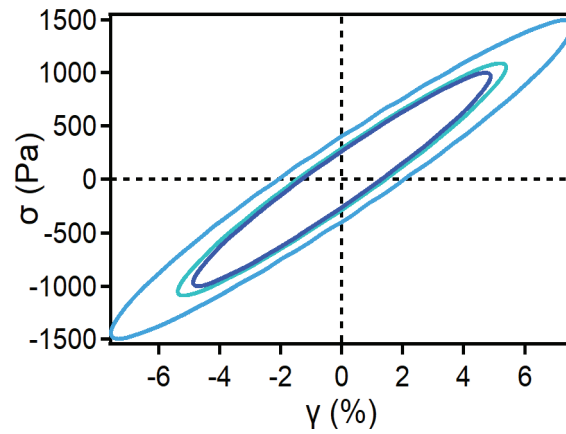


Figure V.14 – *Lissajous curve of NC_D within the viscoelastic regime.*

No significant pattern of non-linear response such as deformation of the ellipses are present, confirming that at these strain values, the response is still linear. The decomposition of the signal into an elastic and a viscous part applied for NC_D is illustrated in figure V.15. This sample is taken as an example, the general behavior being similar for all other samples with well-dispersed silica in the linear regime (NC_A).

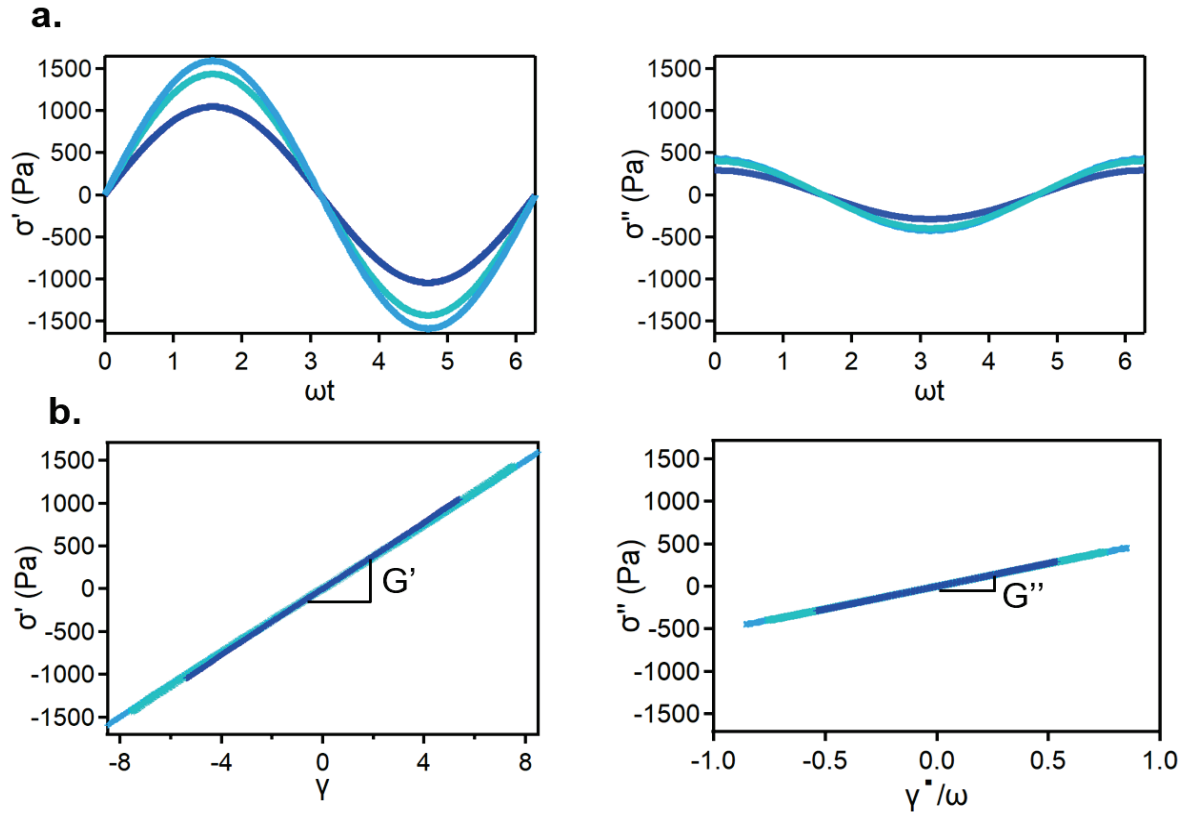


Figure V.15 – Cho's decomposition in the linear regime for three different strain amplitudes ($\gamma_0 = 5\%$, in blue, 7% , in turquoise and 8% , in light blue) for NC_D. **a.** Decomposition into odd (σ' , elastic) and even (σ'' , viscous) parts **b.** σ' and σ'' (in Pa) plotted as a function of γ and $\dot{\gamma}/\omega$, respectively form straight lines with the slopes being equal to the storage (G') and loss (G'') moduli.

The viscoelastic decomposition of the stress in the linear domain gives straight lines that are well described by linear storage and loss moduli, similarly to what was observed for chemical gels to the difference that the viscous part of the stress is much larger for NC_D samples.

4.3 Behavior at large strain of hybrid gels: impact of the monomer nature

4.3.1 Amplitude strain sweep on hybrid gels

The figure V.16 illustrates the evolution of the storage and loss moduli of NC_D and NC_A for increasing strain, up to 250 %. In Chapter III, the difference of stretchability between PDMA and PAAm-based hybrid gels was evidenced through uniaxial tensile tests, the common maximum amplitude of 250 % was then chosen to compare the two compounds and to avoid permanent damage of NC_A during the test. NC_D hybrid gel was tested for increasing strain amplitude up to 800 % to fully assess the non-linear behavior at later stages of deformation.

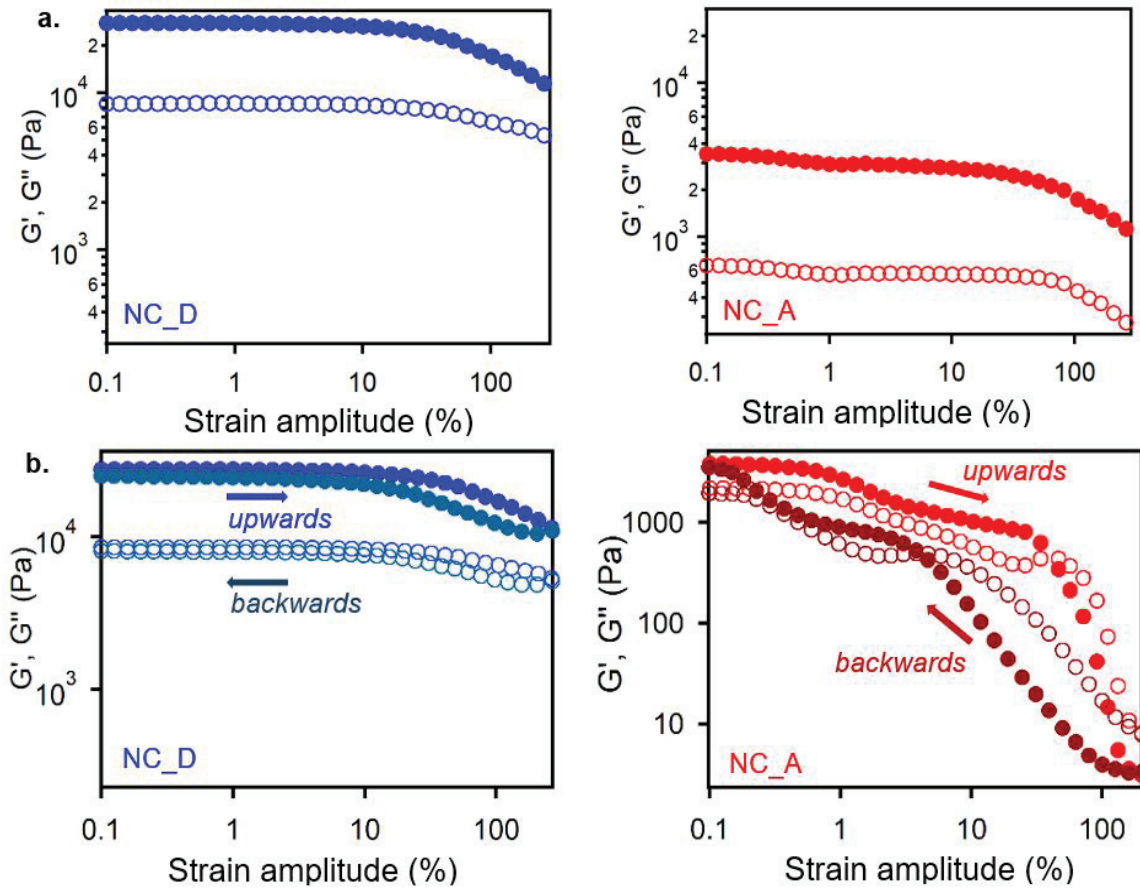


Figure V.16 – **a.** Storage (filled symbols) and loss modulus (empty symbols) of NC_D (blue) and NC_A (red) are plotted against the strain amplitude (%). **b.** Amplitude sweep back and forth of NC_D (blue, upwards and green-blue, backwards) and NC_A (red, upwards and dark red, backwards) from 0.1 to 250 % strain from 0.1 to 250 and 250 to 0.1 % without time of rest. NC_A sample shows signs of slippage at high strain (above 60 %).

