



Elastomer based composites filled with layered fillers and ionic liquids

Anna Laskowska

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Lodz University of Technology



PH.D. THESIS COMPLETED IN "COTUTELLE"

ELASTOMER BASED COMPOSITES FILLED WITH LAYERED FILLERS AND IONIC LIQUIDS

presented by

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and

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COMPOSITES ELASTOMÈRES CHARGÉS AVEC DES CHARGES LAMELLAIRES ET DES LIQUIDES IONIQUES

présentée par

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LIST OF ABBREVIATIONS AND SYMBOLS

AEC	Anion exchange capacity
[AMIM][TFSI]	1-Allyl-3-methylimidazolium <i>bis</i> (trifluoromethylsulfonyl)imide
ATR-FTIR	Attenuated Total Reflection Fourier Transform Infrared Spectroscopy
BDS	Broadband Dielectric Spectroscopy
BET	Brunauer–Emmett–Teller
[BMIM][AlCl₄]	1-Butyl-3-methylimidazolium tetrachloroaluminate
[BMIM][TFSI]	1-Butyl-3-methylimidazolium <i>bis</i> (trifluoromethylsulfonyl)imide
CEC	Cation exchange capacity
CR	Chloroprene rubber
CRI	Cure rate index
d	Interlayer distance
DBPA	Dibutyl phthalate absorption number
DMA	Dynamic Mechanical Analysis
DSC	Differential Scanning Calorimetry
DTG	Derivative Thermogravimetric Analysis
DTA	Differential Thermal Analysis
E'	Storage modulus
E''	Loss modulus
EB	Elongation at break
EDS	Energy Dispersive X-ray Spectrometry
[EMIM][SCN]	1-Ethyl-3-methylimidazolium thiocyanate
[EMIM][TFSI]	1-Ethyl-3-methylimidazolium <i>bis</i> (trifluoromethylsulfonyl)imide
EPDM	Ethylene propylene diene rubber
F	Tear strength
H	Shore Hardness A
[HMIM][TFSI]	1-Hexyl-3-methylimidazolium <i>bis</i> (trifluoromethylsulfonyl)imide
HNBR	Hydrogenated acrylonitrile-butadiene rubber
HT	Hydrotalcite
HXNBR	Hydrogenated carboxylated acrylonitrile-butadiene rubber
IGC	Inverse Gas Chromatography
ILs	Ionic liquids
K_T	Thermo-oxidative aging coefficient
K_{UV}	UV-aging coefficient
LDHs	Layered double hydroxides
LDH30	Pural MG 30 HT
LDH63	Pural MG 63 HT
LDH70	Pural MG 70 HT
LSs	Layered silicates
MBT	Mercaptobenzothiazole
MgAl-LDHs	Magnesium-aluminum layered double hydroxides
MH	Maximum torque
ML	Minimal torque
ML at 200 °C	Mass loss at corresponding temperature
NAT HEC	Hectorite natural
NBR	Acrylonitrile-butadiene rubber

phr	Parts per hundred rubber
ppm	Parts per million
PUR	Polyurethane rubber
rpm	Revolutions per minute
SBR	Styrene-butadiene rubber
S_A	Specific surface area
S_f	Specific interaction parameter
SE₁₀₀, SE₂₀₀, SE₃₀₀	Stress at 100, 200 and 300% deformation
SEM	Scanning Electron Microscopy
SR	Silicone rubber
SYN HEC	Hectorite synthetic
t_{Δ2}	Scorch time
t₉₀	Optimal cure time
T₂, T₅, T₁₀, T₅₀	Temperature corresponding to the 2, 5, 10 and 50 % weight loss
T_g	Glass transition temperature
T_i	Ionic transition temperature
TGA	Thermogravimetric Analysis
TEM	Transmission Electron Microscopy
TS	Tensile strength
XNBR	Carboxylated acrylonitrile-butadiene rubber
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
α_f	Wolff coefficient of activity
γ_S^D	Dispersive component of surface free energy
γ_S^{SF}	Specific or polar component of surface free energy
ΔG_A^{SF}	Molar specific free adsorption energy
ΔH_A^{SF}	Molar enthalpy of specific interactions
ΔM	Torque increment
Δν	Ionic crosslinks content
ε'	Permittivity
tan δ	Loss factor
σ'	Alternating current (AC) conductivity
ν_T	Crosslink density
χ	Huggins parameter for elastomer-solvent interaction

INTRODUCTION

The production of elastomer materials with improved mechanical and thermal properties, and low gas permeability using environmentally friendly processes is highly desirable in various branches of industry. In large-scale production, elastomers are routinely compounded with fillers to improve performance properties (*e.g.*, stiffness, toughness, tensile properties), provide long life service and reduce the cost of the final product. The most widely used reinforcing fillers in the rubber industry have been carbon blacks (CBs) and silicas. Although both fillers effectively strengthen the performance properties and durability of elastomer materials, other types of fillers have been sought as competitive alternatives for commercial scale applications. Layered solids consisting of two-dimensional layers are good candidates for use as reinforcing fillers in elastomer compounds due to their lamellar structure and anisotropic particle shape. Furthermore, plate-like fillers can enhance the gas barrier properties of polymeric matrices, a particularly important advantage of using these materials to produce technical rubber goods with reduced gas permeability. A wide range of layered materials, including phyllosilicates, layered oxides, layered double hydroxides, graphite, and graphene have been studied extensively as promising candidates for the reinforcement of various types of polymer matrices. Advantageously, these types of fillers may simultaneously serve multiple functions in polymer compounds such as flame retardants, gas barrier enhancers, crosslinking agents, UV screeners, etc. However, the disadvantage of layered fillers is their high tendency to agglomerate resulting in undesirable heterogeneity of the material. Thus, various methods have been developed to produce stable filler dispersions that provide optimal performance. Ionic liquids have attracted increasing attention due to their appealing physical and chemical properties and are considered useful processing aids in the preparation of functional elastomer composites with controlled mechanical, morphological and ionic conductivity parameters. This thesis has focused on the preparation and characterization of elastomer composites with layered fillers exhibiting improved mechanical properties, decreased swelling in solvents, reduced gas permeability and increased UV stability. The practical applications of ionic liquids as dispersing agents and conductivity enhancers for rubber systems has also been demonstrated.

This thesis is divided into eight chapters:

Chapter 1 Reviews the current literature relating to the use of layered fillers for rubber reinforcement and the applications of ionic liquids in elastomer composites.

Chapter 2 Outlines the motivation for this thesis and the research aims.

Chapter 3 and Chapter 4 Present the materials and experimental research methodology.

Chapter 5 Is divided into three subchapters with results and discussion:

Subchapter 5.1 (5.1.1) Presents the morphological, structural, thermal and surface properties of layered fillers. (5.1.2) Discusses the effects of layered mineral fillers (natural hectorite, synthetic hectorite and hydrotalcite) on the curing kinetic, crosslink density, mechanical, thermal and morphological properties of nitrile rubber composites. (5.1.3) Presents the impact of structurally differentiated MgAl-LDH on the cure degree, optical, mechanical, thermal, barrier and morphological properties of XNBR composites. Proposes the simultaneous application of magnesium-aluminum layered double hydroxides (MgAl-LDHs) as curing agents and reinforcing fillers for carboxylated acrylonitrile-butadiene rubber (XNBR). The results have been partly published: Laskowska A., *et al.*, *Przemysł Chemiczny* **89**, 461 (2010); Laskowska A., *et al.*, *Przemysł Chemiczny* **90**, 878 (2011); Laskowska A., *et al.*, *Express Polymer Letters* **8**, 374 (2014); Laskowska A., *et al.*, *European Polymer Journal* **60**, 172 (2014).

Subchapter 5.2 Considers the application of hydrophilic and hydrophobic imidazolium ionic liquids, which are characterized by high ionic conductivities, as processing aids for the improvement of filler distribution, facilitating and expediting rubber-filler compounding, and ionic conductivity enhancement of the composites. The concentration and type of ionic liquids were optimized to achieve a good compromise between the mechanical and conductivity properties of the rubber composite.

The results have been partly published: Laskowska A., *et al.*, *Polymer International* **62**, 1575 (2013); Laskowska A., *et al.*, *Macromolecular Symposia* **341**, 7 (2014); Laskowska A., *et al.*, *Macromolecular Symposia* **342**, 35 (2014).

Subchapter 5.3 (5.3.1) Presents the morphological, surface and thermal properties of graphene-based fillers. (5.3.2) Discusses the reinforcing effect of graphene-based fillers on acrylonitrile-butadiene rubber (NBR) and carboxylated acrylonitrile-butadiene rubber (XNBR).

The results have been partly published: Laskowska A. *et al.*, *Journal of Polymer Engineering* (2014).

Chapter 6 Provides general conclusions.

Chapter 7 Contains a list of authored and coauthored publications and a conferences list.

Chapter 8 Includes the reference list.

1. LITERATURE REVIEW

1.1. REINFORCING FILLERS FOR ELASTOMER COMPOSITES

Fillers are relatively inexpensive, solid substances that are added in fairly large volumes to polymers to adjust volume, weight, cost, surface, color, processing behavior, mechanical strength and other properties. In most industrial applications, elastomers are compounded with fillers to improve their performance properties (stiffness, toughness, tensile properties), to enhance the durability of rubber compounds and to reduce the cost of the final product. Fillers can typically be classified in the following categories:

- **diluent or degrading fillers (non-reinforcing):** decrease the strength of the rubber compounds to which they are added and are mainly added to reduce production costs by increasing the volume and mass of the product (however, in reality, there is no filler that is fully inactive and reduces costs only), *e.g., pigments, calcium carbonate (dry ground), talc, barium sulfate*;
- **extending or semi-reinforcing fillers:** have little impact on the strength of the rubber compounds, *e.g., hard clay, precipitated calcium carbonate*;
- **reinforcing fillers:** increase the strength of rubber compounds and substantially enhance their mechanical properties, *e.g., precipitated silica, fumed silica, carbon blacks (CBs)*.

Reinforcement can be defined as the improvement of the mechanical properties of compounds, particularly their strength, hardness, stiffness, abrasion and tear resistance, which consequently improves the service life of rubber products.¹ Carbon black (CB) and precipitated silica are the most important reinforcing fillers for rubber composites due to their large specific area, nanosize and the presence of active functional groups on their surfaces. Due to its strong interactions with hydrocarbon rubbers, CB exhibits strong reinforcement effects and has been employed as a reinforcing filler since 1904. However, due to its polluting nature, the ubiquitous black color of the compounded rubber material, decreased processability at high CB loadings and the dependence of CB on petroleum feedstock (for synthesis), researchers have investigated other “white”, environmentally friendly, reinforcing fillers. Compared to CB, silica particles are less compatible with hydrocarbon rubbers and tend to form a filler-filler network via hydrogen bonding of the silanol groups present on the

particle surfaces.² The development of silica treads in passenger tires inspired extensive research of non-black fillers other than silica. Commercial clay has long been used as an inexpensive, non-reinforcing filler, but a breakthrough occurred when Toyota Co. invented a layered silicate/polyamide nanocomposite.³ Substantial research has since focused on the use of layered mineral fillers as reinforcing fillers in many other polymer matrices. Small particle powders including not only CB and silica, but also layered silicates, layered double hydroxides, graphene, carbon nanotubes, calcium carbonates, calcium silicates, zeolites silica, alumina, starch and many others, have been studied extensively as potential reinforcement additives. In addition to classifications based on their reinforcing effect in the elastomer matrix, fillers can also be distinguished based on their structure and different dimensionalities (**Figure 1**):

- **zero-dimensional (0D):** low aspect ratio, isotropic spheres, cubes, polyhedrons, *e.g.*, *CB*, *calcium carbonate*, *fullerene*;
- **one-dimensional (1D):** filler particles in which one dimension is considerably longer than the others (rods, wires, tubes), *e.g.*, *multiwalled carbon nanotubes*, *carbon nanowires*, *sepiolite*;
- **two-dimensional (2D):** filler particles in which two dimensions are of considerable length (discs, prisms, plates), *e.g.*, *layered silicate*, *graphene*, *graphite*;
- **three-dimensional (3D):** filler particles in which three dimensions are of considerable length, *e.g.*, *boehmite*, *diamond*.

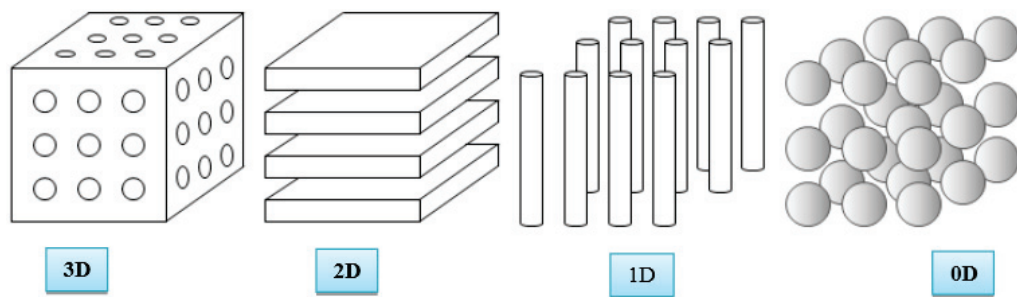


Figure 1 Various types of nanoscale materials.⁴

The mechanical properties of polymer composites can vary dramatically depending on the dimensionality of the filler (1D, 2D, and 3D),⁵ and the reinforcing effect of fillers follows the order: 1D filler > 2D filler > 3D filler. Other factors that determine the reinforcing effect of fillers in a polymer matrix are discussed in detail in subsequent chapters.

The main criteria impacting reinforcement

The crucial parameters that determine the effect of fillers on the properties of composites are the filler geometry (size, shape, aspect ratio) and the filler-matrix interactions.⁶

Particle size

The average particle size is typically the first characteristic of a filler to be considered.⁷ A new generation of nanosized fillers has emerged in response to the importance of small-sized particles in the preparation of functional, high-performance composites with sophisticated architectures. The extent of reinforcement increases as the particle size decreases, providing a higher polymer-filler interface and thus a more efficient interfacial bond when a certain degree of bonding exists between the two phases. Reinforcing fillers usually have particle diameters in the range of 10 to 100 nm. Large agglomerates in the rubber limit the contact between the rubber matrix and the filler surface and act as failure initiation sites that lead to premature failure of the material.

Specific surface area (S_A) and porosity

The term "specific surface area" (S_A) refers to the area/unit mass and is usually expressed as m^2/g . The specific surface area is strictly related to the particle size. A decrease in the average particle size of fillers and the consequent increase in the S_A , increase the polymer/filler interfacial volume and thus are desirable in designing mechanically strong composites.⁸ The specific surface area determines the total surface of the filler that is in contact with the polymer. The S_A is characterized by measuring the adsorption of specific molecules. The most widely used adsorption technique is based on the Brunauer–Emmett–Teller (BET) method of N_2 adsorption, which provides the ‘total’ surface area including porosity. Another approach is the cetyltrimethyl ammonium bromide (CTAB) method (**Figure 2**), which analyzes the external surface area, which corresponds to the accessible surface area of the filler (carbon black) for an elastomer.⁹ A simple method to obtain values related to the S_A is to determine the oil adsorption. The empty space (void volume) between the aggregates and agglomerates can be expressed as the volume of dibutylphthalate (DBP) absorbed by a given amount of filler, which is reflected in the DBPA number value.

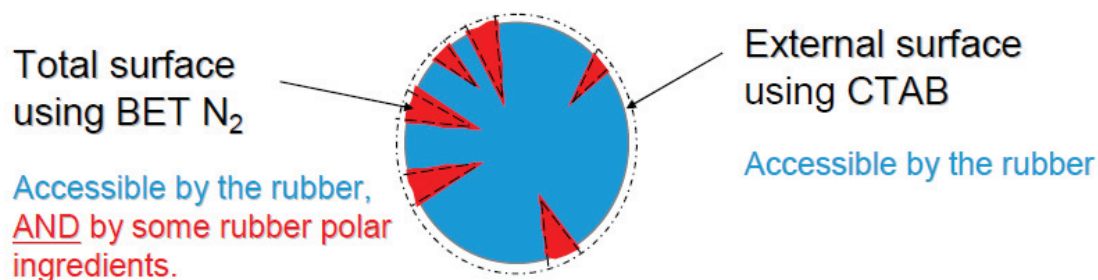


Figure 2 Comparison of methods BET and CTAB.¹⁰

DBPA oil absorption is a technique used to quantify the amount and structural characteristics of a grade of carbon black (CB) by providing information about the degree of porosity and the structure of the filler particles. Higher DBPA oil absorption numbers correspond to higher CB structures. In general, increasing the surface area (decreasing particle size) provides lower resilience and higher Mooney viscosity, tensile strength, abrasion resistance, tear resistance and hysteresis.

Particle shape and aspect ratio

Spherical particles have the closest packing structures, resulting in uniform stress distribution and reduced melt viscosity of the blend. Branched, dendritic particles have a very large surface area, enabling extensive interaction between the filler and polymer particles and enhancing rubber reinforcement. Lamellar structures facilitate orientation, reduce permeability to liquids, vapors and gases and enhance the mechanical properties of elastomer compounds. Longitudinal particle shapes (needles or fibers) with high anisotropy increase the extent of reinforcement, reduce shrinkage and thermal expansion, and exhibit thixotropic properties. Fillers with irregularly shaped particles do not exhibit any specific advantages beyond easy production and low cost.¹¹ Particles with longitudinal shapes are more difficult to disperse in polymers, which causes stress concentrations and a reduction of the reinforcing effect. Inhalation of nanosized, thin or fibrous particles may be harmful to health even when their concentration in the inhaled air is low. Silicosis, the most ancient recognized occupational disease, is exclusively caused by exposure to crystalline silica. Similarly, asbestos, a fibrous filler, was once widely used and is now prohibited because of its health and safety risks.

Some examples of filler with various particles shapes:

- **spherical particles:** *e.g., nanosilica, carbon black, zinc oxide, glass beads, aluminum oxide, titanium dioxide, aluminum powder, polyhedral oligomeric silsesquioxanes;*
- **cubical particles:** *e.g., calcium hydroxide;*
- **dendritic particles:** *e.g., copper powder;*
- **sheet/platelet, lamellar shaped particles:** *e.g., graphite, layered silicates such as smectites group clays, synthetic mica, kaolin, talc;*
- **rod/fiber, longitudinal particles:** *e.g., aramid fibers, carbon fibers, acicular titanium dioxide, cellulose fiber, acicular wollastonite, synthetic whiskers, carbon nanotubes, carbon nanofibers, boehmite, sepiolite, nano CaCO₃;*
- **irregular-shaped particles:** *e.g., oxide and aluminum hydroxide, barite, calcium carbonate, aluminosilicates, dolomite, perlite, fumed silica, anthracite.*

The filler aspect ratio is one of the key factors in improving the properties of polymer nanocomposites and is expressed as the ratio of particle length to particle diameter. Isometric fillers such as CB or fumed silica are typically used to reinforce elastomers. Most fillers have small aspect ratios of less than 10. Acicular fillers such as fibers improve the properties of the composites in one dimension. Platelets are anisometric particles that are significantly larger in two dimensions than the third and thus are expected to exhibit a two-dimensional reinforcing effect on the composite material.¹² As the aspect ratio of the filler particles increases, the viscosity, modulus at elongation of <300% and hysteresis loss of the filled material increase, whereas the resilience, tear resistance and extrusion shrinkage decrease.

Table 1 Aspect ratios of fillers.¹³

Shape	Aspect ratio	Example
Cube	1	Feldspar, calcite
Sphere	1	Glass spheres
Block	1-4	Quartz, calcite, silica and barite
Plate	4-30	Kaolin, talc, hydrous alumina
Flake	50-200 ++	Mica, graphite, montmorillonite
Fiber	20-200 ++	Wollastonite, glass fibers, carbon nanotubes, wood fibers, asbestos fibers, carbon fibers

Surface activity and surface energy

The reinforcement of elastomers by particulate fillers is dependent on the physical interactions between the filler and rubber matrix, which can determine the degree of adhesion at the interfaces. The surface activity is related to the number and type of active functional groups, the surface energy, and energetically different crystallite faces of the filler surfaces. The surface activity is the predominant factor with regard to polymer-filler phase bonding and filler-filler interactions. The surface activity determines the compatibility of the filler with a specific elastomer and the ability of an elastomer to adhere to the inorganic phase. Generally, it is attributed to the distribution of highly active sites for the adsorption of polymer segments on the surface of reinforcing fillers.¹⁴ A filler can have a high surface area and a high aspect ratio but still offer relatively poor reinforcement when its specific surface is characterized by low activity. CB is a good example of a filler that displays high surface activity due to the presence of a variety of chemical groups, such as *carboxylic acid groups*, *quinone*, *phenols*, and *lactones*, on the filler surface, as shown in **Figure 3**.

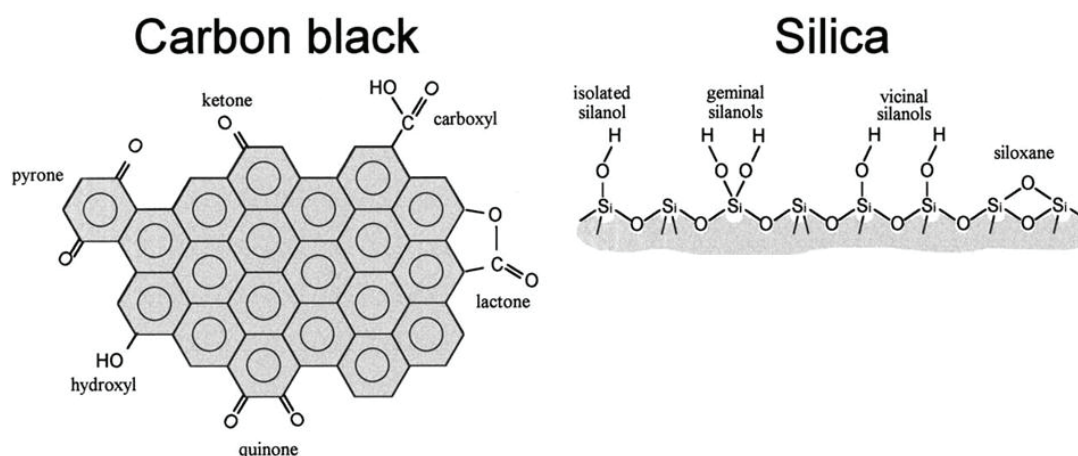
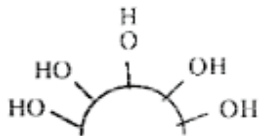
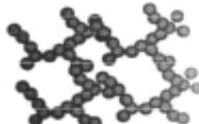


Figure 3 Various chemical groups existing on the surfaces of carbon black and silica.

Due to the presence of numerous active sites on the surface of CB, it is compatible with different types of rubbers and interacts strongly with the elastomer as well as non-polar rubbers such as NR and SBR, without the need for surface modifiers. The formation of the functional groups is controlled during the production of CB. Heat treatment of CBs at temperatures ranging from 1500 to 2700 °C¹⁵ profoundly change the influence of CB on the properties of rubber. Heating CB results in a low level of bound rubber and a drastic reduction in the high strain modulus, tensile strength and abrasion resistance because the nanocrystallites that compose the primary particles of CBs drastically increase in size during

heat treatment, whereas the number of high-energy sites located at the edges of the crystallites drastically decreases.¹⁶

Table 2 Filler morphology and properties.¹⁷

	Morphology	Filler effect	Filler characterization
	Surface chemistry (Å size scale)	Filler-filler Filler-polymer	Surface functional groups
	Primary particle Volume, shape (Å-nm size scale)	Hydrodynamic/ mechanical reinforcement	Size, shape Structure Surface area
	Branched aggregates (nm size scale)	Hydrodynamic Occluded rubber	Structure, Surface area, Fractal dimensions, branching coefficient
	Agglomerated Aggregates (nm - μm size scale)	Filler networking Trapped rubber	Structure Surface area Fractal dimension

In contrast to CBs, silicas are hydrophilic and have silane (Si-OR) and acidic silanol (Si-OH) functional groups attached to the surface, as shown in **Figure 3**. The amount of silanol and silane can vary from pristine fumed silica ($\sim 100\text{s/m}^2$) to precipitated silica ($\sim 100\text{s}-1000\text{s/m}^2$). Because of the highly polar surface, silica does not interact well with non-polar elastomers such as SBR. The presence of silanol groups on the surface leads to strong filler-filler interactions, inducing a high level of aggregation and interparticle interaction in the rubber matrix. A strong interaction between the silica particles increases viscosity, which is not desirable in rubber processing. CB is less polar than silica and therefore appears better suited for the reinforcement of non-polar hydrocarbon elastomers. This finding suggests that the surface of non-black fillers, such as precipitated silica, should be modified to decrease their polarity and hydrophilicity and increase their compatibility with elastomers with improved reinforcing capabilities. For example, the use of bifunctional organosilane coupling agents such as *bis*-(triethoxysilylpropyl) tetrasulfide (TESPT) effectively increases the wettability and compatibility of silica with hydrocarbon elastomers and promotes polymer-filler interactions via the formation of covalent chemical linkages.¹⁸

One of the most sensitive and convenient techniques for the characterization of the surface activity of fillers is inverse gas chromatography (IGC) at infinite dilution. IGC is based on the adsorption and desorption kinetics of the gas molecules in the flow of an inert carrier gas and is widely used to determine the surface energy of fillers and the highly active sites on their surfaces. A good match of surface energies indicates filler-polymer interactions and greater compatibility of the rubber and filler. For instance, a high degree of filler agglomeration in the rubber matrix results from large differences in surface energy between the filler and polymer, strong interparticle forces, and high filler loadings. The surface energy of the filler indicates how compatible it is with the rubber. Generally, the surface energies of fillers are much higher than those of organic polymers. Most inorganic fillers have surface energies greater than 100 mJ/m², whereas polymers typically have surface energies of approximately 35 mJ/m².

Wang and coworkers¹⁹ compared the surface energies of a wide range of commercial CBs and silicas using IGC. The surface energy of fillers can be described by the following basic equation:

$$\gamma_s = \gamma_s^D + \gamma_s^{SP} \quad (1)$$

where γ_s is the surface energy, γ_s^D is the dispersive component, and γ_s^{SP} is the specific or polar component. Fillers with a high filler-filler interaction will have a high specific component of the free surface energy (γ_s^{SP}), and fillers with a high filler-rubber interaction will have a high dispersive component of the surface free energy (γ_s^D).¹⁷ CBs possess a high γ_s^D , which is related to stronger interactions between the filler and hydrocarbon rubber. By contrast, silicas are characterized by a lower γ_s^D and a higher specific component of the surface free energy, represented by a high S_f , which is related to stronger filler-filler interactions.²⁰ The surface characteristics of silica can be altered by surface modification, thereby decreasing the specific component of the surface free energy and consequently, increasing interactions between the silica and rubber, improving dispersion and reducing the viscosity of the compound. The resulting compound exhibits remarkably enhanced processability, and the vulcanized material exhibits improved abrasion and dynamic resistance properties. In addition, other types of fillers, such as montmorillonite, double layered hydroxides or graphene, have been subjected to modification by various types of organic compounds to control the filler surface energy and reduce hydrophilicity as well as to increase the interlayer distance, leading to enhanced contact between the filler and rubber.

Preparation of rubber composites containing layered fillers

Several methods have been developed for the synthesis of elastomer composites containing layered fillers, such as solution intercalation, latex compounding, *in situ* polymerization of intercalated monomers, melt blending and direct two-step melt compounding in a laboratory two roll mill or twin-screw extruder (**Figure 4**). Because most rubbers are available in solid (dry) and latex (solution) forms, melt and latex intercalations are considered the most feasible methods for the industrial preparation of rubber nanocomposites. Although the *in situ* polymerization route is viable, it is not commonly used with rubbers at present.²¹

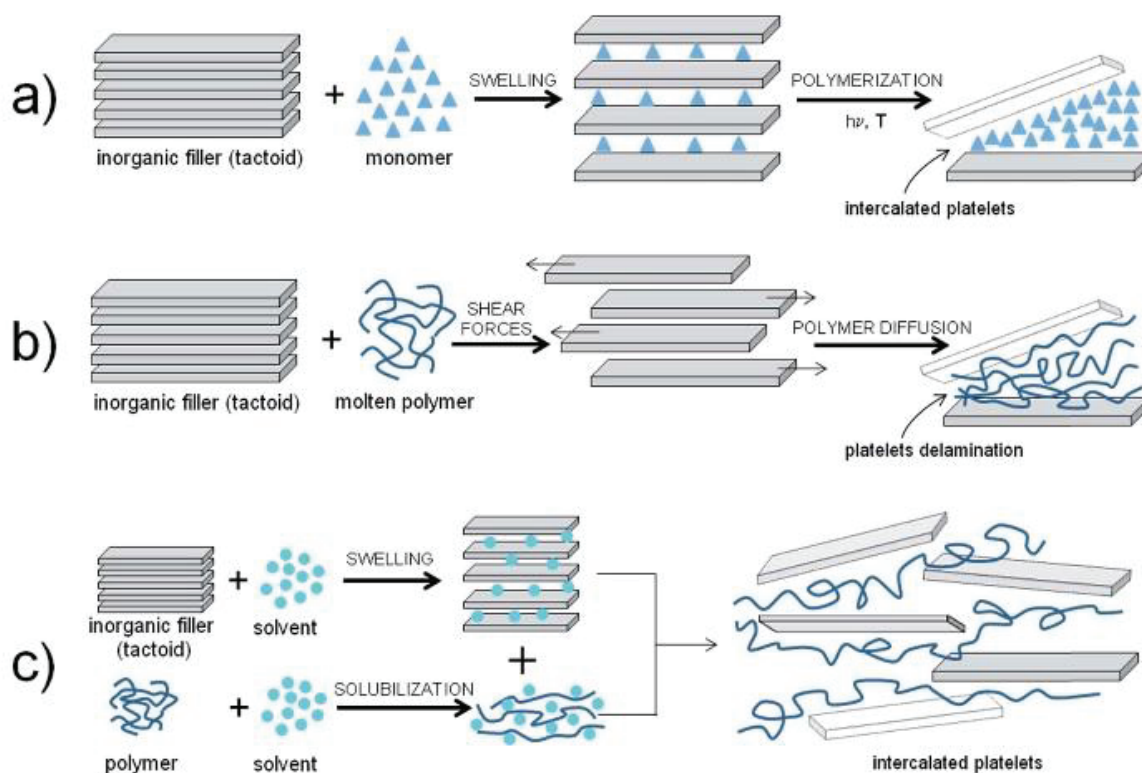


Figure 4 Schematic representation of (a) in situ polymerization, (b) melt processing, and (c) solution casting.²²

Solution blending

Solution blending is used to fabricate polymer-layered filler composites provided the polymer is easy to dissolve in common aqueous or organic solvents, such as water, toluene, chloroform, acetone, DMF. Due to the use of organic solvents, solution blending route is not considered as an eco-friendly technique for the rubber composites preparation. In this method, the desired amount of layered filler is dispersed in a proper solvent. The dispersed solution so obtained is added to a solution of rubber already dissolved in a suitable solvent. The resulting solution is mechanically stirred by vigorous magnetic stirring. After the nanofillers get

dispersed, the solvent is removed. The curatives may be incorporated before solvent evaporation, or may be added to the above solution and stirred altogether. The resultant solution is vacuum dried. Finally, the composites obtained are roll-milled at room temperature followed by compression moulding at specific conditions.²³

Latex compounding

The latex is an aqueous dispersion of elastomer particles in the submicron-micron range. There are some elastomers which are available in the form of latex, for instance, NR, SBR, CR, XSBR, XNBR, PUR. Most of rubber/layered silicate nanocomposites are produced by this method. To the rubber latex pristine clay can be added directly, or in its aqueous dispersion (slurry). Note that clays are strongly hydrophilic and thus adsorb water molecules, which is associated with an expansion of their intergallery spacing. So, hydration decreases the attractive forces between the silicate layers, making easier their exfoliation under stirring. After mixing/stirring of the clay-containing lattices, they are cast in a mold and dried. In this case, the rubber/clay nanocomposite remains unvulcanized or suitable rubber curatives, which can be dispersed in water, may also be mixed with the clay-containing rubber latex. After casting and drying, the related articles can be cured accordingly.²⁷

Melt mixing method

The most commonly applied processing method of direct mechanical mixing of the filler particles and rubber is termed a melt blending technique. From an industrial standpoint, melt blending is the most direct, eco-friendly and the most economically viable (as no organic solvents are involved) method to synthesize rubber composites. On the other hand, a better degree of dispersion is achieved by *in situ* polymerization, followed by solution mixing. The advantage of melt mixing method lies in the absence of utilization of organic solvents, and its applicability to both polar and non-polar elastomers. This involves equipment like internal mixers and open two-roll mills. The mixing temperature and shear rate employed when using mixers and open two roll mills strongly influence the filler dispersion in the rubber matrix; however, the high viscosity of the material often causes non-uniform dispersion of the filler platelets.

Morphology of rubber/layered filler composites

The physical properties of a rubber product depend on the morphology and distribution of particles in the elastomer matrix. The state of dispersion of the layered fillers in rubber compounds is typically characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD). In general, two basic structures of polymer composites containing layered fillers are recognized: intercalated and exfoliated. In the first case, the polymer chains are incorporated between the galleries; however, total separation of the layers does not occur. During exfoliation, these distances increase such that the interaction between adjacent layers and the arrangement of the crystalline materials are lost. Thus, for completely exfoliated clays, no wide-angle X-ray peak is expected for the nanocomposite. If the polymer chains cannot intercalate between the filler sheets, then a traditional microphase-separated structure (conventional or microcomposite) is formed, and there is no shifting of the X-ray d-spacing. The possible dispersions of layered silicate in a polymer are schematically depicted in **Figure 5**.

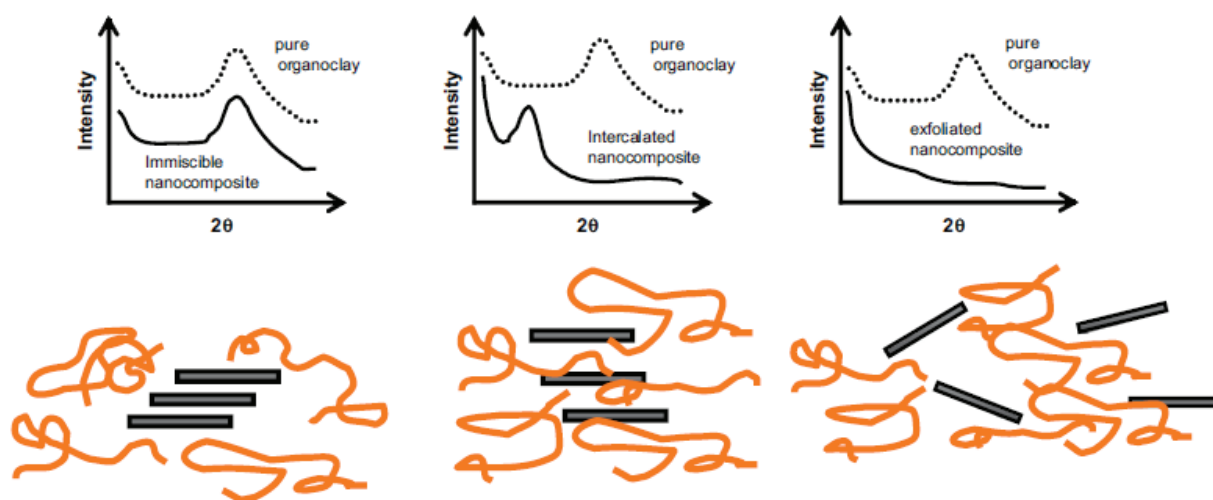


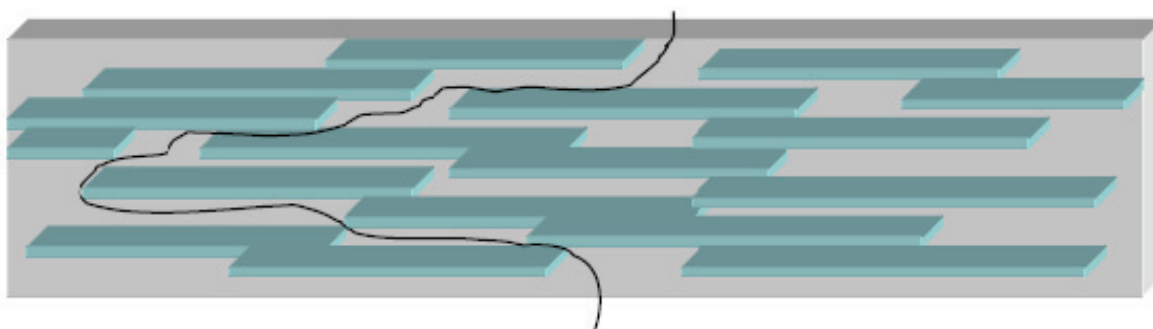
Figure 5 Different structures of polymer (rubber)/clay nanocomposites.²⁴

Exfoliated, intercalated and mixed morphologies are obtained depending on the following factors: (a) the polymer polarity, (b) the properties of the nanofiller (particularly the ion exchange capacity), (c) the alkyl modifier chain length and (d) the method of composite synthesis.

Properties of rubber/layered filler composites

Elastomer composites containing layered fillers are competitive with conventional materials filled with commercial CBs and silicas, mainly due to the eco-friendliness resulting from layered solids origins and their natural abundance, as well as due to the possibility of fabrication of low cost materials with some multifunctional properties. The following advantages of rubber/layered filler composites are anticipated:

- enhanced mechanical properties of the rubber matrix at low filler loadings;²⁵
- improved fire resistance of vulcanizates due to a delay in thermal-oxidative degradation and a decrease in the heat release rate;
- reduced gas permeability of the filled rubber material due to the formation of a tortuous diffusion path by the lamellar filler particles, which retards the diffusion of gas molecules through the material (**Figure 6**);
- and others, such as increased swelling resistance in organic solvents, improved UV resistance, or enhanced conductivity.



Permeation path imposed by nanoplatelet modification of polymer films

Figure 6 Barrier to permeation imposed by nanoparticles imbedded in a polymeric matrix.²⁴

This study presents the characterization of the structural and surface properties of layered fillers with respect to their potential use in the preparation of reinforced elastomer composites with specific functional properties. The layered fillers differed not only in origin and chemical composition but also in particle size, particles aspect ratio, surface area, and surface activity. The incorporation of fillers in their raw state into the elastomer matrix was performed using melt mixing, the most economical and ecological route for the preparation of composite materials.

1.2. TYPES OF LAYERED FILLERS AND THEIR APPLICATIONS IN RUBBER COMPOSITES

1.2.1. CATIONIC CLAYS - HECTORITES

Smectites form a group in the class of minerals known as phyllosilicates or layered silicates (LSs). Other groups in this class include the micas, vermiculites, chlorites, talc and pyrophyllite (**Figure 7**). Hectorite is a rare magnesium lithium clay mineral belonging to a trioctahedral smectite mineral group with unit formula $M_x[Li_xMg_{6-x}Si_8O_{20}(OH)_4]$ where $M=Na, Li, NH_4$.²⁶

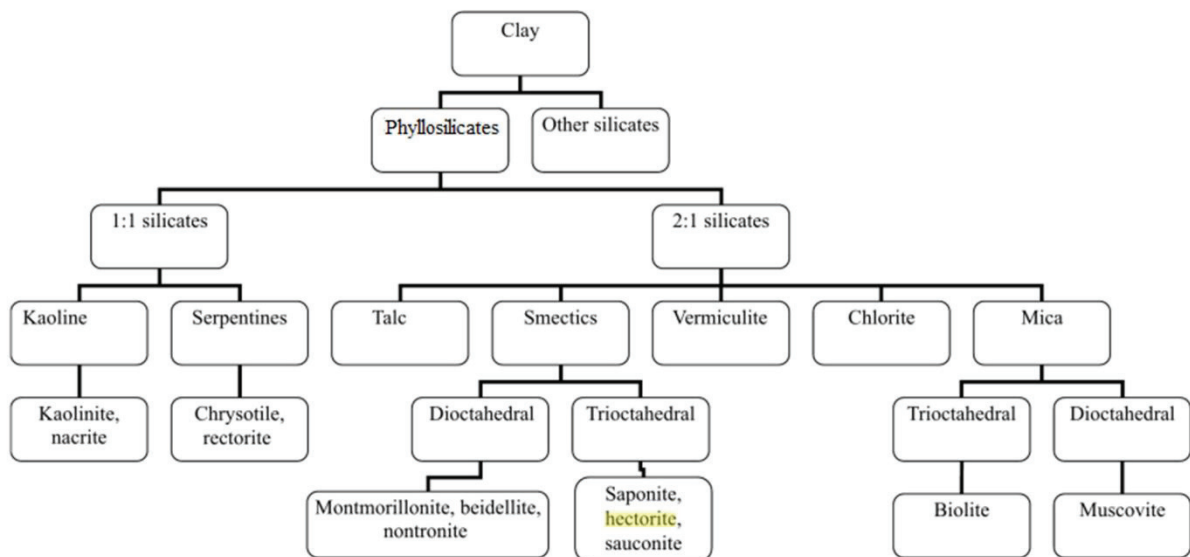


Figure 7 Various types of clays.²⁷

The structure of hectorite corresponds to a 2:1 (TOT) type of phyllosilicate in which a layer of octahedrally coordinated Mg^{2+} or Li^+ ions is bound to two tetrahedral crystalline silicate layers SiO_4 by the sharing of oxygen atoms, as shown in **Figure 8**. Some of the hectorite hydroxyl groups are usually substituted by fluorine atoms. The octahedral sheet may either be dominantly occupied by trivalent cations (dioctahedral smectites – montmorillonite) or divalent cations (trioctahedral smectites – hectorite). Isomorphic partial substitution of divalent cations Mg^{2+} by monovalent cations Li^+ in the octahedral lattice generates permanent negative charges on the layers, which are counterbalanced by the presence of inorganic cations, usually Na^+ , Ca^{2+} , Mg^{2+} . Stacking of the layers forms a regular van der Waals gap between the layers called the interlayer region, interstium or gallery where balancing cations

are localized. The layers are continuous in the length and width directions, but the bonds between sheets are weak and have good cleavage, allowing water and other molecules to enter interlayer region causing expansion in the highness direction.²⁸ A significant amount of water intercalated between the layers gives very plastic properties of the hydrated clay. The water may be held in pores (easily removed by drying under ambient conditions) and may be also associated with layer surfaces and in interlayer region. Upon dispersion in water, the lamellar crystal is swollen and gradually cleaved into discrete platelets with thickness of about 1 nm and diameter of about 30 nm up to several microns or larger, depending on the particular layered silicate.²⁹ By the ion exchange reaction, the interlayer inorganic cations may be replaced by the organic species leading to an increase of the interlayer distance and an alternation of clays surface from a hydrophilic to an organophilic.

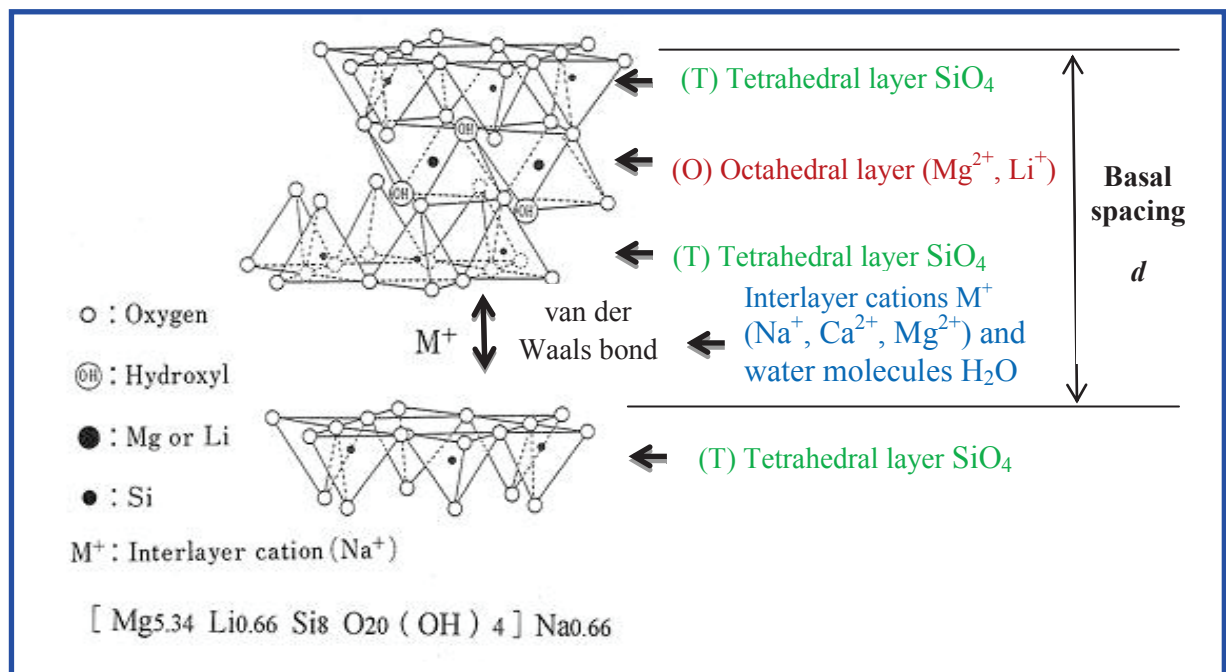


Figure 8 Structure of hectorite.³⁰

The extent of the isomorphic substitution defines the cation exchange capacity (CEC) of the clay. CEC values are expressed in centimole of positive charge per kilogram of dry clay mineral ($\text{cmol}(+)/\text{kg}$) which is numerically equal to the traditional unit of milliequivalents per 100g clay ($\text{meq}/100\text{g}$).⁵⁴ Several methods to determine the CEC have been developed. A common method for determining CEC known as the ammonium acetate method uses 1 M ammonium acetate (NH_4OAc) at pH 7 (neutral NH_4OAc) and is a standard method used for soil surveys by the Natural Resource Conservation Service.³¹ The CEC of smectites available commercially is in the range of 65-150 $\text{meq}/100\text{g}$.

Hectorites are the most common authigenic clay minerals. They form at low temperatures and pressures by the alteration of oceanic and continental basalts and other basic volcanic rocks.³² The naturally occurring clay mineral hectorite is seldom found in soils and mined only in limited localizations. Natural hectorite often contains significant amounts of impurities (iron) and other minerals such as, for example, dolomite or calcite. Smectites can be mined from natural resources, however their synthesis allows to obtain an impurity-free reproducible solid. A classical method of hectorite synthesis involves long hydrothermal treatments with the use of high temperatures or long aging times (from several days to several weeks).³³ Hydrothermal treatment frequently starts with the preparation of slurries consisting of the necessary reagents such as Mg, Li, F, Si, etc., which are aged under reflux or in autoclave at around 333-573 K producing the hectorite with designed composition. A method for incorporating a variety of intercalats directly during hydrothermal synthesis of hectorite was developed by Carrado in 1992.³⁴ This approach was unique in that the organic intercalate was present during synthesis rather than being added later by ion exchange. The microwave-hydrothermal treatment is quite modern technique and it is definitely a faster method used for clay synthesis.³⁵ Most common synthetic clays are hectorite and fluorohectorite. A synthetic hectorite has some obvious advantages over natural ones, for instance:

- controllable pore size distribution;
- higher specific surface area;
- higher purity;
- tunable composition;
- excellent reproducibility.³⁶

Hectorite suspensions display a high viscosity and transparency as well as other attractive rheological properties, which render hectorite a very valuable clay mineral for industrial applications. Due to their high cation exchange capacity (CEC), high specific surface area, small particles size, chemical and mechanical stabilities, thixotropic properties, acid properties together with their swelling ability in water up to thirty five times its weight and to form organic and inorganic interlayer complexes, hectorites are interesting materials widely used in many technological applications such as:²⁶

- ceramics;
- suspending agent in glazes;
- rheology-modifiers;
- plasticizing agent for non-plastic formulations;

- oil drilling fluid;
- supports of metal catalysts and occasionally as catalysts themselves;
- substrate for colloidal systems;
- adsorbents for heavy metal ions, adsorbents for the removal anionic dyes (basic dyes), organic compounds, pesticides, and other environmental applications or waste isolation;
- due to its white color and good gelling properties, hectorites find wide application in paint, cosmetic and paper industries;
- fillers used in polymer composites.

Most of technological uses of smectites are related to reactions that take place in the gallery region where hydrated and exchangeable interlayer cations such as Na^+ , K^+ , Ca^{2+} and Mg^{2+} are localized. Polymeric hydro(oxides) of Al, Fe, Cr, Zn, Ti can intercalate into smectites by cation exchange. After heating, these so-called “pillared clays” exhibit a large surface area, huge porosity, high acidity and catalyzing properties.⁵⁴ In their pristine form montmorillonite and hectorite are hydrophilic in nature, and this property makes them very difficult to disperse into a hydrophobic media. The most common way to make hydrophilic clay surface hydrophobic is to exchange interlayer cations with organic cations by ion exchange reaction.

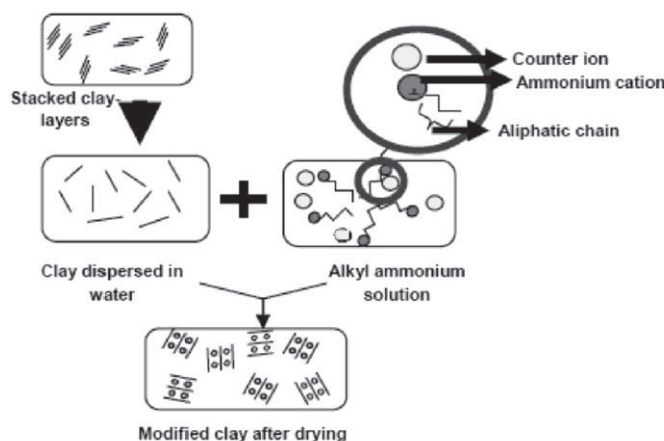


Figure 9 Schematic showing clay modification.³⁷

Small, inorganic cations may be replaced in an aqueous medium by larger, organic cations, such as quaternary ammonium, aliphatic-aromatic or phosphonium cations having long alkyl chains. For example, Sadhu and Bhowmick modified montmorillonite clays with various amines, like stearyl, hexadecyl, dodecyl and decyl amine and subsequently employed them to produce SBR/clay nanocomposites.³⁸ In order to enable each layer to be accessible for the

surfactant molecules from the solution, clay layers need to swell to exfoliate in the solvent (usually water) (as shown in **Figure 9**). Incorporation of large, organic cations into the interlayer not only causes that the silicates become organophilic, but also leads to an increase in the interlayer distance which size depends on the functionality and length of the chains of organic molecules. Organophilization reduces the surface energy of the mineral silicates, facilitates the intercalation of polymer macromolecules and improves the compatibility between the two phases. The quaternary alkylammonium salts are cationic surfactants and the most used organic compounds to prepare organoclays. The advantage of using phosphonium salts over the ammonium salts is higher degradation temperature of the modified silicates up to 350 °C. Silicates modified with phosphonium cations can be used in the preparation of nanocomposites by the melt mixing method. Also, aromatic compounds, such as imidazole or quinolone moieties exhibit greater thermal stability than the commercial cation-pyridine or alkyl ammonium salts.³⁹ Most of the commercially available modified clay minerals is produced by exchanging the metal cations in the interlayer space with the ammonium cations. However, some types of surface modifier, particularly amines, may affect the degree of crosslinking and vulcanization time of elastomer composites. For instance, it has been found that octadecylamine acts as an accelerator for NR vulcanized with sulfur.⁴⁰

Rubber/hectorite composites

In recent years, much attention has been paid to the composites based on layered fillers and rubber matrices, however there are only a few reports concerning the use of hectorite as a reinforcing filler in elastomer composites. For example, Maiti and Bohowmick⁴¹ investigated the influence of natural and synthetic hectorite (at loadings of 4 and 16 phr) on the mechanical, dynamic mechanical, swelling, and thermal properties of fluoroelastomer – a terpolymer of hexafluoropropylene, vinylidene fluoride and tetrafluoroethylene. The composites were prepared by a solution mixing method. First, a mixture of dissolved rubber and layered silicate dispersed in a common solvent methyl ethyl ketone was stirred to make it homogeneous, after solvent evaporation, the sample was cured at optimum cure time in a hydraulic press. The natural hectorite, even after extensive cleaning, still contained CaCO₃, quartz, and (Mg, Fe, Ca)SiO₃ impurities. Moreover, the synthetic clays showed smaller particle size and higher specific surface areas (around 159 m²/g) relative to the natural one (71 m²/g). Compared with natural hectorite, all the synthetic materials impart better properties of elastomer composites due to the lower particle size and higher surface area of synthetic clays which enhance the polymer–filler interaction. Bhattacharya *et al.*⁴²

examined the effects of varying morphological and chemical constitution of nanofillers (montmorillonite, sepiolite, hectorite, carbon nanofiber and expanded graphite) and various dispersion methods on natural rubber (NR) nanocomposites. Incorporation of 4 phr of natural hectorite and Laponite (synthetic hectorite) to the NR matrix during compounding in an internal mixer Brabender did not improve modulus, tensile strength and tear strength and had no effect on the crosslink density of the final NR nanocomposites.

In order to achieve a better compatibility between hydrophobic polyurethane matrix (PUR) and synthetic hectorite Laponite RD, the reactive organifier terminated by hydroxyl end group to react with diisocyanate was synthesized and used for the preparation of organoclay.⁴³ The polyurethane nanocomposites were synthesized by mixing of organoclay suspended in DMF with polyurethane prepolymer PTMG, removing the dispersion medium DMF and subsequent reaction between reagents. The authors reported that the *d*-spacing increased up to 2.08 nm with increasing the molecular weight of organifier. The enhancement of Young's modulus was directly attributed to the reinforcement provided by the dispersed silicate layers and to the strong interactions between polyurethane matrix and silicate layers via the formation of ionic bonding as well as hydrogen bonding. The maximum increase of tensile strength was 45 %.

Many studies have reported the preparation and investigation of elastomer/layered filler composites with improved mechanical, thermal and gas barrier properties. The majority of these studies have used organo-modified montmorillonite as a reinforcing filler in various elastomers, whereas the potential of hectorite in this field has not been sufficiently explored. Hectorite possesses a lamellar structure, high aspect ratio and high thermal stability similar to that of montmorillonite and is an interesting mineral that could act as an active filler for rubbers and produce a reinforced rubber material with improved barrier and thermal properties. The main difference between hectorite and montmorillonite is the presence of magnesium ions in the octahedral layer, therefore, hectorite belongs to the trioctahedral smectite mineral group. The presence of magnesium ions and the polar mineral surface may contribute to possible interactions with polar functionalities attached to the rubber hydrocarbon chains, such as –CN or –COOH. This research focused in part on the evaluation and comparison of the reinforcing effects of natural and synthetic hectorite in two elastomers of differing polarity and curing system.

1.2.2. ANIONIC CLAYS - LAYERED DOUBLE HYDROXIDES (LDHs)

In recent years, there is a growing interest in using layered double hydroxides (LDHs) (also known as hydrotalcite-like compounds) as novel fillers for elastomer composites and in that sense they are competing materials to layered silicates (LSs).⁴⁴ In contrast to the cationic clay minerals with negatively charged layers (1:1, 2:1 type), the LDHs are a kind of anionic clay minerals consisting of positively charged sheets (1:1 type, brucite type) with intercalated water and interlayer exchangeable anions that maintain electroneutrality.

LDHs have been known since 1842. Hydrotalcite is one of the most representative minerals of the LDH group which naturally occurs as a white hydrous mineral with chemical formula given as $\text{Mg}_6\text{Al}_2(\text{OH})_{16}(\text{CO}_3) \cdot 4\text{H}_2\text{O}$.⁴⁵ Natural hydrotalcites are rare in the nature, exist in small quantities and are highly contaminated. The sites of hydrotalcite occurrence are Snarum, Norway, New South Wales and Tasmania, Australia. **Table 3** shows some known naturally occurring minerals with structural composition similar to that of hydrotalcite.

Table 3 Natural hydrotalcite minerals with carbonate in the interlayer.^{46,47}

Divalent cation	Trivalent cation	Composition	Mineral	Unit Cell
Mg	Al	$\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$	Hydrotalcite	Rhombohedral, 3R
Mg	Al	$\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$	Manasseite	Hexagonal, 2H
Mg	Mn	$\text{Mg}_6\text{Mn}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$	Desautelsite	Rhombohedral, 3R
Mg	Fe	$\text{Mg}_6\text{Fe}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$	Pyroaurite	Rhombohedral, 3R
Mg	Fe	$\text{Mg}_6\text{Fe}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$	Sjogrenite	Hexagonal, 2H
Mg	Cr	$\text{Mg}_6\text{Cr}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$	Stichtite	Rhombohedral, 3R
Mg	Cr	$\text{Mg}_6\text{Cr}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$	Babertonite	Hexagonal, 2H
Ni	Fe	$\text{Ni}_6\text{Fe}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$	Reevesite	Rhombohedral, 3R
Ni	Al	$\text{Ni}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$	Takovite	Rhombohedral, 3R

The structure of hydrotalcite shown in **Figure 10**, is related to that of brucite $[\text{Mg}(\text{OH})_2]$, where bivalent octahedrally coordinated M^{II} ions of the Mg^{2+} are partially substituted by the trivalent M^{III} ion having not too different a radius such as the Al^{3+} (Fe^{3+} for pyroaurite, Cr^{3+} for stichtite) yielding positively charged sheets.⁴⁸ This net positive charge is neutralized by $(\text{CO}_3)^{2-}$ anions, which lay in the interlayer region between the two brucite-like sheets. In the free space of this interlayer the water of crystallization also finds a place. The anion and water are randomly located in the interlayer region, being free to move by breaking their bonds and forming new ones (as in liquid water). The oxygen atoms of water molecules and of the $(\text{CO}_3)^{2-}$ groups are distributed approximately closely around the symmetry axes that pass through the hydroxyl groups (0.56 Å apart) of the adjacent brucite-like sheet. These hydroxyls

are tied to the $(\text{CO}_3)^{2-}$ groups directly or via intermediate H_2O through hydrogen bridges: $\text{OH}-\text{CO}_3-\text{HO}$ or $\text{OH}-\text{H}_2\text{O}-\text{CO}_3-\text{HO}$. The $(\text{CO}_3)^{2-}$ are situated flat in the interlayer and H_2O is loosely bound, they can be eliminated without destroying structure.⁴⁷

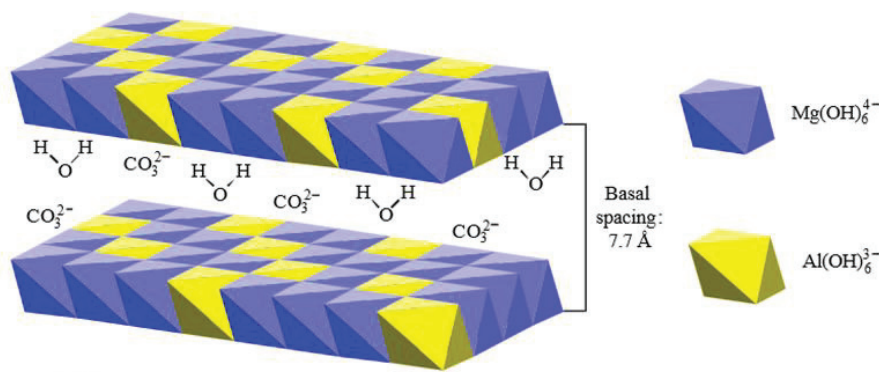


Figure 10 Layered structure of the hydrotalcite $\text{Mg}_2\text{Al}(\text{OH})_6(\text{CO}_3)_{0.5} \cdot 2\text{H}_2\text{O}$ showing edge connected magnesium and aluminium hydroxide octahedrons comprising charge.⁴⁹

The advantages of synthetic LDHs over their natural counterparts are better-defined geometry, crystal structure and purity. Moreover, LDHs can be easily designed using bivalent and trivalent metal ions, and their ratio and the type of anion can be adjusted to obtain various charge densities and interlayer spacing. The general chemical formula for LDH family minerals can be written as:



Where: M^{II} is a bivalent metal ion (Mg^{2+} , Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} etc.), M^{III} is a trivalent metal ion (Al^{3+} , Cr^{3+} , Mn^{3+} , Fe^{3+} , Ga^{3+} , Ni^{3+} and Co^{3+} etc.), x is molar ratio $[\text{M}^{\text{III}}]/[\text{M}^{\text{II}} + \text{M}^{\text{III}}]$ normally varying from $0.2 \leq x \leq 0.4$,⁵⁰ but there are also the claims that LDHs compounds can be formed for x values in the general formula in the range $0.1 - 0.66$,^{51,52} A^{n-} is the interlayer anion with a valence of n (Cl^- , CO_3^{2-} , SO_4^{2-} , NO_3^- , etc.).⁴⁵

Tetravalent cations such as Zr^{4+} and Sn^{4+} can also be incorporated.⁵³ Cation radius (size) is an important parameter in LDH formation and the LDH structure is not stable when the ionic radius of M^{II} is smaller than 0.06 nm.⁵⁴ Currently, Mg–Al and Zn–Al LDHs are the most extensively studied, however there is growing interest in synthesis of transition metal–bearing LDHs such as Co–Al, Fe–Al and Ni–Al,⁵⁵ as they may have special applications due to their magnetic, catalytic and optical properties.⁵⁶ There is no theoretical limit to the intercalation of anions into LDH structure. The following families of anions can be incorporated:

- halides (F^- , Cl^- , Br^- , I^-);
- non-metal oxoanions (BO_3^{3-} , CO_3^{2-} , NO_3^- , $Si_2O_5^{2-}$, HPO_4^{2-} , SO_4^{2-} , ClO_4^- , AsO_4^{3-} , SeO_4^{2-} , BrO^- , etc.);
- oxometallate anions (VO_4^{3-} , CrO_4^{2-} , MnO_4^- , $V_{10}O_{28}^{6-}$, $Cr_2O_7^{2-}$, $Mo_7O_{24}^{6-}$, $PW_{12}O_{40}^{3-}$, etc.);
- anionic complexes of transition metals ($Fe(CN)_6^{2-}$ etc.);
- volatile organic anions (CH_3COO^- , $C_6H_5COO^-$, $C_{12}H_{25}COO^-$, $C_2O_4^{2-}$, $C_6H_5SO_3^-$, etc.);
- anionic polymers (PSS, PVS, etc.).⁵⁴

Table 4 Some common methods of LDH synthesis.

Method	Brief description	Ref.
Coprecipitation	A solution containing M^{II} and M^{III} metal cations in adequate proportions reacts with an alkaline solution.	57
Urea hydrolysis method	This technique provides large, highly crystalline hexagonal-shaped layers of LDH, reaction temperature and reagents concentrations control size of particles.	58
Induced hydrolysis	This technique was used to obtain LDH $[Zn-Cr-Cl]$, $[Zn-Cr-NO_3]$, $[Zn-Al-Cl]$, $[Zn-Al-NO_3]$.	59
Regeneration method (memory effect)	Rehydration of mixed oxides obtained after calcination ($450\text{ }^{\circ}C - 500\text{ }^{\circ}C$) of LDH precursor containing volatile interlayer anions (e.g. CO_3^{2-} or NO_3^-) then regeneration in solution of new anions.	60
Ion exchange reaction	Original LDH is dispersed in an aqueous solution of the desired anionic species and stirred at ambient temperature for several hours.	61
Hydrolysis of a mixture of metal alcoholates	This procedure is suitable to prepare LDHs with low Al^{3+} molar fractions (x_{Al}), $x_{Al} < 0.1$, can produce highly stable intercalates with alkoxy anions.	52

On the contrary to cationic clays that occur abundantly on the Earth, natural stocks of anionic clays are very limited and most LDHs are synthesized at both, laboratory and industrial scales.⁶² LDHs are commercially manufactured (e.g. by FCC in China, Sud Chemie and Sasol in Germany, Ciba in Switzerland, Akzo Nobel, Dulso Sal'a, Slovakia, and Reheis Chemical Co. in the USA) from purified salts, or minerals such as brucite, $Mg(OH)_2$, or quasicrystalline boehmite, $AlO(OH)$,⁶³ mainly as acid-absorbers and catalysts for molecular conversions and reactions.⁶⁴ The most common methods of LDH synthesis are summarized in Table 4.

LDHs have attracted researchers attention for their interesting properties such as:

- high anion-exchange capacity AEC (from 200 to 450 meq/100g);
- structural memory effect;
- layered crystalline structure;
- simplicity of synthesis;
- possibility of controlling particle size and aspect ratio by changing the reaction conditions;
- their highly designable characteristics and rich host-guest chemistry.

LDHs have already been used as controlled release drug carriers in pharmaceutical field,⁶⁵ host for organic UV ray absorbents⁶⁶ or biosensors for human health,⁶⁷ catalysts and catalyst precursors,⁶² anion scavengers in wastewater treatments,⁶⁸ host for flame retardants⁶⁹ or dye adsorbents,^{70,71} a hybrid LDH photoinitiators,⁷² HCl absorbing agents for poly(vinyl chloride) (PVC) and other halogenated polymers.⁷³

Recently, LDHs have been recognized as alternative to some conventional fillers for polymer composites as they exhibit layered structure, high aspect ratio of particles and may play role as flame retardant and thermal stabilizer for polymers.⁷⁴ Research demonstrate that incorporation of LDHs into a polymer matrix can remarkably enhance polymer properties such as mechanical, thermal, and reduce gas permeability and other physicochemical properties compared to neat polymers or composites containing conventional fillers.^{75,76,77} Most publications on polymer/LDH composites refer to thermoplastic matrices or epoxy resins, and comparatively fewer studies have investigated the effects of LDH particles on elastomer matrix properties.

Generally LDHs are similar to layered silicates (LSs) in some aspects, however the main advantages of LDHs over LSs lay in controlling size of particles, purity and a wide range of organic species that can be used to diminish their hydrophilic surface property. On the other hand, the disadvantages of LDHs are strong interactions between positively charged sheets and high charge density which make the exfoliation of LDHs much more difficult than LSs.⁷⁸ Nevertheless, exfoliation may occur by using chemical exfoliation, pre-intercalation or modification of the lamellar surface by mechanical process.⁷⁹ The basal *d*-spacing of typical magnesium-aluminum LDH is 0.76 – 0.77 nm and the small ions presented in interlayer region can be replaced by larger organic species which weakens the electrostatic forces between the hydroxide sheets. In general, the objective of organic modification is to enlarge the basal *d*-spacing, make LDH more polymer-wettable and also reduce of surface energy of

LDHs. In order to obtain homogeneous dispersion in the polymer matrix, the inorganic LDH is made hydrophobic by the replacement of interlayer anions such as Cl^- , NO_3^- or CO_3^{2-} with organic anions. Various methods for LDHs organophilization, such as ion exchange, regeneration and thermal reactions, are used in order to achieve the successful dispersion of layered filler in hydrophobic elastomer matrix.⁸⁰ Mostly, LDHs are organically modified by the rehydration process of calcined LDH (also known as a regeneration technique), which is based on LDHs “structure memory effect”. Pristine LDH is first calcined in a muffle furnace at 500 °C for several hours to convert it into a mixed oxide form known as calcined LDH, then is suspended in a aqueous solution of the surfactant and stirred for around 24h at elevated temperature. The modified solid residue is then separated by filtration and dried to a constant weight.⁸¹ The most common organic anions used for LDH modification are: dodecyl sulfate ($\text{C}_{12}\text{H}_{25}\text{SO}_4^-$),⁸² 1-decanesulfonate ($\text{C}_{10}\text{H}_{21}\text{SO}_3^-$),⁸¹ 1-hexadecanesulfonate ($\text{C}_{16}\text{H}_{33}\text{SO}_3^-$),⁸¹ dodecylbenzenesulfonate ($\text{C}_{18}\text{H}_{29}\text{SO}_3^-$),⁶⁰ stearate ($\text{C}_{18}\text{H}_{35}\text{O}_2^-$).⁸³ Usually wide-angle X-ray diffraction (XRD, WAXS) measurements are used to determine an interlayer distance before and after organic modification of LDH.

Preparation of rubber/LDH composites

One of the most often used technique for the rubber/LDH composite preparation is a two-step melt compounding (**Table 5**). There are two possible procedures: In the first step raw rubber is milled in a two roll mill with curing agents. Subsequently, the compounded rubbers are melted in an internal mixer at elevated temperature with a high speed of rotor, then layered filler is added to the mixture.⁹⁷ Alternatively, in the first step the raw rubber is melted in an internal mixer at elevated temperature at high rotor speed, then the layered mineral is added and further mixed, in the second step all the rest ingredients are added to rubber/filler mix in an open two roll mill at room temperature.⁸¹ Solution blending is used to fabricate polymer-layered filler composites provided the polymer is easily dissolved in common aqueous or organic solvents, such as water, toluene, chloroform, acetone, DMF.

Majority of studies on polymer/LDH composites refer to thermoplastic matrixes, such as polyethylene (PE),⁸⁴ polypropylene (PP),⁸⁵ poly(vinyl alcohol) (PVA),⁸⁶ poly(vinyl chloride) (PVC),⁸⁷ polystyrene (PS),⁸⁸ poly(methyl methacrylate) (PMMA),⁸⁹ poly(ethylene-co-vinyl acetate) (EVA),⁹⁰ poly(ethylene oxide) (PEO),⁹¹ poly(ϵ -caprolactone) (PCL),⁹² poly(ethylene terephthalate) (PET),⁹³ etc., as well as epoxy resins,⁹⁴ whereas not as much works have been devoted to study the interactions between LDH particles and elastomer matrices. There have been several reports published in recent years related to the elastomeric composites.

Table 5 Some methods of rubber/LDH composites preparation.

Rubber	Method of rubber/LDH composites compounding	Ref.
CR	Laboratory two roll mill	83
NBR	Laboratory two roll mill	95
EPDM	Two-step melt compounding method	96
XNBR	Two-step melt compounding method	81,96,97,98
EPDM	Solution intercalation in toluene	99,100
PUR/NBR	Solution blending in THF	23
PUR	Solution intercalation in THF	101
SR	Solution intercalation in CCl ₄	82
EPDM	Twin-screw extruder	102
PUR	<i>In situ</i> polymerization	103
SBR	Laboratory two roll mixing mill	104

Rubber/LDH composites

Polyurethane PUR/LDH nanocomposites

One of the most widely studied material for the preparation of rubber/LDHs composites is polyurethane. Polyurethane elastomers (PUR) have comparable and sometimes identical applications to those of cast elastomers and TPU's. This polymer has high tensile modulus, wear and tear resistance, chemical resistance, however its thermal stability is very poor. With addition of organically modified LDH in PUR the thermal properties are improved what can be attributed to the mass barrier effect of LDH layers to volatile products during thermal decomposition.¹⁰⁵ Kumar's group noted that incorporation of unmodified and modified (sodium stearate) LDH improves mechanical properties of polyurethane elastomer in respect to the neat PUR.¹⁰¹ The reinforcing effect has been attributed to the orientation of LDH particles, high aspect ratio of the LDH platelets as well as to the strong interfacial interaction between the hydroxyl groups of LDH and the polar urethane groups (–NHCOO) through the hydrogen bonding which was confirmed by Fourier transform infrared spectroscopy (FTIR) analysis. Field emission scanning electron microscopy (FESEM) study showed that the modification of LDH with stearate ions led to a transformation of LDH morphology from hexagonal platelet structure into irregular shape upon modification, whereas high-resolution transmission electron microscopy (HRTEM) study revealed that organically modified layers of LDH were well exfoliated in the PUR matrix what contributed to the improvements in mechanical properties. In another study, Guo *et al.*¹⁰³ prepared polyurethane/CoAl layered double hydroxide nanocomposites via *in situ* polymerization. They used anionic clay which was treated with organic dodecyl sulfate anion according to the Liu's method¹⁰⁶ of synthesis.

The authors obtained the nanoscale dispersion of CoAl-LDH layers in PUR matrix what has been verified by the XRD and TEM studies. The real-time FTIR revealed that such prepared nanocomposites had a slower thermo-oxidative rate than the neat PUR in the temperature region from 160 °C to 340 °C, the proposed explanation of this behavior is the barrier effect of LDH layers.¹⁰³

Chloroprene rubber CR/LDH composites

Chloroprene rubber (CR) is well known for its high ozone and weather resistance, low flammability, good adhesion to other materials and high vulcanizate strength arising from strain induced crystallization, therefore CR has many applications in the elastomer field. Despite its excellent physical properties, the influence of small amount of nanofiller such as LDH on CR crystallization behavior was investigated by Das's group.⁸³ It was found that LDHs particles have capability to resist the crystallization of CR whereas organically modified montmorillonite strongly enhances it.

Ethylene propylene diene rubber EPDM/LDH composites

Ethylene propylene diene rubber (EPDM) is an extremely versatile rubber because of high resistance to heat, weather, ozone as well as resistance to polar substances and steam. It is commonly used in general industrial manufacture of seals and other products requiring excellent water, ozone, heat resistance, however it is not recommended for applications with petroleum and mineral oils or fuel exposure.

Acharya *et al.*^{99,100} successfully prepared partially exfoliated EPDM/MgAl-LDH nanocomposites by the solution intercalation method using dodecyl sulfate modified LDH (DS-LDH). The nanocomposites containing 2 – 8 wt% of DS-LDH showed a significant improvements in mechanical properties and thermal stability in comparison to neat EPDM.

Kumar *et al.*¹⁰² investigated the influence of MgAl-LDH on photo-oxidation of EPDM composites with stabilizers prepared by using a twin-screw extruder. According to their results, the rate of photo-oxidative degradation of EPDM/LDH was faster than that of blank EPDM. Such effect could occur because of the adsorption of the stabilizing additives onto the LDH sheets, which partially inhibits their activity.

Another interesting study was carried out by Pradhan *et al.*⁹⁶ who noted that EPDM composites containing organically modified LDH (with decanesulfonate anions) exhibited a decrease in storage modulus with an increasing filler content. The EPDM/LDH nanocomposites displayed a softening effect below glass transition temperature (T_g) which

was attributed to the effect of surfactant that could eventually increase the mobility of the polymer matrix.⁹⁶

Silicone rubber SR/LDH composites

Silicone rubber (SR) is an elastomer material that possesses excellent weatherability, good chemical stability, oxidation resistance, thermal stability, low-temperature toughness, electrical-insulation properties, low surface energy, low toxicity and high optical transparency. However unfilled SR is also well-known for its very poor mechanical properties.

Pradhan's group synthesized SR/dodecyl sulfate intercalated LDH (DS-LDH) composite by a solution-intercalation method.⁸² Composites were filled with 1, 3, 5 and 8 wt% of modified DS-LDH. The great improvements in mechanical properties, thermal stability and solvent resistance were successfully achieved for nanocomposite containing 5 wt% of filler. In their subsequent research, SR filled with 5 phr of stearate ion-modified-LDH exhibited a significant improvement in gas barrier properties.¹⁰⁷

For enhancing mechanical properties of SR, LDH/multiwalled carbon nanotubes (MWCNT) hybrids were prepared by simple dry grinding of Li-Al-LDH, Mg-Al-LDH and Co-Al-LDH with MWCNT. It has been reported that Mg-Al-LDH was most effective in dispersing MWCNT in polar and non-polar solvent due to its cationic charge on the platelet surface and large surface area. The improvement in mechanical properties was due to the synergistic effect of MWCNT and LDH on the SR matrix. In addition, the excellent synergistic effect of Mg-Al-LDH/MWCNT hybrid was related to the highest surface area which contributed to nanolevel dispersion and strong interfacial interaction between Mg-Al-LDH/MWCNT with SR matrix.¹⁰⁸

Solution-based styrene-butadiene rubber S-SBR/LDH composites

Styrene-butadiene rubber (SBR) is one of the most versatile copolymer rubber compounds exhibiting high abrasion resistance. It is used in a wide variety of products, such as automobile tires, mechanical goods, automotive, adhesives. However, SBR shows poor mechanical properties unless reinforcing fillers are incorporated.

Elastomer/LDH composites were prepared based on the solution styrene-butadiene rubber (S-SBR) and zinc-aluminum layered double hydroxide ZnAl-LDH (with a composition of 3:1 (Zn/Al)), using a conventional sulfur cure system.¹⁰⁴ The amounts of filler were 4, 60, 80 and 100 phr and were incorporated without any oil and plasticizers. All filled composites

exhibited an interesting phenomenon of thermoreversible transparency, *i.e.*, the transparent sample becomes opaque at elevated temperature and restores the transparency at room temperature. Moreover, such materials have other advantages, like easy processing (shear mixing), low cost and they are environmentally friendly. The authors proposed that such materials may lead to the development of smart materials, such as temperature sensors for automobile tires.¹⁰⁴

Acrylonitrile-butadiene rubber NBR/LDH composites

Acrylonitrile-butadiene rubber (NBR) provides a material that has versatile applications requiring good processability, elasticity at low temperature and oil resistance. The major drawbacks of the NBR are its poor ozone and weather resistance and moderate heat resistance. Normally sulfur, zinc oxide, stearate acid and accelerators form the cure system for the NBR formulation. With sulfur alone, the vulcanization process would take long time but with this curing system vulcanization time is reduced to a minimum.

Recently Das's group designed and employed of LDH in rubber formulation to prepare environmentally friendly rubber composites.⁹⁵ Since both stearic acid and zinc are indispensable activators in sulfur rubber vulcanization to promote cross-linking of the rubber chains, authors designed and synthesized LDH that was a source of both zinc and stearate ions which could deliver zinc ions in the vulcanization reaction as accelerators, stearate anions as activators to promote vulcanization process as well as where LDH layers acted as highly anisotropic nanofillers to reinforce the rubber matrix. In such system LDH played several roles as a reinforcing filler, reservoir of other ingredients and also provided transparent sulfur cross-linked rubber material. The important advantage of this novel approach is reduction the number of steps of rubber mixing, as well as reduction in necessary Zn^{2+} content what has potentially great importance for the rubber industry. The novel multifunctional LDH has been applied not only to NBR but also to rubbers with different polarity and chemical structure such as carboxylated acrylonitrile-butadiene rubber (XNBR), solution styrene-butadiene rubber (SSBR), butadiene rubber (BR), polychloroprene rubber (CR), natural rubber (NR) and ethylene propylene diene monomer rubber (EPDM).⁹⁵

In another study dealing with the rubber/LDH nanocomposites Kotal's group characterized polyurethane blended with NBR (PUR/NBR; 1:1 w/w) containing 1, 3, 5 and 8 wt% LDH with dodecyl sulfate (DS) anions intercalated.²³ The highest concentration of LDH in PU/NBR blend led to a substantial improvement in thermal stability and solvent resistance property of the nanocomposites. The thermal stability of PUR, NBR, PUR/NBR and

PUR/NBR/DS-LDH followed the order $\text{NBR} > \text{PUR/NBR/DS-LDH} > \text{PUR/NBR} > \text{PUR}$. TEM and XRD studies were performed to show the structure of PUR/NBR/DS-LDH nanocomposite. The authors reported formation of partially distributed layers of DS-LDH in PUR/NBR blends suggesting the formation of partially exfoliated nanocomposites.

Carboxylated acrylonitrile-butadiene rubber XNBR/LDH composites

Carboxylated acrylonitrile-butadiene rubber (XNBR) offers both excellent abrasion resistance and superior chemical resistance (especially to aliphatic hydrocarbons) compared to the straight acrylonitrile-butadiene rubber (NBR). XNBR is a terpolymer of acrylonitrile, butadiene and monomers containing carboxyl groups, such as acrylic and methacrylic acids. Lateral carboxyl groups $-\text{COOH}$ provide additional curing sites and make possible to use curing agents that can react with the carboxyl functionalities.¹⁰⁹

In 2008 Pradhan *et al.*⁹⁶ reported that the mechanical properties of XNBR filled with 5.0 – 10 phr of MgAl-LDH (modified with sodium 1-decanesulfonate) were enhanced due to the acid/base and polar interactions that occur between carboxylated rubber and hydroxide metal filler. A decreased amount of metal oxide curative in sulfur vulcanizing system was used deliberately to keep the $-\text{COOH}$ on XNBR free for possible interaction with LDH particles. Based on mechanical tests and FTIR studies, it has been observed that LDH exhibits a potential as a reinforcing nanofiller in elastomer and also could be used as a curing agent in functionalized elastomers.^{96,110} The advantage of using LDH in such system (XNBR or its hydrogenated counterpart HXNBR) give rise to possibility of replacing a part of conventional curatives like ZnO, MgO by organo-LDH.

In 2009 Thakur's *et al.*⁹⁷ investigated the influence of organically modified and unmodified MgAl-LDH (Mg/Al 63 : 37) on the curing process of XNBR crosslinked with zinc oxide. The authors reported that both pristine and dodecylbenzenesulfonate intercalated MgAl-LDH used in the amount of 5 phr quite significantly inhibit formation of ionic-crosslinks between XNBR and ZnO, what was proven by dynamic mechanical analysis (DMA), FTIR and mechanical studies, however the effect of suppression of ionic-links formation was found to be more pronounced in the presence of unmodified LDH.⁹⁷

The role of organic modifiers on nanofiller dispersion in XNBR/MgAl-LDH composites was examined by Costa *et al.*⁸¹ Authors concluded that higher *d*-value of the organo-clay results in higher degree of exfoliation and homogenous dispersion of filler particles in the uncrosslinked compounds, however after crosslinking more complicated reorganization might occur.

In 2014 Basu *et al.*¹¹¹ studied the effects of unmodified ZnAl-LDH on the mechanical and thermal properties of XNBR matrix. The composites were vulcanized by a standard sulfur cure system containing 4 phr of ZnO and by unconventional sulfur cure system where ZnO was replaced by ZnAl-LDH at concentrations of 4, 10, 40 and 100 phr. It was observed from FTIR studies that Zn^{2+} ions present in the ZnAl-LDH structure react with the $-\text{COOH}$ of the rubber chains, however the ionic transition peak (T_i) which is characteristic for ionic elastomers was not detected during DMA analysis. Their subsequent studies¹¹² aimed at exploration the nature of the ionic crosslinking of XNBR produced by ZnO, ZnCl_2 and ZnAl-LDH. The unmodified ZnAl-LDH was applied as a curing agent for XNBR and such composites were compared to those containing ZnO or ZnCl_2 as curatives. The authors stated that all zinc-containing compounds can react with the carboxylic groups of XNBR under vulcanization conditions, however only ZnO is able to produce microphase separation demonstrated by high-temperature dynamic mechanical relaxation behavior. Such additional ionic transition was not observed in the case of XNBR crosslinked with ZnAl-LDH.

The development of reinforced elastomer/LDH materials based on various types of polymer matrices has been studied extensively, and the number of studies related to the use of LDH in carboxylated acrylonitrile-butadiene rubber (XNBR) is steadily increasing. Most research has focused on the impact of low concentrations (up to 10 phr) of organically modified MgAl-LDH on the mechanical and morphological properties of XNBR crosslinked by a conventional sulfur vulcanizing package. Very recent studies have considered the possibility of the replacement of zinc oxide by ZnAl-LDH in the sulfur cure system to crosslink diene rubbers. However, the simultaneous application of pristine MgAl-LDH as a curing agent and as a reinforcing filler in XNBR for the production of strong, ionic elastomer composites with improved mechanical properties, reduced swelling and enhanced gas barrier properties has not been examined. Therefore, a part of this thesis has been devoted to the employment of pristine MgAl-LDHs with various Mg/Al ratios, surface properties and morphologies as reinforcing fillers and curatives in XNBR and the evaluation of the main factors impacting the reinforcement in such systems.

1.2.3. GRAPHENE

In 2004, isolation of single-layer graphene crystals stable in their free state led to a rapid increase in interest in this material due to its unique thermal, electrical, mechanical and optical properties. Graphene is a two-dimensional monolayer of sp^2 -hybridized carbon atoms closely packed in a honeycomb-like lattice, which is the basic building block of all other carbon nanostructures: fullerene, carbon nanotubes and graphite. Graphene nanosheets have high mechanical strength (>1060 GPa), high thermal conductivity (~ 3000 W/mK) and a high specific surface area (2600 m²/g).¹¹³ Graphene and its derivatives are frequently used in the production of devices for electronics and optoelectronics^{114,115} and in polymer composites as reinforcing nanofillers.¹¹⁶ In the near future, graphene may replace silicon in electronic devices¹¹⁷ and be employed in lithium ion batteries,¹¹⁸ as a hydrogen storage material,¹¹⁹ and in drug delivery systems.¹²⁰ The high aspect ratio of graphene in combination with its unique physical properties support its use as a filler for manufacturing conductive polymer composites.^{121,122} Moreover, polymer composites containing graphene are expected to exhibit improved mechanical, gas barrier and thermal properties.