The behavior of hybrid samples NC_D and NC_A differs from the one observed for the corresponding chemical gels. As expected, the first feature that appears is the large modulus enhancement for NC_D gels in the linear regime compared to the corresponding chemical gel and the weak modulus reinforcement observed for NC_A sample, confirming the observations made in Chapter III concerning the mechanical properties of NC_D and NC_A gels.

For NC_D, at strain values smaller than about 10%, both G' and G'' remain constant indicating that the samples are still in the linear domain. At higher strain (around 20 %), G' and G'' start to decrease as the strain amplitude increases, with a more marked effect on the storage modulus, which is very similar to the Payne effect observed in filled rubbers to the difference that this effect seems to be shifted towards higher strain (usually observed between 1 and 10 % of strain amplitude in filled elastomers [Perez-Aparicio et al., 2013]). Another important feature is the fact that the loss modulus does not increase with the amplitude strain contrary to what is usually observed with filled rubbers.

NC_A samples behave slightly differently with two different regimes observed in the drop of modulus, one first drop happening at low strain (between 0.1 and 1%), very similar to what is observed

in filled rubbers, followed by a plateau at intermediate strain (between 1 and 25 %). Around 25% of strain, dynamic moduli drop again, with a more pronounced effect for the storage moduli, similarly to what is observed for NC_D, as illustrated in figure V.17, where it is clearly shown that the ratio between G' and G'' is no longer a constant at high strain (above 25%). The first drop at small strain could be attributed to filler-filler interactions, as SAXS experiments showed that silica nanoparticles were more prone to aggregate in NC_A samples. Even though no strong aggregation patterns were observed, this small drop could indicate some local aggregation of the silica which would be consistent with what is observed in filled rubbers where aggregation state of the fillers is hard to control. However, this assessment remains purely speculative and would deserve further analysis.

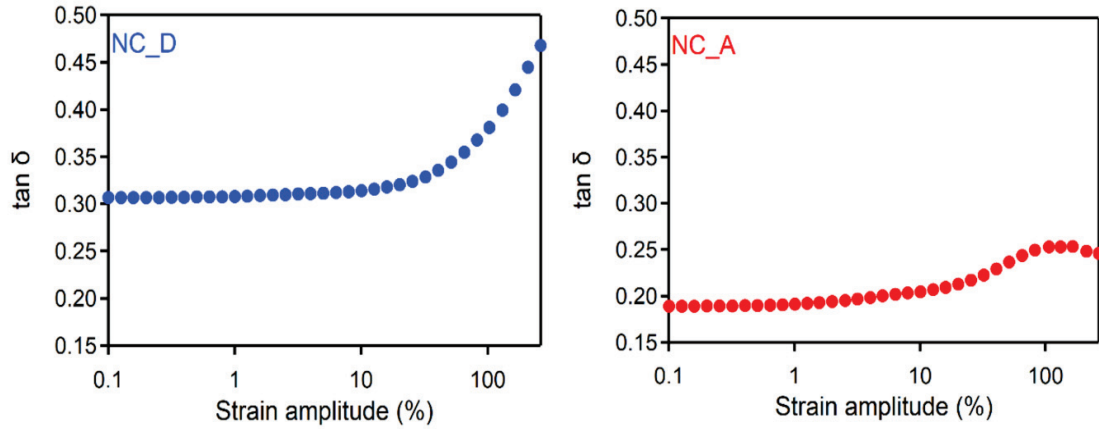


Figure V.17 – $\tan \delta$ defined as the ratio between G'' and G' of NC_D (blue) and NC_A (red) as a function of the strain amplitude (%).

Successive upwards and downwards strain amplitude sweeps (from 0.1 to 250 and from 250 to 0.1%, without resting time) were applied to the samples. While chemical gels do not show any variation of G' and G'' , NC_D and NC_A samples showed decreased dynamic moduli values between the first and the second strain amplitude sweeps, as shown in table V.4. The recovery parameters between the two strain amplitude sweeps are calculated as the ratio of the dynamic moduli (taken at fixed strain, during the back sweep and the forth sweep) with $R_{G'} = G'_{1stsweep}/G'_{2ndsweep}$ and $R_{G''} = G''_{1stsweep}/G''_{2ndsweep}$.

strain amplitude (%)	$R_{G'}$	$R_{G''}$	$R_{G'}$	$R_{G''}$
	NC_D	NC_D	NC_A	NC_A
0.1	0.90	0.94	0.92	0.89
5	0.86	0.91	0.33	0.58
50	0.72	0.84	0.02	0.16
100	0.73	0.81	-	-
200	0.82	0.85	-	-
250	0.96	0.96	-	-

Table V.4 – Recovery parameters $R_{G'}$ and $R_{G''}$ of NC_D and NC_A at fixed strain of 0.1, 5 50, 100, 200 and 250 %. Recovery parameter of NC_A drops very fastly and around 50 % strain, G'' becomes higher than G' indicating very likely slippage of the sample.

Interestingly, the dynamic moduli of NC_D do not fully recover when two loading cycles are applied without resting time, which is in good accordance with the characteristic time associated with adsorption/desorption processes at silica surface (around ten seconds). NC_A sample showed decreased moduli as well but also recovery of the dynamic moduli at small strain. At higher strain, it is clear that slippage has occurred making the amplitude sweeps results hard to analyze at those strain values.

In filled rubbers, the large enhancement of the modulus in the linear regime has been attributed to the transmission of the applied stress through a percolating network of particles. The breaking/reforming or the reorganization of such network under large amplitude strain could lead to the non-linear drop of modulus [Akutagawa et al., 2008; Kluppel and Schuster, 2008]. The latter hypothesis is not relevant at small strain amplitude for the considered systems since the dispersion state of NC_D and NC_A revealed that the particles remain non-aggregated in both polymer matrices even if NC_A favors aggregation of silica nanoparticles. However, at critical strain, the collisions between particles become effective and was evaluated experimentally for uniaxial tensile test at 45-75 % of strain [Rose et al., 2015] which could contribute to the observed Payne effect. Another approach consists in considering the presence of glassy domains due to a shift of glass temperature (T_g) in elastomer matrix near the fillers [Berriot et al., 2002b, 2003; Dequidt et al., 2012]. It is based on the fact that, even though the above mechanisms may play a role in the higher temperature range, they can certainly not explain the very large maximum of reinforcement observed a bit above the T_g of the elastomer matrix. This hypothesis should not be relevant for the systems considered here, since the polymer network is in semi-dilute solution in water, which certainly impair the formation of glassy zones. Another type of approach is focused on the breakage of polymer chains that would release trapped entanglements, or desorption from the filler surface [Maier and Goritz, 1996], leading to disentanglement of bulk rubber matrix from bounded chains [Litvinov et al., 2011]. However, no direct experimental evidences of those hypotheses in filled elastomers have been shown. The relative contribution of the various mechanisms mentioned above may be very different, depending on material and experimental parameters (essentially strain amplitude, strain rate and temperature) and on test conditions. As mentioned above, the effect of a filler network and of glassy bridges may not be relevant in our systems. However, given the presence of an adsorbed polymer layer around the silica nanoparticles with reduced mobility for NC_D, the approach of strong interactions with kinetic adsorption/desorption seems to be relevant to describe the behavior but raises questions as this adsorbed polymer layer was not observed for NC_A. Still,

a drop of modulus is noticeable at high strains for PAAm hybrid gel, pointing to the fact that the observed 'Payne effect' arises from various contributions.