Graphene synthesis and properties

Graphene can be easily fabricated by employing different methods with inexpensive graphite, even at large scales, and is already commercially offered by various companies. However, commercial graphene produced by exfoliation of graphite at the industrial scale is usually not completely exfoliated; thus, it is better described as ultra-thin graphite.¹²³ Various mechanical,¹²⁴ physical,¹²⁵ and chemical¹²⁶ methods have been developed to obtain carbon layers. In 2004, Geim and Novoselov isolated a homogeneous graphene layer through the micro-exfoliation of a small amount of a highly oriented, pyrolytic graphite (micromechanical exfoliation).¹¹⁹ They were awarded the Nobel Prize in Physics in 2010 by the Royal Swedish Academy of Sciences for their discovery. Micro-exfoliation yields graphene with an ideal crystal structure and preserved high electron mobility¹¹⁵ but is time-consuming for the preparation of large quantities of material. An alternative method for the synthesis of high-quality graphene is epitaxial growth of single-domain graphene on a silicon carbide (SiC) substrate.^{127,128} Using controlled sublimation of silicon from the SiC crystal at a temperature of approximately 1500 °C, surfaces of high-quality graphene can be produced that are ideal for building transistors or diodes. The disadvantage of this method is the difficulty of achieving large graphite domains with uniform thicknesses.¹²⁷

So far, the least complicated and most effective method is the production of chemically synthesized graphene flakes. The starting raw material is graphite, which is first treated with concentrated strong mineral acids (H_2SO_4 , KMnO_4 , HNO_3 ; Hummer's method)¹²⁹ or other oxidizing agents. The product of this reaction is graphite oxide (GO) containing numerous oxygen-containing groups attached to the surface and the edges of layers. Epoxy and hydroxyl groups are present in the highest concentrations on the surfaces of the GO layers and the sp^3 hybridized carbon atoms, whereas the carboxyl and carbonyl groups are located on the edges of the layers. Thus, GO is easily dispersed in aqueous media.^{130,131} Due to the strong tendency of water molecules to intercalate into GO sheets, the interlayer distance depends on the ambient humidity and varies between 6 and 12 Å.^{132,133,134} The surface charge (zeta potential) of the oxidized layers of graphene dispersed in an aqueous medium is negative because electrostatic repulsion between the negatively charged layers forms a stable aqueous suspension. GO can be exfoliated by either thermal shock¹³⁵ or chemical reduction.¹³⁴ Although the chemical oxidation of graphite and further exfoliation provides a large number of individual layers of GO, such aggressive treatment inevitably leads to structural defects.^{136,137} Defects in the graphene lattice structure interfere with electron mobility and create a semiconductor. After chemical reduction or annealing (1000 °C), graphene structures can be only partially recovered, as confirmed by X-ray photoelectron spectroscopy (XPS) studies.¹³⁸ In a thermal reduction process, GO is exfoliated by rapid heating to a temperature of 1050 °C in an inert gas atmosphere (5 % H_2 and 95 % Ar).¹³⁹ The preparation time must be sufficiently short (heating rate of 2000 °C/min) to avoid aggregation and graphitization at high temperatures. During pyrolysis, CO_2 mechanically separates layers held by weak van der Waals forces.^{140,141} The resulting product forms a very loosely structured mass with low density and 100- to 300-fold volume expansion.

Thermally reduced graphene oxide (TRG) is characterized by high surface development (1700 m^2/g) and electrical conductivity (10 – 20 S/cm).¹⁴¹ To completely remove the oxygen functionalities located on the edges of the TRG plane, it can be subjected to the further reduction in acetonitrile under ultrasonic irradiation, as shown in **Figure 11**.¹⁴²

TRG forms a highly agglomerated structure that disperses readily in polar solvents such as *N*-methylpyrrolidone, dimethylformamide, 1,2-dichlorobenzene, nitromethane or tetrahydrofuran under ultrasonic irradiation. The GO layers are chemically reduced using reducing agents such as hydrazine¹⁴³ or sodium borohydride¹⁴⁴. Despite its toxicity, hydrazine is the most commonly used chemical in the preparation of graphene sheets. This method delivers reduced GO that is less hydrophilic and precipitates from the aqueous medium due to

the elimination of oxygen groups from its surface. Hydrazine reduces the epoxy and hydroxyl groups.¹³⁷

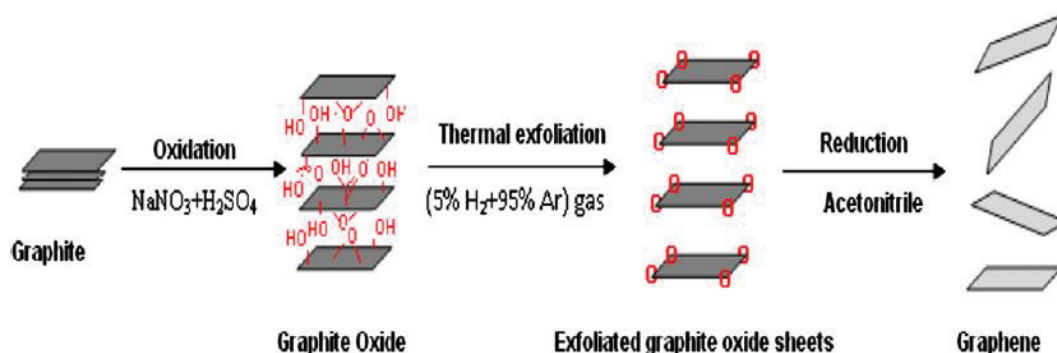


Figure 11 Reduction of GO.¹⁴²

NaBH_4 reduces GO oxygen groups more efficiently than hydrazine but is slowly hydrolyzed in aqueous media. Other methods involve the use of chemical reducing hydroquinone,¹⁴⁵ gas hydrogen (after thermal expansion),¹⁴⁶ strongly alkaline solutions¹⁴⁷ or vitamin C¹⁴⁸. The disadvantages of these methods are pollution, excess reducing agent in the product, process complexity and the toxicity of the reducing agent. The product of the chemical reduction of graphene oxide contains oxygen-containing groups and irreversible crystal lattice defects, which contribute to the deterioration of the conductive properties. Layers of exfoliated graphene and expanded graphite have far fewer defects, enabling high electrical conductivity to be maintained (1000 – 2300 S/m).¹⁴⁹ The advantages of thermal reduction include the production of large quantities of the product and a short reducing cycle by heat that does not require any additional treatments (such as purification of the product). Graphene oxide can also be reduced with iron at ambient temperature.¹⁵⁰

Because of its strong tendency to agglomerate, graphene is not suitable for intercalation of larger organic molecules such as polymeric chains.¹³¹ Therefore, to improve the interaction of graphene with polymer chains and prevent filler agglomeration, graphene must be chemically oxidized, followed by grafting of functional groups on its surface. Functional groups attached to the graphene surface may be either small organic molecules or a long chain polymer. The chemical functionalization of graphene makes it more compatible with the organic matter, promotes interfacial interactions and facilitates the processing of polymer composites. Surface modification of the carbon filler may be performed by amination, esterification,¹⁵¹ reaction with isocyanates¹⁵² or electrochemical modification with an ionic liquid¹⁵³.

Graphene-based fillers in elastomer composites

Among the various nanocomposite systems, those of graphitic based fillers are important due to their multi-functional behavior. They can improve mechanical and tribological properties, thermal stability, microwave absorption, electrical and thermal conductivities, dielectric performances and gas barrier properties of all elastomer matrices.¹⁵⁴ Polymer nanocomposites acquire new characteristic properties due to the presence of graphene layered filler. Increase in strength and electrical conductivity of polymer composites is significantly greater with an addition of graphene filler, when compared to a commonly nanofillers such as silicate or other carbon fillers. Although the strength of carbon nanotubes is similar to that of graphene, they are inferior in terms of thermal and conductive properties,¹⁵⁵ as well as their cost of production. Furthermore, it was observed that this type of filler can play also the role of an anti-aging agent.¹⁵⁶ Reinforcing effect GO has been already observed in various kinds of elastomers as shown in **Table 6**. It was found that the presence of the graphene improves the mechanical strength, enhances the impact resistance, resistance to cracking,¹⁵⁷ gas barrier properties or may influence the vulcanization kinetic of rubbers.

For example, unfunctionalized few layer graphene (FLG) nanoplatelets were mixed with acrylonitrile-butadiene rubber (NBR) by melt mixing method and explored as a reinforcing filler for the NBR matrix. The NBR/FLG composite properties were compared with those of compositions having equal loadings of carbon black (CB), and 1 : 1 mixture of FLG and CB. It was reported that FLG acts as a better reinforcing filler for NBR compared to CB. The rheometer torque values showed the effect of FLG in improving the scorch safety of the compositions. Additionally, the helium leak rate of the composites was decreased by 40 % in the presence of FLG due to its platelet structure. These studies showed that by tuning the rubber formulation, significant improvement in mechanical, dynamic mechanical and gas barrier properties can be achieved with a very low loading of either FLG or a mixture of CB and FLG without adopting challenging steps like functionalization of graphene.¹⁶¹

Table 6 Some examples of rubber/graphene composites and their properties.

Type of rubber	Type of filler	Method of composite preparation	Composite Properties	Ref.
EPDM	Graphene Oxide (GO)	Combination of solution mixing and two-roll mill mixing	Increased the tensile modulus, tensile strength, elongation at break, decreased thermal stability with GO loading	158
HXNBR	Graphene Oxide (GO)	Combination of solution mixing and two-roll mill mixing	Increased tensile strength, modulus at 200% elongation and increased T_g of HXNBR	159
NBR	Graphene (GnPs) with 5, 15, and 25 μm average particle diameters	Dry mixing of graphenes with NBR without softener and with dioctylphthalate	Increased conductivity for the graphene composites in the presence of dioctylphthalate	160
NBR	Unfunctionalized few layer graphene (FLG) nanoplatelets	Melt mixing	Improved the cure characteristics of NBR, improved gas barrier and tensile properties	161
S-SBR	Graphene nanoplatelets (GnPs)	2-stage mixing: in an internal mixer and two-roll mill mixing	The electrical percolation behaviour was found to be started at 15 phr for GnPs	162
XNBR	Graphene Oxide (GO)	Mixing exfoliated GO aqueous dispersion with XNBR latex	Improved thermal stability, thermal conductivity, and thermal diffusivity	163
NR	Graphene Oxide (GO)	Latex compounding	GO took part in the vulcanization process and enhanced crosslinking density of NR	164

Rubber/graphene composites have emerged as a new class of high-performance materials with promising multifunctional properties and a wide range of applications. In this study, commercially available graphene nanoplatelets (GnPs) were directly added to NBR and XNBR matrices without any functionalization and suitably compounded to achieve the required level of reinforcement using a conventional rubber compounding process. The curing behavior, cure degree, mechanical properties and UV stability of the NBR and XNBR composites loaded with different types of graphene and crosslinked by two different systems were investigated.

1.3. IONIC LIQUIDS (ILs) AND THEIR APPLICATIONS IN RUBBER COMPOSITES

1.3.1. IONIC LIQUIDS (ILs) – PROPERTIES AND APPLICATIONS

According to a definition of ionic liquids (ILs), organic molten salts composed entirely of ions that melt at or below 100 °C are categorized as ILs.¹⁶⁵ The current interest in ILs is mainly driven by their proven or potential applications as solvents for "green chemistry" due to their non-volatility which results in low impact on the environment and human health.¹⁶⁶ Ideally, such organic compounds are optically clear, have negligible volatility, low combustibility, high chemical stability and are relatively undemanding and inexpensive to manufacture. Nowadays, the most widely explored ILs consist of imidazolium, ammonium, phosphonium, pyridinium, pyrrolidinium cation which is weakly coordinated to an organic or inorganic anion, such as Cl^- , I^- , Br^- , $[\text{SCN}]^-$, $[\text{AlCl}_4]^-$, $[\text{N}(\text{CN})_2]^-$, $[\text{BF}_4]^-$, $[\text{PF}_6]^-$, $[\text{NO}_3]^-$, $[\text{CH}_3\text{COO}]^-$, $[\text{CF}_3\text{SO}_3]^-$, $[(\text{CF}_3\text{SO}_2)_2\text{N}]^-$ and their chemical structures are showed in **Figure 12**.¹⁶⁷

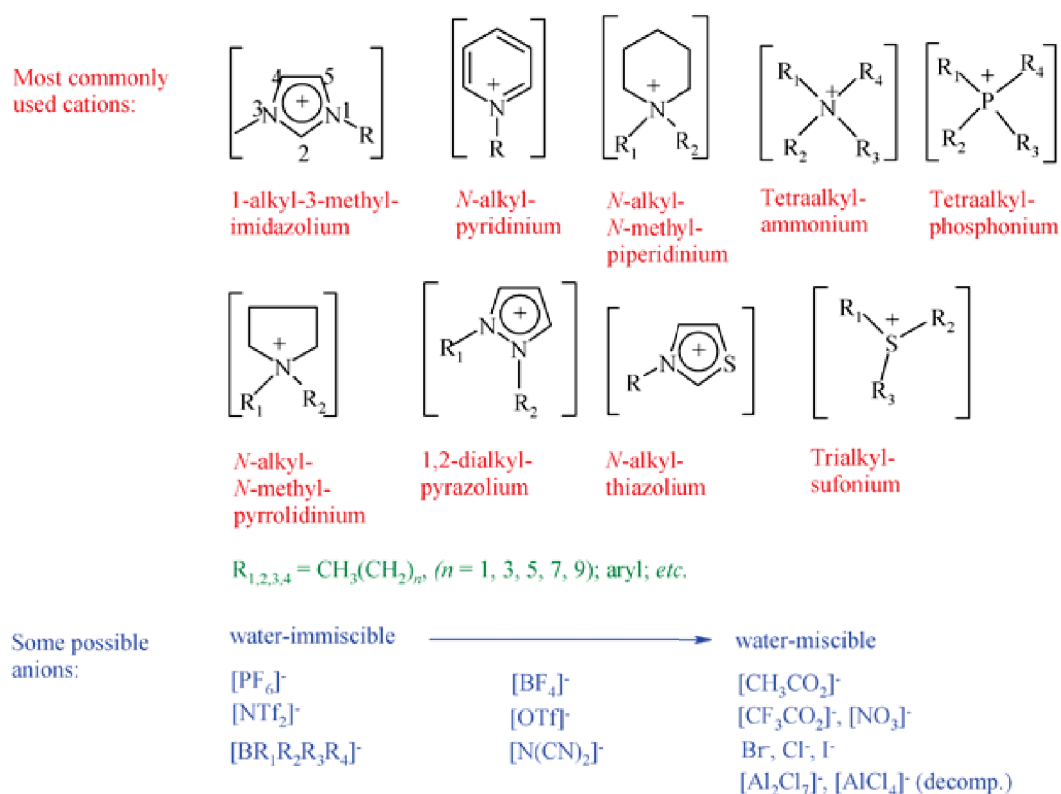


Figure 12 Common cations and anions for ILs.¹⁶⁸

Physicochemical properties such as polarity, hydrophobicity, solvent miscibility, viscosity and density of ILs can be tuned by selecting the various combinations of cations and anions and for this reason ILs are known as designer solvents.¹⁶⁹ For example, the commonly used 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF₆] is immiscible with water, whereas 1-butyl-3-methylimidazolium tetrafluoroborate [BMIM][BF₄] is water soluble, however both are found to be toxic since they release HF on hydrolysis.¹⁷⁰ In general, tetrafluoroborates, chlorides, nitrates, and trifluoroacetates display complete miscibility with water, whereas hexafluorophosphates, triflimides, and other perfluorinated anions impart very low solubilities in water. The properties of ILs such as superacidity, basicity, water miscibility, water immiscibility and hydrophobicity result from the composite properties of the cations and anions. The anion is currently used to control the water miscibility, but anion can also have impact on the hydrophobicity or hydrogen bonding ability.¹⁷¹ The number of available ILs can be easily and significantly increased by considering their binary (yielding over 10¹² combinations) or ternary mixtures (yielding over 10¹⁸ combinations).¹⁷²

Due to the unique properties of ILs, they have been widely applied in many fields including the use:

- as an alternative for traditional volatile organic solvents,¹⁷³ as solvents for polymerization process,¹⁷⁴ as solvents in which cellulose is soluble,¹⁷⁵
- for catalytic reactions, where the main advantages of ionic liquid catalysis are greatly enhanced reaction rates, higher activity at lower temperature, non-volatility and higher selectivity;¹⁷⁶
- for separation of biomacromolecules and biosensing;¹⁷⁷
- in polymerization of polymerizable ILs for production of solid polyelectrolytes;¹⁷⁸
- in electrochemical applications such as: dye-sensitized photoelectrochemical cells;^{179,180} electrochemical mechanical actuator devices,¹⁸¹ electrochemical supercapacitors,^{182,183} lithium-ion batteries;¹⁸⁴
- as antimicrobial agents;¹⁸⁵
- as lubricants;¹⁸⁶
- in solvation of radioactive material.¹⁸⁷

Given their low vapor pressure, non-flammability, high chemical and thermal stability, ILs may serve multiple functions in the preparation of polymer composites. Homogeneous distribution of fillers and increased ionic conductivity are two major reasons for the

incorporation of ionic liquids in elastomer composites, however the presence of ILs may influence many other properties of rubber compounds as it is shown in **Figure 13**.

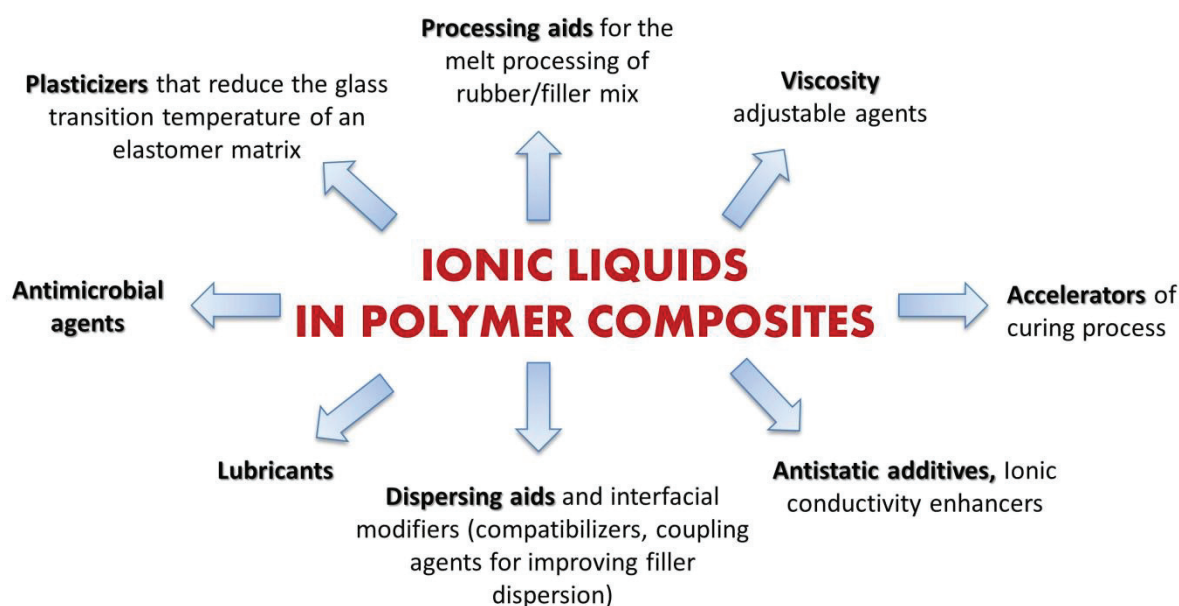


Figure 13 Possible applications of ILs in polymer field.

It has been recently reported that doping rubbers with ionic liquids is an easy way to change their critical properties including mechanical, thermal and antimicrobial and to prepare composites with high ionic conductivity and good elasticity. Their potential applications in elastomer composites include the use as processing aids for the melt processing of rubber/filler composites,¹⁸⁸ plasticizers that reduce the glass transition temperature of an elastomer matrix,¹⁸⁹ interfacial modifiers (compatibilizers, coupling agents for improving filler dispersion)¹⁹⁰ (**Figure 14**), cure accelerators,^{191,192,193} or antistatic additives^{194,195,196}. The high ionic conductivity enables ILs to act as ion reservoirs to increase the ionic conductivity of polymer composites.¹⁹⁷

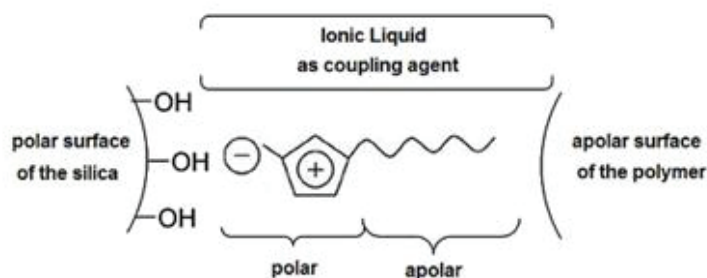


Figure 14 Ionic liquid as coupling agent between inorganic filler and polymer matrix.¹⁹⁸

1.3.2. PROPERTIES AND APPLICATIONS OF ROOM TEMPERATURE IMIDAZOLIUM IONIC LIQUIDS (RTILs) CONTAINING TETRACHLOROALUMINATE $[AlCl_4]^-$, THIOCYANATE $[SCN]^-$ AND BIS(TRIFLUOROMETHYLSULFONYL)IMIDE $[TFSI]^-$ ANIONS

The properties and applications of imidazolium ionic liquids containing tetrachloroaluminate anion $[AlCl_4]^-$

In 1981, Wilkes *et al.*¹⁹⁹ announced dialkylimidazolium chloroaluminate melts as a new class of RTILs for electrochemistry, spectroscopy and synthesis. A few years later, the physicochemical properties of $[BMIM]Cl/AlCl_3$ were studied by Fannin *et al.*²⁰⁰ Depending on the ratio of cation/anion, the IL can be Lewis-acidic, neutral, or Lewis-basic.²⁰¹ The acidity of these ILs can be tuned by changing the molar ratio of organic chloride salt ($[R]Cl$) to $AlCl_3$. When the apparent mole fraction, x , of $AlCl_3$ is higher than 0.5, the ILs are acidic due to an excess of Lewis acidic $AlCl_3$. The most widely studied apparent mole fraction range of $AlCl_3$ is 0.50 to 0.66, and the main species of Lewis acidic anions are confirmed as $[Al_2Cl_7]^-$ in these ILs.²⁰² Chloroaluminate ionic liquids display Lewis acidity what makes them attractive alternative solvent-catalyst systems.²⁰² For example, the synthesis of high molecular weight poly(isobutylene) in acidic $[EMIM][AlCl_4]$ ionic liquid without an additional catalyst has been reported.²⁰³ Another example involves the application of $[BMIM][AlCl_4]$ ionic liquid in biphasic ethylene polymerization as a medium of Cp_2TiCl_2 titanocene catalyst.^{207,204}

The relatively high conductivity (23.0 mS/cm for $[EMIM]^+$ at 20 °C,²⁰⁰ 9.5 mS/cm for $[BMIM]^+$ at 20 °C,²⁰²) low viscosity (18 cP at 20 °C for $[EMIM]^+$ ²⁰⁰) wide electrochemical window, and tunable acidity render these ILs as potential electrolytes and catalysts. Over the past decades, Lewis acidic chloroaluminate ILs have been widely applied in the low-temperature metal electrodeposition,²⁰⁵ in the desulfurization of model diesel fuels,²⁰¹ in biphasic ethylene polymerization.^{206,207} and as catalyst.²⁰⁸ De Castro *et al.*²⁰⁹ applied $[BMIM][AlCl_4]$ ionic liquid immobilized on a range of alumina and silica supports as a Lewis acid catalyst for Friedel–Crafts alkylation reactions. Another example involves application of imidazolium tetrachloroaluminate as the electrolyte/separator in solid-state lithium batteries, however exposure to atmospheric moisture of tetrachloroaluminate results in release of heat and HCl due to an extremely high moisture sensitivity of anion $[AlCl_4]^-$. For a certain time, chloroaluminate ILs were investigated as a potential RTIL electrolyte,²¹⁰ but due to elimination of the safety advantages of $[AlCl_4]^-$ the interest in the use of non-chloroaluminate ionic liquids has gradually increased.

The properties and applications of imidazolium ionic liquids containing thiocyanate anion [SCN]⁻

1-Ethyl-3-methylimidazolium thiocyanate [EMIM][SCN] is hydrophilic, low-viscous (22 cP at 20 °C)²¹¹ and highly-conductive (21.0 mS/cm at 20 °C)^{212,217} ionic liquid. As used herein “hydrophilic ionic liquid” means an ionic liquid which is partially or wholly miscible with water. The crystallization and the melting point occur at -94 and -6 °C, respectively. [EMIM][SCN] shows quite good thermal stability with weight loss beginning above 237 °C. The thiocyanate is a strongly coordinating ion and, as such, the ionic liquids produced with this anion are expected to display similar physical properties to the ionic liquids containing the dicyanamide anion [DCN]⁻, also a pseudo-halide.^{213,214} The species is electrochemically stable down to -1.4 V and up to 0.8 V vs. Ag/Ag⁺. This is a small electrochemical window compared to those of other ionic liquids such as [BMIM][PF₆], largely due to the electrochemical instability of the anion. This is thought to be related to the pseudo-halide behavior of the anion, oxidation producing the neutral dimeric species [SCN]₂. While the thermal stability of the thiocyanate salts was confirmed as relatively good, the optical stability of the species is less certain. The salts are often yellow or orange in color and darken on extended exposure to sunlight. The thiocyanate ion is known to dimerise to thiocyanogen [SCN]₂ under chemically or electrochemically oxidative conditions in melts, or in solutions of alkali metal thiocyanates.²¹⁵ Thiocyanogen is itself unstable and polymerizes to polythiocyanogen [SCN]_x, a linear polymer whose structure has only recently been established.^{214,216}

The main advantages of [EMIM][SCN] are high conductivity and low viscosity at room temperature which makes it an interesting electrolyte for the preparation of an electrochemical double layer capacitors (EDLC)^{217,218} or an alternative extraction solvent.^{219,220} Due to the electrostatic nature of ionic liquids, [EMIM][SCN] interacts strongly with cellulose acetate (CA) molecules through pronounced hydrogen bonding, Coulombic forces and van der Waals interactions, which play an important role in dissolving CA.²²¹

The properties and applications of imidazolium ionic liquids containing bis(trifluoromethylsulfonyl)imide anion [TFSI]⁻

Dialkylimidazolium bis(trifluoromethylsulfonyl)imides [TFSI]⁻ are hydrophobic ionic liquids saturated by less than 2 % of water which were first time synthesized by Bonhote *et al.*²²² Dialkylimidazolium [TFSI]⁻ salts are easy to prepare and they combine low viscosity, high thermal and electrochemical stability. Their immiscibility with water and solvents of low polarity (ethers, haloalkanes, alkanes) opens interesting perspectives for synthetic and electrochemical applications (supercapacitors, sensors, biosensors).²²²

The cation structure influences the salt viscosity which is an important feature of electrolytes. One of the most fluid ionic liquids is 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide [EMIM][TFSI] which has viscosity of 34 cP at 20 °C.²²³ The minimal viscosity value of [EMIM][TFSI] salt results from its sufficient side chain mobility and low molecular weight. Alkyl chain lengthening or fluorination makes the salt more viscous, due to increased van der Waals interactions. The effect of the viscosity on ionic conductivity is equally as important as the influence of ion size and weight. For instance, the conductivity of [EMIM][TFSI] and [BMIM][TFSI] was found to be 8.8 and 3.9 mS/cm at 20 °C, respectively.²²² Generally, ionic liquids have excellent ionic conductivity up to their decomposition temperature. Unlike other highly conductive but less electrochemically and thermally stable ILs (*e.g.*, those containing dicyanamide [DCN]⁻ (28 mS/cm at 20 °C for [EMIM]DCN)²²⁴ or thiocyanate [SCN]⁻ ions), TFSI-based imidazolium salts are characterized by high chemical and thermal stability up to 380 °C^{222,225} whereas for [EMIM][TFSI] it was found to be 439 °C.²²⁶ The thermal stability decreases with increasing number of carbon atoms in the alkyl chain from methyl to butyl after which no noticeable changes in the decomposition temperature are observed.²²⁶

The thermal stability of ILs is a critical factor in their suitability at the high temperatures involved in the melt-blending process. Hydrophobicity (immiscibility with water) is another advantage of TFSI-based imidazolium ILs making them more compatible with hydrophobic rubber matrices, preventing leakage (migration within the polymer matrix), facilitating rubber processing and improving filler dispersion throughout the elastomer matrix. Additionally, the immiscibility with water increases with increasing length of the cation side chain due to the increased surface activity of longer-chain cations.²²⁷

The use of TFSI-based imidazolium ILs as processing aids, filler-matrix compatibilizers (interfacial modifiers) and conductivity enhancers in elastomers has been already reported for

hydrogenated nitrile rubber (HNBR),²²⁸ chloroprene rubber (CR),^{229,230,231,232,233,234} nitrile rubber (NBR)^{197,235,236,237,238} and solution styrene butadiene rubber (SSBR).²³⁹ Most publications present the ability of IL-modified carbon nanotubes (CNTs)^{228,231} or carbon black (CB)²⁴⁵ to improve rubber conductivity and filler dispersion. Few studies have investigated the ability of high levels of pure ionic liquids to improve the ionic conductivity of unfilled rubber materials.^{197,236} Another example involves the use of TFSI-based ILs for enhanced antistatic properties of polyurethane films. It was found that addition of [BMIM][TFSI] in the amount of 10 ppm results in the reduction of surface resistivity (ρ_s) from 2.1×10^{12} to 9.4×10^{10} ohm/sq. Because a such small concentration is not sufficient to generate a successive conduction pathway, the antistatic effect cannot be explained by the percolation theory. The authors suggested that the antistatic effect may be derived from the conduction of free ions generated in polymer network.¹⁹⁵

1.3.3. IONIC LIQUIDS (ILs) IN ELASTOMER COMPOSITES

Acrylonitrile-butadiene rubber (NBR)

For applications in electrochemical devices, where flexibility, thermal stability and high ionic conductivity are required, polymer electrolytes are frequently based on acrylonitrile-butadiene rubber (NBR) combined with an ionic liquid. For example, polymer electrolytes with high ionic conductivity and good elasticity were prepared by Marwanta *et al.*²³⁶ by mixing NBR with ionic liquid, *N*-ethylimidazolium *bis*(trifluoromethanesulfonyl)imide, [EMIM][TFSI]. Sample with ionic liquid content of 50 wt% displayed the ionic conductivity of 1.2×10^5 S/cm at 30 °C. Incorporation of lithium salt to this composite further increased the ionic conductivity to about 10^4 S/cm without deterioration of the mechanical properties. Marwanta *et al.*²³⁶ reported the Raman study of NBR/[EMIM][TFSI] composites to confirm the existence of interaction between the anion of imidazolium ionic liquid and –CN group of NBR. A similar studies on the solid polymer electrolyte preparation were carried out by Cho *et al.*²³⁵ The combination of 1-butyl-3-methylimidazolium *bis*(trifluoromethylsulfonyl)-imide [BMIM][TFSI] and NBR with 40 mol% of acrylonitrile content (ACN) delivered material exhibiting high conductivity of 2.54×10^{-4} S/cm at 20 °C as well as high electrical stability. Moreover, the investigations showed that both the dielectric constant and the uptake of the ionic liquid in the NBR films increased with increasing ACN level.

The imidazolium, benzalkonium and phosphonium ILs combined with the 2-mercaptobenzothiazolate anion were prepared for the application as vulcanization

accelerators in NBR compounds crosslinked with sulfur-based cure systems. The synthesized ionic liquids allowed to reduce amount of 2-mercaptobenzothiazol which is a conventional vulcanization accelerator that is widely used in the rubber industry.¹⁹¹ In the another work, a series of alkylimidazolium and alkylammonium ILs added in the amount of 1 phr to the unfilled NBR was studied for the effect of anions (chloride, bromide, hexafluorophosphate, tetrafluoroborate) on zinc oxide nanoparticles activity in sulfur vulcanization of NBR.¹⁹² The authors concluded that alkylimidazolium and alkylammonium salts catalyze the interface crosslinking reactions, and consequently, the vulcanization time of the rubber compounds remarkably decreases whereas the crosslink density of the vulcanizates increases. The cure rate and crosslink density of NBR vulcanizates increased with the length of alkyl chains present in the alkylimidazolium or alkylammonium salt. Higher cure rate of rubber compounds was observed in the presence of alkylimidazolium Cl^- and Br^- anions, whereas the longest vulcanization times were displayed by the rubber compounds with alkylimidazolium hexafluorophosphate. Considering mechanical properties of vulcanizates, the most effective ones were ILs with 1-butyl-3-methylimidazolium cation, especially tetrafluoroborate and bromide.¹⁹²

Hydrogenated acrylonitrile-butadiene rubber (HNBR)

Likoza *et al.*^{228,240} prepared solid electrolytes by following steps: (1st step) melt compounding of the carbon nanotubes (MWCNT-OH) with hydrogenated acrylonitrile-butadiene rubber (HNBR), (2nd step) mixing it with peroxide curing system, (3rd step) curing, and (4th step) immersion of HNBR/MWCNT-OH films into the diluted ionic liquid (dialkylimidazolium and pyrrolidinium-based ILs with tetrafluoroborate, hexafluorophosphate, *bis*(trifluoromethylsulfonyl)imide anions). The elastomer based electrolytes exhibited high tensile strength and elongation at break. A plasticizing effect of TFSI-based ILs on HNBR matrix was observed as the glass transition temperature (T_g) of HNBR/MWCNT-OH/IL compounds decreased as a function of increasing IL content, whereas the presence of the ILs with $[\text{PF}_6]^-$ and $[\text{BF}_4]^-$ anions caused the opposite effect and led to the elevation of T_g by 5 °C. The author suggested that ionic liquids bearing *bis*(trifluoromethylsulfonyl)imide anions have good miscibility with HNBR/MWCNT-OH compounds due to the interaction of the dipoles of HNBR-originating nitrile group with $[\text{TFSI}]^-$ -originating sulfonyl groups and negatively charged nitrogen atom, causing van der Waals forces. Moreover, ILs with $[\text{BMIM}]^+$ had better miscibility with nitrile rubber than the most commonly known ionic liquids with $[\text{EMIM}]^+$.

Maciejewska *et al.*²⁴¹ investigated the activity of several ionic liquids (alkylimidazolium (allyl-, ethyl-, butyl-, hexyl-, and octyl-) salts containing bromide, chloride, tetrafluoroborate, and hexafluorophosphate ions) that were used to improve the dispersion of coagent particles in peroxide-crosslinked HNBR. It was found that alkylimidazolium salts displayed a positive impact on the coagent dispersion in the elastomer matrix. The results obtained for a series of tetrafluoroborates indicated that crosslink density and tensile strength of vulcanizates decreased with increasing alkyl chain lengths.

Chloroprene rubber (CR)

In numerous studies, the conductivity of chloroprene rubber (CR)/carbon-nanotubes (CNTs) composites has been enhanced by using imidazolium salts as dispersion agents.^{229,231,232,234} Subramaniam *et al.*²²⁹ reported that combining commercial grade multi-walled carbon nanotubes (MWCNTs) with 1-butyl-3-methylimidazolium *bis*(trifluoromethylsulfonyl)imide [BMIM][TFSI] in CR produces composite with an electrical conductivity of 0.1 S/cm with a stretchability >500 %. The increased conductivity of the composite was ascribed to the synergistic effect of electrons and ions and to the formation of percolating network with the IL modified tubes. The authors did not observe a proportional increase in the conductivity by increasing the loading of pure IL. The ionic conductivity of the CR/[BMIM][TFSI] mixture increased from 10^{-11} S/cm (neat CR) to 10^{-9} S/cm in the presence of 5 phr of IL and remained unaltered upon amount till 20 phr of IL. DMA measurements showed that the presence of IL had no effect on the glass transition temperature (T_g) of composites.²²⁹ In later work on CR/IL-CNTs composites, Subramaniam *et al.*²³¹ reported that the physical (cation- π - π) interaction existing between [BMIM][TFSI] and MWCNTs result in enhanced thermal stability of the rubber composite and promote to obtain homogenous dispersion of nanotubes in elastomer matrix. This was confirmed by subsequent investigation.²³⁰ In other studies, the electrical conductivity of IL- CR/CNTs composites increased upon accelerated thermal aging, and therefore, the authors suggested that these composites may be useful for applications where conductivity at elevated temperatures is required.²³³

Steinhauser *et al.*²³² investigated the influence of [BMIM][TFSI] on the dielectric relaxation behavior of CR/CNTs nanocomposites. Composite contained: 0.5 phr of stearic acid, 5 phr zinc of oxide (ZnO), 4 phr of magnesium oxide (MgO), 1 phr of ethylene thiourea and 20 phr of [BMIM][TFSI] for unfilled sample, or 15 phr of [BMIM][TFSI] for composites loaded with 3 phr of CNTs. The improvement of the conductivity over more than two orders

of magnitude, which was found in the presence of IL in the composite, was explained through the role of [BMIM][TFSI] as a coupling agent which leads to the enhanced CR-CNTs interaction.

Solution-styrene-butadiene rubber (SSBR)

Two types of thiol ILs, 1-methylimidazolium mercaptopropionate [MIM][MP] and *bis*(1-methylimidazolium) mercaptosuccinate [BMIM][MS], were studied as interfacial modifiers for SBR/halloysite nanotubes (SBR/HNTs) composites. Significant mechanical improvements and lowered mechanical loss in the temperature range of 50 – 80 °C were ascribed to the enhanced HNTs dispersion and strengthened interfacial interactions.¹⁹⁰ In another study, the role of 1-methylimidazolium mercaptopropionate [MIM][MP] as a modifier for SBR/silica composites was evaluated,²⁴² also the effects of 1-methylimidazolium methacrylate [MIM][MA] were investigated in SBR/silica composites.²⁴³

The IL-coated HNTs (1-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF₆]) were used for reinforcement of SBR compounds. Compared with the rubber composites with pristine HNTs, the uncured compounds with modified HNTs exhibited accelerated curing, and the resulting vulcanizates showed substantially higher tensile properties and much lower hardness. The unique changes in the compounds were ascribed to the interaction between IL and HNTs and improvements in the state of filler dispersion.²⁴⁴

In order to ensure better compatibility between the blend of SSBR/polybutadiene rubber (BR) and multi-walled carbon nanotubes (MWCNTs) and to enhance the state of filler dispersion in the rubber matrix, a series of ionic liquids was tested ([AMIM][Cl], [EMIM][SCN], [MOIM][Cl], 3-(triphenylphosphonic)-1-sulfonic acid tosylate, trihexyl(tetradecyl)phosphonium decanoate). It was found that in the presence of especially one ionic liquid, 1-allyl-3-methylimidazolium chloride [AMIM][Cl], for the blend of SSBR/BR, a threefold increase of tensile strength was achieved with only at ~3 wt% of MWCNTs loading. The enhancement in the mechanical properties was explained through the chemical coupling between MWCNTs and rubber chains by 1-allyl-3-methylimidazolium chloride [AMIM][Cl], as it was evidenced by Raman spectra, dynamic mechanical analysis (DMA) and electrical properties.²⁴⁵

Kreyenschulte²⁴⁶ conducted investigations on the interaction between 1-allyl-3-methylimidazolium chloride [AMIM][Cl] and carbon black (CB) and its influence on the properties of the blend of SSBR/BR and EPDM. An improvement in composites conductivity was achieved, however the addition of [AMIM][Cl] contributed to a significant increase in the

elongation at break resulting from the reduction in the crosslink density of the rubber composites.

Table 7 Some applications of ILs in the rubber composites and their influence on the characteristic properties.

Type of rubber	Type of filler	Type of IL	Composite Properties	Ref.
NBR	-	[Li][TFSI], imidazolium-type zwitterion	High ionic conductivity at 25 wt% salt content, at 9.2 wt% imidazolium-type zwitterion $\sigma = 5.6 \times 10^{-6}$ S/cm.	197
NBR	-	[BMIM][TFSI]	Solid polymer electrolyte, high ionic conductivity of $\sigma = 2.54 \times 10^{-4}$ S/cm.	235
NBR	-	1,3-dialkylimidazolium benzalkonium and phosphonium cations with 2-mercaptobenzothiazolate anion	Antimicrobial activity, accelerated vulcanization process, reduction of 2-mecrcaptobenzothiazole in sulfur-based cure system.	191
NBR	ZnO	alkylimidazolium [Cl], [Br], [PF ₆], [BF ₄], alkylphosphonium [Br], alkylammonium [Br]	Accelerated vulcanization process, homogenous distribution of ZnO in elastomer matrix.	192
SBR	Silica	1-methylimidazlium mercaptopropionate	Considerably improved mechanical properties and abrasion resistance.	242
SBR	Halloysite nanotubes (HNTs)	[BMIM][PF ₆]	Accelerated curing process, superior mechanical properties, improved filler dispersion.	244
SBR	Halloysite nanotubes (HNTs)	1-methylimidazolium mercaptopropionate, <i>bis</i> (1-methylimidazolium) mercaptosuccinate	Substantial hydrogen bond between HNTs and ILs largely facilitated the HNTs dispersion in the rubber matrix. Significant improvement in mechanical properties.	190
S-SBR	MWCNTs	[AMIM][Cl],[EMIM][SCN], [MOIM][Cl]. 3-(Triphenylphosphonic)-1-sulfonic acid tosylate. Trihexyl(tetradecyl) phosphonium decanoate.	Strong level of reinforcement and dispersion of MWCNTs in the presence of [AMIM][Cl], superior electrical properties.	245

SSBR/ BR	Carbon black	[AMIM][Cl]	Increased conductivity and slightly increased <i>EB</i> , [AMIM][Cl] acts as a local plasticizer at the carbon black surface, weaker filler network.	246
EPDM	Carbon black	[AMIM][Cl]	A huge increase in <i>EB</i> and reduction in crosslink density.	246
HNBR	MWCNT-OH	Cations: [EMIM] ⁺ , [BMIM] ⁺ , [BMPyr] ⁺ . Anions: [BF ₄] ⁻ , [PF ₆] ⁻ , [TFSI] ⁻	Reinforcing effect, homogenous solids, tensile strength and <i>T_g</i> decreased with increasing IL content.	228
CR	MWCNTs	[BMIM][TFSI]	Highly electro-conducting and elastic materials $\sigma = 0.1$ S/cm, <i>EB</i> > 500 %.	229

Due to the growing interest in developing conductive materials, composites based on various combinations of polymer matrices, fillers and ionic liquids have been synthesized and investigated to identify the relationship between the material composition, processing parameters and final product properties. Such information is indispensable for designing a material with specific characteristics and applications. Most studies have examined the ability of IL-modified carbon nanotubes or carbon black to improve rubber conductivity and microstructure homogeneity, while studies of the impact of high levels of pure ionic liquids on the conductivity and mechanical properties of neat rubbers or composites containing nonconductive fillers have been limited. Moreover, the majority of studies have examined the use of ionic liquids in sulfur-vulcanized systems containing active curing reagents such as accelerators, activators and sulfur. In this study, an ionic elastomer based on XNBR and LDH was doped with different types of ionic liquids at various concentrations to obtain a material representing the best compromise between mechanical properties and ionic conductivity. The results presented in this thesis are novel and could be interesting for researchers in the field.

2. AIM OF THE WORK

Fillers are important for enhancing the properties of elastomers and can therefore be used for the development of a new generation of composite materials with improved or new functionalities. This work focused on the fabrication and characterization of elastomer composites containing layered fillers and ionic liquids with improved mechanical and ionic conductivity properties. The impact of layered fillers of different origins with various particle aspect ratios, specific surface areas and elemental compositions on the reinforcement of nitrile rubbers (acrylonitrile-butadiene rubber (NBR), and carboxylated acrylonitrile-butadiene rubber, (XNBR)) composites was explored. Some of the layered minerals were investigated not only in terms of their use as reinforcing fillers for rubbers but also as crosslinking agents, gas barriers and UV stability enhancers. The multifunctionality of these fillers makes them interesting materials with broad potential applicability for the manufacture of high-performance elastomers. The layered fillers included cationic clays (natural and synthetic hectorite), anionic clays (hydrotalcites or magnesium-aluminum layered double hydroxides (MgAl-LDHs)) and graphene-based materials.