4.3.2 Behavior at large strain

At high strains, the stress of hybrid gels is not described by a simple sine wave anymore, non-linearity appears. This is quite obvious when the response is plotted as stress-strain curve (Lissajou curve) as illustrated in figure V.18. Two phenomena can be noticed for NC_D: a strong deviation of the ellipse obtained in the linear case, with intra-cycle strain-stiffening and a drop of the slope at the origin at high strains that can be compared with the Payne effect observed for filled rubbers. NC_A gels display a different behavior. First, the drop of the dynamic moduli with increasing strains is less pronounced than that of NC_D. Then, the Lissajou curves remain well-defined ellipses with no visible strain-stiffening pattern, highlighting once more the impact of the nature of the monomer on the mechanical behavior of the hybrid gels.

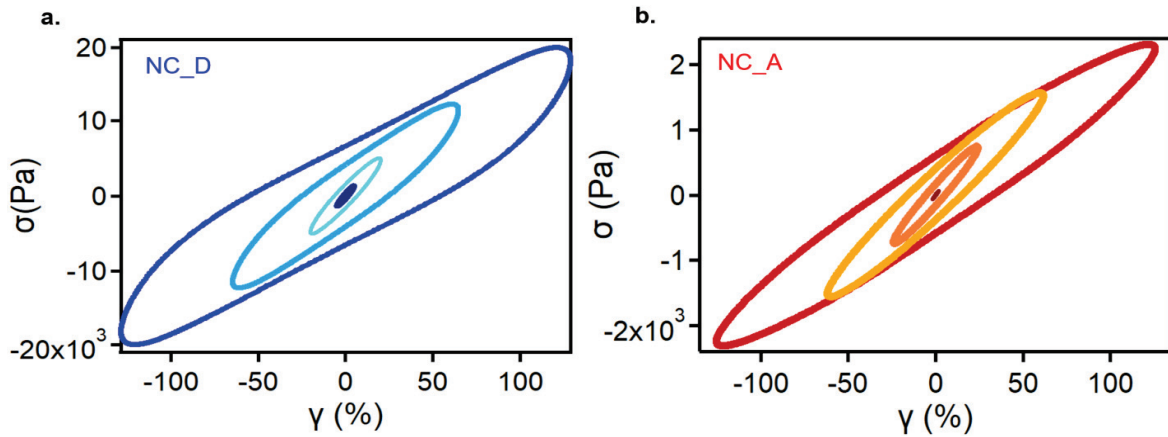


Figure V.18 – **a.** Stress (σ) as a function of the strain (Lissajou curves) of NC_D (on the left) at = 4 (dark blue), 25 (turquoise), 64 (light blue) and 120 (blue) % and **b.** Lissajou curves of NC_A at the same levels of strain: 4 (dark red), 25 (orange), 64 (yellow) and 120 (red) %.

The observed behavior is completely different from that of a material which would be described by a non-linear hyperelastic constitutive equation relating σ' to γ . This would be the case for example in a material in which strain hardening would be due to finite extensibility of the gel network chains. For such a hyperelastic material, the σ' vs γ curves obtained at various amplitudes would superpose in their common regime. In particular the slope at $\gamma = 0$ would not change as a function of the maximum strain amplitude. Thus the observed behavior proves that the state of the material changes depending on the maximum strain applied.

The elastic σ' and viscous σ'' stresses can no longer be described by the dynamic moduli G' and G'' . In this regime, the measured moduli have no clear physical meaning, this is why the stress is analyzed following the decomposition into elastic and viscous parts as proposed by Cho *et al.* as illustrated in figure V.19. To analyze the stress at higher strains, the generalized moduli Γ' and Γ'' which are function of $\gamma(t)$ and $\dot{\gamma}(t)/\omega$ in each cycle are introduced.

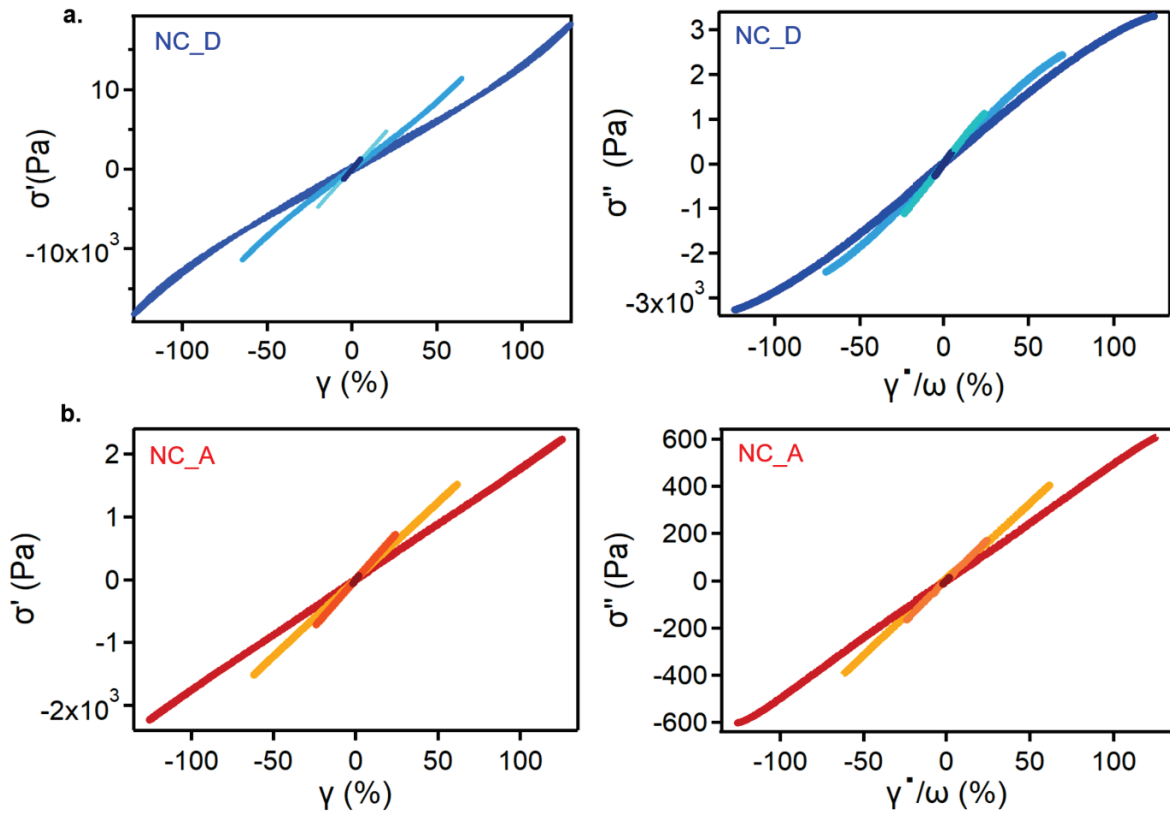


Figure V.19 – **a.** Cho's decomposition in the non-linear regime for different strain amplitudes ($\gamma_0 = 4, 25, 64$ and 120%) for NC_D into odd (σ' , elastic) and even (σ'' , viscous) parts. **b.** Decomposition into odd (σ' , elastic) and even (σ'' , viscous) parts for NC_A samples at $\gamma_0 = 4, 25, 64$ and 120% (obtained from the data in Figure V.18).

To study the generalized moduli, Ewoldt et al. [Ewoldt et al., 2008, 2007] chose to decompose the stress in Chebyshev series. As the interpretation of the various coefficients obtained remains rather complex, here the decomposition is limited to two terms, one describing the linear behavior and the other describing the nonlinear one.

Then the variations of Γ'_0 , Γ''_0 (the slopes at origin in figure V.19) and of Γ'_2 and Γ''_2 (the slope at the maximum strain and strain rate of each cycle respectively) with the strain amplitude γ_0 are studied.

On all the samples, we can observe the same general behavior, more or less pronounced depending on the nature of the monomer. As shown in figure V.20, Γ'_0 decreases with increasing γ_0 : this behavior is coherent with the Payne effect, meaning that the storage modulus decreases with the strain amplitude as observed for filled rubbers [Papon et al., 2010].

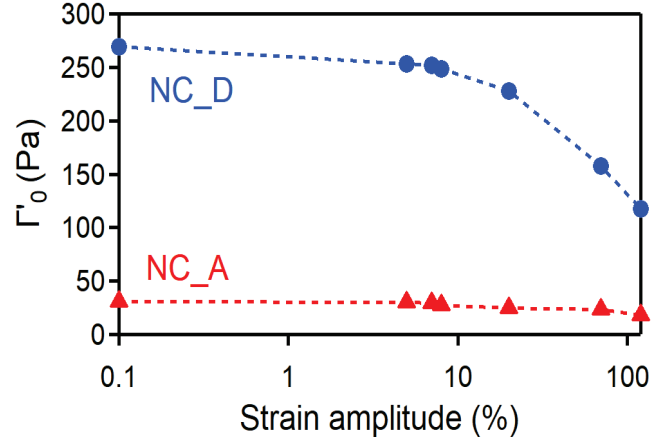


Figure V.20 – Γ'_0 (slope at $\gamma = 0$) obtained from the curves in figure V.20 for NC_D (blue dots) and NC_A (red triangles).

As NC_D and NC_A samples possess different stretching abilities, the behavior of NC_D only was evaluated at higher strain. As displayed in figure V.21, the obtained curve of viscous and elastic stress possess are characterized by strong non-linear patterns.

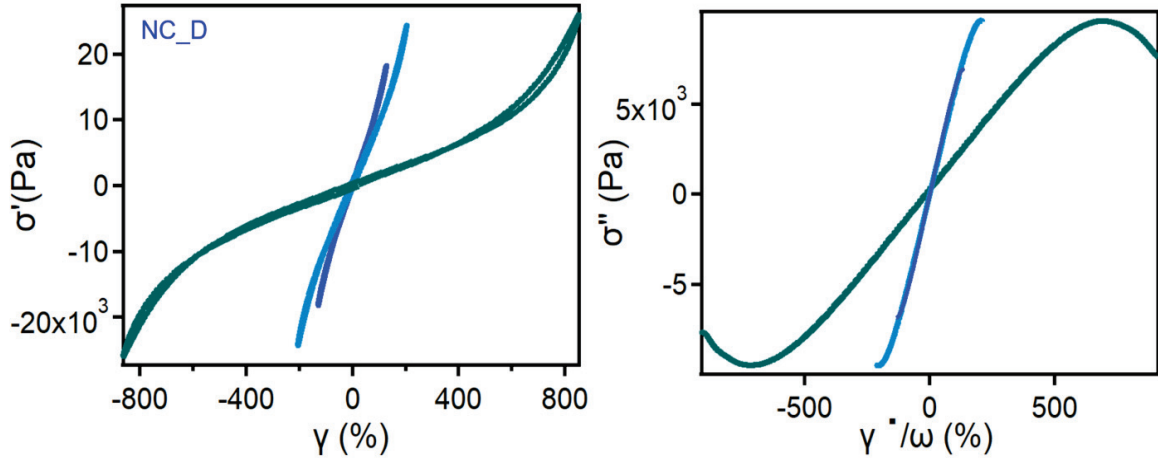


Figure V.21 – Decomposition into odd (σ' , elastic) and even (σ'' , viscous) parts for NC_D samples at $\gamma_0 = 130$ (blue), 200 (light blue), and 800% (green-blue).

For all NC_D samples, strain-stiffening is observed with increasing γ ($\Gamma'_2 > \Gamma'_0$ within one strain cycle). At these strain values, Γ'_0 decreases more smoothly for increasing strain and Γ''_2 remains positive, contrary to what is observed in filled rubbers [Papon et al., 2010]. At higher strain, it becomes higher and Γ''_2 becomes negative, indicating shear-thinning of the sample. Interestingly, NC_A gels show no difference between Γ'_0 and Γ'_2 , the non-linearity of the behavior seems to be visible in the drop of the Γ'_0 modulus only. This could indicate that the presence of fillers in a non-interactive matrix can have an impact, even weak, on the mechanical behavior since it was evidenced that PAAm possesses only few affinity towards silica. These results confirm the fact that the main contribution for reinforcement in hybrid gels comes from the reversible adsorption/desorption of polymer chains at silica surface as it is the case for NC_D samples. This

hypothesis can be supported with the mechanical properties reported for NC_A in Chapter III showing a weak reinforcement compared to the chemical gels and also with the LAOS experiments conducted on chemical gels showing pure linear behavior.

The non-linear parameter is defined by the ratio $\Gamma'_2(\gamma_0)/\Gamma'_0(\gamma_0 = 0)$ and is shown in figure V.22 for NC_D and NC_A and allows to evaluate the non-linear effects. The strain-stiffening is increasing drastically with strain amplitude for NC_D while it remains moderate for NC_A samples. In previous paper [Papon et al., 2012], the non-linear behavior of filled elastomers was modeled by considering the kinetics of melting/reformation of glassy bridges. Specifically, a new non-linear mechanism denoted ‘slowing-down-hardening’ was proposed. At the maximum strain in an oscillatory cycle, the strain rate goes down to zero, which gives more time for glassy bridges to reform. It follows that the number of glassy bridges which contribute to the modulus is modulated along one cycle, with more bridges at the maximum of a cycle. The similarity with the behavior observed in our systems suggests that a similar mechanism dealing with the adsorption of polymer chains on silica nanoparticles may be effective in hybrid gels. Applying a large amplitude strain modifies the polymer/filler adsorption/desorption dynamics, which explains the drop of modulus. Then, it takes some time for chain segments to re-adsorb, which would explain that more chains can re-adsorb when the strain goes to zero, hence the observed apparent strain hardening. This hypothesis would explain as well that strain hardening is not present in NC_A, in which chain adsorption is weak.

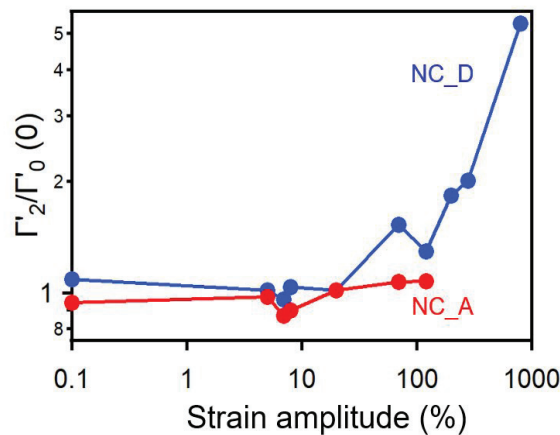


Figure V.22 – Nonlinear parameter $\Gamma'_2(\gamma_0)/\Gamma'_0(\gamma_0 = 0)$ as a function of the strain amplitude γ_0 of NC_D (blue) and NC_A (red).

At equivalent strain, strain-stiffening is larger for the NC_D samples compared with the NC_A samples. This means that the strain-stiffening does not only come from non-linear dissipation as both samples are subject to it. Another explanation could be the finite extensibility of polymer chains confined between chemical cross-linking points and silica nano-particles that act as supplementary cross-linking. When the polymer chains are completely stretched, the stress increases drastically. Since the silica particles cannot be distorted under the shear, the effective strain felt by the polymer confined between solid particles can be higher than the macroscopic strain applied. For NC_A samples, non-interacting with the silica nanoparticles the lesser significance of the strain-stiffening might be due to a slippage effect (depletion zone) of the polymer matrix at the surface of the particles, which could lower the strain amplification between the particles. This also could

explain why the decrease of modulus happens at earlier stage of deformation in the case of NC_A (8 % of strain to reach 10% of decrease of the initial storage modulus of NC_A against 15% of deformation for NC_D sample).