The use of layered minerals in rubber formulations has ecological and economic importance and offers the potential for environmentally friendly rubber products. Moreover, the melt mixing method used in this work for the preparation of rubber/layered filler composites is one of the most eco-friendly routes that excludes the use of organic solvents and is the most suitable for industrial-scale production.

Moreover, to enhance the ionic conductivity of the selected rubber/layered filler composites characterized by significantly improved mechanical properties, room temperature imidazolium ionic liquids (RTILs) exhibiting high ionic conductivity were employed. Such organic compounds may play a role not only as ionic conductivity enhancers in the rubber material but also as processing and dispersion aids in the preparation of elastomer composites. This work sought a compromise between the type and concentration of imidazolium ionic liquids and the enhancement in mechanical strength and ionic conductivity of elastomer composites.

3. MATERIALS

3.1. ELASTOMERS AND CURING AGENTS

■ **Acrylonitrile-butadiene rubber (NBR)** – Perbunan 2845 F, bound acrylonitrile content 28 wt%, Mooney viscosity (ML1+4(100 °C):45) was provided by LANXESS, (Leverkusen, Germany). The NBR compounds were crosslinked using conventional sulfur cure system. The NBR rubber mixture composition was as follows: NBR rubber (100 phr), sulfur (2 phr), mercaptobenzothiazole (2 phr), zinc oxide (5 phr), stearic acid (1 phr).

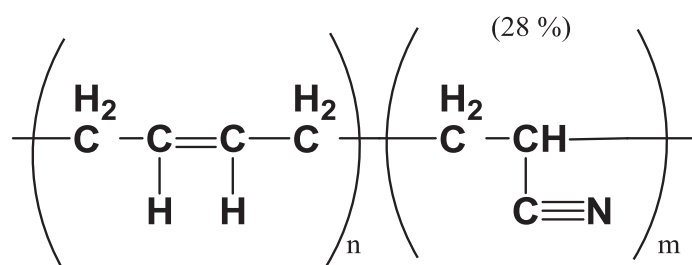


Figure 15 NBR chain structure.

■ **Carboxylated acrylonitrile-butadiene rubber (XNBR)** – Krynac X 750 (7 wt% carboxyl groups content, 27 wt% acrylonitrile content, Mooney viscosity (ML1+4(100 °C):47)) was supplied by LANXESS (Leverkusen, Germany). The XNBR compounds contained 5 phr of zinc oxide (used as a curing agent) of the same company.

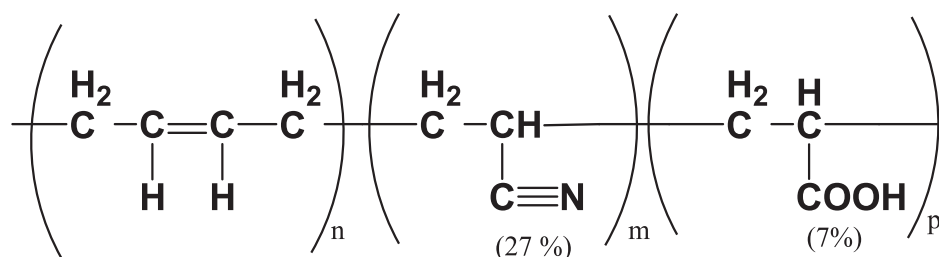


Figure 16 XNBR chain structure.

3.2. LAYERED FILLERS

- **Natural hectorite (NAT HEC)** – A naturally occurring magnesium lithium smectite, named hectorite (chemical formula: $\text{Na}_{0.3}(\text{Mg}, \text{Li})_3\text{Si}_4\text{O}_{10}(\text{OH})_2$), was obtained from a raw hectorite material deposit (Hector) located in San Bernardino County, California (USA) (*Ward's Natural Science Establishment, Inc.*). The smectite used in this study contained approximately 50 % carbonated impurities.

- **Synthetic hectorite (SYN HEC)** – Synthetic hectorite clay silicate with the chemical formula: $\text{Na}_{(0.67)}(\text{Mg}, \text{Li})_6\text{Si}_8\text{O}_{20}(\text{OH}, \text{F})_4$ was supplied by *ABCR* (Karlsruhe, Germany GmbH). The product code was AB111153.

- **PURAL® MG 30 HT (LDH30), PURAL® MG 63 HT (LDH63), PURAL® MG 70 HT (LDH70)** – Hydrotalcite-like compounds (magnesium-aluminum hydroxycarbonates) with the chemical formula: $\text{Mg}_{2x}\text{Al}_2(\text{OH})_{4x+4}\text{CO}_3 \cdot n\text{H}_2\text{O}$ synthesized by hydrolysis of heterometallic alcoholates were kindly supplied by *Sasol GmbH* (Hamburg, Germany). The three types of MgAl-LDH investigated were designated as LDH30, LDH63 and LDH70, respectively.

Table 8 Product information about magnesium-aluminum hydroxycarbonates according to producer Sasol technical data sheets.

Characterization:	Pural MG 30 HT	Pural MG 63 HT	Pural MG 70 HT
Surface	hydrophilic	hydrophilic	hydrophilic
MgO [%]	28.8	63.4	69.7
Al ₂ O ₃ [%]	71.2	36.6	30.3
Surface area [m ² /g] after activation 3h, 550° C	276	200	196
L.O.I. [%]	34.2	44.1	45.0 max
SiO ₂ [ppm]	350 max	350 max	350 max
Fe ₂ O ₃ [ppm]	200 max	200 max	200 max
Loose bulk density [g/ml]	0.4	0.35	0.5
Particle size < 25 µm, [%]	25.2	-	41.1
Particle size < 45 µm, [%]	48.2	-	72.4
Particle size < 90 µm, [%]	91.5	-	99.8

- **Hydrotalcite (HT)** – Synthetic hydrotalcite, magnesium-aluminum double layered hydroxide MgAl-LDH (magnesium-aluminum hydroxycarbonate) (chemical formula: $\text{Mg}_6\text{Al}_2(\text{CO}_3)(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$) with a density of 2.0 g/mL at 25 °C was obtained from *Sigma Aldrich* (Schnelldorf, Germany GmbH).
- **xGnP-C-300, xGnP-C-500, xGnP-C-750** – xGnP® graphene nanoplatelets (grade C) consisting of aggregates of sub-micron platelets with a particle diameter of less than two microns, a typical particle thickness of a few nanometers, and a surface area ranging from 300 to 750 m²/g, were purchased from *XG Science Inc.* (Lansing, Michigan, USA). The three types of graphene nanoplatelets employed were designated as xGnP-C-300, xGnP-C-500, xGnP-C-750 and had specific surface areas of 300, 500, 750 m²/g, respectively.
- **xGnP-M-5** – xGnP® graphene nanoplatelets (Grade M) with an average thickness of approximately 6 nanometers and a typical surface area of 120 to 150 m²/g was supplied by *XG Science Inc.* (Lansing, Michigan, USA). Grade M is available with average particle diameters of 5, 15 or 25 microns.
- **Exfoliated graphene** – Exfoliated graphene with the trade name exfoliated graphene nanopowder 0541DX (Graphene NanoPowder (C, 6-8 nm)) was supplied in platelet and pristine forms by *Skyspring Nanomaterials, Inc.* (Westhollow Drive, Houston, USA). According to the technical data sheet, the product had an average layer thickness of approximately 6-8 nanometers, an average particle diameter of 15 microns and a typical surface area of 120-150 m²/g.

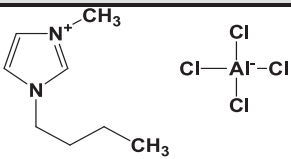
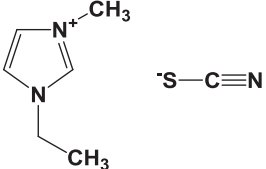
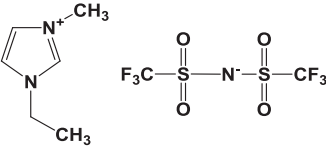
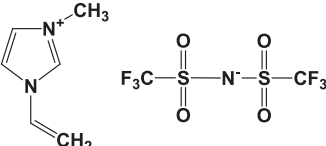
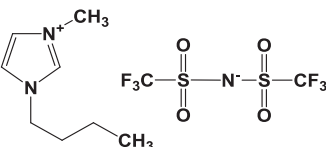
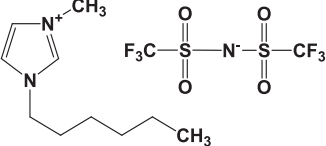
Table 9 Product information about xGnP-M according to producer XG Science technical data sheets.

Characterization:		Parallel to surface	Perpendicular to surface
Density	[g/c ³]		2.2
Carbon content	[%]		>99.5
Thermal conductivity	[W/mK]	3 000	6
Tensile modulus	[GPa]	1 000	N/A
Tensile strength	[GPa]	5	N/A
Electrical conductivity	[S/m]	107	102

3.3. IMIDAZOLIUM IONIC LIQUIDS (ILs)

- 1-Butyl-3-methylimidazolium tetrachloroaluminate [BMIM][AlCl₄], assay $\geq 94.5\%$
- 1-Ethyl-3-methylimidazolium thiocyanate [EMIM][SCN] assay $\geq 95\%$, impurities $< 1\%$ water anion traces: chloride (Cl⁻) $\leq 1\%$, were supplied by *Sigma Aldrich* (Germany).

Table 10 Some of physicochemical properties of ionic liquids (at 20 °C) according to producer technical data sheet and literature.

IL	Chemical structure	MM ^a	MP ^b	Vis. ^c	EW ^d	σ ^e
		[g/mol]	[°C]	[cP]	[V]	[mS/cm]
[BMIM][AlCl ₄]		308.01	-10	32	-	9.5 ²⁰²
[EMIM][SCN]		169.25	-6	22 ²¹¹	3.2	21.0 ^{212,217}
[EMIM][TFSI]		391.31	-16	34 ²²³	4.7	8.8 ²²²
[AMIM][TFSI]		403.32	-2	35	5.3	2.8
[BMIM][TFSI]		419.36	-4	61	5.0	3.9 ²²²
[HMIM][TFSI]		447.42	-7	102	4.7	1.9

^a Molecular mass; ^b melting point; ^c viscosity; ^d electrochemical window; ^e conductivity.

- 1-Ethyl-3-methylimidazolium *bis*(trifluoromethylsulfonyl)imide [EMIM][TFSI],
 - 1-Allyl-3-methylimidazolium *bis*(trifluoromethylsulfonyl)imide [AMIM][TFSI],
 - 1-Butyl-3-methylimidazolium *bis*(trifluoromethylsulfonyl)imide [BMIM][TFSI],
 - 1-Hexyl-3-methylimidazolium *bis*(trifluoromethylsulfonyl)imide [HMIM][TFSI]
- were supplied by *IoLiTec* Ionic Liquids Technologies GmbH (Heilbronn, Germany).

3.4. OTHER MATERIALS

- Toluene pure – *POCh* (Gliwice, Poland);
- Ammonia 25 % solution – *POCh* (Gliwice, Poland);
- Sulfur S₈ – curing substance, *ZCh Siarkopol* (Tarnobrzeg, Poland);
- Mercaptobenzothiazole (MBT) – accelerator in the sulfur vulcanization, *Chemical Worldwide Business* Sp. z o.o. (Słupca, Poland);
- Zinc oxide (ZnO) – activator in the sulfur vulcanization or curative for XNBR, *Lanxess* (Leverkusen, Germany);
- Stearic acid – activator in the sulfur vulcanization, *Sigma Aldrich* (Germany).

4. CHARACTERIZATION TECHNIQUES

4.1. SCANNING ELECTRON MICROSCOPY (SEM)

The morphology of the layered filler particles was evaluated by scanning electron microscopy (SEM) with a LEO 1530 Gemini scanning electron microscope (Zeiss/LEO, Oberkochen, Germany).

The fractured surfaces of rubber composites were inspected using a scanning electron microscopy equipped with an energy dispersive spectrometer (EDS) with a microscope SEM HITACHI S800 (Tokyo, Japan) at the accelerating voltage of 15 kV. Prior to SEM observations, liquid nitrogen-fractured surfaces of the composites were Au/Pd sputtered (with a thickness of approximately 10 nm).

4.2. BET N₂ ADSORPTION MEASUREMENTS

Specific surface area was measured based on nitrogen adsorption at 77 K over the relative pressure (P/P_0) range of $10^{-6} - 1$ using a Gemini 2360 V2.01 porosimeter (Micromeritics, USA). Measurements were performed according to the Brunauer-Emmett-Teller (BET) nitrogen adsorption method. The samples were degassed for 20 hours at 100 °C under vacuum. The samples were then subjected to a 99-point BET surface area analysis and full adsorption isotherms were collected.

4.3. X-RAY DIFFRACTION (XRD)

Powder X-ray diffraction patterns were collected at room temperature using a PANalytical X'Pert Pro MPD diffractometer with a Bragg-Brentano reflecting geometry and CuK α radiation from a sealed tube (Almelo, Netherlands). Data were collected in the 2θ range of $2 - 70^\circ$ with a 0.0167° step size and a 20-s exposure per step. The interlayer distance of mineral layers d was calculated according to the Bragg's equation, **Equation (2)**.

$$n\lambda = 2d \sin\theta \quad (2)$$

$$\lambda = 1.54178 \text{ \AA} \quad (3)$$

where: λ – wavelength (**Equation (3)**), d – distance between layers, θ – Bragg's angle.

4.4. OIL ABSORPTION PARAMETER DBPA

The oil absorption parameter (DBPA) of fillers was measured according to ASTM D2414 using Absorptometer C equipment Brabender Measuring Mixer N50 (Duisburg, Germany). The process parameters were: sample weight 20 g, titration rate 4.0 ml/min. The oil used in this study was dibutyl phthalate DBP.

4.5. THERMOGRAVIMETRIC ANALYSIS (TGA)

Thermal decomposition of the rubber compounds was performed using a TA Instruments Q500 Thermogravimetric Analyzer (TGA) (New Castle, USA). Samples were analyzed in the presence of nitrogen or air atmosphere from 10 °C to 600 °C using a heating rate of 10 °C/min.

4.6. X-RAY PHOTOELECTRON SPECTROSCOPY ANALYSIS (XPS)

The surface elemental composition of the fillers and XNBR composites was determined by X-ray photoelectron spectroscopy (XPS) analysis. XPS spectra were recorded on a Prevac X-ray photoelectron spectrometer (Rogow, Poland) equipped with a SES 2002, VG Scienta hemispheric electron energy analyzer (Uppsala, Sweden) and an aluminum (mono) K_{α} source (1486.6 eV). The aluminum K_{α} source was operated at 15 kV and 25 mA. The spectrometer was calibrated using Ag 3D BE = 368.27 eV core-level photoemission spectra. For rubber samples, a high-resolution survey (pass energy 50 eV) was performed in the appropriate spectral regions. All core level spectra were referenced to the C 1s neutral carbon peak at 284.6 eV.

4.7. INVERSE GAS CHROMATOGRAPHY (IGC)

Inverse gas chromatography (IGC) was used to determine the surface properties of the mineral fillers: natural hectorite²⁴⁷ and synthetic hydrotalcite.⁹⁸ IGC measurements at infinite dilution conditions were performed with a Hewlett Packard 5890A gas chromatograph equipped with a high-sensitivity flame ionization detector. Measurements were carried out using steel columns measuring with the inner diameter of 3.17 mm and the length of 360 mm. The measurements for each of the powders were performed at four temperatures. The columns were conditioned at 100 °C for 24 h before all measurements. Helium was used as the carrier gas with a flow rate of 20 cm³/min, measured with a soap flow-meter. To ensure adsorption at infinite dilution conditions, the amount of the gas probe

(about 10 μL) injected into the column approached the detector sensitivity limit. Each probe was injected into the column three times. The hold-up volume of the columns was determined by injecting methane. The calculation method for retention time was based on the maximum of chromatographic peak. IGC measurements were performed at temperature ranges of 70 – 100 $^{\circ}\text{C}$ and 240 – 270 $^{\circ}\text{C}$ because of the different surface properties of the examined fillers at such temperatures.

The surface interactions of the fillers with various polar and non-polar molecular probes were investigated.²⁴⁸ The non-polar probes used were *n*-alkanes, from pentane to decane ($\text{C}_5 - \text{C}_{10}$), and branched alkanes, 2,5-dimethylhexane (DMH) and 2,3,4-trimethylpentane (TMP). Diethyl ether (Et_2O) and tetrahydrofuran (THF) were used as electron donors, chloroform (CHCl_3) was used as an electron acceptor, and bipolar solvents of acetonitrile (ACN) and benzene (C_6H_6) were used as polar probes. The probe characteristics are presented in **Table 11**.

Table 11 Characteristics of molecular probes (DN , AN^* – Gutmann's electron donor (DN) and acceptor (AN^*) numbers, χ_T – topology indices).²⁴⁹

Probe	DN [kcal/mol]	AN*	DN/AN	χ_T
Tetrahydrofuran (THF)	20.6	0.5	41.20	4.85
Chloroform (CHCl_3)	0.0	5.4	0.0	3.21
Diethyl ether (Et_2O)	19.2	1.4	13.71	4.77
Benzene (C_6H_6)	3.5	0.17	20.59	4.88
Acetonitrile (ACN)	14.1	4.7	3.00	2.60
Pentane	0	0	0	5.00
Hexane	0	0	0	6.00
Heptane	0	0	0	7.00
Octane	0	0	0	8.00
Nonane	0	0	0	9.00
Decane	0	0	0	10.00
2,3,4-trimethylpentane (TMP)	0	0	0	7.40
2,5-dimethylhexane (DMH)	0	0	0	7.68

The free adsorption energy was calculated according **Equation (4)**:

$$-\Delta G_A = RT \ln \frac{B \times V_n}{S \times W} \quad (4)$$

where: V_n – the retention volume of a known substance injected into a column; $B = 2.99 \times 10^2$ if De Boer's definition of surface pressure in the standard adsorbed state is

applied;²⁵⁰ S – the specific surface area of the adsorbent; W – the mass of adsorbent in column. For a given system, B , S and W are constant and **Equation (4)** changes^{251,252} to **Equation (5)**:

$$-\Delta G_A = RT \ln V_n + K \quad (5)$$

where: K – a constant that is dependent on the choice of the reference state of the adsorbed probe. The net retention volume was determined by **Equation (6)**:

$$V_n = jD'(t_R - t_0) = jD't_n \quad (6)$$

with

$$D' = D \frac{T_E}{T_R} \frac{P_0 - P_{0W}}{P_0} \quad (7)$$

where: j – the James-Martin correction factor related to the gas compressibility; t_R – the time the probes occupied the column; t_0 – the zero retention reference time (determined for methane); t_n – the adjusted retention time; D – the flow rate of the carrier gas measured by flow-meter; T_E – the column temperature; T_R – the flow-meter temperature; P_0 – the atmospheric pressure; P_{0W} – the vapor pressure of water at flow-meter temperature.

Two types of interactions between the adsorbate and the adsorbent are considered: the London's dispersive interactions and the specific interactions (**Equation (8)**). Such interactions occur simultaneously and are evaluated indirectly because they are impossible to determine separately from one another.

$$\Delta G = \Delta G^D + \Delta G^{SP} \quad (8)$$

The dispersive component γ_s^D of the surface energy was determined using Dorris and Gray's method²⁵³ with the retention times of n -alkanes and taking into account that non-polar probes exclusively undergo London's dispersive interactions with solid surfaces with $\Delta G^{SP} = 0$ in **Equation (8)**.

The dispersive component of the surface energy is provided by **Equation (9)**:

$$\gamma_s^D = \frac{(-\Delta G_{CH_2})^2}{4N_A^2 \cdot a_{CH_2} \cdot \gamma_{CH_2}} \quad (9)$$

whereas

$$\Delta G_{CH_2} = -RT \ln \left(\frac{V_{n+1}(C_{n+1}H_{2n+4})}{V_n(C_nH_{2n+2})} \right) \quad (10)$$

where: $-\Delta G_{CH_2}$ – the slope of the straight line referred to as the “alkane line” and represents the specific free energy of a single CH_2 group adsorption (desorption); N_A – Avogadro’s number, a_{CH_2} is the area occupied by a CH_2 group (0.06 nm^2 , according to Gray); γ_{CH_2} – the surface energy of a solid consisting only of CH_2 groups (*e.g.* polyethylene)²⁵⁴ as given by **Equation (11)**, where t is the temperature in °C.

$$\gamma_S^D = 35.6 - 0.058(t - 20)(\text{mJ/m}^2) \quad (11)$$

The relationship between the dispersive interaction parameter and the molar free energy of adsorption for n -alkanes is linear. The polar probes interact more strongly with the solid, and their corresponding points are situated above the “alkane line”. The specific adsorption energy can be measured by taking the difference between the values of adsorption energy of polar probes and the energy of n -alkane adsorption. According to the Papirer and coworkers,²⁵⁵ the specific adsorption energy is provided by **Equation (12)**, where: $V_{n(s.p.)}$ – the net retention volume of a polar probe; $V_{n(s.w.)}$ – net the retention volume of a non-polar probe (alkane).

$$-\Delta G_A^{SP} = RT \ln \frac{V_{n(s.p.)}}{V_{n(s.w.)}} \quad (12)$$

The ability of a solid to undergo specific interactions is also characterized by the specific interaction parameter, S_f (**Equation (13)**)²⁵⁶ and is calculated as the ratio of the polar probe molar adsorption energy on the solid surface ΔG_A to the adsorption energy of a true or hypothetical alkane with the same structural characteristics and London’s parameter as the given polar probe, $\Delta G_{alk.}$ ²⁵⁷

$$S_f = \frac{\Delta G_A}{\Delta G_{alk}} \quad (13)$$

The molar enthalpy ΔH_A of the adsorption interaction is determined according to **Equation (14)** and **Equation (15)** and from values of ΔG_A measured at various temperatures, where T is the absolute temperature in K.²⁵⁸ ΔH_A^{SP} was calculated from ΔG_A^{SP} using the same relationship.

$$\Delta H_A = \frac{d(\frac{\Delta G_A}{T})}{d(\frac{1}{T})} \quad (14)$$

Interactions between the adsorbate and the adsorbent (solid molecular probe) can be considered as acid-base interactions.^{259,260} therefore, the acceptor K_A and donor K_D interactions parameters were estimated based on **Equation (15)**. Parameters K_A and K_D characterize the degree of Lewis acidity of the electron acceptors and the degree of Lewis basicity of the electron donors, respectively, on solid surfaces.

$$-\Delta H_A^{SP} = K_A DN + K_D AN^* \quad (15)$$

The measurement of ΔH_A^{SP} for various probes with different values of Gutmann's donor (DN) and acceptor (AN^*) numbers enables plotting of **Equation (16)** from which the K_A and K_D parameters can be determined as the coefficients of a straight line.

$$\frac{-\Delta H_A^{SP}}{AN^*} = K_A \frac{DN}{AN^*} + K_D \quad (16)$$

Depending on the structural heterogeneity of the solid surface, there are differences in the energy of interaction with isomeric alkanes. The values of adsorbate surface roughness are morphological indexes, and could be determined based on the retention volume ratio of octane and its branched isomers, such as 2,3,4-trimethylpentane and 2,5-dimethylhexane (**Equation (17)** and **Equation (18)**).²⁶¹

$$IM_{TMP} = \frac{V_{N(octane)}}{V_{N(TMP)}} \quad (17)$$

$$IM_{DMH} = \frac{V_{N(octane)}}{V_{N(DMH)}} \quad (18)$$

4.8. CURING CHARACTERISTICS

The curing characteristics of the rubber composites were determined using a MonTech Moving Die Rheometer MDR 3000 (Buchen, Germany) at 160 °C for 120 minutes. A sinusoidal strain of 7 % was applied at a frequency of 1.67 Hz. The optimum cure time t_{90} , scorch time t_{A2} , minimum torque ML , maximum torque MH , and delta torque ΔM were determined from the curing curves. The mixed stocks were cured in a standard hot press at 160 °C for t_{90} . The difference between MH and ML of the vulcanization curve was defined as the ultimate rheometric torque ΔM . The time required to reach 90 % of ΔM was termed t_{90} – optimal curing time; t_{A2} – (scorch time) the time at which the torque rises above ML by 2.0 dNm.

Reinforcing activity of tested fillers was compared using Wolff coefficient of activity α_f .²⁶² M_{spec} and α_f were calculated according to **Equation (19)** and **Equation (20)**.

$$M_{spec} = \frac{\Delta M_x}{\Delta M_0} - 1 \quad (19)$$

$$M_{spec} = \alpha_f \cdot \frac{m_x}{m_p} \quad (20)$$

where: ΔM_x – the torque increment of the rubber mix containing x phr of filler during vulcanization; ΔM_0 – the torque increment of non-filled rubber during vulcanization; m_x – weight of added filler; m_p – weight of polymer in the mix.

Cure rate index (CRI) was calculated according to **Equation (21)**:

$$CRI = \frac{100}{(t_{90} - t_{42})} \quad (21)$$

4.9. CROSSLINK DENSITY MEASUREMENTS

The crosslinking density in the cured network was determined by the method of equilibrium swelling. The vulcanizates were swollen in toluene for 48 h at room temperature. The swollen samples were then weighed on a torsion balance, dried in a dryer at a temperature of 60 °C to a constant weight, and reweighed after 48 h. The volume fraction of rubber in the swollen gel (V_r) was calculated from the following equation which is based the simple additive rule of volumes as follows:

$$V_r = \frac{(D - FH)/\rho_r}{\frac{D - FH}{\rho_r} + A_0/\rho_s} \quad (22)$$

where: H – initial weight of the test specimen; D – deswollen weight of the test specimen (until constant weight); F – weight fraction of the insoluble components of the rubber mix, such as fillers; A_0 – weight of the absorbed solvent ($A_0 = \text{immediate weight} - H$); ρ_r – density of the rubber; ρ_s – density of the solvent, here density of toluene $\rho_s = 0.867$ [g/cm³] (20 °C).

The crosslink density (v_T) was calculated using the Flory-Rehner equation, **Equation (23)**,²⁶³ and the Huggins parameter χ for elastomer-solvent interaction at a temperature of 20 °C are given by **Equation (24)** and **Equation (25)**.

$$v_T = - \frac{\ln(1 - V_r) + V_r + \chi \cdot V_r^2}{V_s \left(\frac{1}{V_r^3} - \frac{V_r}{2} \right)} \quad (23)$$

where: v_T – crosslink density; V_r – the volume fraction of elastomer in the swollen gel; and V_S – the molar volume of solvent.

For NBR elastomer: $\chi = 0.381 + 0.671 \cdot V_r$ (24)

For XNBR elastomer:²⁶⁴ $\chi = 0.487 + 0.228 \cdot V_r$ (25)

To determine the content of ionic crosslinks in the elastomer network, samples were swollen in toluene in a desiccator with saturated ammonia vapor (25% aqueous solution). The percentage of ionic crosslinks (Δv) formed in XNBR was determined by their decomposition under the influence of ammonia²⁶⁵ and was calculated from **Equation (26)**.²⁶⁶

$$\Delta v = \frac{v_T - v_A}{v_T} \cdot 100 \% \quad (26)$$

where: v_A – the crosslink density determined for samples treated with ammonia vapour using the Huggins elastomer-solvent interaction parameter χ described by **Equation (27)**.²⁶⁶

$$\chi = 0.483 + 0.320 \cdot V_p \quad (27)$$

4.10. FOURIER-TRANSFORM INFRARED SPECTROSCOPY (FTIR)

Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra were recorded on a Thermo Scientific Nicolet 6700 FT-IR spectrometer (Waltham, MA, USA) at room temperature with a resolution of 4 cm⁻¹ and a 64-scan signal from 600 – 4000 cm⁻¹ in absorbance mode.

4.11. DYNAMIC MECHANICAL ANALYSIS (DMA)

Dynamic mechanical analysis (DMA) was performed on a TA Instruments Q 800 Dynamic Mechanical Analyzer (New Castle, USA) operating in tension mode at a frequency of 10 Hz. Storage modulus (E'), loss modulus (E'') and loss tangent ($\tan \delta$) were measured in tension mode in the temperature range of -80 to 100 °C, at frequency 1, 3, 5, 10, 20, 30, 70 and 100 Hz with a heating rate of 2 °C/min.

4.12. DIFFERENTIAL SCANNING CALORIMETRY (DSC)

DSC measurements (Q 200 DSC, TA Instrument, USA) of samples were performed at a heating rate of 10 °C/min in the temperature range -80 to 180 °C under a nitrogen atmosphere. The glass transition temperatures were determined at the midpoint of the step.

4.13. BROADBAND DIELECTRIC SPECTROSCOPY (BDS)

Dielectric measurements were conducted with broadband dielectric spectroscopy (Novocontrol alpha analyser, Hundsagen, Germany) in the frequency range from 10^{-1} to 10^7 Hz at room temperature. The samples were placed between two copper electrodes with diameters of 20 mm.

4.14. AIR PERMEABILITY

The through-plane air permeability of composites was determined by manometric method in accordance with the ASTM standard D1434, using circular samples 30 mm in diameter and 1 mm in thickness. The tests were conducted by using atmospheric air at room temperature. Gas permeability P was determined as volume of gas passing through a membrane of unit thickness, per unit area and unit time, under unit partial - pressure difference between the two sides of the material. P is expressed in mole meters per square meter second Pascal [$\text{mol}\cdot\text{m}/\text{m}^2\cdot\text{s}\cdot\text{Pa}$].

4.15. TENSILE TESTING

Tensile properties were characterized on a ZWICK 1435 tensile testing machine from the Zwick Roell Group (Ulm, Germany). The moduli at 100 %, 200 % and 300 % elongation (SE_{100} , SE_{200} , SE_{300}), tensile strength (TS) and elongation at break (EB) were measured at room temperature with a crosshead speed of 500 mm/min. For testing, type 2 dumb-bell specimens were prepared according to the ISO-37-2005 standard. Five different dumbbell-shaped specimens were tested, and the average value for each formulation was reported.

4.16. HARDNESS SHORE A

Hardness testing of vulcanizates was performed with Shore type A durometer Zwick Roell Group (Ulm, Germany) at room temperature according to the standard PN-80/C-04238. The measuring error $\pm 1^\circ\text{Sh}$.

4.17. TEAR STRENGTH

Tear strength tests were performed with a universal material testing machine Zwick Roell Group (Ulm, Germany) at room temperature according to the standard ISO 34-1:2010. The measuring error ± 10 %.

4.18. THERMO-OXIDATIVE AGING AND RESISTANCE TO UV RADIATION

(A) The thermo-oxidative aging test. Samples were subjected to the action of air at elevated temperature (100 °C) for 10 days in a dryer with thermo-circulation (Binder Inc., New York, USA).

(B) The UV-aging test. Accelerated UV aging studies were carried out for rubber composites using a UV2000 Atlas solar simulation chamber (Linsengericht, Germany) (UV-A, $\lambda = 342$ nm). Sample aging lasted for 120 h during which alternating day (radiation intensity 0.7 W/m^2 , temperature 60 °C, duration 8 h) and night (without UV radiation, temperature 50 °C, duration 4 h) segments were repeated.

After aging, stress-strain tests were performed. The thermo-oxidative aging coefficients (K_T) and UV aging coefficients (K_{UV}) were calculated according to the **Equation (28)**.

$$K = \frac{(TS \cdot EB)_{after \text{ aging}}}{(TS \cdot EB)_{before \text{ aging}}} \quad (28)$$

where: TS – tensile strength [MPa], EB – elongation at break [%]. In addition, the crosslink densities of the samples subjected to UV radiation were measured by the swelling method using toluene as the solvent, as described above.

4.19. COLORIMETRIC STUDIES

The color of the obtained composites was measured using a CM-3600d spectrophotometer from Konica Minolta Sensing, Inc. (Osaka, Japan). The instrument provided the color in terms of the CIE L^*a^*b color space system, where L represents the lightness (or brightness), a and b are color coordinates, where $+a^*$ is the red direction, $-a^*$ is the green direction, $+b^*$ is the yellow direction, and $-b^*$ is the blue direction. Changes in the individual components allowed estimation of the total change of color ΔE for composites subjected to elevated temperature. The spectral range of the apparatus was 360 – 740 nm and ΔE was calculated by **Equation (31)**.

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2} \quad (29)$$

where ΔL corresponds to the difference in the brightness intensity between light and dark, Δa corresponds to the difference of intensity between green and red, Δb corresponds to the difference of intensity between blue and yellow, and the ΔE implies the difference in the color of the sample before and after heating.

5. RESULTS AND DISCUSSION

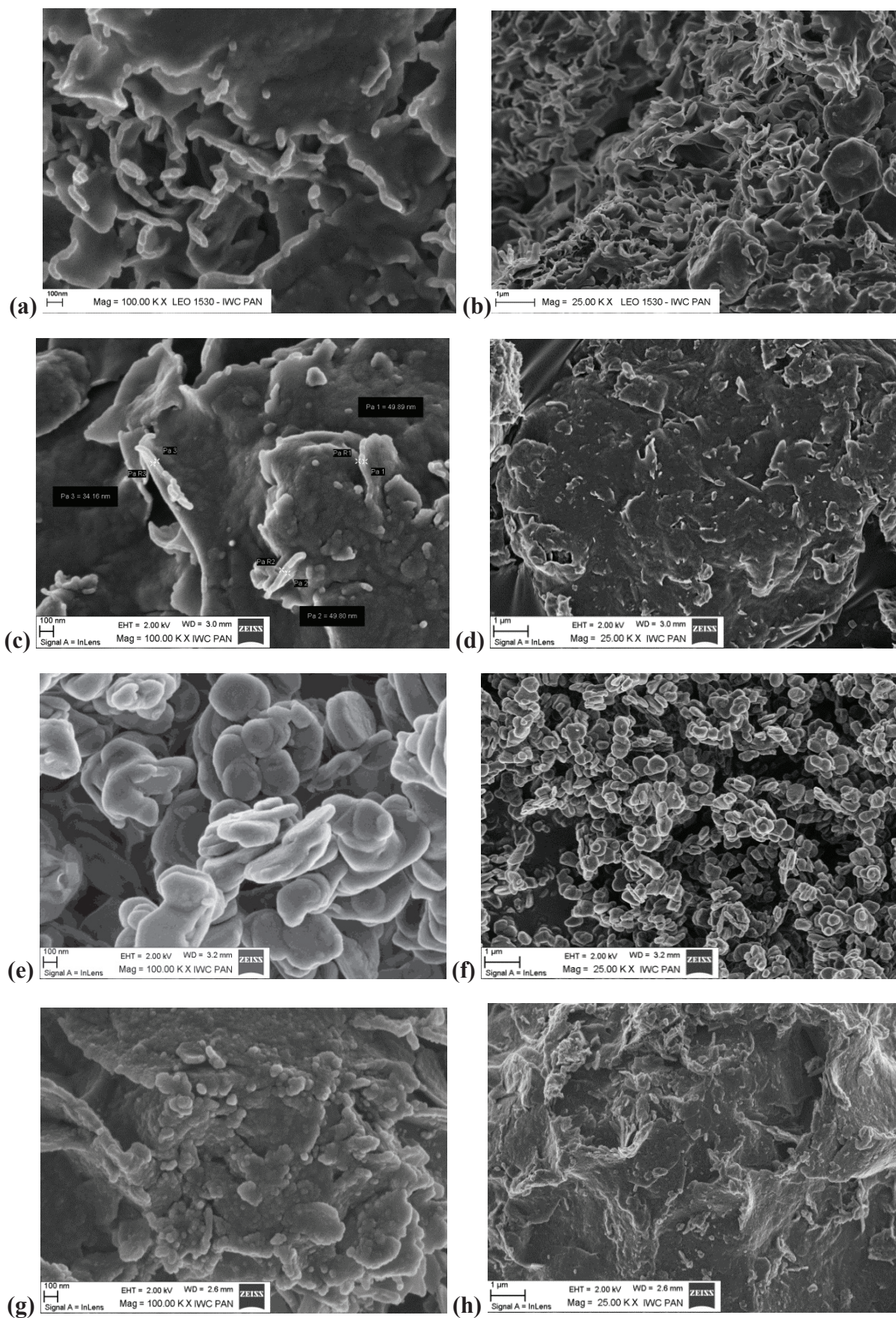
5.1. RUBBER COMPOSITES CONTAINING MINERAL LAYERED FILLERS

5.1.1. CHARACTERIZATION OF THE MORPHOLOGICAL, STRUCTURAL, THERMAL AND SURFACE PROPERTIES OF LAYERED FILLERS

INTRODUCTION: This section focuses on the evaluation of the morphological, structural, thermal and surface characteristics of the layered minerals (natural hectorite (NAT HEC), synthetic hectorite (SYN HEC) and the magnesium-aluminum layered double hydroxides (HT, LDH30, LDH63, LDH70)) using the following techniques: scanning electron microscopy (SEM), X-ray powder diffraction (XRD), N₂ adsorption measurements, Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS) and inverse gas chromatography (IGC).

5.1.1.1. SEM observations of filler particles morphology

Scanning electron microscopy micrographs at various magnifications (**Figure 17 a-l**) revealed that the layers of cationic clays (NAT HEC, SYN HEC) and synthetic anionic clays LDH (HT, LDH30, LDH63 and LDH70) possessed different shapes, layers and dimensionalities and formed highly agglomerated structures. The agglomeration tendency of the layered particles was due to the strong electrostatic attraction between the sheets and interlayer anions because of the surface charge density. The particle morphologies of NAT HEC and SYN HEC were quite similar, however, the thickness of the layers of NAT HEC (ranging from 20 to 30 nm) was slightly smaller than that of SYN HEC (30-50 nm). As shown in **Figure 17 b**, in addition to the layers of NAT HEC, single crystals of another phase were observed, most likely calcite and dolomite because a highly complex combination of calcium-, magnesium- and carbonate-rich minerals is typically present in hectorite due to its natural origin. The aspect ratio of the platelets of both cationic minerals was high, the lateral dimensions were several hundred times greater than the thickness of a single plate.



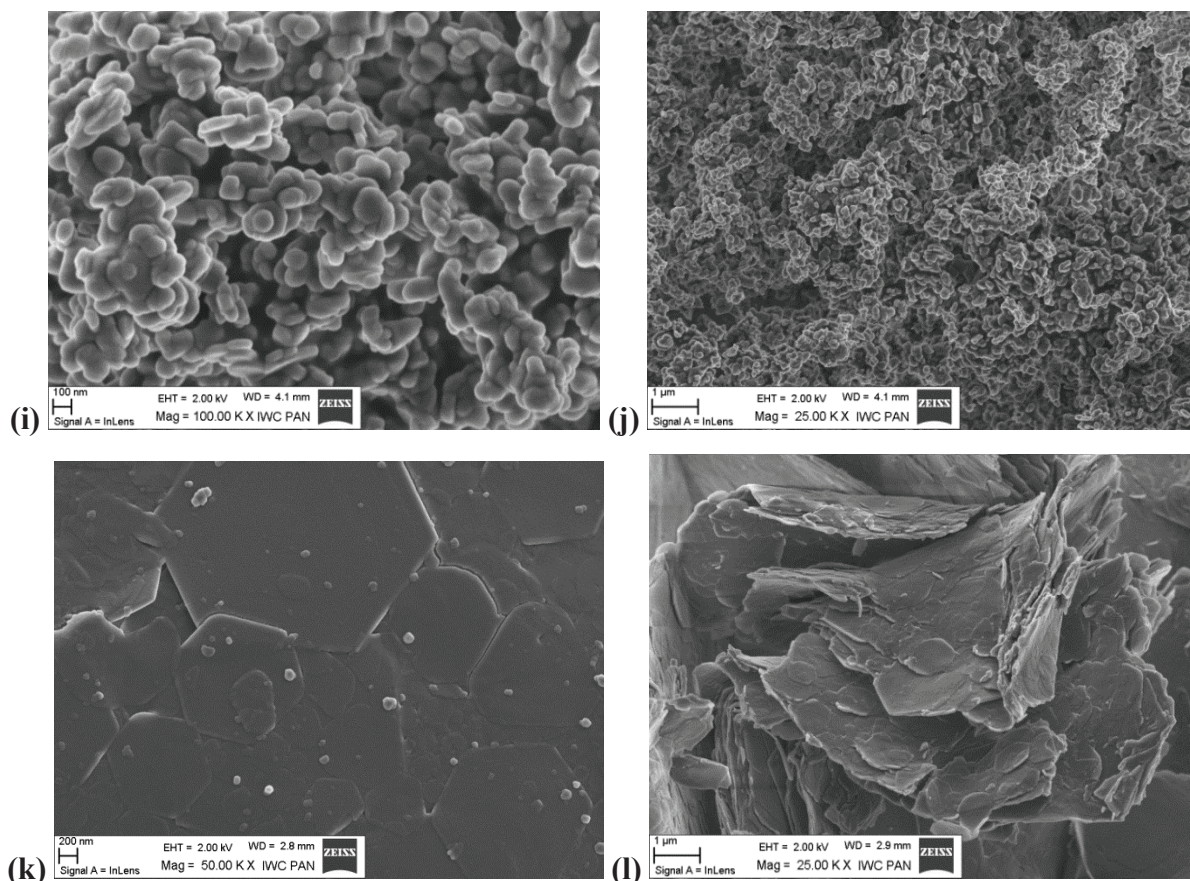


Figure 17 SEM images of (a, b) natural hectorite (HEC NAT), (c, d) synthetic hectorite (HEC SYN), (e, f) hydrotalcite (HT), (g, h) LDH30, (i, j) LDH63, (k, l) LDH70.

The size and shape of LDH layers are usually dependent on the synthesis method and experimental conditions. SEM micrographs of the LDHs revealed that the HT-like compounds exhibited platy-like shape, however, the dimensions of the sheets varied, and a tendency toward particle aggregation due to the electrostatic interactions and hydrogen bonds between the layers and counter-ions was observed. LDH is typically characterized by a layered structure of hexagonally shaped, uniform, thin platelets with lateral dimensions of 200 – 500 nm and, occasionally, up to 5 μm. A standard shape of two-dimensional hexagonal plates lying flat upon one another can clearly be observed in the case of LDH70 (**Figure 17 k, l**). The Mg-ion-rich LDH (LDH70) was also characterized by the highest platelet aspect ratio, with layer dimensions of greater than 500 nm in width and approximately 10 – 50 nm in thickness. Micrographs of HT and LDH63 also revealed the presence of hexagonal plate-like particles stacked on top of each other, however, the layer diameter, and thus the aspect ratio, was much smaller than that of LDH70. SEM images of LDH30 (**Figure 17 c, d**) revealed a collapsed layer structure with no apparent ordering.