4.4 LAOS on hybrid gels with aggregated silica

4.4.1 Small strain linear viscoelasticity of hybrid gels with clustered silica

The mechanical properties of NC_D_ag and NC_A_ag are first studied at small deformations within the viscoelastic linear regime to specifically investigate the impact of the presence of the aggregation state of the nanoparticles on the dynamic moduli, probing the mechanical response of the microstructure without perturbations from its conformation at rest, as illustrated in figure V.23. The frequency-dependence was assessed from 0.1 to 100 rad.s⁻¹. For NC_D_ag gels, the aggregation of silica nanoparticles lead to an increase of G' and G'' and of the frequency dependence, similarly to what is observed for ND_D gels to the difference that the moduli values are higher. Both G' and G'' follow a power-law frequency response, similar to the one reported for physical gels [Kong et al., 2003; Ng and McKinley, 2008, 2011] or hydrophobically-modified systems [Hao and Weiss, 2011] . These measurements do not give the possibility to define a characteristic time that would correspond to a maximum in the loss modulus, indicating that there is a large distribution of relaxation processes. It is worth noticing that $\tan \delta$ decreases from 0.5 to 0.2 with increasing frequency as illustrated in figure V.23.b.

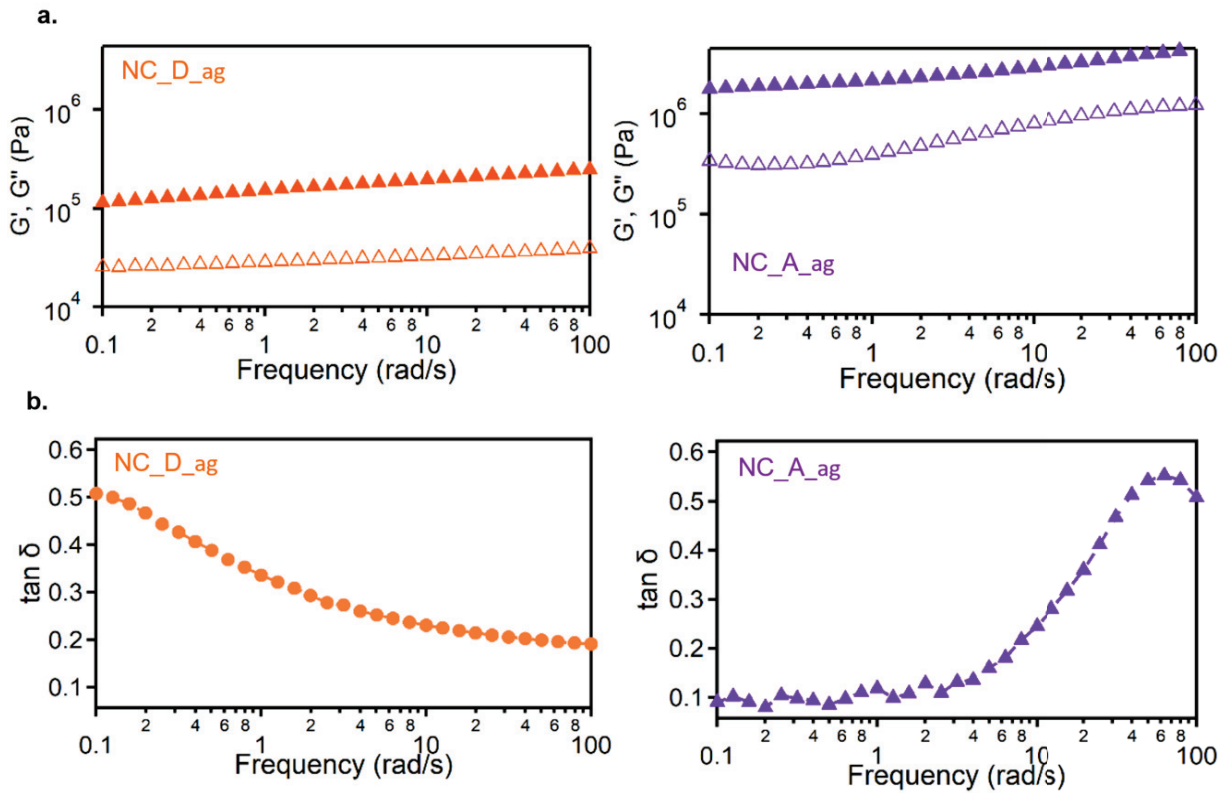


Figure V.23 – **a.** Frequency dependence of the storage (filled symbols, G') and the loss (open symbols, G'') moduli of PDMA (NC_D_ag, orange triangles) and PAAm (NC_A_ag, purple triangles) hybrid gels at oscillation strain = 0.1%. **b.** $\tan \delta$ defined as G'' / G' of NC_D_ag (orange dots) and NC_A_ag (purple triangles) plotted as a function of the frequency.

The NC_A gels displays a slightly different behavior, with a drastic increase of the dynamic moduli (of the order of the MPa). G'' seems to slightly decrease first, before increasing as the frequency increases which could be due to the hard filler network response. The values of calculated Young modulus from the rheology experiments and of the experimentally determined ones from the uniaxial tensile tests at low strain are shown in table V.5. Both values coincide very well. As shown in figure V.23.b, a maximum in $\tan \delta$ is observed at high frequencies.

	NC_A_ag	NC_D_ag	NC_A	NC_D
n ($G' \approx \omega^n$)	0.32 ± 0.004	0.06 ± 0.003	0.07 ± 0.001	0.18 ± 0.0001
m ($G'' \approx \omega^m$)	-	0.14 ± 0.006	0.17 ± 0.002	0.17 ± 0.001
$E_{calc} \ 3(G'^2 + G''^2)^{1/2}$ (kPa, at 0.37 rad/s)	5859	613	19	85
$E_{tensile}$ at 0.06 s^{-1} (kPa)	4960 ± 1709	1016 ± 240	23 ± 1	92 ± 5

Table V.5 – Experimental values of power laws of storage and loss moduli, and calculated value of modulus (at frequency corresponding at 0.06 s^{-1}), compared to experimental values of initial modulus obtain in tensile tests at 0.06 s^{-1} for NC_D_ag and NC_A_ag. NC_D and NC_A values are displayed as a comparison.

4.4.2 PDMA gels with aggregated silica

The same measurements were performed on hybrid gels with aggregated silica. As previously demonstrated with the mechanical tests conducted on those samples, their behavior is very different depending on the monomer used. In figure V.24 are displayed the evolution of the elastic and loss moduli with the strain amplitude on NC_D_ag sample. To avoid any damage to the sample, the maximal strain is fixed below the strain at break obtained during the tensile tests. Similarly to what was observed during the mechanical tests, the obtained modulus are higher than those of NC_D, by one order of magnitude which can be explained by the aggregation state of the inorganic fillers that provides supplementary reinforcement.

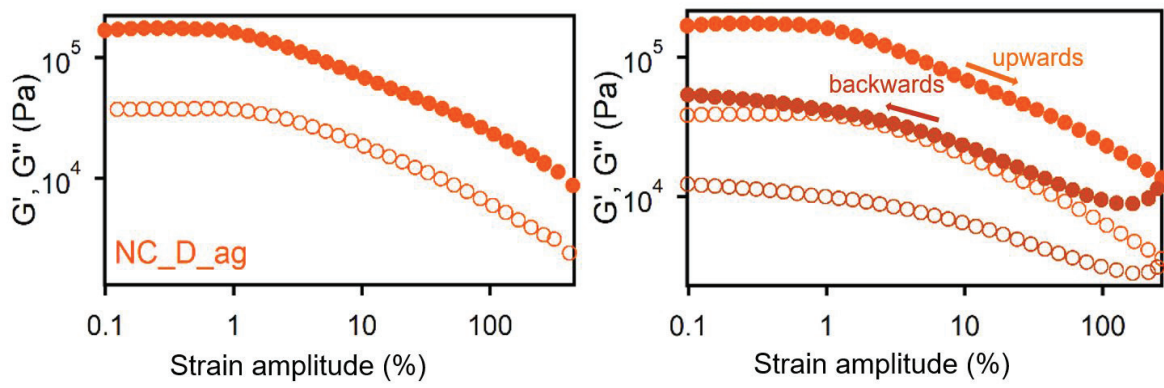


Figure V.24 – Storage (filled symbols) and loss modulus (empty symbols) of NC_D_ag vs the oscillation strain, varying from 0.1 to 400%. The measurements are performed at fixed frequency of 1 Hz. On the right, storage (filled symbols) and loss modulus (empty symbols) of NC_D_ag vs the oscillation strain from 0.1 to 250 % and from 250 to 0.1 % without time of rest.

The behavior is similar to what is obtained for NC_D gels to the difference that the observed drop of modulus seems to happen at earlier stage of deformation, around 1%. Surprisingly, a slight enhancement of the storage modulus is systematically observed correlatively to the first drop, between 0.1 and 0.3% of oscillation strain which remains quite puzzling. The first drop is similar to what is observed in filled rubbers and might be attributed to the breaking of the silica network, or alternatively to a stretching of polymer chains tightly constrained between silica clusters. The second step of decrease is similar to what is observed in the NC_D gels and may be attributed to the desorption of a fraction of chains. Beyond 1% of deformation the dynamic moduli are decreasing with a more marked effect for G' . For those samples, the hypothesis of a hard network of nanoparticles or hard clusters linked with interacting polymers chains can be taken into account to explain both the enhance of the dynamic moduli (by an order two of magnitude compared to the pure chemical polymer matrix) and the non-linear drop of modulus.

The recovery was also investigated by performing successive strain amplitude sweeps, first without time of rest (from 0.1 to 250% then from 250% to 1%), then after 24 hours of rest (from 1 to 250 %) to assess the recovery processes. The results are illustrated in table V.6.

strain amplitude (%)	$R_{G'}$	$R_{G''}$	$R_{G'}-24h$	$R_{G''}-24h$
0.1	0.32	0.32	-	-
0.5	0.29	0.27	-	-
1	0.26	0.26	0.90	1.14
5	0.32	0.29	0.92	1.12
10	0.35	0.34	0.89	1.09
20	0.36	0.37	0.83	1.02
50	0.36	0.42	0.78	0.96
100	0.41	0.50	0.83	1.01
200	0.61	0.69	0.94	1.11
250	0.83	0.87	0.97	1.14

Table V.6 – Recovery parameters $R_{G'}$ and $R_{G''}$ of NC_D_ag at fixed strain, between two successive amplitude strain sweeps without rest and with 24 hours of rest between sweeps ($R_{G'}-24h$ and $R_{G''}-24h$). The recovery parameters between the two amplitude strain sweeps are calculated as the ratio of the dynamic moduli of the two sweeps at fixed strain, with $R_{G'} = G'_{1stsweep}/G'_{2ndsweep}$ and $R_{G''} = G''_{1stsweep}/G''_{2ndsweep}$ and $R_{G'}-24h = G'_{1stsweep}/G' - 24h$ and $R_{G''} = G''_{1stsweep}/G'' - 24h$

Right after the first amplitude sweep, the sample seems permanently damaged compared to NC_D, with a recovery parameter not exceeding 0.32 at small strains. However, after 24 hours of rest, the sample seems to have fully recovered. The obtained G' values remains a little bit inferior to the one obtained during the first amplitude strain sweep, on the contrary G'' is slightly superior which indicates that the sample undergoes polymer/silica rearrangement after stretching. NC_D samples were already demonstrated to be able to recover due to the re-formation of silica/PDMA interactions. The same mechanism seems to be at play here, maybe delayed by the smaller available silica surface due to aggregation state. Reorganisation of silica clusters could also be involved in the overall rearrangement.

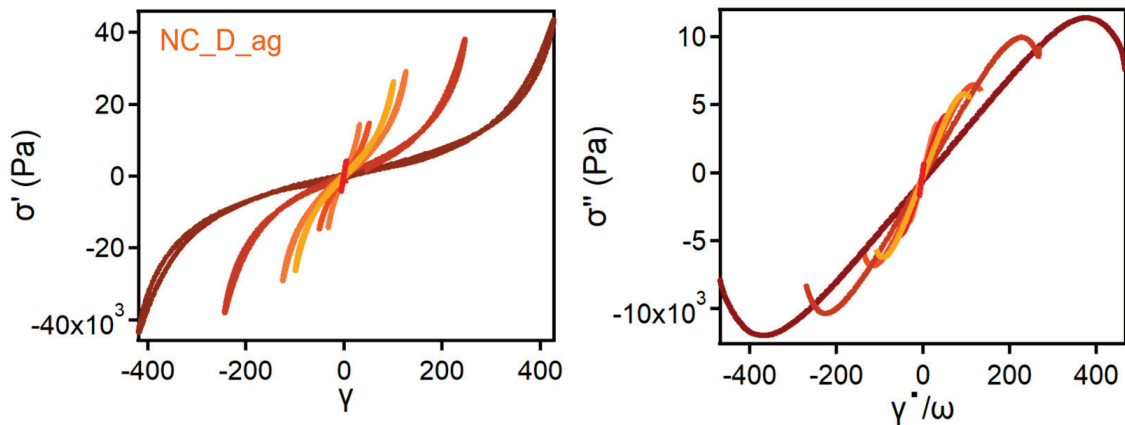


Figure V.25 – Decomposition into odd (σ' , elastic) and even (σ'' , viscous) parts for NC_D_ag samples at $\gamma_0 = 4, 25, 64, 105, 130, 250$ and 410% .

In figure V.25 are displayed the obtained curves of the elastic and viscous stresses of NC_D_ag. Non-linear effects are pronounced, more than for NC_D with a strong deviation from the linear

behavior happening at low stages of deformation. At small strain, inferior to 0.5%, a slight increase of Γ'_0 is noticed before dropping with increasing strain. Γ''_0 decreases also but more smoothly than its elastic counterpart. Strain-stiffening is increasing along with the strain amplitude (Γ'_2 being positive with each strain cycle). Γ''_2 stays positive until $\approx 60\%$ of strain then becomes negative, pointing to shear-thinning of the sample. When the non-linear parameter is plotted as a function of the strain as displayed in figure V.26, it is quite clear that the strain-stiffening effect is more important when silica is aggregated. This might be due to the finite extensibility of adsorbed polymer chains onto the silica clusters but also to the presence of anisotropic silica aggregates.

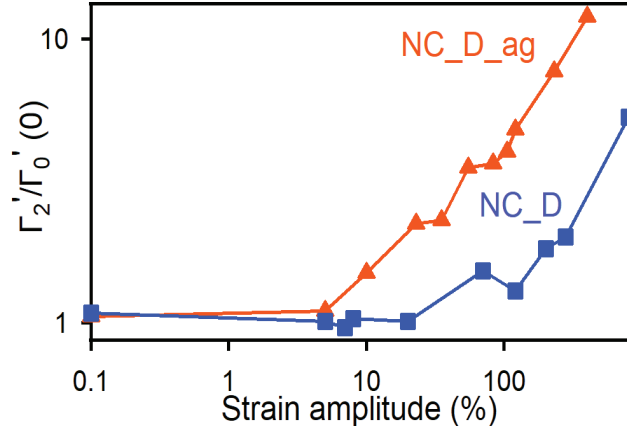


Figure V.26 – Non-linear parameter $\Gamma'_2(\gamma_0)/\Gamma'_0(\gamma_0 = 0)$ as a function of the strain amplitude γ_0 (%) of NC_D (blue) and NC_D_ag (orange).

4.4.3 PAAm gels with aggregated silica

Under the shear, NC_A_ag samples undergo permanent damages so that the usable data are confined to low strain only (inferior to 10%) as illustrated in figure V.27. Beyond 10% of strain, G' drops suddenly and follows the same trend as G'' before collapsing completely. The more likely hypothesis is that silica nanoparticles strongly aggregate during the polymerization of AAm, leading to a hard percolating silica network that irreversibly breaks under the shear, whatever the resting time allocated, explaining both the very high modulus obtained for those gels and the observed damages.