5.1.1.2. Specific surface area and interlayer distance of layered fillers

Figure 18 a includes the powder XRD data for hydrotalcite (HT) and natural hectorite (NAT HEC), whereas **Figure 18 b** depicts the powder XRD data for LDH30, LDH63 and LDH70. The interlayer distances d for all of the crystalline layered minerals were calculated using Bragg's equation and are presented in **Table 12**.

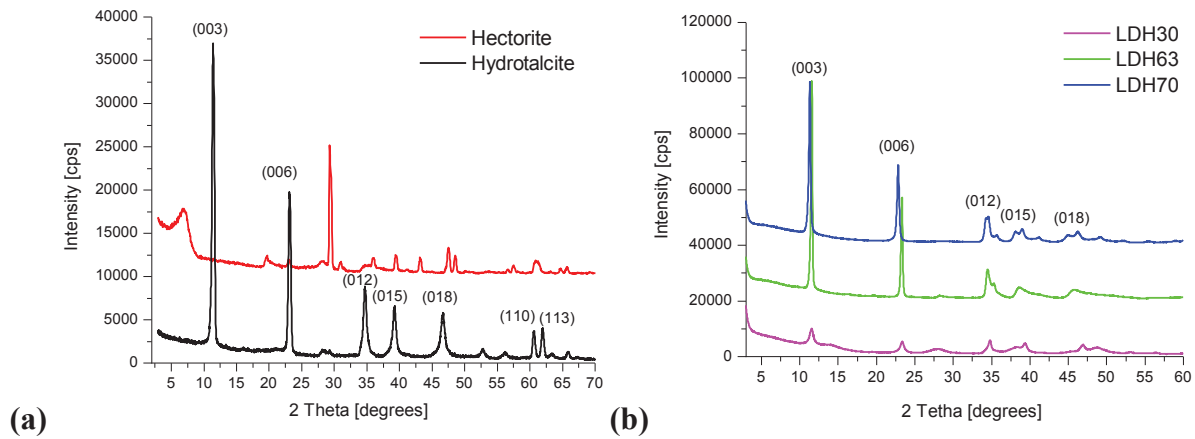


Figure 18 X-ray diffraction patterns of (a) natural hectorite (NAT HEC) and hydrotalcite (HT) and the (b) MgAl-LDH series.

The structure of natural hectorite (NAT HEC) was characterized by a (00l) d -spacing of 12.8 Å, corresponding to a Bragg diffraction peak at $2\theta = 6.75^\circ$. The sample of natural silicate contained many impurities, particularly calcite, CaCO_3 and dolomite. The presence of dolomite is not surprising because hectorite is generally formed in Mg-, Ca- and carbonate-rich environments.

Table 12 Structural properties of layered fillers.

Filler type	d -spacing [nm]	S_A , specific surface area BET (Multipoint method) [m^2/g]	DBPA number [g/100g]
NAT NEC	1.28	52.0	66.3
SYN HEC	1.28	13.0	57.4
HT	0.77	8.7	42.9
LDH30	0.76	129.4	172.9
LDH63	0.76	18.9	104.2
LDH70	0.78	13.0	86.5

XRD analysis of the unmodified HT structure revealed basal reflections at (003), (006), (012), corresponding to d -spacings of 0.77, 0.34 and 0.26 nm, respectively. As expected, the HT sample did not contain any impurities because such materials are easily synthesized with a

high degree of purity. All MgAl-CO₃-LDH types featured a similar interlayer distance with a *d*-value of approximately 0.77 nm, as presented in **Table 12**. However, the intensities of the basal reflections of LDH30 were remarkably reduced compared with those of the two other types of LDH, as shown in **Figure 18 b**. This result indicates a less-ordered, less-lamellar shape of the particles, in agreement with the collapsed layer structure of LDH30 observed by scanning electron microscopy. The X-ray patterns of LDH63 and LDH70 were comparable to that of hydrotalcite (HT), and in agreement with the X-ray patterns of MgAl-LDHs reported in the literature.²⁶⁷

The specific surface area (*S_A*) of SYN HEC was much smaller than that of NAT HEC which is in accordance with the larger size of the layered particles of SYN HEC observed by SEM. In general, HT-like compounds are known for their relatively low specific surface areas. Due to a lack of layer ordering and their irregular shape, LDH30 exhibited the highest *S_A* value of 129.4 m²/g and a high *DBPA* value of 172.9 g/100 g, reflecting the significant development of the structure, its porosity and strong tendency to form agglomerates.

5.1.1.3. ATR-FTIR studies of layered fillers

FTIR spectra of the hectorites and LDH minerals are presented in **Figure 19 a-b**, and the interpretation of the observed peaks is presented in **Table 13**.

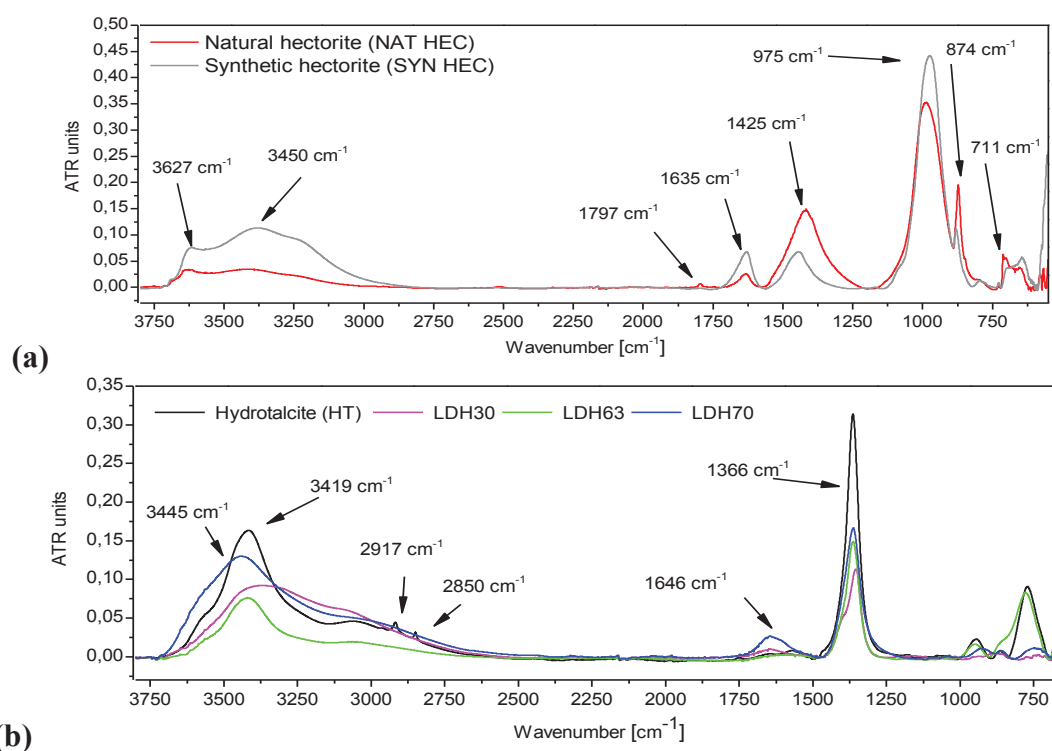


Figure 19 ATR-IR spectra of (a) hectorites, (b) MgAl-LDHs.

The FTIR spectra presented in **Figure 19 a** reveal that both types of hectorites exhibited the same characteristic bands at corresponding wavelengths, although their intensities differ slightly. For example, the intensity of the band corresponding to the stretching of the O–H group derived from adsorbed water was higher for SYN HEC than NAT HEC, whereas the higher intensity of the peak at 1425 cm^{-1} , assigned to the impurities like quartz,⁴¹ was characteristic of natural silicate (NAT HEC), but also for synthetic hectorite. Moreover, in the spectrum of NAT HEC, a band at 1797 cm^{-1} due to the presence of calcite was observed. The FTIR data for the hectorites were in good agreement with those reported in the literature.⁴¹

Table 13 Assignment of FT-IR spectra of hectorite and hydrotalcite.

	Wavenumber [cm^{-1}]	Assignment
HECTORITE	3627	Stretching of O–H
	3450	H ₂ O OH stretching
	1797	Calcite
	1650 – 1620	H ₂ O deformation (bending vibration), bending vibration of the interlayer
	1640	–Mg–O ⁴¹
	975	Si–O stretch
	874	Calcite CO ₃ bend
	711	Calcite
	655	Bending vibration of –OH attached to Mg ⁴¹
HYDROTALCITE	3600 – 3200	Stretching of O–H H ₂ O, O–H stretching vibration of the surface and interlayer water molecules
	Shoulder at 3000	Hydrogen bonding between water and carbonate anions in the interlayer galleries
	2917	Asymmetric stretching of methylene groups
	2850	Symmetric stretching of methylene groups
	1650 – 1620	H ₂ O deformation (bending vibration), bending vibration of the interlayer water molecules ($\delta_{(\text{HOH})}$)
	1366	Asymmetric stretching of carbonate counter-ions CO ₃ ^{2–}
	943	Doublet “Al–OH” deformation or asymmetric stretching of carbonate counter-ions CO ₃ ^{2–}
	782	Stretching of M–OH, Al–O, Mg–Al–O bond vibrations in the brucite-like layer
	670 – 620	Bending vibrations of carbonate bonds

As shown in **Figure 19 b**, all MgAl-LDHs exhibited a broad, strong band in the range of $3600 - 3200\text{ cm}^{-1}$, which is characteristic of the O–H stretching modes of the surface and interlayer water molecules. The broad shoulder near 3000 cm^{-1} visible in **Figure 19 b** is due

to hydrogen bonding between water and CO_3^{2-} counter-ions in the interlayer galleries. The high peak located at approximately 1366 cm^{-1} was assigned to the asymmetric stretching vibration of CO_3^{2-} counter-ions in the interlayer galleries. HT exhibited the strongest 1366 cm^{-1} peak, whereas the intensity of this band was comparable among the remaining LDHs. The peak located at approximately 782 cm^{-1} was assigned to the Al–O or Mg–Al–O bond. The FTIR data for the LDH layered minerals were also in good agreement with those reported in the literature.²⁶⁸

5.1.1.4. Thermal stability of layered fillers

The thermal stability of the layered minerals was determined by TGA in air, and the recorded data are presented in **Table 14**. The TGA profiles and the differential curves (DTG) of the layered minerals are shown in **Figure 20 a-b**. Due to the substantial amount of partially intercalated water molecules in the interlayers of the clay materials, a characteristic weight loss peak is typically observed at approximately $100\text{ }^\circ\text{C}$, however, this peak was observed only for the cationic clays (hectorites). The first mass loss (ML) below $200\text{ }^\circ\text{C}$ corresponding to the loss of partially intercalated water molecules was reported to occur at levels of 7.0 and 3.9 % by weight for SYN HEC and NAT HEC, respectively. This result indicates that the SYN HEC contained a higher percentage of interlayer water and water adsorbed on the external surfaces of the cationic clay than NAT HEC. The shape of the TGA curves revealed that NAT HEC had the highest thermal stability among the investigated types of mineral layered fillers. The decomposition temperature of synthetic hectorite was slightly lower than that of natural one at corresponding weight loss (ML) values.

Table 14 Thermal stability of layered fillers.

Filler type	T _{2%} [°C]	T _{5%} [°C]	T _{10%} [°C]	ML at 200 °C [wt%]	ML at 400° °C [wt%]	Char residue [wt%]
NAT HEC	84	592	720	3.9	4.5	78
SYN HEC	85	125	600	7.0	8.3	81
HT	165	216	240	3.8	29.8	54
LDH30	94	153	219	7.5	24.8	66
LDH63	150	202	232	4.8	29.4	54
LDH70	135	186	226	6.3	26.1	56

The thermal stability of LDHs typically depends on several factors, such as the nature of the cation, the cationic composition in the brucite-like layers, the nature of the interlayer anions, and crystallinity. Similar to the cationic clays, the first weight loss in the temperature

range of 100 – 225 °C is attributed to the removal of intercalated water molecules (dehydration) in the interlayered galleries, whereas the relatively sharp second transition at 225 – 315 °C is due to removal of hydroxyl groups (dehydroxylation) from the brucite layers as water molecules. The synthetic MgAl-LDHs also exhibited a very broad, small endothermic peak at approximately 334 °C (before the second main transition at 411 °C). This peak has been assigned to the partial loss of OH⁻ in the brucite-like layer. The last peak at 411 °C, which was more intense, was due to the completion of dehydroxylation and removal of interlayer carbonate anions as CO₂ (decarbonization). The thermal decomposition through calcinations of LDHs is a well-known method for preparing homogeneous mixed oxides, here magnesium and aluminum oxides. The residues after the thermal decomposition of the MgAl-LDHs were 66, 54 and 56 wt% for LDH30, LDH63 and LDH70, respectively.

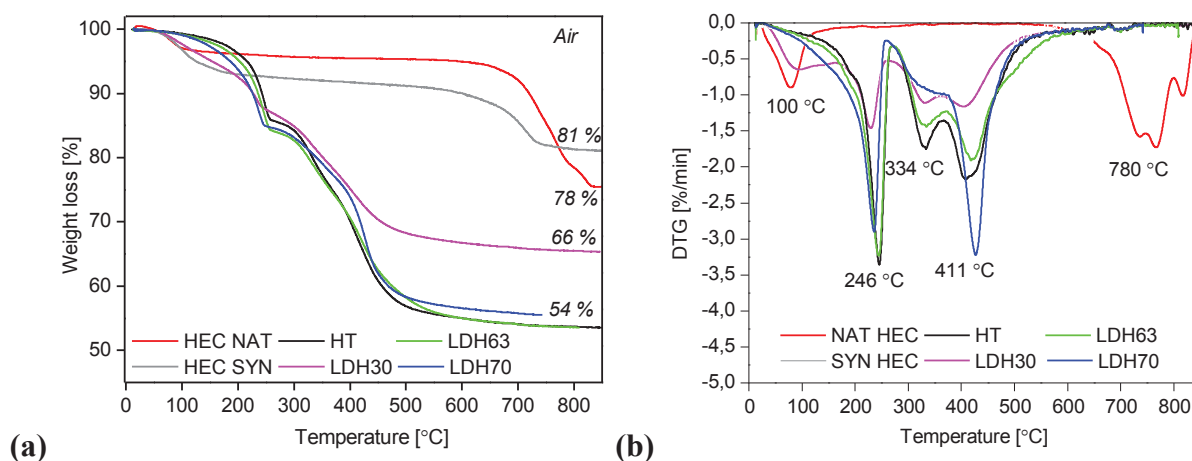


Figure 20 (a) TGA and (b) DTG profiles of layered minerals (under air atmosphere).

5.1.1.5. Examination of the surface chemical composition of layered fillers by XPS

The atomic content of the surface composition of the layered fillers was determined by XPS analysis. The total amount of specific elements of particulate solid was taken to be 100%, and their atomic percentages are given in **Table 15**. Analysis of the sample of natural hectorite revealed the presence of (the surface atomic percentage is shown in parentheses) oxygen (53.6 %), carbon (12.2 %), sodium (2.3%), silicon (17.0 %), magnesium (10.5 %) and fluorine (4.3 %). Comparison of the observed ratios to the stoichiometric composition of hectorite revealed close agreement, with a slight excess of sodium atoms at the expense of magnesium atoms. Carbon pollution was also observed. Fluorine occurs on the surface and does not enter the hectorite in the deployed source, thus, fluoride should be treated as an impurity. The hectorite samples approximately corresponded to the hectorite composition

with a surface coated with fluorine and carbon. Whether the fluorine is present as a separate compound (for example NaF) or its atoms are built into the structure of hectorite could not be resolved based on these studies.

Table 15 XPS Atomic content for surface composition of layered fillers.

Atom [% at.]	NAT HEC	SYN HEC	HT	LDH30	LDH63	LDH70
Carbon	12.2	11.4	39.2	25.6	21.3	19.4
Oxygen	53.6	55.2	42.3	50.6	51.8	56.2
Aluminum	-	-	4.5	13.6	5.2	5.8
Magnesium	10.5	11.0	14.0	7.3	15.6	13.8
Silicon	17.0	18.5	-	2.9	6.1	4.8
Fluorine	4.3	3.6	-	-	-	-
Sodium	2.3	0.3	-	-	-	-

The obtained data confirmed that the ratio of magnesium to aluminum in hydrotalcite (HT) was approximately the same as the stoichiometric ratio of the specified elements based on the chemical formula $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$. However, in the case of LDH70, the atomic percentage of magnesium on the surface of the filler particles was slightly lower than the expected value. LDH70 was also characterized by the highest atomic percentage of oxygen (56.2 %) on the particles surface among all types of filler investigated. **Table 16** shows the binding energies of the main peaks for the samples.

Table 16 Binding energies (EB) of the main peaks for the layered fillers.

Photoelectron line position		Chemical environment
Al 2p	73.9 eV	Al–OH
Mg 2p	49.3 eV	Mg–OH
Mg 2p	50.6 eV	Mg–CO ₃
Si 2p	102.8 eV	Si–O
O 1s	531.6 eV	Oxygen bonds in hydroxyl groups
C 1s	284.6 eV	Adventitious carbon
C 1s	289.0 eV	CO ₃ ²⁻
Na 1	1072.7 eV	Na–F

For XPS C1s, two components were observed: one at $EB = 284.6$ eV, which corresponds to the so-called “adventitious carbon” layer (C–C bonds, contamination), and one at $EB = 289.0$ eV, which corresponds to inorganic carbonates (CO₃²⁻).

5.1.1.6. Examination of the surface energetic characteristics of layered fillers using IGC

IGC was applied at infinite dilution to evaluate the surface properties of the layered nanoparticles and their donor-acceptor characteristics. The dispersive components (γ_s^D) of the free energy of the minerals were determined using Gray's method, whereas their tendency to undergo specific interactions was evaluated based on the electron donor-acceptor approach proposed by Papirer. The specific interactions were characterized by the molar free energy (ΔG_A^{SP}) and molar enthalpy (ΔH_A^{SP}) of adsorption and the donor and acceptor interaction parameters (K_A , K_D).

As shown in **Figure 21**, the dispersive component (γ_s^D) of the surface energy calculated for the two types of layered fillers, namely natural hectorite (NAT HEC) and synthetic hectorite (SYN HEC), decreased with temperature, as evidenced by the decrease in adsorption with temperature. The values of γ_s^D were determined at four temperatures, which differed for both types of fillers, and then extrapolated to room temperature (20 °C). The dispersive component (γ_s^D) of the surface energy estimated for hectorite at 20 °C was 260 mJ/m². By contrast, the value of the dispersive component (γ_s^D) of the surface energy of the synthetic anionic clay HT calculated at room temperature was much smaller (approximately 50 mJ/m²), which is very close to the value of γ_s^D for nitrile rubber. Similar γ_s^D values of the rubber and filler favor compatibility between components and the formation of a homogeneous mixture. A large difference between these values results in a tendency of filler particles to agglomerate and form a heterogeneous dispersion. Thus, these results suggest that HT particles will disperse more homogeneously in an elastomer than the layers of NAT HEC.

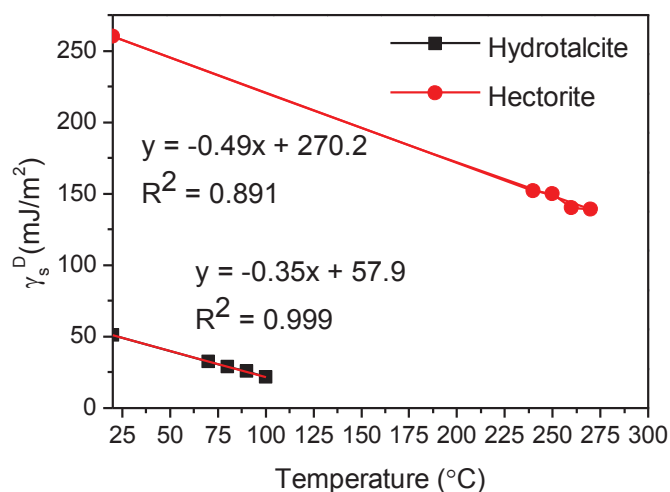


Figure 21 Variation of the γ_s^D values for hydrotalcite (HT) and hectorite (NAT HEC) at different temperatures.

The nature of the mineral surface can be characterized based on the differences between the adsorption energy values of suitably chosen polar probes with electron donor or acceptor characteristics. In this experiment, diethyl ether (Et₂O) and THF were chosen as electron donor probes, whereas chloroform (CHCl₃) was employed as an electron acceptor.²⁴⁸ The energy of the specific interaction (ΔG_A^{SP}) and specific interaction parameter (S_f) are presented in **Table 17** and **Table 18**. The ΔG_A^{SP} slightly decreased with increasing measurement temperature. Among the polar probes, the retention times of acetonitrile (ACN) and THF on the hectorite surface were too long, making it impossible to determine ΔG_A^{SP} . The highest value of ΔG_A^{SP} was measured for diethyl ether (Et₂O) (donor), whereas the lowest was observed for chloroform (CHCl₃) (acceptor). This result may indicate that the surface of NAT HEC is in a greater degree preoccupied by acceptor centers than donor sites.

Table 17 Molar enthalpies of specific interactions (ΔH_A^{SP}) between probes and hectorite, molar specific free adsorption energies (ΔG_A^{SP} , [kJ/mol]), specific interaction parameters (S_f) and (DN/AN) parameters.

Probe	DN/ AN	$-\Delta H_A^{SP}$, [kJ/mol]	240 °C		250 °C		260 °C		270 °C	
			$-\Delta G_A^{SP}$	S_f	$-\Delta G_A^{SP}$	S_f	$-\Delta G_A^{SP}$	S_f	$-\Delta G_A^{SP}$	S_f
CHCl ₃	0.00	37.7	10.1	1.7	7.5	1.6	8.1	1.6	8.1	1.6
C ₆ H ₆	0.85	33.9	12.6	1.6	11.3	1.5	11.7	1.5	11.2	1.5
Et ₂ O	4.3	14.4	16.4	1.8	15.6	1.8	11.5	1.6	9.5	1.5

The ΔG_A^{SP} values for hydrotalcite (HT) determined at 70, 80, 90 and 100 °C are shown in **Table 18**. In contrast to hectorite, the surface of HT seems to be dominated by donor sites rather than acceptor centers. The highest value of ΔG_A^{SP} was determined for acetonitrile (ACN) (amphoteric), a slightly lower ΔG_A^{SP} was reported for THF (donor), benzene (C₆H₆) (amphoteric) and chloroform (CHCl₃) (acceptor), whereas the smallest HT surface interactions occurred with diethyl ether (Et₂O) (donor). The interaction of the adsorbent material with polar hydrocarbon probes permitted the evaluation of the acceptor and donor interaction parameters (acid-base parameters) (K_a and K_d) of the mineral (**Figure 22**) for a more complete evaluation of the Lewis acid-base properties. The higher value of the K_d constant when compared to the K_a constant calculated for HT and the fact that the K_a/K_d ratio was less than 1, confirmed the assumption that the surface of HT was dominated by active sites with donor characteristics that interact with acidic groups (or compound). On the

contrary, the surface of natural silicate (NAT HEC) was predominantly occupied by acceptor sites, as the value of K_a was higher than the value of K_d and the $K_a/K_d > 1$.²⁶⁹

Table 18 Molar enthalpies of specific interactions (ΔH_A^{SP}) between probes and hydrotalcite, molar specific free adsorption energies (ΔG_A^{SP}), [kJ/mol]), specific interaction parameters (S_f) and (DN/AN) parameters.

Probe	DN/ AN	$-\Delta H_A^{SP}$, [kJ/mol]	70 °C		80 °C		90 °C		100 °C	
			$-\Delta G_A^{SP}$	S_f	$-\Delta G_A^{SP}$	S_f	$-\Delta G_A^{SP}$	S_f	$-\Delta G_A^{SP}$	S_f
CHCl ₃	0.00	62.7	7.3	2.0	7.2	2.0	6.5	2.0	5.9	2.0
C ₆ H ₆	0.01	48.9	6.9	1.6	6.7	1.6	6.9	1.6	6.1	1.6
Et ₂ O	4.92	34.2	1.1	1.1	0.3	1.0	0.3	1.0	0.9	1.1
THF	2.50	48.3	7.4	1.7	7.1	1.7	7.0	1.7	6.4	1.7
ACN	0.75	51.5	10.7	2.8	10.6	2.9	9.7	2.8	8.6	2.8

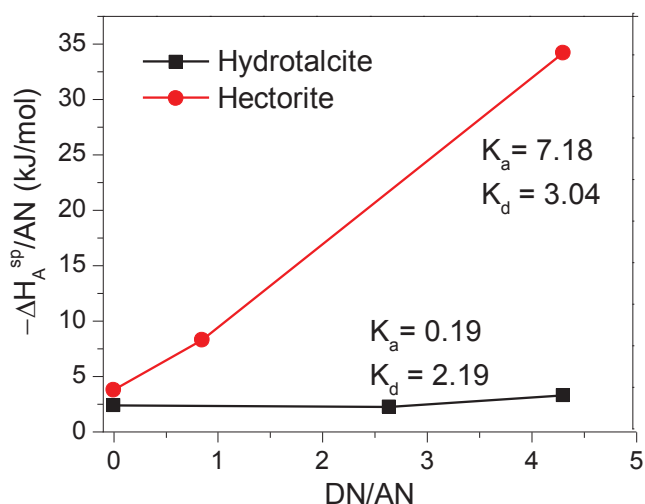


Figure 22 Relationship of $\Delta H_A^{SP}/AN$ versus DN/AN donor-acceptor properties of polar probes adsorbed on the hydrotalcite and hectorite surfaces.

5.1.1.7. Conclusions

The investigated types of hectorites (natural hectorite and synthetic hectorite) were hydrophilic with high sorption capacities and displayed high decomposition temperatures (approximately 750 °C). The natural silicate was characterized by a high specific surface area (S_A) of 52 m²/g, whereas the synthetic hectorite possessed a much lower specific surface area (S_A) of 13 m²/g. Both types of cationic clays exhibited similar particle morphologies and layer dimensionalities, as determined by SEM. XPS revealed that the surface chemical compositions of the hectorites were comparable, as evidenced by the similar surface atomic percentages of specific elements. Only the surface of synthetic silicate was characterized by a higher atomic percentage of oxygen and magnesium and lack of sodium in its composition. Moreover, FTIR analysis showed that when comparing both hectorites, the surface of synthetic hectorite contained a higher level of adsorbed water and interlayer water molecules, as evidenced by which provided a characteristic band in the range of 3600-3200 cm⁻¹. The natural silicate was most likely contaminated with mixtures of other minerals such as calcite and dolomite. The surface of NAT HEC was acidic, and acceptor centers were predominant. The dispersive component of the surface energy (γ_s^D) was very high (approximately 260 mJ/m²) at 20 °C. In contrast to the cationic clay, the surface of hydrotalcite (HT) was dominated by active sites with donor characteristics. Moreover, the dispersive component of the surface energy (γ_s^D) calculated for the synthetic anionic clay was approximately 50 mJ/m² at 20 °C. The layered particles of HT were much smaller than those of the cationic clays, however, the specific surface area of HT was also quite small (8.7 m²/g). The particle size, morphology and the specific surface area (S_A) varied depending on the type of MgAl-LDH. The particles size and shape as well as the surface characteristics of HT were comparable to those of LDH63. Among the MgAl-LDHs, LDH70 exhibited the highest aspect ratio, with plate-shaped hexagonal layers. LDH30 exhibited a high specific surface area of 124 m²/g and a high sorption capacity, however, SEM analysis of its particle morphology revealed a collapsed layer structure that exhibited a small degree of order confirmed by XRD studies. The MgAl-LDHs were much less thermally stable than the silicates, and LDHs underwent thermal decomposition in several steps, leading to the formation of a mixture of metal oxides known as “calcined LDH”.

5.1.2. COMARPISON OF THE INFLUENCE OF HECTORITE AND HYDROTALCITE ON MECHANICAL AND MORPHOLOGICAL PROPERTIES OF ACRYLONITRILE-BUTADIENE RUBBER (NBR) AND CARBOXYLATED ACRYLONITRILE-BUTADIENE RUBBER (XNBR) COMPOSITES

INTRODUCTION: The effects of layered fillers and their loadings on the rheometric, mechanical, morphological and thermal properties of nitrile butadiene rubber (NBR) and carboxylated nitrile butadiene rubber (XNBR) were studied. Natural hectorite (NAT HEC), synthetic hectorite (SYN HEC) and magnesium–aluminium layered double hydroxide (hydrotalcite, HT) were incorporated at loadings of 5, 10, 20, 30 and 40 parts per hundred rubber (phr).

5.1.2.1. Preparation of NBR and XNBR composites containing layered fillers

The filler and curing agents were mixed with NBR and XNBR in a laboratory two roll mill at a temperature of approximately 40 °C. The total compounding cycle was less than 10 min. The friction ratio of the rolling mill was 1:1.1 during the mixing period. The raw rubber was masticated prior to the addition of filler and curative.

5.1.2.2. Curing studies and crosslink densities of NBR and XNBR composites

Table 19 and **Table 20** present the influence of the layered fillers on the torque parameters of the NBR and XNBR gum vulcanizates. The cure rate index (CRI) is a measurement of the vulcanization rate based on the difference between the optimum cure time (t_{90}) and the incipient scorch time ($t_{\Delta 2}$) at which vulcanization begins. The incorporation of minerals increased the optimum cure time (t_{90}) and lowered the *CRI* of the NBR composites compared to the control NBR sample (without filler). At higher filler loadings, the rate of crosslinking (*CRI*) remarkably decreased, particularly for the sample filled with HT. The increase in t_{90} may be attributable to the absorption of the curative substance on the filler surface. The scorch time ($t_{\Delta 2}$) of the NBR composites remained almost unchanged in the presence of fillers. Increased loadings of HT and SYN HEC tended to slightly decrease the number of crosslinks formed during the vulcanization of NBR.

Table 19 Rheometric properties and crosslink densities of NBR composites.

Sample name content [phr]	ML [dNm]	MH [dNm]	ΔM [dNm]	$t_{\Delta 2}$ [min]	t_{90} [min]	CRI [min ⁻¹]	α_f [-]	$v_T \cdot 10^{-5}$ [mol/cm ³]
NBR unfilled	0.6	8.8	8.2	0.7	7.0	15.8	-	5.74 ± 0.29
NAT HEC 5	0.6	8.8	8.2	0.7	7.3	15.2	0	5.57 ± 0.04
NAT HEC 10	0.7	9.9	9.2	0.7	8.1	13.5	1.2	5.94 ± 0.11
NAT HEC 20	0.8	11.0	10.2	0.6	9.7	11.0	1.2	5.93 ± 0.17
NAT HEC 30	1.0	13.2	12.2	0.6	10.6	10.0	1.6	6.02 ± 0.08
NAT HEC 40	1.0	14.0	13.0	0.6	11.2	9.4	1.5	6.44 ± 0.70
SYN HEC 5	0.6	8.8	8.2	1.2	9.7	11.8	0	5.60 ± 0.05
SYN HEC 10	0.6	8.9	8.3	1.0	8.8	12.8	0.1	5.52 ± 0.03
SYN HEC 20	0.8	10.4	9.6	0.9	9.9	11.1	0.9	5.54 ± 0.03
SYN HEC 30	0.8	11.3	10.5	0.8	10.6	10.2	0.9	5.71 ± 0.04
SYN HEC 40	1.0	12.1	11.1	0.8	12.8	8.3	0.9	5.59 ± 0.06
HT 5	0.7	9.8	9.1	0.7	21.0	5.0	2.2	6.03 ± 0.04
HT 10	0.7	10.3	9.6	0.7	21.0	5.0	1.7	5.94 ± 0.01
HT 20	0.8	11.1	10.3	0.7	20.2	5.1	1.3	5.80 ± 0.11
HT 30	0.8	11.8	11.0	0.7	20.0	5.2	1.1	5.52 ± 0.50
HT 40	0.8	12.3	11.5	0.7	20.0	5.2	1.0	5.59 ± 0.04

Table 20 Rheometric properties and crosslink densities of XNBR composites.

Sample name content [phr]	ML [dNm]	MH [dNm]	ΔM [dNm]	$t_{\Delta 2}$ [min]	t_{90} [min]	CRI [min ⁻¹]	α_f [-]	$v_T \cdot 10^{-5}$ [mol/cm ³]
XNBR unfill.	0.5	4.7	4.2	4.1	27.5	4.3	-	1.11 ± 0.12
NAT HEC 5	0.7	5.0	4.3	3.5	24.1	4.9	0.5	0.97 ± 0.01
NAT HEC 10	0.7	5.3	4.6	2.6	22.0	5.2	1.0	1.27 ± 0.05
NAT HEC 20	0.9	6.2	5.3	1.7	20.9	5.2	1.3	1.51 ± 0.07
NAT HEC 30	0.9	6.5	5.6	1.3	20.0	5.3	1.1	1.52 ± 0.07
NAT HEC 40	1.0	7.2	6.2	1.1	18.8	5.6	1.2	1.57 ± 0.05
SYN HEC 5	0.7	5.0	4.3	2.1	18.6	6.1	0.5	1.61 ± 0.07
SYN HEC 10	0.7	5.3	4.6	1.5	19.9	5.4	1.0	1.54 ± 0.03
SYN HEC 20	1.3	6.1	4.8	1.0	20.1	3.7	0.7	1.88 ± 0.12
SYN HEC 30	1.3	6.6	5.3	0.9	22.0	4.3	0.9	2.81 ± 0.18
SYN HEC 40	1.4	6.9	5.5	0.8	22.0	4.1	1.3	3.10 ± 0.53
HT 5	0.7	4.0	3.3	9.9	47.8	2.6	0	2.39 ± 0.21
HT 10	0.7	4.6	3.9	6.9	45.4	2.6	0	3.69 ± 0.07
HT 20	0.9	5.8	4.9	3.3	37.1	2.9	0.8	4.56 ± 0.21
HT 30	1.1	6.3	5.2	2.0	26.7	4.0	0.8	5.25 ± 0.17
HT 40	1.2	6.8	5.6	1.2	18.1	5.9	0.8	5.19 ± 0.33

In contrast to NBR and the unfilled XNBR gum, the incorporation of both types of hectorite (natural and synthetic) accelerated the crosslinking process of XNBR composites by reducing the t_{90} parameter, whereas the addition of HT at loadings of 5 – 20 phr significantly extended t_{90} and t_{A2} . HT layers were previously reported to have a detrimental effect on the ionic crosslinks formed between XNBR and ZnO.⁹⁷

ΔM is a characteristic of the cured rubbers and represents the degree of chemical crosslinking. The reaction of rubbers with curing agents is merely one factor influencing the crosslinking process. Other factors include the chemical bonding of rubbers with the functional groups on the filler surface or physical interactions between the matrix and the filler, which increase the overall degree of curing. This interaction implies that the state of cure of rubber compounds might change in the presence of filler. Measurements of the crosslink density by equilibrium swelling method revealed that increasing the amount of HT added to XNBR led to a proportional increase in the crosslink density of the rubber composite (**Table 20**). The changes in the cure degree of XNBR/HT were greater than those observed for the compounds loaded with hectorites. The remarkable increases in the crosslink density of XNBR/HT compounds may be attributed to the existence of strong rubber-filler interactions as well as reactions between the basic hydroxyl groups present on the HT surface and the acidic carboxylic groups of XNBR.

Compared with the control sample, the extent of the cure (ΔM) increased with increasing filler content. As a result, the chain mobility of the macromolecular was reduced, hence, an increased difference in torque (*i.e.*, state of cure) was observed.

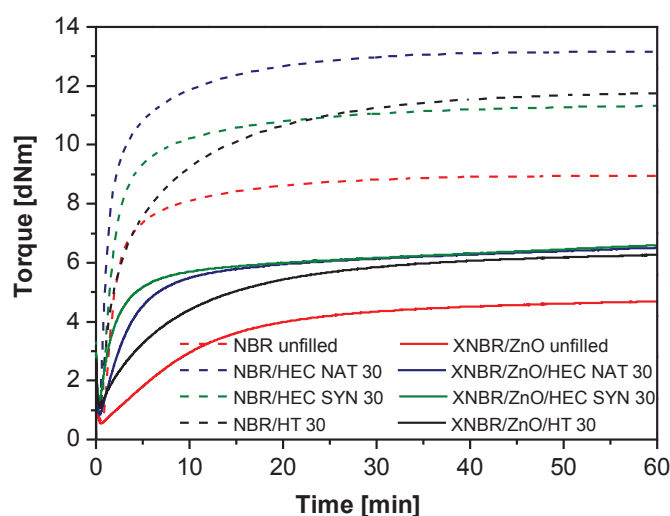


Figure 23 Comparison of the effects of fillers at 30 phr loading on the torque of NBR and XNBR compounds.

5.1.2.3. Mechanical and morphological properties of NBR and XNBR composites

Analysis of the mechanical properties indicated that both types of cationic clays have greater interactions with the NBR rubber than magnesium-aluminum double hydroxide (HT). (Table 21). Both the hardness (H) and tear strength (F) gradually improved as the filler content increased, particularly for hectorites, whereas the impact of HT was minor. Insignificant reinforcing effect of HT particles on the NBR matrix may be due to the small aspect ratio of the HT layers, the small surface area and due to the possible absorption active ingredients of the vulcanizing package on the filler surface. Increased levels of HT and synthetic hectorite (SYN HEC) induced a steady increase in the elongation at break (EB) of the NBR compounds, most likely due to the absorption of curing agents of the sulfur-based curing system. Although the anionic clay particles were much more uniformly distributed throughout the NBR matrix compared to those containing cationic clays (Figure 24 a-d), a homogenous microstructure of the composite material does not seem to be sufficient to obtain a reinforced elastomer material. On the contrary, both hectorites exhibited a tendency to form agglomerates of approximately 10 – 50 microns in the NBR matrix due to their large aspect ratios, hydrophilic nature and strong filler-filler interactions.

Table 21 Mechanical properties of NBR composites.

Sample name and content [phr]	SE ₁₀₀ [MPa]	SE ₂₀₀ [MPa]	SE ₃₀₀ [MPa]	TS [MPa]	EB [%]	F [N/mm]	H [°Sh]
NBR unfilled	1.2 ± 0.1	1.6 ± 0.3	1.9 ± 0.4	3.8 ± 0.3	499 ± 32	1.3	58
NAT HEC 5	1.2 ± 0.1	1.8 ± 0.1	2.4 ± 0.1	3.8 ± 0.7	444 ± 40	2.2	59
NAT HEC 10	1.2 ± 0.1	1.8 ± 0.1	2.3 ± 0.2	4.9 ± 0.8	494 ± 50	3.7	60
NAT HEC 20	1.4 ± 0.1	2.0 ± 0.2	2.7 ± 0.4	5.9 ± 0.1	486 ± 50	3.9	63
NAT HEC 30	1.9 ± 0.1	3.0 ± 0.1	3.9 ± 0.1	4.8 ± 0.8	462 ± 50	5.1	64
NAT HEC 40	1.7 ± 0.1	2.4 ± 0.2	3.0 ± 0.3	4.4 ± 0.5	441 ± 60	3.9	66
SYN HEC 5	1.3 ± 0.1	1.9 ± 0.2	2.4 ± 0.3	3.8 ± 0.3	460 ± 22	2.7	60
SYN HEC 10	1.3 ± 0.1	1.8 ± 0.3	2.3 ± 0.4	4.8 ± 0.6	541 ± 36	3.6	61
SYN HEC 20	1.6 ± 0.1	2.0 ± 0.1	2.4 ± 0.1	4.5 ± 0.1	541 ± 25	3.9	64
SYN HEC 30	1.6 ± 0.1	2.1 ± 0.1	2.5 ± 0.1	5.1 ± 0.2	548 ± 35	4.6	66
SYN HEC 40	1.6 ± 0.1	2.2 ± 0.1	2.7 ± 0.1	7.2 ± 0.5	641 ± 25	6.7	67
HT 5	1.1 ± 0.1	1.8 ± 0.1	2.6 ± 0.2	4.5 ± 0.2	417 ± 16	1.2	60
HT 10	1.2 ± 0.1	1.7 ± 0.1	2.2 ± 0.2	5.2 ± 0.2	488 ± 4	1.4	61
HT 20	1.4 ± 0.1	1.8 ± 0.1	2.3 ± 0.2	5.6 ± 0.7	517 ± 4	2.1	62
HT 30	1.6 ± 0.1	1.8 ± 0.2	2.1 ± 0.2	5.1 ± 0.3	500 ± 11	2.8	63
HT 40	1.3 ± 0.1	1.6 ± 0.1	1.9 ± 0.1	4.8 ± 0.9	511 ± 20	2.3	64

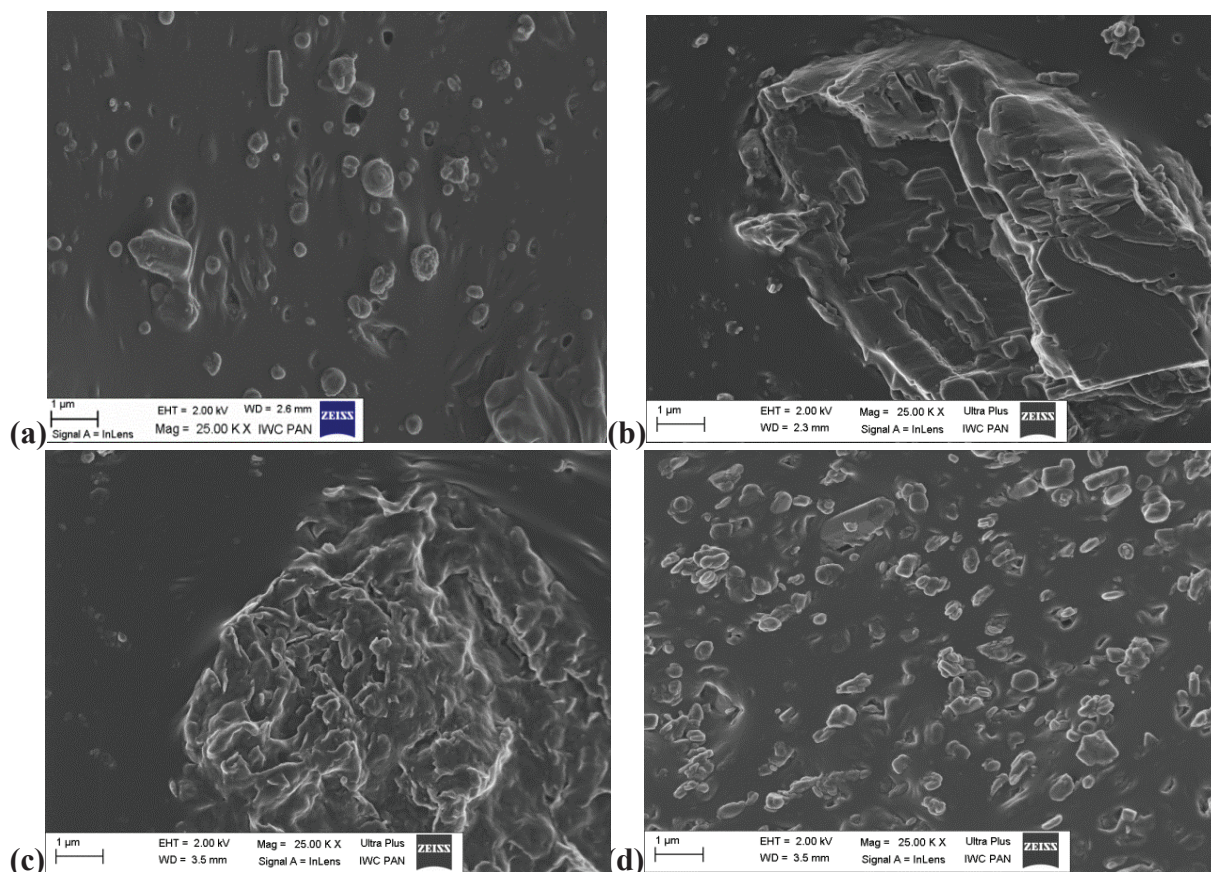


Figure 24 SEM of NBR composites containing 30 phr of: (a) unfilled, (b) natural hectorite (NAT HEC), (c) synthetic hectorite (SYN HEC), (d) hydrotalcite (HT).