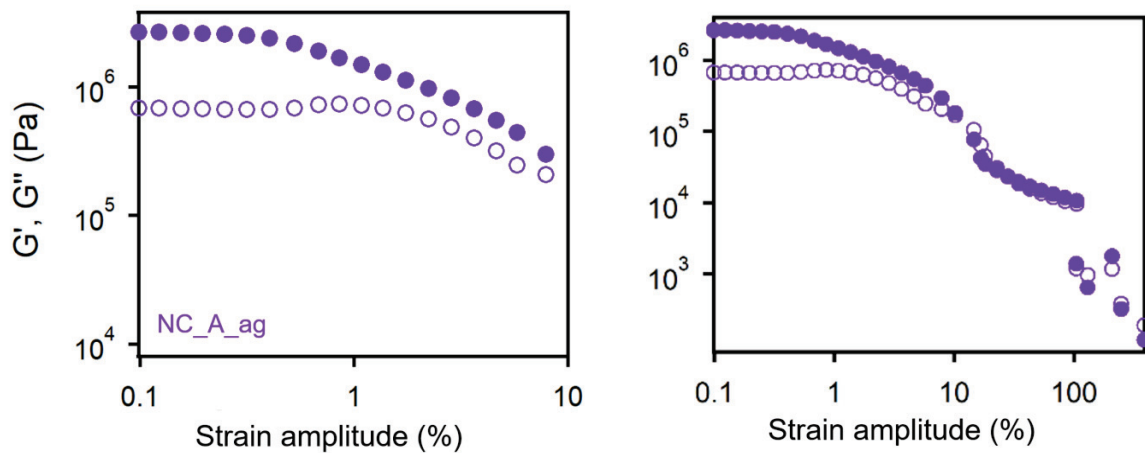


Figure V.27 – On the left, storage (filled symbols) and loss modulus (empty symbols) of NC_A_ag vs the oscillation strain, varying from 0.1 to 10 %. The measurements are performed at fixed frequency of 1 Hz. On the right, full amplitude sweep of NC_A_ag, showing the damages above 10% of strain.

The values of the dynamic moduli are high (of the order of 2 MPa for G'), pointing to strong aggregation of the silica nanoparticles within the network. PAAm hybrid gels with well-dispersed silica did not show strong reinforcement with G' values of the order of a few 10^3 Pa, ruling out the polymer/filler interactions as a reinforcement mechanism. Furthermore such high values of the dynamic moduli were never reached during this study, even with an interacting polymer matrix. The stronger level of aggregation is attributed to the destabilization of the silica nanoparticles due to the depletion zone around the fillers generated by the presence of a non-interacting polymer. When the strain increases, the storage modulus decreases quite abruptly at early stages of strain (G' decreases by 10% at 0.5% of strain). The loss modulus remains quite stable before increasing a little around 1% of strain, before dropping. This behavior seems to be more in accordance to the Payne effect observed in filled rubbers but this remains difficult to discuss further as the samples are too much damaged during the experiment to explore the behavior at large strains.

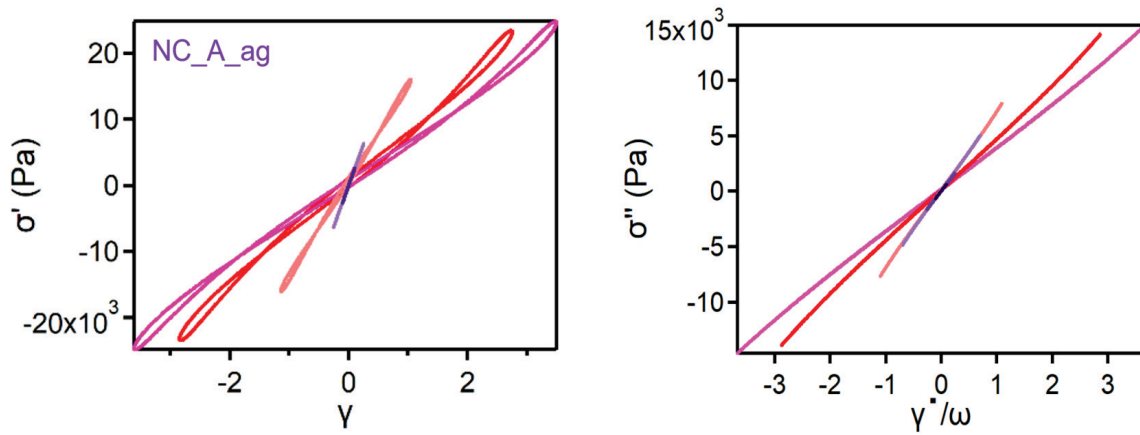


Figure V.28 – Decomposition into odd (σ' , elastic) and even (σ'' , viscous) parts for NC_A_ag samples at $\gamma_0 = 0.25$ (dark blue), 0.25 (light purple), 0.5 (purple), 1 (light pink), 2.8 (red) and 3.4 (pink)%. The small apparent hysteresis observed in the σ' cycles is an artifact due to imperfect strain regulation by the rheometer which impairs signal analysis. Only the general shape of the cycles should be considered.

Even at low strain, non-linearity is clearly visible as shown in figure V.28 with an important drop of the dynamic moduli, larger than that of NC_D_ag at the same level of deformation. At these strain values, other features of non-linearity (strain-stiffening or shear-thinning) are not very pronounced but it is difficult to discuss whether they are not appearing at these low strain or if the non-interacting character of the monomer is also playing a role.

The obtained non-linear parameter illustrated in figure V.29 for those samples indicates stronger non-linear effects than that of NC_D_ag samples at the same strain amplitude, underlying the fact that stronger silica aggregation leads to pronounced non-linearity. However, the permanent damages limit the exploitation of the data so that the behavior at large strain cannot be assessed.

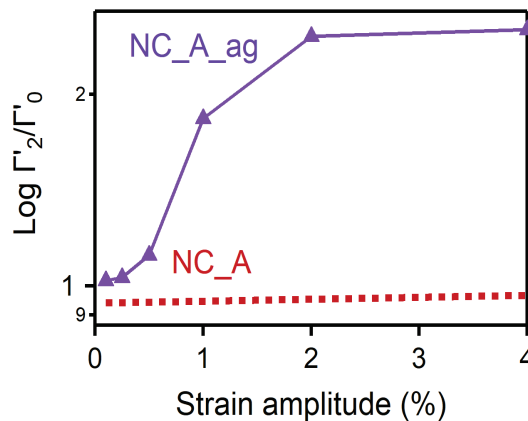


Figure V.29 – Log of the non linear parameter $\Gamma'_2(\gamma_0)/\Gamma'_0(\gamma_0 = 0)$ of NC_A_ag (purple triangles) as a function of the strain amplitude γ_0 , for strain varying from 0.1 to 3.7 %. The non linear parameter of NC_A is also displayed for the corresponding strain amplitudes, as a reference.

5 Conclusion

Tuning the surface chemistry of the nanoparticles to promote aggregation leads to gels exhibiting a behavior completely different from those where silica is well-dispersed within the matrix. The obtained hybrid gels display strong stiffening along with dissipative capabilities and high fracture energies. For NC_D_ag samples, enhanced stiffness and fracture energies are obtained and more surprisingly, recovery processes seem to be preserved but the characteristic times needed to fully recover is extended from a few seconds to several hours. For those gels the reinforcement is certainly due to the nanoparticles dispersion state but also to the reversible interactions that seem to be still effective in spite of the clustered silica. Since the surface chemistry has been changed, one can wonder whether the observed recovery is favored by the higher density of silanols groups at the silica surface that would strengthen the interactions with the polymer. The silica dispersion state remains better than that of PAAm-based samples, the deformation is homogeneous and the silica clusters seem to provide a efficient way to delay crack propagation. For PAAm based gels, no recovery processes are observed, implying that the reinforcement (very high linear tensile modulus, high dissipated energies and enhanced fracture energies) is only due to aggregation of the nanoparticles within the network, that provides high dissipative capabilities, especially compared with NC_A gels that remain soft and fragile. However, these gels reveal a highly inhomogeneous structure with permanent damages under elongation.

The LAOS experiments allowed to probe the non-linear behavior of both chemical and hybrid gels. Chemical gels showed no signs of non-linearity whatever the amplitude of the applied strain. On the contrary, marked non-linear effects are noticed for NC_D, certainly due polymer adsorption onto the nanoparticles. NC_A samples also show non-linearity with a drop of moduli for increasing strain, but no strain-stiffening effects, indicating that the presence of fillers alone can induce non-linearity of the mechanical behavior but with a limited impact on the reinforcement which is in good agreement with what was observed in the previous chapters. The analysis of the non-linear behavior suggests the importance of the kinetics of re-adsorption of polymer chains desorbed under large amplitude strain.

The measurements conducted on NC_A_ag and NC_D_ag showed marked non-linear behavior, similar to the ones observed in filled elastomers. For those samples, the reinforcement can be attributed to two specific features: the reversible interactions between PDMA and silica nanoparticles, that provide the strain-stiffening and the recovery processes, and the silica aggregation that lead to enhanced stiffness, dissipative processes, high fracture energies and pronounced strain-stiffening effects.