XNBR crosslinked with ZnO is characterized by high tensile strength (TS) because of the formation of ionic bonds between the acidic carboxylic groups ($-\text{COOH}$) and zinc ions (Zn^{2+}). Compared with the sulfur-vulcanized NBR composites, the addition of both types of cationic clays led to a decrease in elongation at break (EB). Only the composites containing HT exhibited a higher value of *EB* than that of the reference sample. Thakur *et al.* reported that LDHs have a tendency to suppress the reaction between $-\text{COOH}$ groups and zinc ions (Zn^{2+}), leading to a reduced number of ionic bonds in the composite.⁹⁷

In general, due to the presence of the $-\text{CN}$ and $-\text{COOH}$ functionalities attached to the hydrocarbon chain, XNBR is regarded as a partially polar elastomer, therefore, good compatibility with polar fillers is expected. Increasing the amount of NAT HEC gradually improved the mechanical properties of XNBR, including tensile strength (TS), tear strength (F) and composite hardness (H). However, the incorporation of loadings greater than 30 phr led to a decrease in tensile properties, most likely due to the presence of large filler agglomerates, which cause stress concentrations and lead to the loss of mechanical strength.

Table 22 Mechanical properties of XNBR composites.

Sample name and content [phr]	SE ₁₀₀ [MPa]	SE ₂₀₀ [MPa]	SE ₃₀₀ [MPa]	TS [MPa]	EB [%]	F [N/mm]	H [°Sh]
XNBR unfill.	1.6 ± 0.3	2.3 ± 0.3	3.2 ± 0.6	19.6 ± 2.0	520 ± 20	7.0	60
NAT HEC 5	1.6 ± 0.1	2.4 ± 0.1	4.1 ± 0.4	19.4 ± 1.3	462 ± 26	7.7	65
NAT HEC 10	1.8 ± 0.2	2.6 ± 0.2	4.3 ± 0.2	21.0 ± 1.0	460 ± 29	11.5	67
NAT HEC 20	2.3 ± 0.1	3.3 ± 0.2	5.5 ± 0.3	22.0 ± 1.0	444 ± 10	10.9	67
NAT HEC 30	2.9 ± 0.2	4.2 ± 0.3	6.6 ± 0.4	23.5 ± 0.8	440 ± 15	16.9	73
NAT HEC 40	3.1 ± 0.2	4.3 ± 0.3	6.7 ± 0.4	21.5 ± 1.2	442 ± 10	18.1	77
SYN HEC 5	2.1 ± 0.1	3.0 ± 0.1	5.5 ± 0.1	22.6 ± 0.1	458 ± 10	10.8	66
SYN HEC 10	2.7 ± 0.3	4.3 ± 0.6	7.5 ± 1.0	27.3 ± 0.1	437 ± 15	15.0	69
SYN HEC 20	4.4 ± 0.1	6.7 ± 0.1	10.7 ± 0.3	27.8 ± 2.3	436 ± 15	17.0	70
SYN HEC 30	6.5 ± 0.1	9.5 ± 0.1	13.0 ± 0.1	29.8 ± 0.5	440 ± 20	17.4	70
SYN HEC 40	7.2 ± 0.1	10.5 ± 0.1	13.9 ± 0.2	31.1 ± 0.8	403 ± 10	28.3	73
HT 5	1.2 ± 0.1	1.6 ± 0.1	2.0 ± 0.1	14.0 ± 1.0	566 ± 10	7.6	62
HT 10	1.6 ± 0.1	2.3 ± 0.1	3.4 ± 0.2	15.0 ± 1.2	540 ± 10	9.3	64
HT 20	2.0 ± 0.1	3.4 ± 0.1	5.2 ± 0.1	21.0 ± 2.2	544 ± 8	10.8	67
HT 30	3.0 ± 0.2	5.1 ± 0.4	7.3 ± 0.7	25.6 ± 3.2	523 ± 5	14.3	70
HT 40	3.4 ± 0.2	5.7 ± 0.3	7.9 ± 0.3	26.2 ± 1.4	507 ± 10	22.0	73

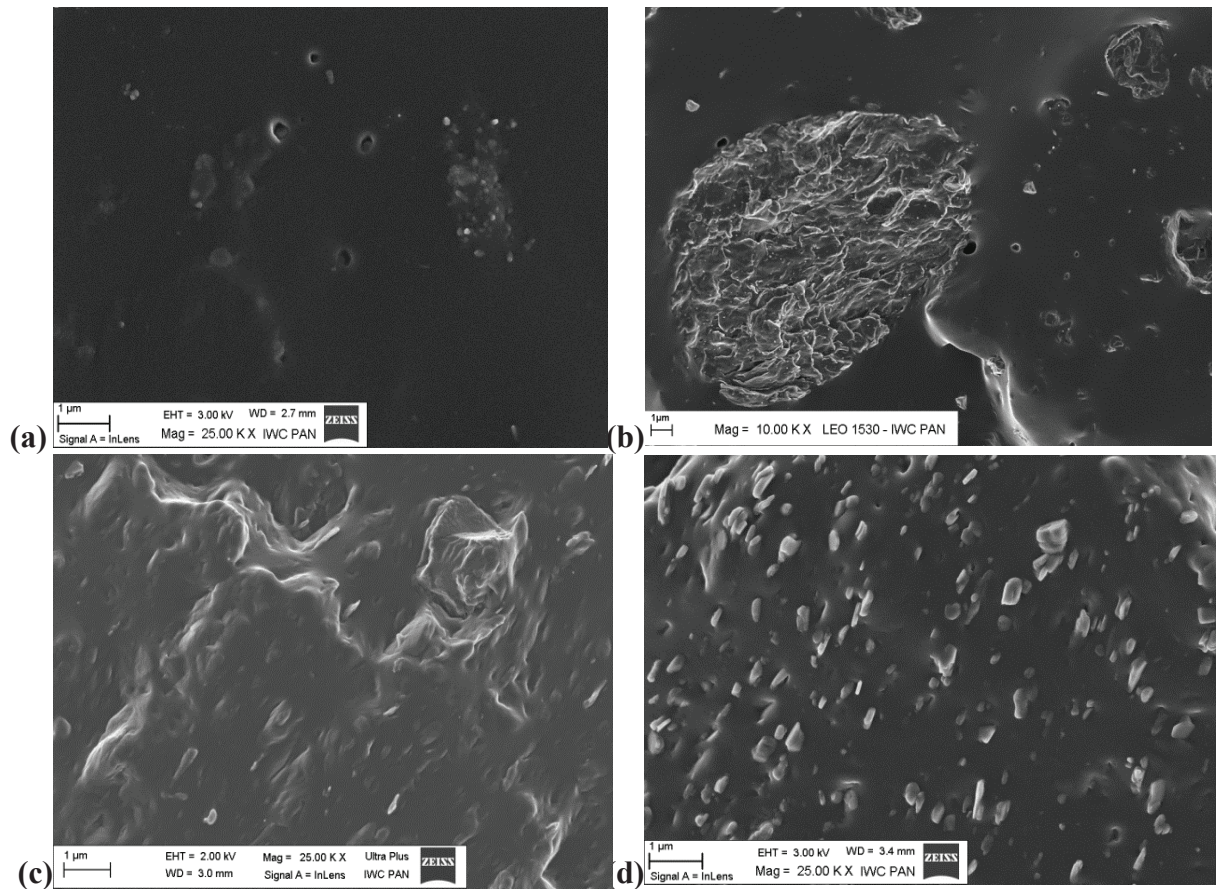


Figure 25 SEM of XNBR composites containing 30 phr of: (a) unfilled, (b) natural hectorite (NAT HEC), (c) synthetic hectorite (SYN HEC), (d) hydrotalcite (HT).

Natural silicate (NAT HEC) exhibited a strong tendency to form agglomerates with a size of 10 – 20 μm , as shown in **Figure 25 b**. This agglomeration resulted from the high dispersive component of the surface free energy of NAT HEC. A large difference between the surface energies of the rubber and filler is a major reason for the heterogenic distribution of filler in elastomer matrix. Significant improvements in mechanical properties were obtained in the presence of SYN HEC, which showed an evident reinforcing effect on the XNBR matrix. A steady upward trend in tensile strength (TS), tear strength (F) and hardness (H) was observed with increased SYN HEC loadings. The difference in the reinforcing ability of both clays (natural and synthetic cationic clays) most likely arises from their different degrees of purity. Moreover, as shown in **Figure 25 c**, the layers of SYN HEC are quite uniformly distributed throughout the XNBR matrix and seem to orient themselves in the direction of high shear force during mixing. A quite homogenous morphology was also observed for the XNBR composites containing hydrotalcite particles (HT) (**Figure 25 d**).

5.1.2.4. Thermal stability of NBR and XNBR composites

The thermal stabilities of the NBR and XNBR composites containing natural silicate (NAT HEC) and synthetic hydrotalcite (HT) were investigated by TGA in an air atmosphere (**Figure 26 a, b**). Analyzing the thermal stability of unfilled elastomers it can be seen that the XNBR exhibited a lower decomposition temperature at 2% of mass loss (T_2) than the NBR, which might be related to the presence of pedant carboxylic groups in the XNBR rubber chain (**Table 23**). The addition of NAT HEC at 30 phr loading to both types of rubber slightly decreased the value of T_2 because of the loss of interlayer water and desorption of water adsorbed on the filler surface.

Table 23 Thermal properties of NBR and XNBR composites containing layered fillers (under air atmosphere).

Sample name content [phr]	T_2 [°C]	T_5 [°C]	T_{10} [°C]	T_{50} [°C]	Char residue [wt%]
NBR unfilled	350	396	412	458	6.33
NBR/HEC NAT 30	327	395	414	477	20.62
XNBR/ZnO unfilled	307	389	415	464	4.94
XNBR/ZnO/HT 10	202	349	409	468	8.58
XNBR/ZnO/HT 20	168	285	359	423	12.97
XNBR/ZnO/HT 30	153	267	361	430	15.23
XNBR/ZnO/HEC NAT 30	291	395	420	495	20.62

The data presented in **Table 23** demonstrate that the T_5 , T_{10} and T_{50} of the compounds loaded with natural silicate are a few degrees Celsius higher than those of the unfilled gums. The incorporation of hectorite significantly increased the char residue of the rubber composites due to the high thermal stability of mineral. By contrast, the much less thermally stable HT tended to decrease the thermal stability of the rubbers. Increasing the amount of HT added to XNBR lowered the observed decomposition temperatures at corresponding mass loss values by a few degrees Celsius compared to pristine rubber. This trend is due to the thermal behavior of pristine LDHs, which undergo multiple steps of thermal decomposition, leading to a mix of metal oxides.

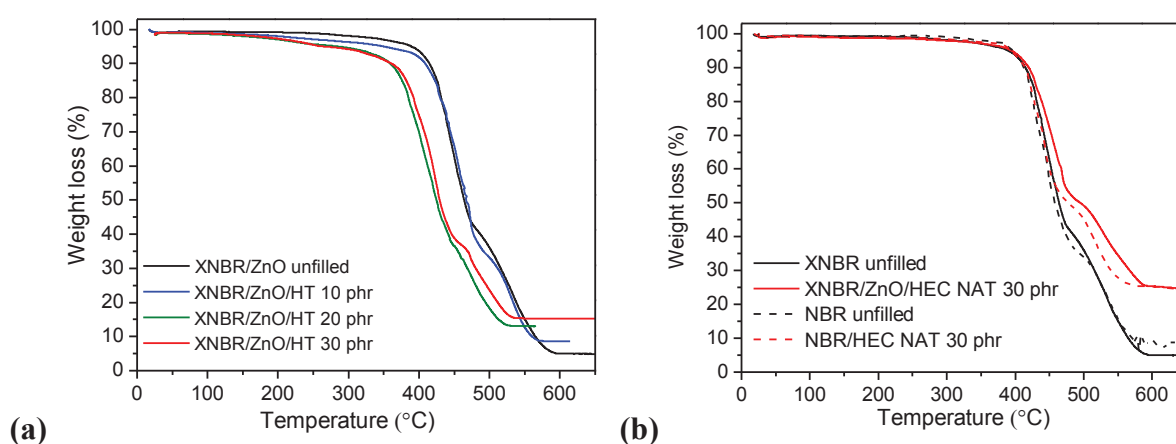


Figure 26 TGA curves of (a) XNBR/ZnO composites with HT filler, (b) NBR and XNBR composites containing 30 phr of hectorite natural (under air atmosphere).

5.1.2.5. Accelerated UV aging of NBR and XNBR composites

Nitrile rubbers typically have poor resistance to atmospheric elements such as ozone and UV radiation because of the presence of unsaturated double bond in the polybutadiene segment. The changes in the mechanical properties and crosslink densities of the NBR and XNBR composites induced by UV aging conditions are presented in **Table 24** and **Table 25**, respectively. The NBR samples subjected to accelerated UV-aging exhibited remarkably decreased tensile strength (TS) and elongation at break (EB), and increased modulus at 100 and 200 % of elongation (SE_{100} , SE_{200}). The incorporation of layered minerals into the NBR matrix did not lead to improvements in the UV stability of the composites, as evidenced by the lack of meaningful changes in the aging coefficient K_{UV} with the increasing loadings of all types of fillers. Moreover, the crosslink density of the filled composites was comparable to those of the reference sample (NBR) and corresponding unaged samples.

Table 24 Mechanical properties and crosslink densities of NBR/layered fillers composites subjected to UV-aging conditions.

Sample name content [phr]	SE ₁₀₀ [MPa]	SE ₂₀₀ [MPa]	SE ₃₀₀ [MPa]	TS [MPa]	EB [%]	K _{UV} [-]	v _T · 10 ⁻⁵ [mol/cm ³]
NBR unfilled	1.5 ± 0.1	-	-	1.5 ± 0.1	189 ± 30	0.2	6.21 ± 0.07
HEC NAT 5	1.4 ± 0.1	1.8 ± 0.1	-	2.1 ± 0.1	249 ± 18	0.3	6.19 ± 0.06
HEC NAT 10	1.5 ± 0.1	2.0 ± 0.1	-	2.4 ± 0.1	257 ± 17	0.3	6.14 ± 0.04
HEC NAT 20	1.5 ± 0.1	2.0 ± 0.1	-	2.6 ± 0.1	268 ± 15	0.3	6.23 ± 0.11
HEC NAT 30	1.8 ± 0.2	2.5 ± 0.2	-	2.7 ± 0.2	244 ± 17	0.3	6.59 ± 0.02
HEC NAT 40	1.9 ± 0.1	2.6 ± 0.1	-	2.7 ± 0.2	237 ± 16	0.3	6.56 ± 0.15
HEC SYN 5	1.3 ± 0.1	1.7 ± 0.1	-	1.8 ± 0.1	237 ± 15	0.2	6.12 ± 0.01
HEC SYN 10	1.4 ± 0.1	1.8 ± 0.1	-	2.0 ± 0.1	263 ± 20	0.2	5.94 ± 0.10
HEC SYN 20	1.6 ± 0.1	2.1 ± 0.1	-	2.4 ± 0.1	263 ± 17	0.2	5.96 ± 0.05
HEC SYN 30	1.9 ± 0.1	2.5 ± 0.1	-	2.7 ± 0.2	273 ± 10	0.2	6.11 ± 0.07
HEC SYN 40	2.0 ± 0.1	2.7 ± 0.1	3.0 ± 0.1	3.1 ± 0.2	311 ± 10	0.2	6.07 ± 0.06
HT 5	1.6 ± 0.1	2.0 ± 0.1	-	2.0 ± 0.1	207 ± 15	0.2	6.40 ± 0.04
HT 10	1.5 ± 0.1	1.9 ± 0.1	-	2.0 ± 0.1	222 ± 15	0.2	6.01 ± 0.03
HT 20	1.6 ± 0.1	1.9 ± 0.1	-	1.9 ± 0.1	233 ± 10	0.2	5.96 ± 0.05
HT 30	1.6 ± 0.1	1.9 ± 0.1	-	2.1 ± 0.2	275 ± 10	0.2	6.03 ± 0.01
HT 40	1.5 ± 0.1	1.9 ± 0.1	2.3 ± 0.1	2.4 ± 0.2	310 ± 15	0.2	5.89 ± 0.02

Table 25 Mechanical properties and crosslink densities of XNBR/layered fillers composites subjected to UV-aging conditions.

Sample name content [phr]	SE ₁₀₀ [MPa]	SE ₂₀₀ [MPa]	SE ₃₀₀ [MPa]	TS [MPa]	EB [%]	K _{UV} [-]	v _T · 10 ⁻⁵ [mol/cm ³]
XNBR unfill.	2.1 ± 0.2	2.6 ± 0.2	3.5 ± 0.2	6.0 ± 0.4	400 ± 20	0.2	2.70 ± 0.30
HEC NAT 5	2.6 ± 0.1	4.0 ± 0.3	7.1 ± 1.3	10.3 ± 0.7	345 ± 30	0.4	2.55 ± 0.33
HEC NAT 10	2.5 ± 0.1	3.8 ± 0.2	6.5 ± 0.2	10.3 ± 1.0	363 ± 20	0.4	2.46 ± 0.05
HEC NAT 20	3.3 ± 0.1	4.7 ± 0.2	7.8 ± 0.4	12.7 ± 1.5	366 ± 20	0.5	2.70 ± 0.20
HEC NAT 30	4.5 ± 0.1	6.5 ± 0.1	10.5 ± 0.1	14.4 ± 0.1	350 ± 6	0.5	3.29 ± 0.06
HEC NAT 40	4.6 ± 0.1	6.4 ± 0.1	9.9 ± 0.1	14.0 ± 0.1	360 ± 5	0.5	3.40 ± 0.27
HEC SYN 5	3.0 ± 0.1	5.0 ± 0.1	10.0 ± 0.1	12.5 ± 0.6	330 ± 20	0.4	3.25 ± 0.17
HEC SYN 10	3.7 ± 0.1	6.0 ± 0.1	10.9 ± 0.1	17.8 ± 1.3	360 ± 20	0.5	3.00 ± 0.46
HEC SYN 20	6.2 ± 0.1	9.5 ± 0.2	14.5 ± 0.3	29.7 ± 1.8	413 ± 10	1.0	3.05 ± 0.32
HEC SYN 30	9.6 ± 0.2	13.6 ± 0.2	18.9 ± 0.3	25.9 ± 2.5	372 ± 17	0.7	4.03 ± 0.41
HEC SYN 40	13.5 ± 0.2	16.2 ± 0.2	20.1 ± 0.4	23.4 ± 2.0	353 ± 10	0.7	4.30 ± 0.40
HT 5	2.2 ± 0.1	3.3 ± 0.2	5.4 ± 0.6	8.8 ± 0.9	316 ± 15	0.4	3.61 ± 0.16
HT 10	3.3 ± 0.1	5.6 ± 0.3	8.3 ± 0.5	10.9 ± 1.1	327 ± 10	0.4	5.55 ± 0.02
HT 20	3.2 ± 0.1	5.4 ± 0.2	7.7 ± 0.5	17.3 ± 0.8	426 ± 15	0.6	6.39 ± 0.13
HT 30	4.1 ± 0.2	6.9 ± 0.3	9.9 ± 0.4	19.0 ± 0.7	406 ± 10	0.6	6.71 ± 0.10
HT 40	5.1 ± 0.1	8.0 ± 0.2	10.7 ± 0.4	18.4 ± 1.1	401 ± 10	0.6	6.92 ± 0.09

On the contrary to the NBR, the exposure of XNBR compounds to UV-aging conditions led to considerably increased stiffness of the material, which is reflected in the higher modulus (SE) and reduced elongation at break (EB). The enhanced stiffness of the composites resulted from the further crosslinking process which was induced by elevated temperature conditions. Thus, the UV-aged XNBR materials exhibited higher number of crosslinks (ν_T) of XNBR when compared to the corresponding unaged samples. The XNBR containing synthetic hectorite (SYN HEC) exhibited the highest mechanical parameters among all investigated composites after UV-aging, whereas increasing concentrations of synthetic HT resulted in a formation of greater number of crosslinks in the XNBR matrix when exposed to UV aging conditions.

5.1.2.6. Conclusions

The slight effect of natural silicate on the improvements in tensile strength of NBR and XNBR composites may result from the tendency of the hydrophilic filler particles to agglomerate in the hydrophobic medium, the lack of compatibility between the components and weak filler-rubber interaction. Rubber composites containing synthetic hectorite exhibited superior mechanical parameters compared with those filled with natural hectorite. Increasing concentrations of the synthetic silicate led to steady increases in the modulus, tensile strength, tear strength and hardness of the composites. In general, greater reinforcement by layered fillers was observed in the XNBR matrix compared to the NBR due to the presence of acidic $-\text{COOH}$ functionalities in the XNBR chain structure, which may contribute to enhanced rubber-filler interactions and greater reinforcement. Moreover, the addition of increasing amounts of synthetic hydrotalcite with a lamellar structure consisting of Mg^{2+} and Al^{3+} ions contributed to a steady increment in the number of crosslinks of XNBR. This result may be useful for the application of magnesium-aluminum layered double hydroxides to fulfill dual roles: as a filler and as a curative in functionalized rubber free of other crosslinking agents.

5.1.3. APPLICATION OF MAGNESIUM-ALUMINUM LAYERED DOUBLE HYDROXIDES (MgAl-LDHs) AS REINFORCING FILLERS AND CURING AGENTS FOR CARBOXYLATED BUTADIENE-ACRYLONITRILE RUBBER (XNBR)

INTRODUCTION: From the research presented in the previous section, it could be observed that incorporation of hydrotalcite to carboxylated acrylonitrile-butadiene rubber (XNBR) remarkably increased the cure degree of the composite. At present, the frequently used curing agents for XNBR, leading to the formation of ionic bonds, are based on bivalent metal oxides, such as ZnO, MgO, CaO. Possible application of magnesium-aluminum layered double hydroxide MgAl-LDH as a crosslinking agent for XNBR (or its hydrogenated counterpart XNBR) could be an interesting alternative to conventional ZnO which is believed to be harmful for the environment. In this section, the effects of LDHs with various platelets structures, specific surface areas and Mg/Al ratios for the potential use as curing agents and possible replacements for ZnO were investigated. The influences of MgAl-LDHs on the curing behavior, crosslink density, mechano-dynamical properties, thermo-optical properties and morphology of XNBR composites were presented and the results of XNBR/LDH composites were compared with XNBR compound crosslinked with zinc oxide (ZnO).

5.1.3.1. Preparation of XNBR/MgAl-LDH composites

The rubber compounds were processed in an internal mixer Brabender Measuring Mixer N50 at a rotor speed of 50 rpm (revolutions per minute), and the initial temperature was set to 70 °C. After approximately 5 minutes of rubber mastication, the LDH filler (2.5, 5, 10, 20 and 30 phr) was added. The total time of compounding was 20 minutes. Subsequently, the compounded rubbers were milled in a laboratory-scale open two-roll mixing mill. The compounding ingredients and the amounts are presented in **Table 26**.

Table 26 Formulation of XNBR/LDH compounds, [phr].

Component	XNBR	XZnO 5	XLDH 2.5	XLDH 5	XLDH 10	XLDH 20	XLDH 30
XNBR	100	100	100	100	100	100	100
HT	0	0	2.5	5	10	20	30
ZnO	0	5	0	0	0	0	0

5.1.3.2. Curing studies and crosslink densities of XNBR/MgAl-LDH composites

The presence of reactive functional groups $-\text{COOH}$ in the carboxylated acrylonitrile-butadiene rubber XNBR structure allows it to be cured with many compounds.¹⁰⁹ Zinc oxide is commonly exploited as a curing agent for XNBR which leads to the formation of ionic bonds through the reaction of carboxylic groups with the Zn^{2+} ions and the formation of the corresponding metal carboxylate salt.^{266,270} Whereas the employment of ZnO as a curative for functionalized elastomers is already well known as its curing mechanism has been studied extensively, the application of magnesium-aluminum layered double hydroxides MgAl-LDHs for the curing process of XNBR is still a relatively new approach that is not yet well understood. There is only an assumption that the crosslinking reaction of XNBR/LDH system might proceed via a direct chemical interaction between the carboxyl groups $-\text{COOH}$ and metal ions delivered by magnesium-aluminum double layered hydroxides.^{44 110}

Figure 27 a-d shows the curing curves of the XNBR composites, separated into the elastic and viscous force components, M' and M'' , respectively, at 160 °C. **Figure 27 a** illustrates the effects of increasing concentration of HT on the rheometric curves compared with the curves for the crosslinking XNBR with 5 phr of zinc oxide (ZnO) and pure XNBR. For the pure XNBR, a slight increase in the torque M' can be observed. This may be explained through the possible self-crosslinking of raw XNBR due to the condensation of carboxyl groups to form anhydride crosslinks, however this process occurs rather at higher temperature than 160 °C.^{97,109,271} Compared to the pure XNBR, the extent of cure was markedly elevated with the incorporation of the ZnO and alternatively HT, which increasing loadings resulted in a steady growth of the elastic component M' of the torque versus time. However, from data illustrated in **Table 27** and **Figure 27 d** it can be clearly seen that the rheometric characteristics of the filled compounds are strongly influenced by the following parameters of LDHs: the amount in the rubber matrix, the Mg/Al ratio in the brucite-like layer, the specific surface area and the particles aspect ratio.

As shown in **Figure 27 c**, the torque increased M' instantly for all rubber mixes and leveled off for some samples. As it can be observed from the curves, there is practically no induction time as the compounds begin to cure almost immediately, what is characteristic of crosslinking with metal oxides.²⁷² Generally, the initial decrease in torque to a minimum value (ML) is caused by the lowering viscosity of the rubber matrix, whereas the increase in torque (MH) results from the formation of crosslinks between rubber macromolecules. As shown in **Figure 18 c**, for the XNBR loaded with 30 phr of LDH30 and LDH63 neither the M'

nor M'' reached a plateau over the entire cure time of 2 h. Inversely, the curves corresponding to the XLDH70 composites reached a plateau almost immediately. The high values of ML of the XLDH70 compounds resulted from their high viscosity evolving from the crosslinking that started at the mixing step in the internal mixer under high temperature and shear stress conditions.

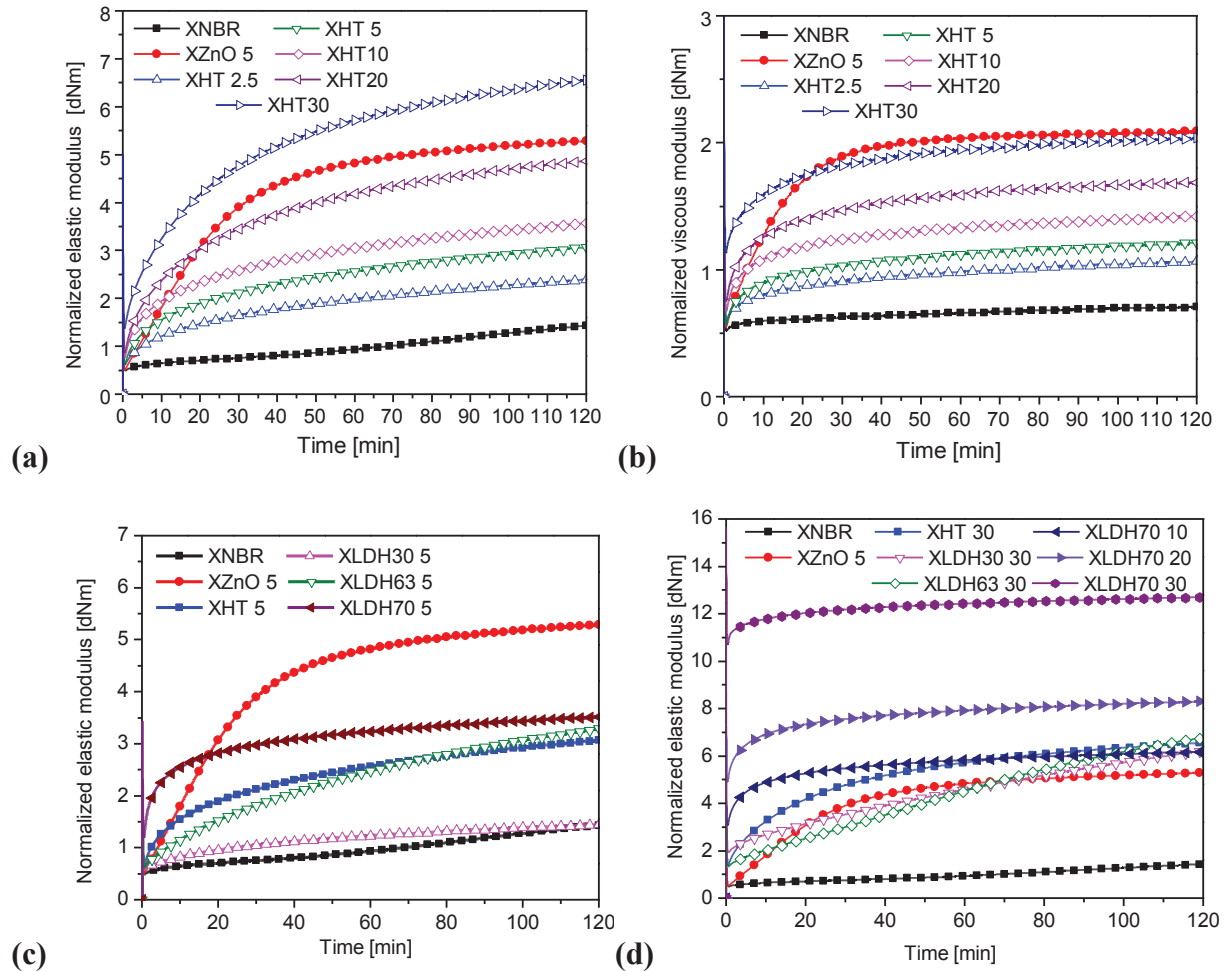


Figure 27 (a) Normalized elastic component M' , (b) normalized viscous component M'' of the torque as a function of time for XHT compounds, (c) comparing the effects of curing XNBR by 5 phr of ZnO and 5 phr of LDH on the normalized elastic component M' of the torque, (d) comparing the effects of curing XNBR by 5 phr of ZnO and 30 phr of LDH on the normalized elastic component M' of the torque.

The efficiency of XNBR crosslinking by LDHs was greater with the use of Mg-rich LDH platelets with a large aspect ratio (**Figure 17 e-i**). The loading of 10 phr of LDH70 is sufficient to increase the torque during crosslinking of XNBR to a level equivalent to 5 phr of ZnO and 30 phr of HT, LDH30 and LDH63. The activity of LDH63 and HT in the

crosslinking process is higher than that of aluminum-rich LDH30 because of greater magnesium content in brucite-like layer, as it is showed in **Figure 27 d**. However, with an addition of higher amounts of LDH30, the XNBR curing behavior was comparable to that of containing HT and LDH63 (**Figure 27 c**).

Table 27 Rheometric properties and crosslink densities of XNBR/LDH composites crosslinked at 160 °C (normalized elastic modulus M').

Sample name	ML [dNm]	MH [dNm]	ΔM [dNm]	t_{A2} [min]	t_{90} [min]	CRI [min^{-1}]	$v_T \cdot 10^{-5}$ [mol/cm^3]	Δv [%]
XNBR	0.5	1.4	0.9	0	0	-	-	-
XZnO 5	0.5	5.3	4.8	7.9	59	1.9	3.11 ± 0.29	20.0
XHT 2.5	0.6	2.4	1.8	27.6	90	1.6	2.90 ± 0.21	4.4
XHT 5	0.6	3.1	2.5	11.8	87	1.3	3.24 ± 0.21	12.0
XHT 10	0.8	3.6	2.8	7.0	83	1.3	4.28 ± 0.16	16.8
XHT 20	0.9	4.9	4.0	5.1	79	1.4	5.40 ± 0.23	26.5
XHT 30	1.4	6.6	5.2	4.1	77	1.4	8.00 ± 0.21	46.5
XLDH30 2.5	0.6	1.3	0.7	0	100	1.0	1.03 ± 0.04	0
XLDH30 5	0.6	1.5	0.9	0	96	1.0	1.19 ± 0.07	0
XLDH30 10	0.9	3.2	2.3	28.3	95	1.5	2.95 ± 0.27	0
XLDH30 20	1.2	6.2	5.0	6.9	90	1.2	5.86 ± 0.26	29.6
XLDH30 30	2.1	7.8	5.7	8.8	90	1.1	6.19 ± 0.43	34.1
XLDH63 2.5	0.5	2.5	2.0	29.1	96	1.5	2.81 ± 0.21	0
XLDH63 5	0.6	3.3	2.7	22.8	96	1.4	2.82 ± 0.29	0
XLDH63 10	0.7	3.7	3.0	25.5	98	1.4	4.42 ± 0.24	12.0
XLDH63 20	0.9	5.2	4.3	15.0	92	1.3	6.13 ± 0.22	30.3
XLDH63 30	1.1	6.6	5.5	6.7	84	1.3	7.00 ± 0.29	35.4
XLDH70 2.5	0.7	2.2	1.5	22.1	95	1.4	2.80 ± 0.22	7.1
XLDH70 5	1.2	3.5	2.3	4.2	68	1.6	4.46 ± 0.21	12.8
XLDH70 10	3.1	6.2	3.1	2.6	65	1.6	8.11 ± 0.28	42.0
XLDH70 20	4.9	8.3	3.4	2.0	65	1.6	8.62 ± 0.21	51.7
XLDH70 30	10.7	12.7	2.0	-	-	-	10.4 ± 0.11	57.7

The rationale behind such a trend could be attributed to the high specific surface area of LDH30 ($192.4 \text{ m}^2/\text{g}$) and its more irregularly shaped particles, which, along with their higher porosity, increases the possibility for interaction with the rubber (**Figure 17 g-h**). In the case of HT and LDH63, their specific surface areas are much smaller, only 8.7 and $18.9 \text{ m}^2/\text{g}$, respectively. Moreover, the aspect ratio of LDH63 particles is quite small and its shape slightly resembles plate-like, lamellar structures (**Figure 17 i-j**). The Mg-ion rich LDH (LDH70) is characterized by the lowest specific surface area ($13 \text{ m}^2/\text{g}$) but has the highest platelet aspect ratio. It is well known that a high aspect ratio of layered structures is a desirable property leading to the reinforcement of rubber matrix because of the increased

contact between the filler surface and rubber. In addition, this could be important for the improvement in curing efficiency.

Although the cure rate index (CRI) indicates that a faster curing reaction was achieved when ZnO was used compared to that of XNBR/LDH, both the optimal cure time t_{90} and the scorch time t_{A2} are shortened with the incorporation of increasing amounts of LDH filler. The global crosslinking reaction rate presented by the *CRI* parameter exhibited a steady upward trend with increasing Mg/Al ratio in the LDH (**Table 27**). A faster reaction was achieved when Mg-rich LDH was used, whereas a slower, progressive curing process was observed in the presence of Al-rich LDH.

The crosslinking of XNBR with LDH takes place through polar interactions, which can occur between the functional groups of XNBR ($-\text{CN}$, $-\text{COOH}$) and the basic hydroxyl groups present $-\text{OH}$ on the filler surface as well as through the formation of ionic crosslinks between the $-\text{COOH}$ groups and metal ions provided by MgAl-LDH. From the rheometry studies, we can observe that the viscous component of the torque M'' curve rises with the curing time (**Figure 27 b**), which according to the literature, is characteristic for ionic vulcanization with metal oxides.^{271,272,273,274} Experimental confirmation of the existence of ionic bonds in XNBR/LDH composites was achieved by measuring the percent content of ionic crosslinks via decomposition under the influence of ammonia (Δv) (**Table 27**). Mandal *et al.*²⁶⁵ have shown that ammonia acts as a strong plasticizer of the ionic aggregates present in the vulcanized rubber, therefore when cured compound is exposed to saturated ammonia vapor the ionic aggregates are supposed to disappear. **Table 27** shows the effect of the filler type and loading amount on the crosslinking density (v_T) of the rubber composites. Compared to the unfilled sample XNBR, which did not contain any curing agent and was dissolved in toluene, increasing levels of LDH filler in the rubber matrix contributed to an increase in the network density (v_T) and the formation of a higher number of ionic bonds (Δv). This trend agrees with the extent of the cure, which was assessed based on the maximum torque (MH) measured during the moving-die rheometer studies. It can be clearly observed that XNBR became more crosslinked in the presence of LDH70, which provided the highest number of ionic crosslinks (Δv) (57.7 %) compared to the other composites. However, crosslinking XNBR with of ZnO yielded a higher number of Δv compared to that of XNBR/LDH at the corresponding concentration of 5 phr. This may be explained through the existence of stronger interaction between Zn^{2+} and $-\text{COOH}$ groups due to the accessibility of Zn^{2+} derived from ZnO for reaction with acid groups. The lower value of Δv found for XNBR cured with

MgAl-LDH might result from limited availability of magnesium ions as the Mg^{2+} make up only a small percentage of the total structure of $MgAl-CO_3$. Moreover, the LDH layers have a strong tendency to agglomerate what additionally makes potential reaction sites less accessible. Presumably, there is only a small fraction of Mg^{2+} ions comparing to their total number, that actually take part in metal-carboxylate crosslinking.

5.1.3.3. Optical and thermotropic properties of XNBR/MgAl-LDH composites

The elastomer composites loaded with HT, LDH63 and LDH70 exhibited good optical transparency, even when a such high amount as 30 phr of filler was added to the XNBR matrix (**Figure 28**). Optical transparency, which can be a desirable characteristic, was not observed in the presence of 5 phr of ZnO and LDH30 as their composites were opaque. The XNBR composites containing Al-rich LDH become less transparent with the increasing filler concentration probably due to a significant amount of boehmite (alumina monohydrate) in the LDH30 composition.



Figure 28 Optical image of XNBR matrix crosslinked with ZnO and different types of LDHs.

Das *et al.*⁹⁵ previously reported that the application of ZnAl-LDH modified with stearic acid allows the production of transparent sulfur vulcanized acrylonitrile-butadiene rubbers (NBR). Moreover, in their another study, highly filled ZnAl-LDH/SSBR composites vulcanized using a conventional sulfur cure system exhibited an interesting phenomenon of thermoreversible transparency, *i.e.*, the transparent sample became opaque at elevated temperature and regained its transparency at room temperature.¹⁰⁴

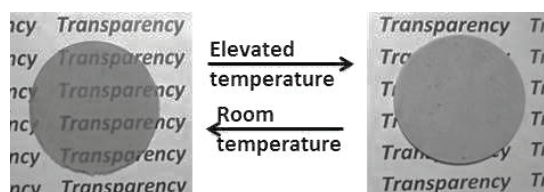


Figure 29 Temperature responsive behavior of XNBR composites with 30 phr of HT or LDH63.

This elastomer composite could be termed a “thermotropic elastomer”. Similar temperature responsive behavior (**Figure 29**) was observed here for the case of XNBR crosslinked with two types of LDH: HT and LDH63. Colorimetric studies in the CIE L*a*b system provided information on the optical changes of the composites when they were subjected to an elevated temperature of 150 °C and then cooled to 25 °C (**Figure 30** and **Figure 31**).

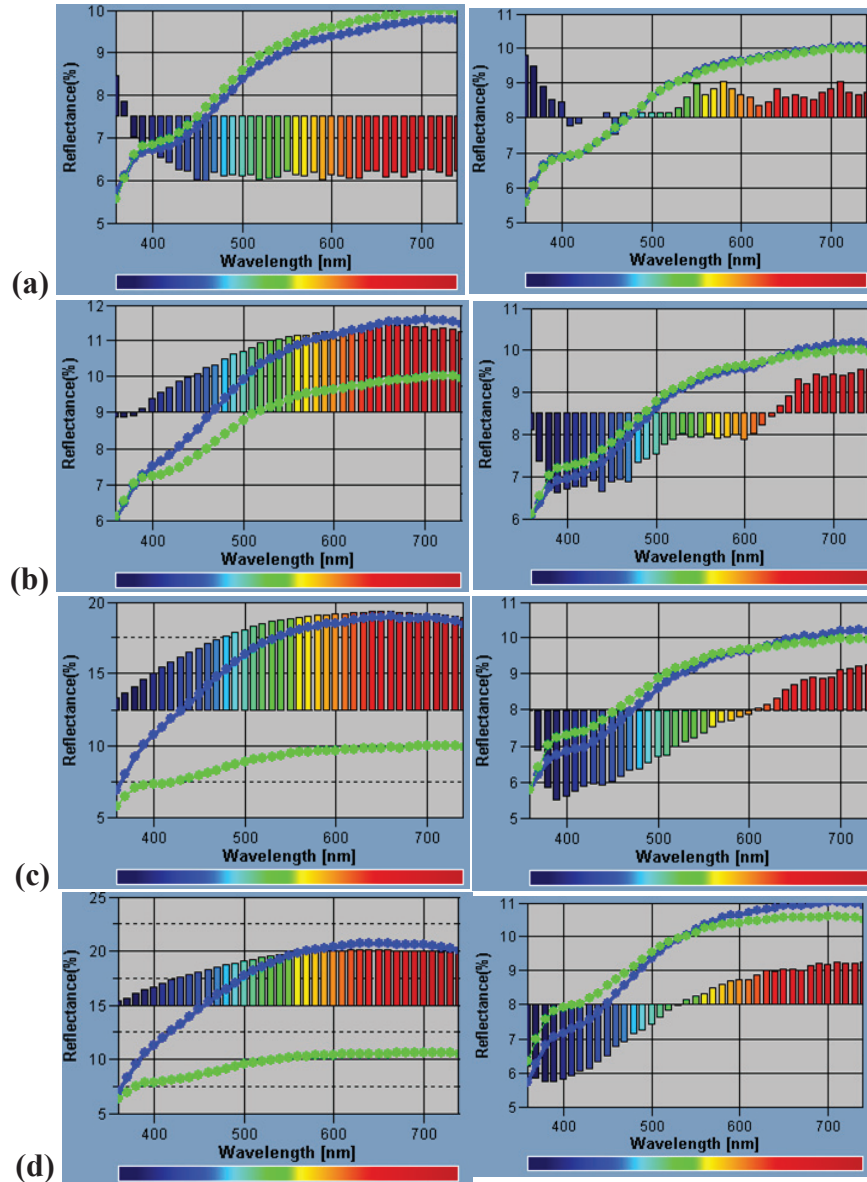


Figure 30 Reflectance spectrum of color for XNBR/HT sample containing (a) 5 phr of HT, (b) 10 phr of HT, (c) 20 phr of HT, (d) 30 phr of HT. Green line is a reference line for the sample at room temperature of 25 °C, the blue line corresponds to the sample after heating to 150 °C (1st chart) and after cooling to 25 °C (2nd chart).

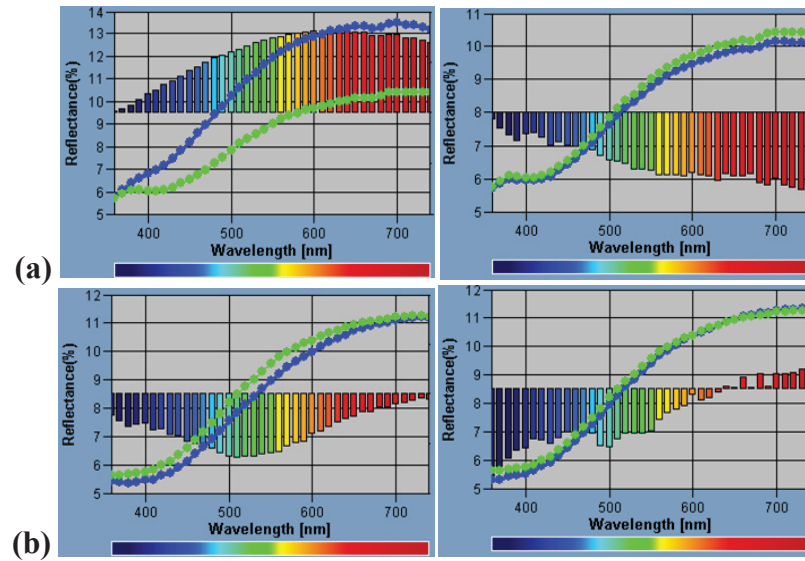


Figure 31 Reflectance spectrum of color for XNBR/LDH sample containing: (a) 30 phr of LDH63 (b) 30 phr of LDH70. Green line is a reference line for the sample at room temperature of 25 °C, the blue line corresponds to the sample after heating to 150 °C (1st chart) and after cooling to 25 °C (2nd chart).

As we can see from **Figure 31 b**, the transparent sample containing Mg-rich LDH did not show thermo-responsive behavior. Such reversible phenomenon was only found for the XNBR samples containing HT and LDH63 (**Figure 30 a-d** and **Figure 31 a**). The most evident composites color transition from being transparent to a milky state induced by high temperature was observed for XNBR sample containing a large filler contents of 20 and 30 phr (**Figure 30 c, d**), whereas a small loading of HT or LDH63 in the rubber matrix (2.5 or 5 phr) did not markedly affect the thermotropic behavior of the material (**Figure 30 a, b**). After cooling to room temperature of 25 °C, the milky, cloudy color state of the these samples was restored to the initial transparency.

The coefficient ΔE defines to what extent the color of the samples changed under the influence of 150 °C. The values presented in **Table 28**, indicate that the XNBR samples containing hydrotalcite HT at 20 and 30 phr concentration were the most sensitive to high temperature. Both the L (lightness) and ΔE (color change) parameters exhibited the highest increment when the samples were heated. Along with the increasing filler content in the composite, we can observe the slight increase in b parameter value, which corresponds to the yellow color, and no important changes for parameter a corresponding to the red color.

Heating of the samples resulted in an increase in the parameter b and decrease in parameter a comparing to those after cooling to room temperature of 25 °C.

Table 28 L , a , b parameters of XNBR/LDH composites subjected to elevated temperature of 150 °C and after cooling back to room temperature of 25 °C.

Sample name	State	L	a	b	dL	da	db	ΔE
XHT 2.5	warm	34.87	0.20	6.29	-0.71	0.33	0.46	0.91
	cool	35.47	-0.02	6.49	-0.11	0.11	0.66	0.68
XHT 5	warm	34.35	-0.10	5.65	3.17	0.14	-0.53	3.22
	cool	36.31	-0.09	5.59	0.07	0.01	0.12	0.14
XHT 10	warm	35.61	-0.21	7.06	2.75	0.09	1.86	3.32
	cool	36.28	-0.17	5.31	-0.19	-0.03	0.60	0.63
XHT 20	warm	48.91	-0.64	8.79	12.34	-0.41	4.17	13.03
	cool	36.33	0.01	5.58	-0.24	0.25	0.96	1.02
XHT 30	warm	50.83	-0.50	9.57	12.98	-0.31	5.01	13.92
	cool	37.95	-0.04	6.36	0.10	0.15	1.80	1.81
XLDH63 10	warm	37.80	-0.31	6.84	1.30	0.04	0.22	1.32
	cool	37.46	-0.25	6.81	0.96	0.10	0.18	0.98
XLDH63 20	warm	36.97	2.89	13.29	3.49	2.02	2.63	4.81
	cool	37.52	0.64	9.11	0.14	-0.18	-0.44	0.50
XLDH63 30	warm	40.71	0.63	10.42	5.01	-0.30	2.37	5.55
	cool	35.25	0.95	7.81	-0.44	0.02	-0.23	0.50
XLDH70 10	warm	41.93	-0.12	6.10	0.71	0.14	0.22	0.76
	cool	40.91	-0.28	5.87	-0.30	-0.02	-0.01	0.30
XLDH70 20	warm	28.07	0.59	13.04	-0.56	0.17	1.64	1.75
	cool	36.65	0.74	10.80	-0.02	-0.11	0.31	0.33
XLDH70 30	warm	35.68	1.78	9.70	-1.01	0.76	0.18	1.28
	cool	34.86	1.35	10.03	-0.10	0.31	0.50	0.60

According to the work of Das *et al.*,⁹⁵ one possible explanation for the thermo-reversibility phenomenon observed for these elastomer/LDH composites is a refractive index mismatch between the pristine rubber and LDH. Of the XNBR/LDH composites tested, this behavior only occurred in the presence of HT and LDH63. Both fillers are characterized by Mg/Al ratio $\approx 2:1$ and their structural and surface characteristics and Mg/Al ratios are very similar. The application Al-rich LDH30 and Mg-rich LDH70 into the XNBR matrix is not effective for the production of the thermotropic elastomer composite.

5.1.3.4. ATR-FTIR studies of XNBR/MgAl-LDH composites

The bands observed in the FTIR-ATR spectra were analyzed to investigate the contribution of carboxylic acid groups to the crosslinking process. The MgAl-LDH filler may provide metal ions for reaction with the -COOH groups (only 7 % in XNBR chain structure), thereby leading to the formation of ionic bonds.

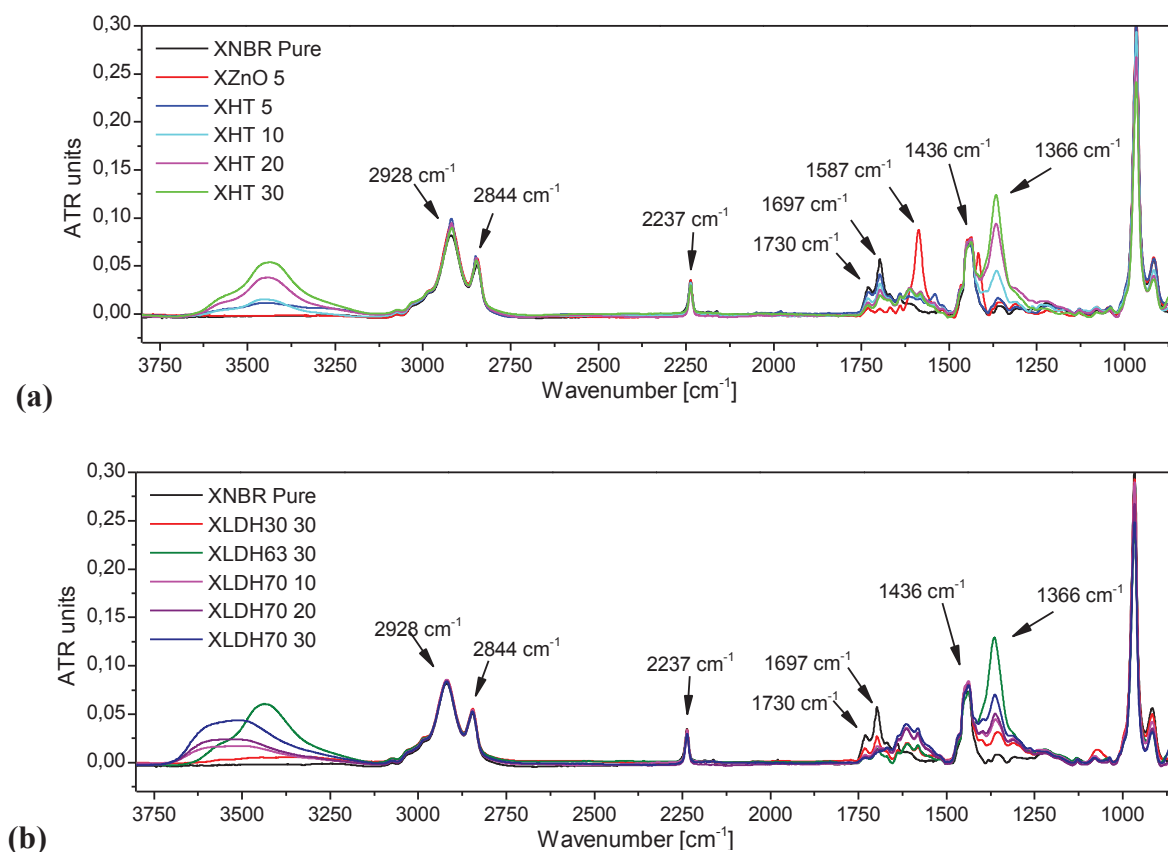


Figure 32 ATR spectra of (a) XZnO 5 and XHT 5-30 composites, (b) XLDH30, XLDH63 and XLDH70 10 – 30 compounds.

Figure 32 a, b shows the 3750 – 750 cm⁻¹ region of the infrared spectra of the sample without crosslinking agent (XNBR), the sample cured with ZnO and crosslinked with various amounts of LDH. The two absorbance bands at 2928 and 2844 cm⁻¹ correspond to the asymmetric and symmetric stretching vibrations of the methylene group -CH_2 , respectively. The peak at approximately 2237 cm⁻¹ corresponds to the stretching vibration of the nitrile triple bonds of CN-groups in the acrylonitrile component.²⁷⁵ These bands were not changed by the crosslinking process for all samples.

The most important region of spectrum is the range between 1800 and 1500 cm⁻¹, where peaks result from the >C=O group of the carboxylic component in the rubber (**Figure 33**).

In pure XNBR, the carboxylic acid groups exist predominantly as hydrogen bonded acid dimers, which have a characteristic infrared stretching vibration located at 1697 cm^{-1} . The carbonyl stretching vibration of the monomeric carboxylic group is converted to an ester by transesterification, and this group is characterized by absorbance at 1730 cm^{-1} . These bands disappear in the sample crosslinked with ZnO and their intensities decrease when XNBR is cured with increasing amount of HT (**Figure 33 a**) and other types of LDHs (**Figure 33 b**). This is due to the chemical change from weak acid to ionic bonds or salt formation. The peak for -COOH appearing at a wavelength of 1697 cm^{-1} is reduced and a new peak at 1587 cm^{-1} is observed for the sample cured with ZnO, that is attributed to the formation of ionic clusters between -COO^- groups and Zn^{2+} ions of ZnO.⁹⁷

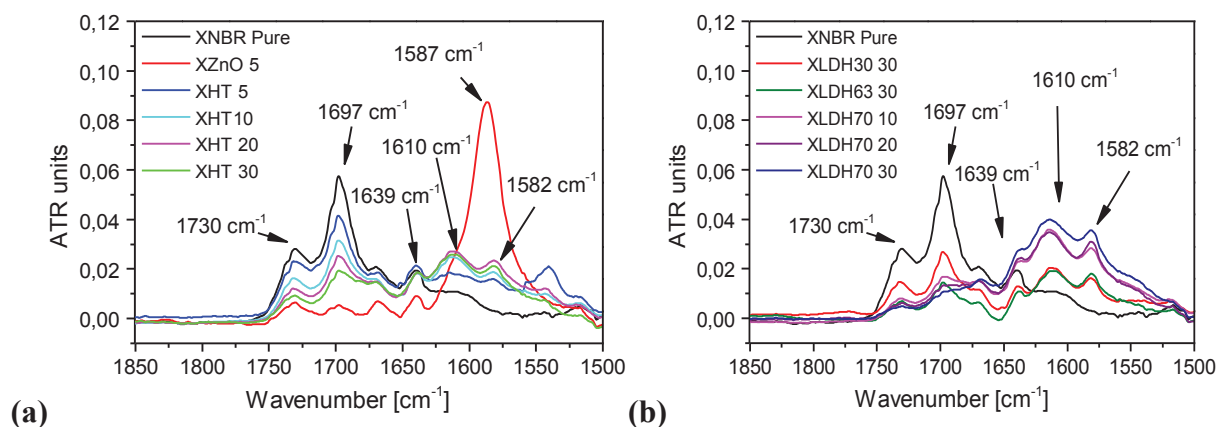


Figure 33 ATR spectra ($1850 - 1500\text{ cm}^{-1}$) of (a) XZnO 5 and XHT 5 – 30 composites, (b) XLDH30, XLDH63 and XLDH70 10-30 compounds.

As it is shown in **Figure 33 a**, for the samples crosslinked with HT the intensity of peaks at 1697 cm^{-1} and 1730 cm^{-1} , related to carboxylic groups, gradually decreases with increasing content of filler, what suggests that HT has evident influence in the dimer formation¹⁰⁹, and emphasizes the decrease of free acid groups with increasing HT amount.

From **Figure 33 b**, we can see that the incorporation of 10 – 30 phr LDH70 in the XNBR matrix most significantly reduced the bands located at 1697 and 1730 cm^{-1} compared to the other LDHs added at 30 phr. For the sample containing LDH30, absorbance peaks characteristic of carboxylic acid groups were still detected, which indicates that in this case, only partial neutralization of the -COOH groups occurred.

According to the obtained data it can be assumed that the crosslinking occurs only with the -COOH groups of the elastomeric chain. The ionic bonds formed from the carboxylic groups and the magnesium aluminium layered double hydroxide generate some new bands at

1639 cm^{-1} , 1610 cm^{-1} and 1582 cm^{-1} , which intensities slightly increased with HT content. The intensity of a strong peak at 1582 cm^{-1} , assigned to the C=O stretching vibration of the metal carboxylate salt, increased with the concentration of LDH filler. The highest absorbance peaks at 1610 and 1582 cm^{-1} were found for the samples containing Mg-rich LDH. **Table 29** shows the interpretation of existing peaks.

Table 29 Peak assignments of FTIR spectra for XNBR/LDH composites.

Wavenumber [cm^{-1}]	Assignment
3420	Stretching of –O-H
2928	Asymmetric stretching of the methylene group –CH ₂
2844	Symmetric stretching of the methylene group –CH ₂
2237	Stretching vibration of nitrile triple bonds in XNBR
1730	Carbonyl stretching of monocarboxylic acid
1697	Carbonyl stretching vibration of H-bonded –COOH group
1640-1670	Stretching of C=C
1610	Carbonyl stretching of magnesium hydroxycarboxylate salt
1587	Asymmetric carbonyl stretching vibration of zinc carboxylate salt
1582	Asymmetric carbonyl stretching vibration of magnesium carboxylate salt
1436	CH deformation, in-plane deformation of methylene group
1366	Asymmetric stretching of carbonate counter-ions CO_3^{2-}

5.1.3.5. XPS studies of XNBR/MgAl-LDH composites

Chemical changes on the surface of the XLDH70 sample were investigated by X-ray photoelectron spectroscopy (XPS). The percentage of individual components in the C1s spectrum of the composite is shown in **Table 30**.

Table 30 The percentage of individual components in the spectra of C1s [%] for the XNBR composite containing 30 phr of LDH70.

Sample name	C–C (285 eV)	C–OH/C–N (286.3 eV)	C=O (287.5 eV)	COOH (288.8 eV)
XLDH70 30	84.5	11.2	4.3	-

Peaks at 286.3, 287.5 and 288.8 eV are typical of carbon atoms bound to one oxygen atom by a single bond (*e.g.*, alcohol, ester), to one oxygen atom by a double bond (*e.g.*, ketone, aldehyde) and to two oxygen atoms (*e.g.*, ester, carboxylic acid), respectively.²⁷⁶ The XLDH70 30 sample did not show a peak at 288.8 eV, which corresponds to the carboxylic acid functionalities in the XNBR chain structure. Thus, because no free carboxylic acid groups are detected in C1s spectra, it can be assumed that the Mg-rich filler completely

neutralizes –COOH groups and contributes to the formation of ionic bonds in the elastomer network. This result corresponds well with the ATR-IR spectra recorded for the same sample, where the disappearance of peaks at 1730 and 1697 cm^{-1} corresponding to free carboxylic acid groups was observed.

5.1.3.6. Dynamic mechanical analysis (DMA) of XNBR/MgAl-LDH composites

Figure 34 a-d and **Figure 35 a-d** show the variation in loss tangent ($\tan \delta$), storage modulus (E') and loss modulus (E'') with temperature for the XNBR compounds at an oscillation frequency of 10 Hz. The values of T_g , T_i and E' are showed in **Table 31**.

The neat XNBR presented only one transition corresponding to the glass transition temperature (T_g) of elastomer at temperature of -9.9 °C. As shown in **Table 31**, the addition of LDHs to the XNBR matrix had less impact on the changes in T_g in comparison to the ZnO. The presence of the LDH filler at each concentration contributed to a constant shift of approximately 3.3 degrees in the T_g , from -9.9 to -6.7 °C, whereas incorporation of 5 phr of ZnO into XNBR elastomer induced a shift in T_g to higher temperature of -5.9 °C.

Table 31 Dynamic mechanical properties of XNBR/LDH composites measured at vibration frequency of 10 [Hz].

Sample name	T_g from E'' [°C]	T_g from $\tan \delta$ [°C]	Height of T_g [-]	T_i from $\tan \delta$ [°C]	Height of T_i [-]	E' at 25 °C [MPa]
XNBR	-22.2	-9.9	1.59	-	-	2.3
XZnO 5	-18.2	-5.9	1.06	77.0	0.30	5.2
XHT 10	-18.0	-6.8	1.30	45.6	0.20	5.6
XHT 20	-18.0	-6.8	1.20	45.6	0.21	7.1
XHT 30	-18.0	-6.8	1.16	51.6	0.21	10.4
XLDH30 10	-18.6	-6.8	1.36	-	-	5.7
XLDH30 20	-18.1	-6.8	1.27	47.3	0.18	9.1
XLDH30 30	-17.1	-6.8	1.20	51.6	0.19	12.1
XLDH63 10	-18.4	-6.8	1.31	47.9	0.19	6.0
XLDH63 20	-18.3	-6.8	1.28	52.1	0.20	6.7
XLDH63 30	-18.1	-6.7	1.21	53.8	0.21	9.2
XLDH70 10	-18.1	-6.7	1.17	45.6	0.22	10.9
XLDH70 20	-17.2	-6.7	1.13	45.4	0.24	20.5
XLDH70 30	-16.9	-6.7	1.09	47.3	0.24	26.5

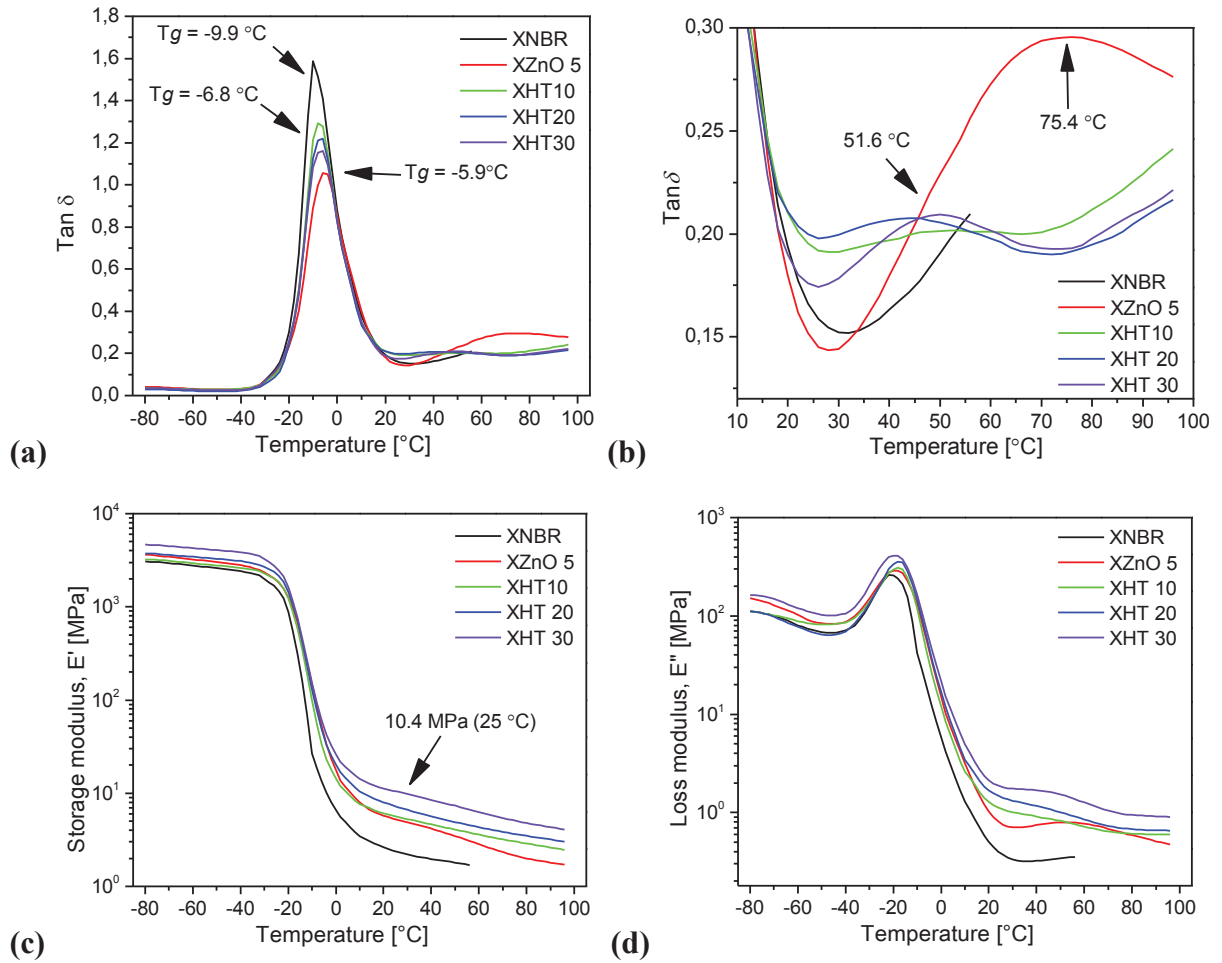


Figure 34 (a) Plot of $\tan \delta$ (loss factor), (b) ionic transition region T_i , (c) plot of storage modulus E' , (d) plot of loss modulus E'' versus temperature for XNBR cured with ZnO and HT composites. Vibration frequency, 10 [Hz].

Moreover, curing XNBR with ZnO significantly declined amplitude of the $\tan \delta$ main peak and caused the emergence of an additional high temperature $\tan \delta$ shoulder at 75.4°C which also known as ionic transition T_i (**Figure 34 b**). This transition, is associated with the formation of ionic structures and occurs over a wide range of temperatures. XNBR/ZnO belongs to a class of elastomeric ionomers that behave as ionic thermoplastics elastomers due to the existence of carboxylic acid salt formed in the presence of ZnO.²⁷⁷ These salts tend to associate and form an independent microphase (clusters), which is immersed in the elastomer matrix.^{278,279} Such types of ionic crosslinks have thermolabile nature that enables the material to be recycled and processed like thermoplastic at elevated temperature.^{272,277} During DMA analysis the hard phase arising from the formation of ionic clusters or conglomerates begin to relax and weaken at ionic transition temperature T_i and in the consequence the elastomer loses its rigidity.

For the XNBR/LDH, in the curves of E'' and $\tan \delta$ versus temperature a high temperature relaxation typical of ionic elastomers occurred (**Figure 34 b, d** and **Figure 35 b, d**). The ionic transition temperature T_i and the ionic transition peak height of XLDH composites were found to be lower than that of XZnO 5. This is probably due to the lower accessibility of metal ions which would participate in the reaction with carboxyl groups of XNBR and produce carboxylate metal salts. As the Mg/Al ratio and concentration of LDH raises, the height of T_i peak increases and shifts towards higher temperatures (**Table 31, Figure 35 b**). This trend supports the hypothesis that the enhancement of the mechanical properties of XNBR/MgAl-LDH composites results from the formation of ionic bonds between $-\text{COOH}$ groups and metal ions (particularly magnesium ions) provided by LDH.

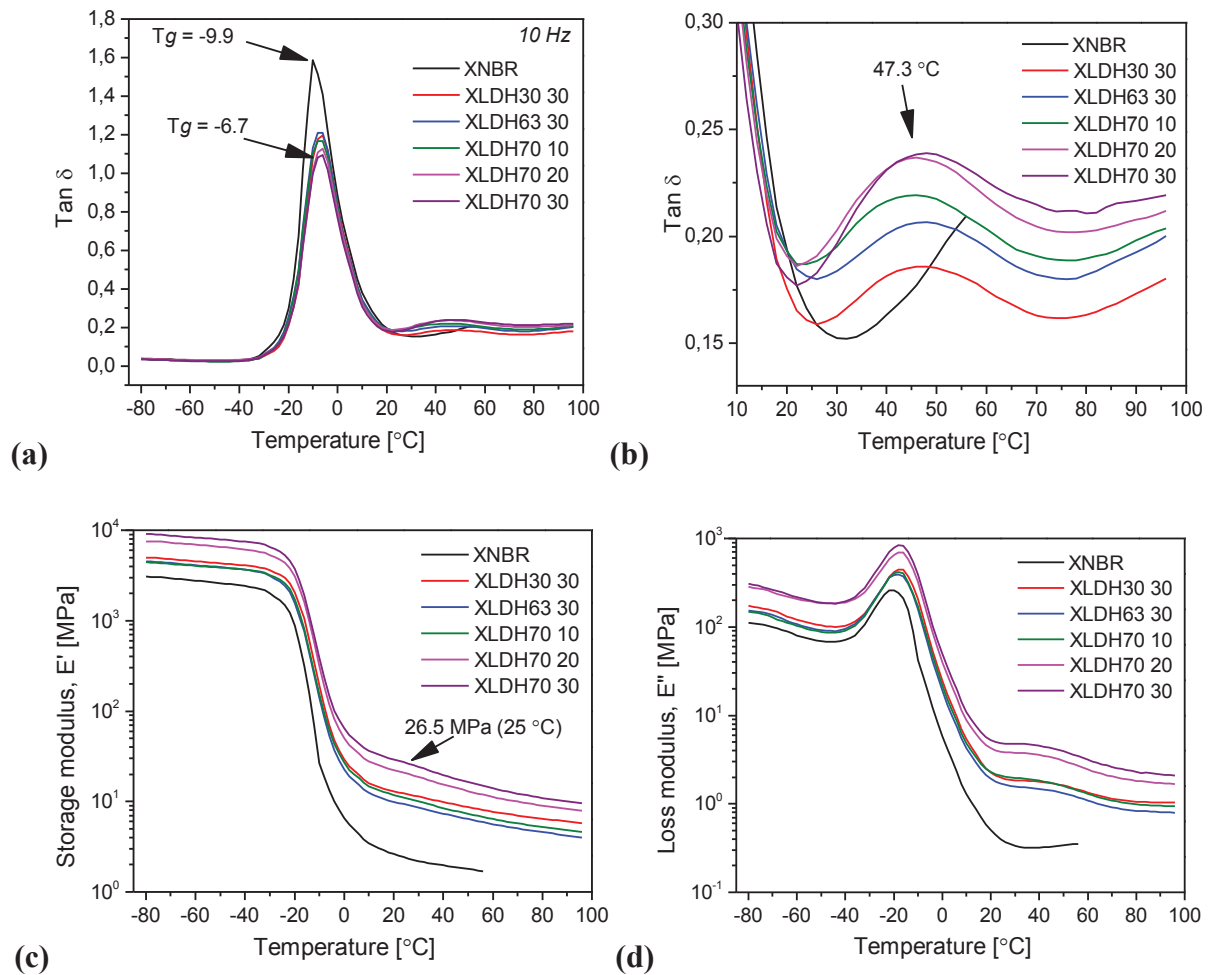


Figure 35 (a) Plot of $\tan \delta$ (loss factor), (b) ionic transition region T_i , (c) plot of storage modulus E' , (d) plot of loss modulus E'' versus temperature for XNBR composites cured with LDH30, LDH63 and LDH70. Vibration frequency, 10 [Hz].

The increased loss modulus E'' maximum and a shift $\tan \delta$ toward higher temperature in comparison to the neat XNBR from $-9.9\text{ }^{\circ}\text{C}$ to $-6.8\text{ }^{\circ}\text{C}$ is associated to the reduced segmental mobility of XNBR macromolecular chains by the formation of immobilized rubber shell on the filler surface. Increasing the Mg/Al ratio and the filler content in the elastomer matrix did not have a significant impact on T_g , which remained virtually unaltered, regardless of the LDH type and amount. However, the peak height of alpha relaxation declined consistently with increasing filler content, and this effect was most pronounced for the samples containing Mg-rich LDH (**Figure 35 a**). Lowered $\tan \delta$ peak intensities indicate the restricted mobility of the rubber chains and reflect the toughness or stiffness of a material at the relaxation temperature.

The plots of storage modulus (E') versus temperature showed a strong reinforcing effect of LDH filler, as E' is increased over the whole temperature range (**Table 31**, **Figure 34 c** and **Figure 35 c**). As the filler content raised, the value of the storage modulus E' also increased as a consequence of the strong interfacial interactions between LDH particles and XNBR matrix and the existence of a hard phase. The composite containing 30 phr of LDH70 had the highest modulus E' of all tested materials (26.5 MPa at $25\text{ }^{\circ}\text{C}$).

5.1.3.7. Mechanical properties of XNBR/MgAl-LDH composites

Table 32 shows the mechanical properties of the XNBR compounds cured with ZnO or alternatively with LDH at various loadings. Additionally, stress-strain curves of representative samples are presented in **Figure 36**.

In general, the incorporation of ZnO in XNBR produces an ionic elastomer with increased modulus, tensile strength, hardness and tear strength what is ascribed to strong interactions between ZnO particles and rubber matrix.²⁷⁷ Mechanical testing results showed that quite high loadings of LDH filler are needed for the preparation of composites with mechanical parameters that are comparable to those of XZnO 5. The addition of LDHs to XNBR matrix resulted in significant improvements in the stress-strain behavior, hardness and tear strength for all vulcanizates compared with the neat XNBR, however the magnitude of reinforcement was dependent on the LDH type.

Table 32 Mechanical properties of XNBR/LDH composites.

Sample name	SE ₁₀₀ [MPa]	SE ₂₀₀ [MPa]	SE ₃₀₀ [MPa]	TS [MPa]	EB [%]	F [N/mm]	H [°Sh]
XNBR	0.7 ± 0.1	0.7 ± 0.1	0.6 ± 0.1	0.7 ± 0.1	1401 ± 12	3.1	50
XZnO 5	1.6 ± 0.3	2.3 ± 0.3	3.2 ± 0.6	19.6 ± 2.0	520 ± 20	6.3	60
XHT 2.5	1.0 ± 0.1	1.2 ± 0.1	1.4 ± 0.1	4.5 ± 0.1	727 ± 10	8.2	54
XHT 5	1.2 ± 0.1	1.7 ± 0.1	2.3 ± 0.1	8.4 ± 0.1	688 ± 50	9.2	55
XHT 10	1.9 ± 0.1	2.8 ± 0.1	4.1 ± 0.1	14.5 ± 1.5	536 ± 40	12.8	60
XHT 20	2.5 ± 0.2	4.3 ± 0.3	6.4 ± 0.4	16.0 ± 1.5	542 ± 33	12.6	61
XHT 30	3.3 ± 0.3	5.8 ± 0.5	8.3 ± 0.6	18.6 ± 1.0	519 ± 30	14.3	62
XLDH30 2.5	1.1 ± 0.4	1.1 ± 0.4	1.1 ± 0.4	1.7 ± 0.4	1163 ± 80	4.5	52
XLDH30 5	1.3 ± 0.2	1.3 ± 0.2	1.3 ± 0.2	2.1 ± 0.2	1100 ± 31	5.2	53
XLDH30 10	1.8 ± 0.1	2.5 ± 0.1	3.2 ± 0.1	10.0 ± 0.5	650 ± 30	13.6	58
XLDH30 20	2.6 ± 0.1	3.8 ± 0.1	4.8 ± 0.2	11.1 ± 1.4	571 ± 10	15.6	64
XLDH30 30	3.4 ± 0.1	5.1 ± 0.1	6.4 ± 0.1	14.9 ± 0.2	580 ± 15	16.5	67
XLDH63 2.5	1.0 ± 0.1	1.2 ± 0.1	1.5 ± 0.1	4.4 ± 0.2	707 ± 10	7.4	53
XLDH63 5	1.1 ± 0.1	1.4 ± 0.1	1.7 ± 0.1	6.3 ± 0.1	700 ± 50	8.6	54
XLDH63 10	1.6 ± 0.1	2.4 ± 0.1	3.5 ± 0.2	14.5 ± 1.6	650 ± 28	13.7	57
XLDH63 20	2.2 ± 0.1	3.7 ± 0.1	5.8 ± 0.1	18.7 ± 1.5	603 ± 30	17.0	60
XLDH30 30	2.7 ± 0.1	4.9 ± 0.2	7.1 ± 0.3	20.0 ± 1.0	610 ± 30	19.7	63
XLDH70 2.5	1.1 ± 0.1	1.4 ± 0.1	1.6 ± 0.1	5.0 ± 0.3	711 ± 30	8.2	57
XLDH70 5	1.7 ± 0.2	2.8 ± 0.5	4.0 ± 0.7	15.5 ± 0.1	634 ± 10	14.0	59
XLDH70 10	4.9 ± 0.1	7.8 ± 0.1	9.3 ± 0.2	17.5 ± 0.5	560 ± 10	18.7	65
XLDH70 20	6.4 ± 0.1	8.8 ± 0.1	11.4 ± 0.1	24.0 ± 0.2	558 ± 10	21.8	68
XLDH70 30	7.8 ± 0.2	10.4 ± 0.2	12.7 ± 0.3	24.8 ± 1.0	521 ± 15	21.5	70

From the values summarized in **Table 32**, it can be clearly seen that increasing the high aspect ratio and Mg²⁺ content of the LDH structure has a strong impact on the mechanical properties of XNBR elastomer. All composites showed improvements in tensile strength *TS* and decreases in elongation at break *EB* relative to pure XNBR because of the reinforcing effect of the LDH filler as well as the increased crosslink density in the rubber network. Furthermore, it was found that the hardness *H*, tear strength *F*, and modulus at 100, 200 and 300 % of elongation *SE* increased with increasing filler content. The greatest changes in the mechanical properties were observed for samples containing LDH70 with the highest anisotropy degree of layers.

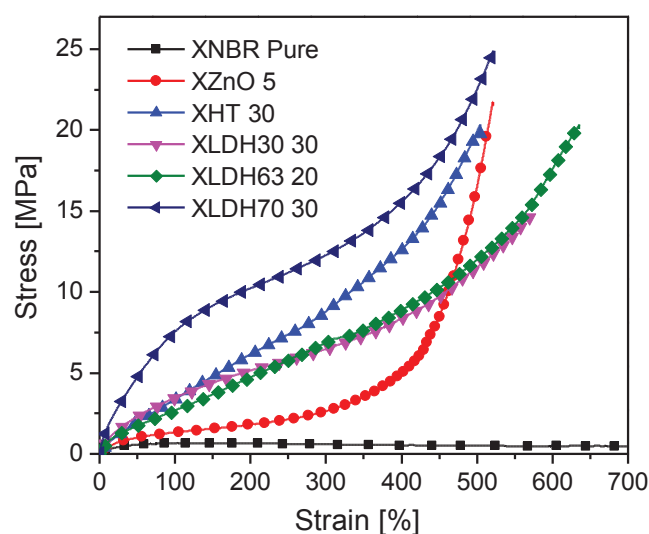


Figure 36 Stress-strain curves of XNBR/LDH composites.

The high values of TS reported for the XLDH70 samples at low filler concentrations indicated that the reinforcing effect of LDH70 in the XNBR matrix was superior compared to the other types of LDHs. The observed improvements in the mechanical properties are possibly due to the high aspect ratio of this LDH and the high Mg content. The incorporation of small quantities of magnesium rich filler at 5 phr resulted in a remarkable increase in the tensile strength (15 MPa). However, the addition of loadings higher than 20 phr only led to a slight improvement in mechanical strength from 24.0 to 24.8 MPa. The percentage of elongation EB decreased drastically with the addition of filler, particularly for the highly filled composites. This trend could be due to the reduced free volume and mobility of the macromolecule chains resulting from interactions between the filler and the matrix. Moreover, the enhancements in tensile strength are directly attributed to the dispersion of LDH layers in the XNBR matrix.

5.1.3.8. Microstructure and morphological analysis of XNBR/MgAl-LDH composites

Micrographs of XNBR composites containing 30 phr of LDHs obtained by SEM are shown in **Figure 37 a-h**. Because of the polar surface of LDHs, good compatibility with XNBR, which contains polar nitrile and carboxyl groups, is expected.

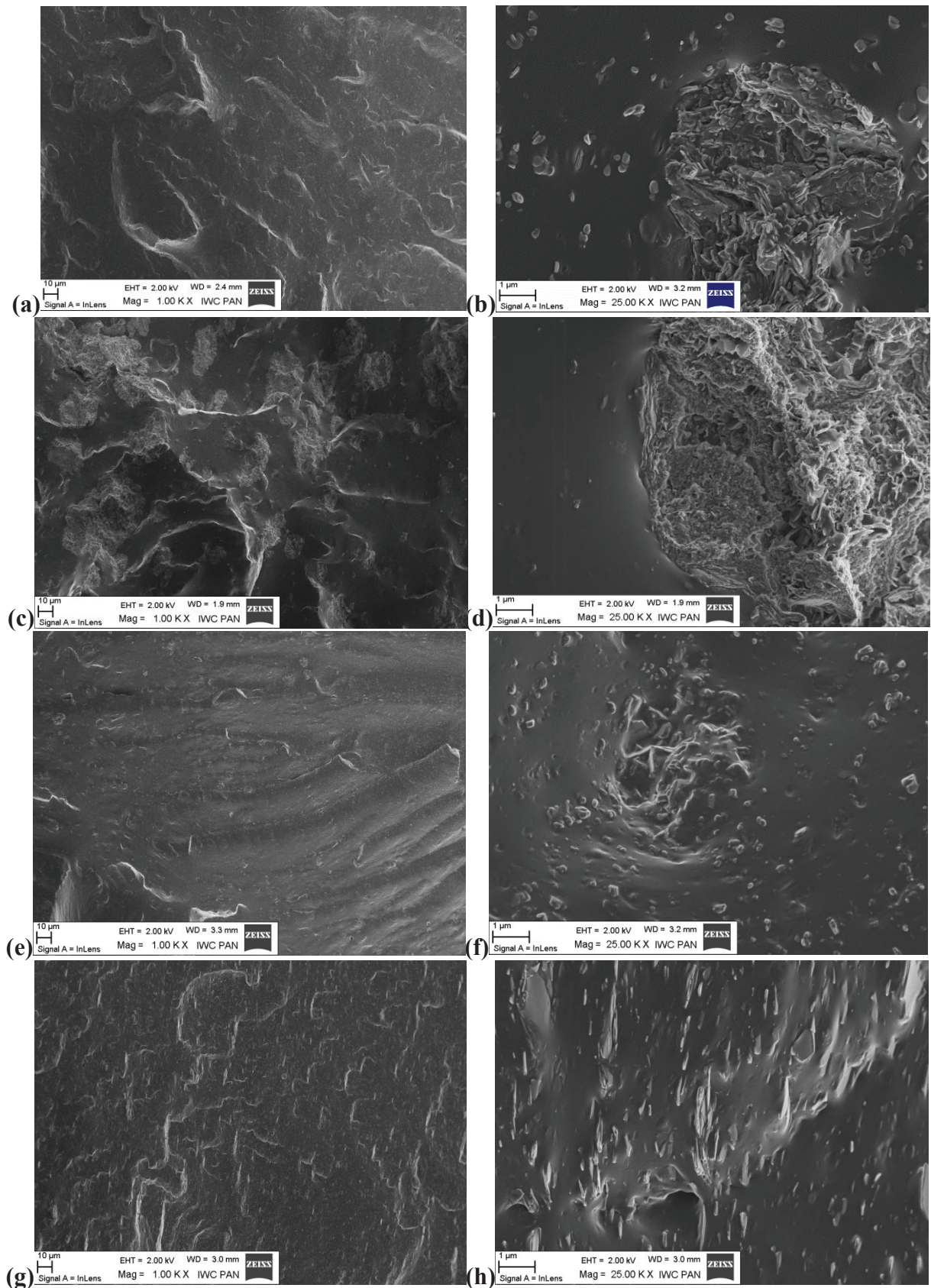


Figure 37 SEM micrographs of XNBR filled with 30 phr of (a, b) HT, (c, d) LDH30, (e, f) LDH63 (g, h) LDH70.

The results indicated that the dispersion state of LDHs in the XNBR composites prepared by the melt mixing method was dependent on the LDH morphology, particle size, aspect ratio and specific surface area. Among LDHs series, LDH70 is characterized by a typical layered structure and hexagonal-shaped particles with lateral dimensions of 500 – 800 nm, particles of HT and LDH63 exhibit smaller aspect ratios and lateral dimensions of 50 – 400 nm and 100 – 200 nm respectively, whereas particles of LDH30 possess plate-like shapes and have a high degree of irregularity. It can be clearly observed from **Figure 37 c-d** that the sheets of LDH30 form the largest agglomerates, with sizes ranging from approximately 5 to 30 μm and more. This tendency to agglomerate arises from the hydrophilicity of these particles, their large specific surface area of 129.4 m^2/g and strong filler-filler interactions. Moreover, the irregular shape of these particles does not favor organization in the rubber matrix during melt-compounding in a high-shear mixer. In contrast, HT, LDH63 were distributed more uniformly in the XNBR matrix (**Figure 37 a, b, e-h**) however their vulcanizates showed no preferential orientation of the layers and still some randomly distributed agglomerates with an average size of 5 and 3 μm were detected. These fillers possess much smaller specific surface areas of 8.7 and 18.9 m^2/g respectively, and much smaller aspect ratios in comparison with LDH70. **Figure 37 g-h** clearly illustrates the parallel orientation of highly anisotropic LDH70 layers with a large aspect ratio in the rubber matrix during mixing (*i.e.*, the shearing action of two winged rotors and the walls of the mixing chamber) in the internal mixer under high shear stress and elevated temperature conditions.