In NC_A_ag samples, the reinforcement is induced by the silica dispersion state that lead to the very high stiffness and the good dissipative properties but at the expenses of the stretchability. Also, the structure seem permanently damaged under the applied stress, revealing the importance of silica/polymer interactions for mechanical reinforcement.

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General Conclusion

Hybrid gels consisting of a covalently cross-linked network interacting physically with silica nanoparticles were developed and studied so as to better understand the reinforcement mechanisms that were reported for those systems. Indeed, polymer adsorption was shown to provide an efficient and transient anchorage of the polymer chains onto the silica surface leading to strong mechanical reinforcement. The idea was to tune these reversible interactions either by substituting the interacting monomer (DMA) with a non-interacting one (AAm) while keeping every other parameters constant (surface chemistry, gel composition), or to purposely modulate the surface chemistry of the nanoparticles to weaken the polymer/silica interactions.

Modulating the surface chemistry also enabled tuning the dispersion state of the silica nanoparticles so as to generate hydrogels with aggregated silica, thus creating hybrid gels containing a double network, one permanently cross-linked, elastic network and one constituted by a percolating filler network.

First, the adsorption abilities of the linear polymer chains onto silica nanoparticles were characterized using three different analysis methods. For that purpose, a synthesis route of homopolymers and copolymers of PDMA and PAAm was developed using Atom Radical Transfer Polymerization. The characteristics and the behavior of the Ludox TM-50 silica suspension used in this study was investigated and underlined the importance of controlling the chemical environment of the nanoparticles. We chose the pH as a way to control the surface chemistry of the silica. The adsorption experiments revealed a good affinity of PDMA chains towards silica surface (at pH 9) and almost no adsorption for PAAm polymer chains under the same conditions. The copolymers showed decreased affinity for increasing AAm content, which confirmed our choice for PAAm as the non-interacting polymer.

The following step was to synthesize hybrid gels based either on PAAm or PDMA. The study focuses on gels with a silica content fixed at 0.2 v/v to reach the maximum reinforcement, weakly cross-linked (0.1 mol%) with a fixed polymer/water molar ratio. The pH was either fixed at 9 (PDMA and PAAm gels) or at 11 (PDMA gels only). Using Small Angle X-Ray Scattering experiments, we verified that the polymerization and the cross-linking of DMA and AAm in the presence of silica nanoparticles does not affect their initial dispersion and we have shown that, while silica is well-dispersed in both matrices, it is more prone to aggregate in PAAm network probably due to the polymer depletion zone induced by the non-interacting character of PAAm. The polymer matrices were first characterized using thermodynamic and mechanic investigations. The mechanical behavior of the corresponding hybrid gels was investigated in details. As reported prior to this study, the attractive potential between PDMA and silica gives rise to a drastic reinforcement of the mechanical behaviour, in terms of linear tensile modulus and strain at failure. The silica nanoparticles acting as multifunctional physical platform of cross-links. The presence of the PDMA/silica interactions is evidenced by the time-dependence of the mechanical behavior. On the contrary, hybrid gels based on PAAm show weak reinforcement and the time-dependence observed for PDMA vanishes, pointing to the lack of reversible interactions between PAAm and the silica. Linear modulus, strain at break, dissipative properties and fracture resistance decreased altogether and the behavior becomes quantitatively similar to the one of an elastic unfilled gel matrix. The covalent polymer network drives the elasticity, recoverability and the strong, highly time-dependent stiffening effect that was observed for PDMA gels vanishes as the physical network does not exist in PAAm gels. Experiments

conducted at the swelling equilibrium state revealed a loss of reinforcement and dissipation for both PAAm and PDMA with a more marked effect for PAAm. The mechanical behavior of PDMA gels synthesized at pH 11 was then assessed to attempt to identify more precisely the nature of interactions between the polymer and the nanoparticles and evidenced the crucial importance of the silanol groups at the silica surface for polymer adsorption and thus gel toughening.

Concomitantly, ^1H NMR experiments were performed on PAAm and PDMA hybrid gels at various chemical cross-linker and silica content to study their structure and dynamics. In PDMA gels at pH 9, the presence of a rigid polymer fraction, interpreted as an adsorbed layer was demonstrated. Conversely, no rigid fraction was measured in PDMA at pH 11 and PAAm gels, underlying once more the importance of polymer dynamics at the solid/liquid interface for gel reinforcement. Double-Quanta experiments showed that in PDMA gels at pH 9, silica nanoparticles contribute significantly to increase the overall effective cross-linking density of the network to the condition that the silica content is high enough (around 10 vol%). On the contrary, for PDMA at pH 11 and PAAm gels, the presence of silica nanoparticles seems to be detrimental to the network cross-linking. The impact of the silica aggregation state in PDMA and PAAm hybrid gels was then investigated by tuning the surface chemistry of the silica nanoparticles, using acidic synthesis conditions (pH ranging between 5-6). The dispersion state of the nanoparticles was also assessed using Small Angle X-Ray Scattering. The study of the mechanical behavior of these double networks revealed a dramatic reinforcement of the modulus, dissipative properties and fracture resistance for PDMA. The time-dependence of their behavior show that the reversible interactions still take place even though the specific surface available for polymer adsorption is decreased. As a consequence, the time needed to reform the interactions and to fully recover is increased, from a few seconds to a few hours. PAAm gels with aggregated silica displayed very high modulus at the expense of a much reduced the strain at break and did not possess recovery processes. However, the aggregation state remained really hard to control leading to great disparities between samples.

Finally, Large Amplitude Oscillatory Shear experiments were developed for hydrogels to further study the reinforcement mechanisms on hybrid gels with either well-dispersed or clustered silica. These measurements showed similarities between hydrogels and filled elastomers, with a drop of modulus observed for all samples (Payne effect) and revealed that PDMA hybrid gels with well-dispersed silica show strain-stiffening patterns for increasing strain amplitude, attributed to the reversible interactions with the silica. The fact that PAAm hybrid gels do not display any strain-stiffening patterns but still present a drop of modulus at increasing strain amplitude indicates that the fillers alone have a weak impact on reinforcement in those gels. The experiments conducted on hybrid gels with clustered silica revealed the strong impact of the aggregation state on the reinforcement, with marked Payne effect and strain-stiffening patterns for PDMA. PAAm gels showed also strong non-linearities of the mechanical response but were permanently damaged under the shear, showing the lack of recovery processes. The formation of a hard silica network provides great stiffness and fracture resistance but the reversible interactions allow for the recovery processes and the strain-stiffening behavior.

As a conclusion, the silica/polymer interactions in hybrid gels are at the core of a wide range of properties and their tuning allowed us to develop hybrid materials with a broad spectrum of

mechanical behavior, which enabled identifying more precisely the reinforcement mechanisms at stake. As a perspective, this project could be continued following various ideas. For example, ^1H NMR experiments, usually dedicated to the study of filled rubbers were developed for this study and would deserve further research to provide useful insight on the gel structure and dynamics and on the reinforcement mechanisms. Stimuli-responsive systems could also be designed mixing several types of interactions, in matrices with either well-dispersed or aggregated silica. The impact of the inorganic fillers on the macroscopic behaviour could be investigated further in other experimental conditions, by changing either the particles size and thus their surface or by introducing anisotropic fillers into the network. We saw briefly that the swelling state of hydrogels is a key parameter to tune the macroscopic properties. It would be interesting to swell the different kind of hydrogels in order to study their properties at intermediate states since the understanding of the mechanical behaviour at the swelling equilibrium remains a challenging question.

Recent research have been conducted on ion gels, swollen with ionic liquid. They have attracted considerable interest for the past years for their potential application in electrochemical devices, actuators and gas-separation membranes. A possible exploration could be to synthesize nanocomposite gels similar to the ones developed throughout this study, swollen with ionic liquids. Indeed, ionic liquid possess unique properties such as non-volatility, non-flammability, and thermal, chemical, and electrochemical stabilities. We demonstrated that the mechanical properties of hybrid gels could be easily tuned by playing on the polymer/filler interactions or the fillers dispersion state, a further step could be to perform similar experiments by developing nanocomposite ion-gels to design strong and tough materials displaying interesting electrochemical properties to provide soft materials for practical applications.