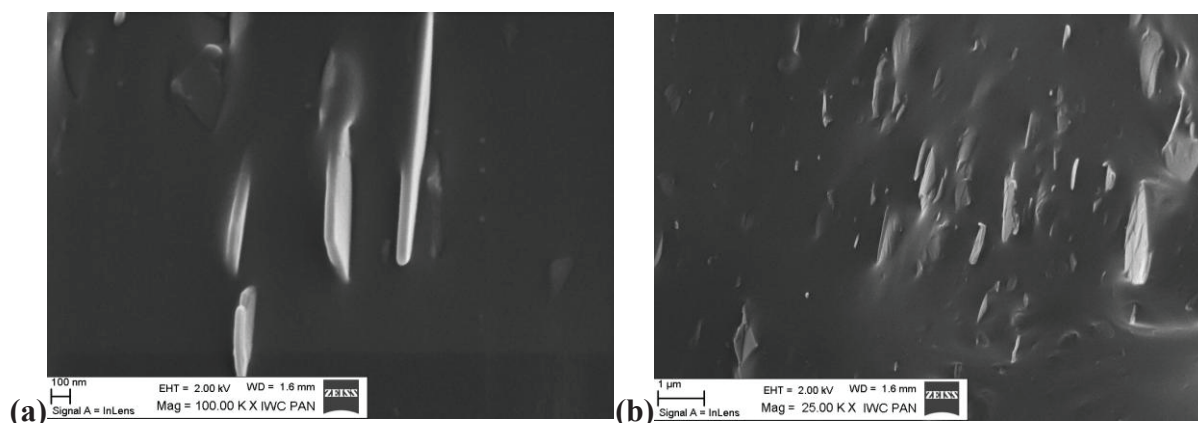


Figure 38 SEM images of XNBR containing 10 phr of LDH70.

An SEM micrograph of XNBR containing 10 phr of LDH70 was also recorded to provide additional insight regarding the composite microstructure. From **Figure 38**, we can observe that the composite exhibited good dispersion of intercalated/exfoliated layers with a thickness of approximately 30 nm. The orientation of anisotropic filler layers in the elastomer matrix in

the direction of the shear force during compounding is advantageous and produces elastomer composites with improved mechanical and morphological properties.

Nevertheless, the melt mixing of high quantities of LDHs did not provide good enough dispersion, as some agglomerates in the XNBR matrix were detected. Because of a high amount of LDH in elastomer, which is necessary to obtain composites with enhanced mechanical parameters, the problem of homogenous distribution of filler particles in elastomer might occur.

5.1.3.9. Gas barrier properties of XNBR/MgAl-LDH composites

It is well known that the presence of layered fillers can help to enhance the gas barrier properties of rubber materials by the formation of a tortuous diffusion path.^{280,281} The influence of LDH type on the air permeability of XNBR is presented in **Figure 39**. An uncrosslinked, neat XNBR sample was too weak mechanically and was destroyed almost immediately by the pressure of the gas at the very beginning of the experiment.

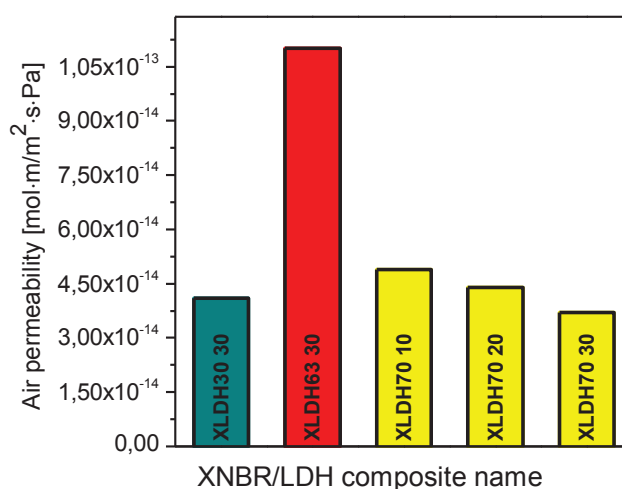


Figure 39 Air permeability of XNBR/LDH composites.

As expected, the air permeability of the composites was found to be much lower in the presence of LDH70 particles. This result is attributed to the very high aspect ratio of the LDH70 particles and their hexagonal plate-like shape, both of which prevent the permeation of gaseous molecules through the composites. Moreover, increasing the filler concentration from 10 to 30 phr slightly but progressively reduced gas permeation through the rubber. The minor differences between the air permeability coefficient values of composites containing various filler contents may be explained by the parallel organization of the highly anisotropic layers in the elastomer matrix under the high shearing forces, which efficiently reduces

permeation of gas molecules through the composite material, even when low amounts of highly anisotropic filler are added. The presence of 30 phr of LDH30 particles, which exhibit a high aspect ratio but have a less ordered structure, had a similar effect on the gas barrier properties as LDH70 at corresponding filler concentration of 30 phr. The composite filled with LDH63 had the highest air permeability, likely due to the small aspect ratio of these LDH particles. Similarly, due to the small aspect ratio of HT particles, the air permeability coefficients of XHT composites were at levels of 1.4×10^{-12} , 2.0×10^{-13} and 4.0×10^{-14} ($\text{mol} \cdot \text{m}^2 \cdot \text{s} \cdot \text{Pa}$) respectively for 10, 20 and 30 phr contents of HT in rubber matrix.

5.1.3.10. Thermal stability of XNBR/MgAl-LDH composites

Thermogravimetric (TGA) and derivate thermogravimetric (DTG) curves of pure XNBR and XNBR loaded with 30 phr of LDH are displayed in **Figure 40**. **Table 33** summarizes the thermal degradation temperatures corresponding to 2% (T_2), 5 % (T_5), 10 % (T_{10}) and 50% weight loss (T_{50}), as well as the char residue at 600 °C. It is evident from **Table 33** that T_2 , T_5 and T_{10} of the XNBR/LDH composites are lower than those of pure XNBR.

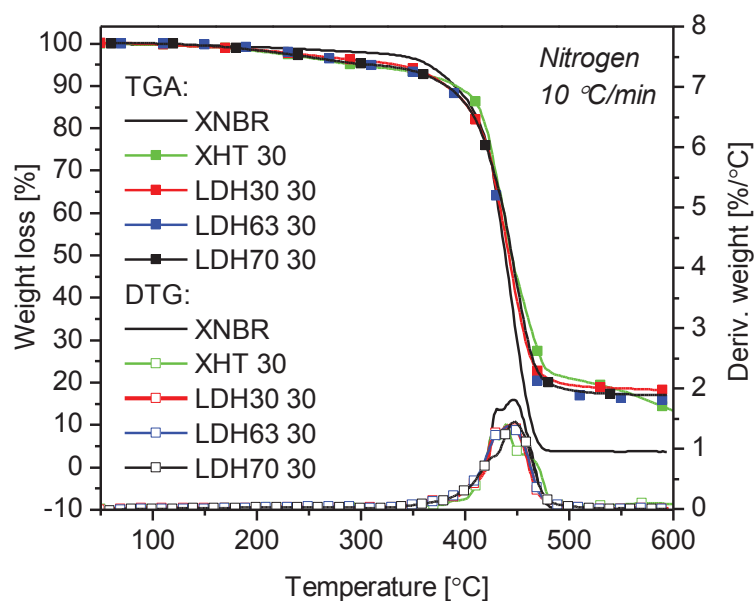


Figure 40 TGA/DTG profiles of XNBR/LDH composites containing 30 phr of filler (under nitrogen).

This result is most likely due to the thermal behavior of pristine MgAl-LDH, which may release intercalated water molecules in the interlayered galleries, the loss of hydroxyl groups from the brucite-like layer structure and the loss of CO_3^{2-} anions as CO_2 in the temperature range of 350-500 °C.

Table 33 Thermal properties of XNBR/LDH composites containing 30 phr of filler (under nitrogen).

Sample name	T ₂ [°C]	T ₅ [°C]	T ₁₀ [°C]	T ₅₀ [°C]	Char residue [wt%]
XNBR	294	364	390	438	3.73
XHT 30	207	291	391	445	13.45
XLDH30 30	223	333	382	442	18.21
XLDH63 30	231	302	379	441	15.95
XLDH70 30	215	309	382	445	17.05

When 50 % weight loss (T₅₀) is selected as the point of comparison, it is observed that the thermal decomposition temperatures of the composites are a few degrees Celsius higher than that of pure XNBR. The residues after thermal decomposition of the XNBR/MgAl-LDH compounds were higher compared to the neat rubber.

5.1.3.11. UV-aging and thermo-oxidative aging of XNBR/MgAl-LDH composites

The mechanical properties and crosslink densities of XNBR composites exposed to the photo-oxidative aging (hv, O₂, T) are summarized in **Table 34**. XNBR generally has poor resistance to ozone, UV radiation and weathering because double bonds are present in polybutadiene segment of the chemical backbone. Inorganic compounds, such as metal oxides are known for their effective UV screening.²⁸² The exposure of XNBR composites to UV radiation resulted in higher stiffness and a loss of elasticity, which is reflected by the significantly reduced elongation at break (EB) as well as the higher modulus values at 100, 200 and 300 % of elongation SE. Based on the obtained K_{UV} values, which reflect the UV stability, the highest UV protection was provided by LDH70. Despite its high stiffness, composite filled with LDH70 showed high tensile strength TS with increasing filler content and, therefore, had enhanced UV stability. This behavior may be explained by the tendency to increase the crosslink density (v_T) of XNBR/MgAl-LDH composites under elevated temperature conditions because higher crosslink density could balance the deleterious effects of UV radiation, which breaks the polymer chains.

Figure 41 shows the changes in the crosslink densities of XNBR/MgAl-LDH composites subjected to the action of hot air at temperature of 100 °C up to 17 days. There is an evident that such materials became more stiff and crosslinked under conditions of the oxygen (O₂) and elevated temperature (T).

Table 34 Mechanical properties and crosslink densities of XNBR/LDH composites subjected to UV radiation.

Sample name	SE ₁₀₀ [MPa]	SE ₂₀₀ [MPa]	SE ₃₀₀ [MPa]	TS [MPa]	EB [%]	K _{UV} [-]	v _T · 10 ⁻⁵ [mol/cm ³]
XNBR	0.8 ± 0.1	0.8 ± 0.1	0.8 ± 0.1	1.1 ± 0.1	1167 ± 48	-	1.90 ± 0.17
XZnO 5	2.1 ± 0.2	2.6 ± 0.2	3.5 ± 0.2	6.0 ± 0.4	400 ± 10	0.2	2.80 ± 0.29
XHT 2.5	1.5 ± 0.1	1.7 ± 0.2	2.0 ± 0.2	2.8 ± 0.3	510 ± 20	0.2	4.91 ± 0.35
XHT 5	1.6 ± 0.1	1.9 ± 0.1	2.3 ± 0.1	3.2 ± 0.1	470 ± 20	0.2	5.12 ± 0.61
XHT 10	2.0 ± 0.1	2.7 ± 0.1	3.8 ± 0.3	5.3 ± 0.5	460 ± 10	0.3	7.08 ± 0.91
XHT 20	3.2 ± 0.1	4.7 ± 0.1	6.1 ± 0.1	8.0 ± 0.6	420 ± 20	0.4	9.40 ± 0.80
XHT 30	3.8 ± 0.1	5.6 ± 0.1	7.2 ± 0.1	11.1 ± 0.1	480 ± 10	0.6	10.73 ± 0.91
XLDH30 2.5	1.2 ± 0.1	1.2 ± 0.1	1.2 ± 0.1	1.3 ± 0.1	700 ± 40	0.3	2.71 ± 0.18
XLDH30 5	1.3 ± 0.1	1.3 ± 0.1	1.4 ± 0.1	2.3 ± 0.2	780 ± 50	0.4	3.33 ± 0.56
XLDH30 10	2.2 ± 0.1	3.0 ± 0.2	3.7 ± 0.3	5.2 ± 0.2	450 ± 40	0.4	8.69 ± 0.59
XLDH30 20	3.4 ± 0.2	4.7 ± 0.3	5.5 ± 0.3	6.9 ± 0.2	440 ± 10	0.4	10.61 ± 0.50
XLDH30 30	4.3 ± 0.2	6.0 ± 0.3	7.2 ± 0.3	8.8 ± 0.5	410 ± 10	0.4	10.99 ± 0.87
XLDH63 2.5	1.3 ± 0.1	1.4 ± 0.1	1.6 ± 0.1	2.1 ± 0.2	490 ± 40	0.3	4.81 ± 0.21
XLDH63 5	1.6 ± 0.2	1.9 ± 0.2	2.1 ± 0.2	2.9 ± 0.1	450 ± 10	0.3	5.00 ± 0.29
XLDH63 10	2.2 ± 0.1	2.9 ± 0.1	3.9 ± 0.1	6.2 ± 0.1	471 ± 10	0.3	7.81 ± 0.49
XLDH63 20	2.9 ± 0.1	4.5 ± 0.1	6.0 ± 0.1	8.9 ± 0.1	460 ± 10	0.4	9.30 ± 0.78
XLDH30 30	3.5 ± 0.1	5.5 ± 0.1	7.3 ± 0.1	10.5 ± 0.2	450 ± 10	0.4	10.90 ± 0.55
XLDH70 2.5	1.5 ± 0.1	1.8 ± 0.1	2.0 ± 0.1	3.1 ± 0.1	550 ± 15	0.5	4.37 ± 0.23
XLDH70 5	2.0 ± 0.1	2.8 ± 0.1	3.6 ± 0.2	6.0 ± 0.1	480 ± 10	0.3	7.31 ± 0.71
XLDH70 10	4.7 ± 0.3	6.4 ± 0.3	8.0 ± 0.3	14.5 ± 0.1	490 ± 30	0.7	11.77 ± 1.05
XLDH70 20	6.1 ± 0.5	7.8 ± 0.6	9.4 ± 0.7	16.0 ± 2.0	440 ± 30	0.5	13.33 ± 0.55
XLDH70 30	9.9 ± 0.6	12.4 ± 1.0	14.2 ± 1.0	21.5 ± 2.0	480 ± 40	0.9	18.75 ± 1.89

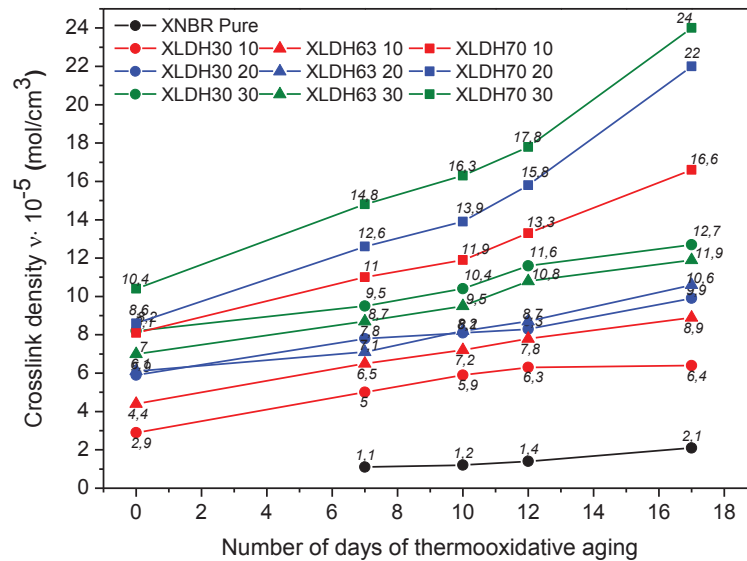


Figure 41 The influence of thermo-oxidative aging time on the crosslink density v_T of XNBR/LDHs composites.

5.1.3.12. Conclusions

The simultaneous application of magnesium-aluminum layered double hydroxide (MgAl-LDH) as a filler and as a crosslinking agent in carboxylated nitrile butadiene rubber (XNBR) produces mechanically strong and transparent elastomer composites without requiring the addition of standard curatives, such as zinc oxide, or a sulfur cure system, which is an important ecological and economical advantage. In addition, it was found that the optical properties of XNBR/LDH composites are reversible, depending on temperature and the type of MgAl-LDH. The addition of high levels of LDH with a Mg/Al ratio $\approx 2:1$ to the XNBR matrix produced composites that exhibited thermoreversible transparency. In contrast, the application of aluminum rich LDH resulted in opaque materials, whereas XNBR filled with Mg-rich LDH exhibited transparency but did not show thermotropic behavior. It was found that the LDHs effectively participate in the crosslinking reaction of XNBR and contributes to obtaining strong and stiff elastomeric composites. The high aspect ratio of the layers and the high magnesium content in the LDH structure resulted in significant improvements in mechanical and barrier properties and promoted the formation of a higher number of ionic crosslinks between the XNBR and filler. The parallel orientation of highly anisotropic filler layers in the rubber matrix under the conditions of high shearing force in the internal mixer is advantageous and produces elastomer composites with improved physical properties. The dynamic mechanical analysis revealed a remarkable enhancement in the storage moduli and increase in glass transition temperature when LDH is present in the XNBR matrix. The increase in crosslink density and the improvement in mechanical properties of XNBR/HT composites may result from the following types of interactions between: (a) acidic functionalities of XNBR and basic hydroxyl groups existing on the filler sheets, (b) polar functional groups of XNBR and polar surface of filler, (c) $-\text{COOH}$ and metal ions provided by HT (ionic bonds). The incorporation of LDH delivers not only an environmentally friendly, zinc oxide-free rubber product but also an ionic elastomer composite with excellent mechanical, barrier and transparent properties. However, obtaining material with aforementioned parameters requires quite high loadings of layered mineral. Application of large amounts of an inexpensive and easily synthesized filler is economically beneficial due to the reduction of the cost of the final product, however, in consequence, the problem of uniform distribution might occur.

5.2. EFFECTS OF IONIC LIQUIDS (ILs) ON THE PROPERTIES OF ELASTOMER COMPOSITES BASED ON CARBOXYLATED ACRYLONITRILE-BUTADIENE RUBBER (XNBR) AND LAYERED DOUBLE HYDROXIDE (LDH)

INTRODUCTION: Application of room temperature ionic liquids (RTILs) can help accelerate the curing process of rubbers, enhance the ionic conductivity and improve the state of filler dispersion of elastomer composites. Therefore, this chapter mainly focuses on investigation the influence of IL structure, hydrophilicity-hydrophobicity and concentration on the aforementioned properties of rubber composites. The effects of an increasing concentration of 2.5 phr to 15 phr (parts per hundred rubber) of imidazolium ionic liquids on carboxylated acrylonitrile-butadiene rubber (XNBR) composites filled with magnesium-aluminum layered double hydroxide (LDH) were investigated. The effects of anion type (tetrachloroaluminate $[\text{AlCl}_4]^-$, thiocyanate $[\text{SCN}]^-$ and *bis*(trifluoromethylsulfonyl)imide $[\text{TFSI}]^-$) of imidazolium ionic liquid and the impacts of the length of alkyl chain of 1-*n*-alkyl-3-methylimidazolium salt consisting with *bis*(trifluoromethylsulfonyl)imide anion $[\text{Cn-MIM}][\text{TFSI}]$ on the properties of XNBR/LDH compounds were analyzed.

5.2.1. Preparation of XNBR/IL-LDH composites

The magnesium-aluminum layered double hydroxide (LDH) in an amount of 30 phr was mixed with different contents (2.5, 5, 10 and 15 phr) of imidazolium ionic liquid (IL) by grinding it till a homogeneous paste was obtained. The rubber compounds were processed in an internal mixer Brabender Measuring Mixer N50 at 50 rpm rotors speed and the initial temperature was set at 70 °C. After around 5 minutes of rubber mastication, the mix composed of LDH and IL was added and homogenized for around 10 minutes. Subsequently the compounded rubbers were milled in a laboratory two-roll mill. The compounding ingredients and the amounts are presented in **Table 35**.

Table 35 Formulation of XNBR/IL-LDH compounds, [phr].

Component	XNBR/LDH	IL 2.5	IL 5	IL 10	IL 15
XNBR	100	100	100	100	100
LDH	30	30	30	30	30
Ionic Liquid IL	0	2.5	5	10	15

5.2.2. Curing studies and crosslink densities of XNBR/IL-LDH composites

The effects of the type of imidazolium salts were analyzed with regards to the curing behavior and crosslink density of the XNBR/IL-LDH composites. Results for curing kinetics and crosslink densities of the composites are summarized in **Table 36**.

Table 36 Cure characteristics and crosslink densities of XNBR/IL-LDH composites crosslinked at 160 °C.

Sample name and IL content [phr]	ML [dNm]	MH [dNm]	ΔM [dNm]	$t_{\Delta 2}$ [min]	t_{90} [min]	CRI [min ⁻¹]	$v_T \cdot 10^{-5}$ [mol/cm ³]
XNBR/LDH	1.4	6.6	5.2	4.1	77	1.4	8.2 ± 0.17
[BMIM][AlCl ₄] 2.5	2.1	9.6	7.5	1.2	30	3.5	12.03 ± 0.66
[BMIM][AlCl ₄] 5	3.8	13.7	9.9	0.9	33	3.1	12.83 ± 0.55
[BMIM][AlCl ₄] 10	4.6	17.0	12.4	0.7	32	3.4	13.36 ± 0.77
[BMIM][AlCl ₄] 15	4.8	19.6	14.8	0.5	28	3.6	16.08 ± 0.66
[EMIM][SCN] 2.5	1.5	5.9	4.4	1.4	36	3.0	9.96 ± 0.60
[EMIM][SCN] 5	1.6	6.0	4.4	1.5	35	3.0	10.16 ± 0.49
[EMIM][SCN] 10	1.2	4.8	3.6	1.3	35	3.0	8.06 ± 0.56
[EMIM][SCN] 15	1.1	4.4	3.3	1.9	37	2.9	7.53 ± 0.88
[EMIM][TFSI] 2.5	1.1	5.3	4.2	2.6	62	1.7	8.00 ± 0.45
[EMIM][TFSI] 5	1.2	5.0	3.8	2.5	59	1.7	7.61 ± 0.40
[EMIM][TFSI] 10	1.0	4.6	3.6	3.2	63	1.7	6.90 ± 0.40
[EMIM][TFSI] 15	1.0	5.2	4.2	2.0	61	1.7	6.51 ± 0.22
[AMIM][TFSI] 2.5	1.1	5.3	4.2	2.6	64	1.6	7.55 ± 0.55
[AMIM][TFSI] 5	1.1	5.1	4.0	2.3	60	1.7	7.11 ± 0.17
[AMIM][TFSI] 10	1.1	5.0	4.9	2.8	62	1.7	6.62 ± 0.33
[AMIM][TFSI] 15	0.7	4.4	3.7	2.9	60	1.8	6.40 ± 0.28
[BMIM][TFSI] 2.5	1.2	5.4	4.2	2.6	65	1.6	8.21 ± 0.50
[BMIM][TFSI] 5	1.1	5.3	4.2	2.5	63	1.6	7.63 ± 0.45
[BMIM][TFSI] 10	1.1	4.8	3.7	3.2	64	1.6	6.91 ± 0.36
[BMIM][TFSI] 15	0.8	4.0	3.2	3.9	63	1.7	6.59 ± 0.30
[HMIM][TFSI] 2.5	1.1	5.3	4.2	2.6	58	1.8	6.41 ± 0.25
[HMIM][TFSI] 5	1.1	4.9	3.8	2.5	56	1.9	6.28 ± 0.30
[HMIM][TFSI] 10	0.8	4.3	3.5	3.4	65	1.6	6.02 ± 0.10
[HMIM][TFSI] 15	0.7	3.9	3.2	3.9	66	1.6	5.39 ± 0.28

Applying the tetrachloroaluminate [BMIM][AlCl₄] and thiocyanate [EMIM][SCN], which are hydrophilic ionic liquids, markedly accelerated the curing process of the XNBR/LDH composite in comparison with the reference sample (XNBR/LDH). The faster curing process is reflected in a doubled cure rate index (CRI) value reported for rubber compounds containing hydrophilic ILs. The increased concentration of tetrachloroaluminate ionic liquid reduced the scorch time ($t_{\Delta 2}$) and shortened the curing time (t_{90}) from 77 min (0 phr) to 28

min (15 phr). The ability of certain types of imidazolium ionic liquids to influence the rate of crosslinking process is a phenomenon particularly known for the rubber compounds vulcanized with the conventional sulfur cure system. It has been stated that ILs may act as catalysts of interface reactions thus significantly affect the rheometric parameters. The type of anion has been found to have a decisive influence on the extent of the vulcanization acceleration whereas the length of alkyl chains in the ionic liquid molecule has less importance in this regard.^{191,192}

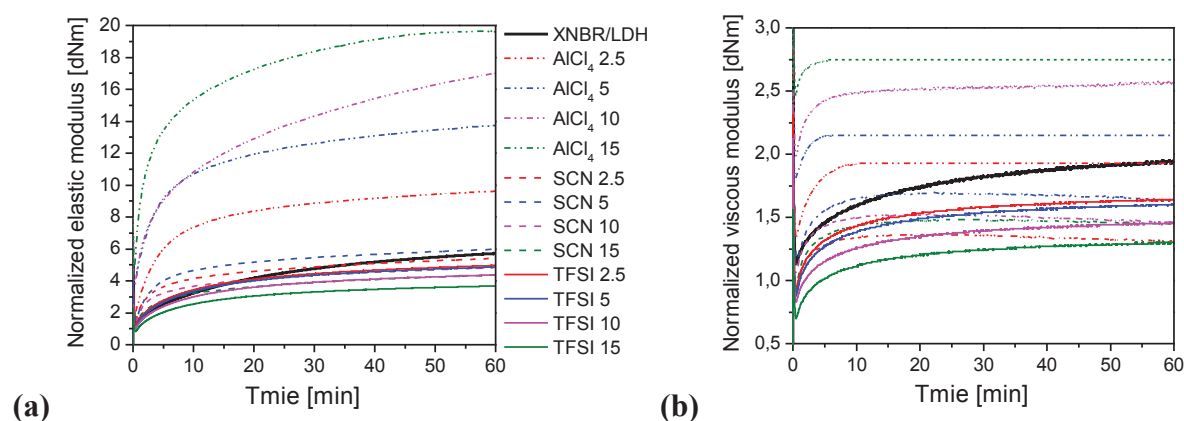


Figure 42 (a) Normalized elastic modulus M' of the torque as a function of time, (b) normalized viscous modulus M'' of the torque as a function of time for XNBR/IL-LDH compounds crosslinked at 160 °C.

In contrast to the hydrophilic ILs, the incorporation of the hydrophobic TFSI-based imidazolium ILs in the elastomer matrix had only a slight impact on the acceleration of curing process of XNBR by LDH. Apparently, TFSI-based imidazolium salts caused the reduction of t_{A2} the most remarkably when added in small amount of 2.5 phr, whereas further IL addition resulted in a proportional extension of t_{A2} . The value of optimal curing time t_{90} was reduced from 77 to 65 min in the presence of *bis*(trifluoromethylsulfonyl)imide anions and remained almost unchanged regardless of the alkyl side length and the imidazolium salt content.

From the rheometric data we can observe changes in the minimum torque (ML), which is a representative of rubber mix viscosity and the maximum torque (MH), which is an indicator of the extent of crosslinking between rubber chains and reinforcement by the filler particles. It can be clearly seen from rheometric data showed in **Table 36** and **Figure 42**, that the increased concentration of tetrachloroaluminate ions led to a significant increase in the rubber mix viscosity ML and crosslink density reflected in MH due to the crosslinking reaction that took place during the rubber compounding. The considerably higher crosslink densities of

composites containing tetrachloroaluminate anions were also confirmed by the study of equilibrium swelling in toluene and is represented by the v_T parameter. The value of v_T increased gradually with increasing amounts of [BMIM][AlCl₄] from $8.2 \cdot 10^{-5}$ (0 phr) up to $16.0 \cdot 10^{-5}$ mol/cm³ at 15 phr content of IL. This results from the curing effect of anion of alkylimidazolium salt in the XNBR compound. Similarly, application of hydrophilic thiocyanate ionic liquid [EMIM][SCN] at small concentrations 2.5 – 5 phr increased mix viscosity and promoted obtaining higher crosslink densities of XNBR/LDH. When the amounts of thiocyanate salt exceeded 10 phr, the torque parameters and the number of bonds formed between macromolecules in the elastomer network were slightly reduced. This can be explained through the fact that excess of IL acts as a plasticizer and may weaken filler-rubber interactions thus reduces the formation of network nodes between the chains of elastomer.

The opposite effects of the imidazolium salt concentration on the torque parameters were observed for the composites containing a series of hydrophobic TFSI-based ILs. Their increased loadings resulted in the reduction of all the torque values compared to the control sample thereby manifesting their plasticizing effect on XNBR matrix. It is noticeable that increasing the alkyl chain length of imidazolium cation from ethyl to hexyl lowered the mix viscosity and hindered network formation, which is reflected in reduced ΔM values in comparison with the reference sample. For TFSI-based IL series, the plasticizing effect of [HMIM]⁺ was found to be the highest likely due to its bulky structure. The results from a moving die rheometer are in good agreement with the results of crosslink density obtained on the base of equilibrium swelling method. The number of crosslinks (v_T) formed in the presence of [TFSI]⁻ anions was inversely proportional to the IL amount. Most likely, the hydrophobic IL present onto the filler surface acted like plasticizer.

5.2.3. Dynamic mechanical analysis (DMA) of XNBR/IL-LDH composites

The glass transition temperatures T_g of the XNBR/IL-LDH composites were measured by differential scanning calorimetry DSC and dynamic mechanical analysis DMA thermoanalytical techniques and are summarized in **Table 37**. The loss tangent ($\tan \delta$), storage modulus (E') and loss modulus (E'') as functions of temperature are illustrated in **Figure 43 a-d** and **Figure 44 a-d**. DMA experiments were performed at a vibration frequency of 10 Hz.

According to the data showed in **Table 37**, both techniques showed a single T_g for all composites suggesting no microscopic phase separation and compatibility of the polymer

matrix with the imidazolium salts used. DMA method provided more precise values as it is a more sensitive technique for measuring the T_g than the DSC method.

Table 37 Glass transition temperatures T_g and dynamic mechanical properties of XNBR/IL-LDH composites. Vibrational frequency of 10 Hz.

Sample name and IL content [phr]	T_g from DSC [°C]	T_g from E'' [°C]	T_g from $\tan \delta$ [°C]	Height of T_g [-]	T_i from $\tan \delta$ [°C]	Height of T_i [-]	E' at 25 °C [MPa]
XNBR/LDH	-23	-18.0	-6.8	1.16	51.6	0.21	10.4
[EMIM][SCN] 15	-23	-18.8	-6.8	1.15	31.4	0.23	10.4
[BMIM][AlCl ₄]							
2.5	-23	-16.9	-6.6	1.15	-	-	10.2
5	-23	-19.2	-6.6	1.15	-	-	10.6
10	-24	-19.0	-7.4	1.10	-	-	12.2
15	-24	-20.0	-9.7	1.10	-	-	12.7
[BMIM][TFSI]							
2.5	-24	-18.2	-8.0	1.18	45.7	0.22	11.2
5	-26	-20.3	-9.7	1.22	46.7	0.22	9.1
10	-28	-24.1	-12.9	1.21	45.7	0.23	9.3
15	-33	-24.4	-14.4	1.21	41.3	0.23	9.7
[EMIM][TFSI] 15	-31	-22.0	-10.9	1.20	48.3	0.22	8.1
[AMIM][TFSI] 15	-31	-23.3	-12.9	1.20	47.6	0.22	7.8
[HMIM][TFSI] 15	-33	-24.4	-14.4	1.20	45.7	0.23	7.9

The presence of hydrophilic ILs had less impact on the changes in the glass transition temperature T_g of XNBR/LDH composite in comparison to the hydrophobic ones. Hydrophilic [BMIM][AlCl₄] and hydrophobic [BMIM][TFSI] were selected as representative ionic liquids to demonstrate the effects of their increasing concentrations from 2.5 to 15 phr on the XNBR matrix relaxation processes. As it can be seen in **Figure 43 a**, the maximum height of the $\tan \delta$ peak of the XNBR/[BMIM][TFSI]-LDH composites displaced towards lower temperatures from -6.8 °C (reference sample) up to -14.4 °C ([BMIM][TFSI] 15) with increasing levels of the IL, indicating the plasticizing behavior of [BMIM][TFSI] in the XNBR matrix. On the other hand, a high concentration of tetrachloroaluminate ions caused a shift in T_g only by three degrees to -9.7 °C thus showing a much smaller effect of plasticization.

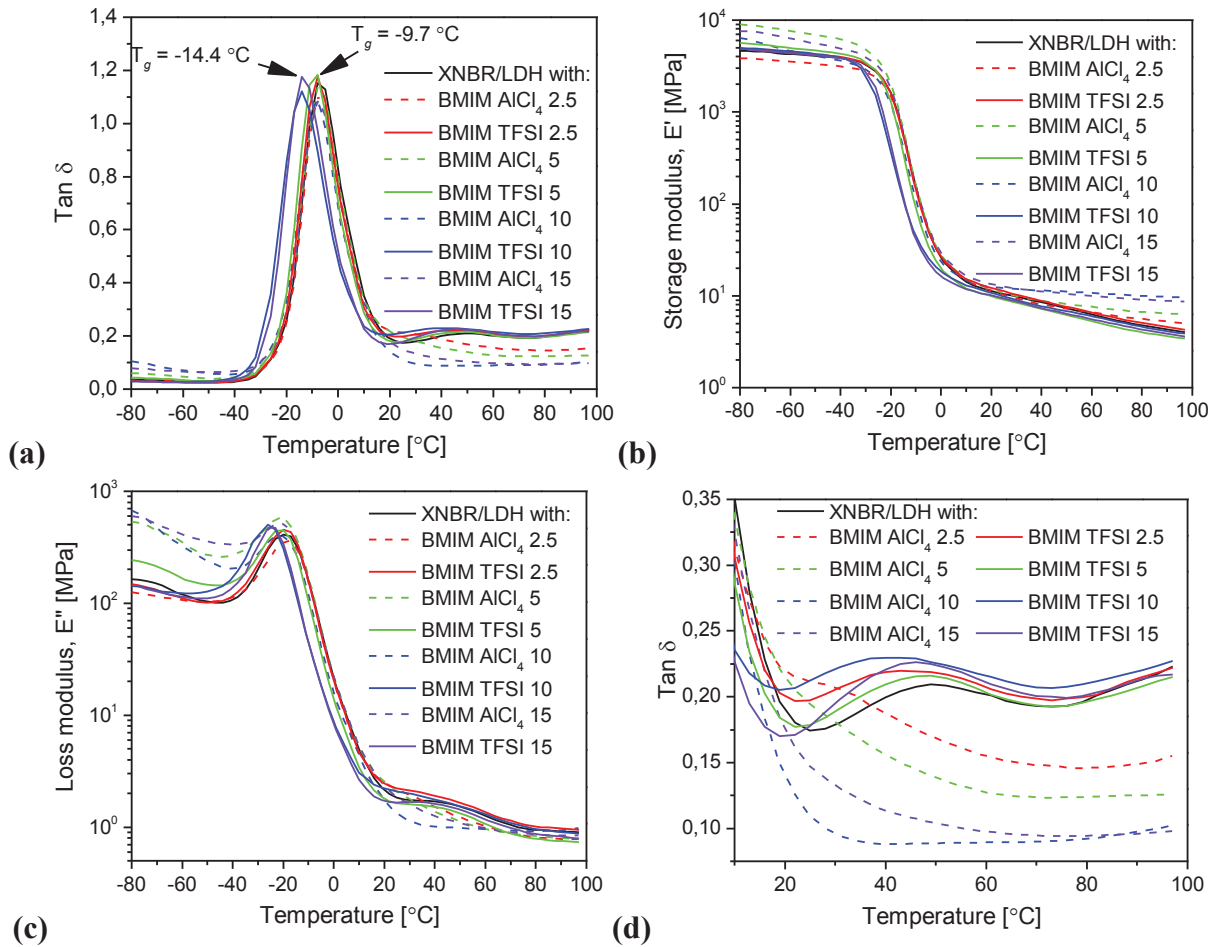


Figure 43 (a) Plot of $\tan \delta$, (b) plot of storage modulus E' , (c) plot of loss modulus E'' versus temperature, (d) ionic transition region T_i for XNBR composites containing [BMIM][AlCl_4] and [BMIM][TFSI]. Vibration frequency, 10 [Hz].

It can be seen from **Figure 43 b** that increasing the hydrophilic tetrachloroaluminate salt amount contributed to an increase in storage modulus (E') of the composites over the whole temperature region, whereas the presence of TFSI-based IL caused a decrease in E' in the glassy state as well as in the rubbery region. This is due to the fact that in the glass transition region, the motion of molecules is governed by the crosslink density, which in this case was increased by the presence of [BMIM][AlCl_4] and lowered by the presence of [BMIM][TFSI]. **Figure 43 d** shows an additional shoulder in the $\tan \delta$ peak plot, also known as ionic transition peak (T_i) which ascribed to the existence of ionic bonds in the XNBR/LDH network. Increasing hydrophilic IL content resulted in the gradual disappearance of the T_i peak whereas this shoulder remained almost unchanged in the presence of the hydrophobic IL and slightly displaced towards lower temperatures by the increased [TFSI]⁻ anions levels in XNBR/LDH composite.

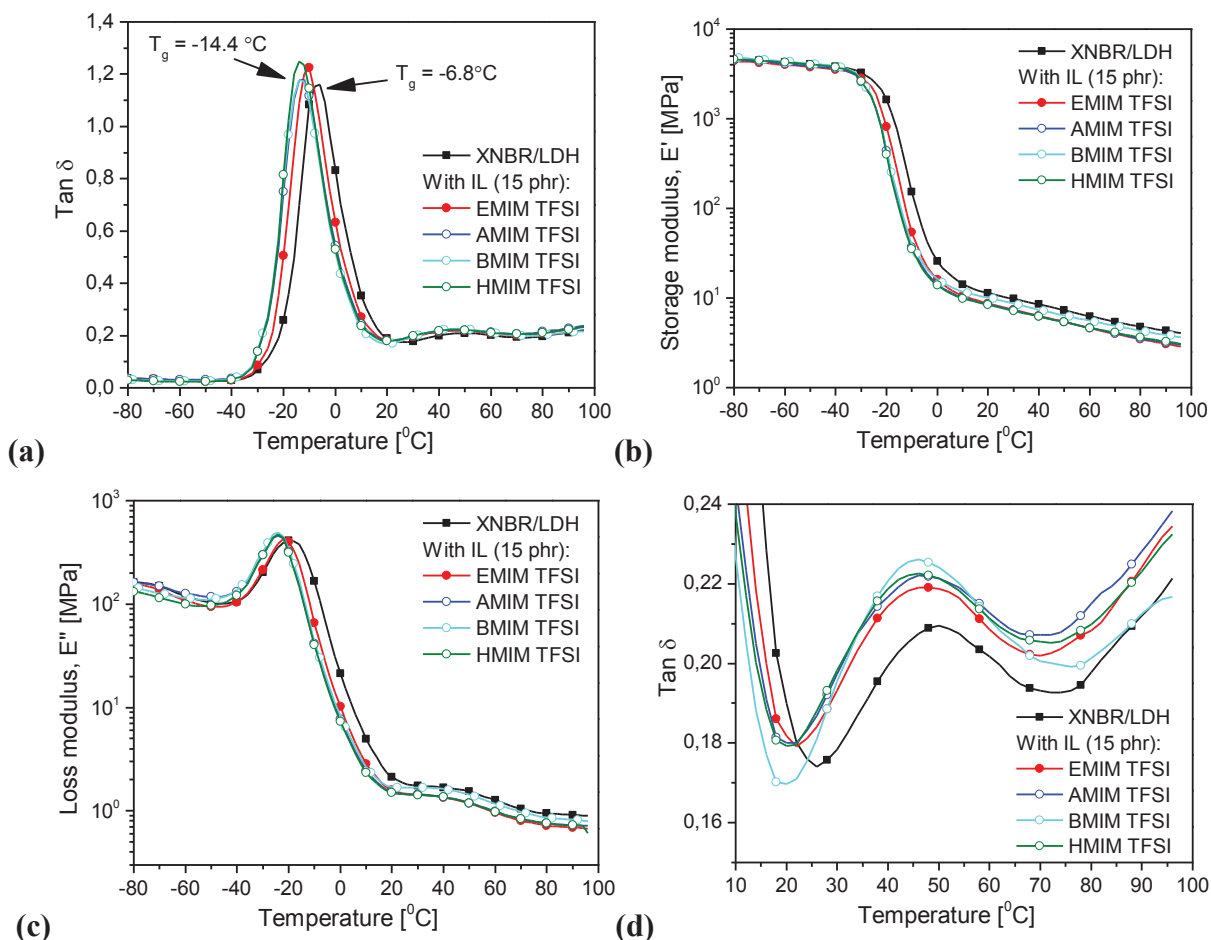


Figure 44 (a) Plot of $\tan \delta$, (b) plot of storage modulus E' , (c) plot of loss modulus E'' versus temperature, (d) ionic transition region T_i for XNBR composites containing 15 phr of TFSI-based ILs. Vibration frequency, 10 [Hz].

The effects of the length of the alkyl backbone of the imidazolium ring TFSI-based IL on T_g (Table 37) and dynamic mechanical properties (Figure 44 a-d) of XNBR/IL-LDH composites were analyzed for the samples containing the highest IL concentration of 15 phr. Increasing the length of the alkyl backbone chain from ethyl to hexyl contributed to a slight drop in T_g (DSC) from -31°C for the sample with [EMIM] and [AMIM][TFSI]s to -33°C for the sample with [BMIM] and [HMIM][TFSI]s. It can be seen from Figure 36a, that $\tan \delta$ peak maximum shifted toward lower temperature from -6.8 (control sample) to -10.9°C (15 phr [EMIM][TFSI]) and around -14.4°C (15 phr [HMIM][TFSI]). The changes in T_g in the XNBR/IL-LDH composites depended slightly on the alkyl backbone length in the imidazolium ring of the incorporated IL, however the greatest plasticization was reported for sample containing the 1-hexyl-methylimidazolium *bis*(trifluoromethylsulfonyl)-imide. The plasticizing effect of [TFSI]-containing ionic liquids on acrylonitrile-butadiene

rubber NBR has been already reported by Marwanta²³⁶ hydrogenated nitrile butadiene rubber HNBR by Likozar,²²⁸ and also solution styrene butadiene rubber SSBR²³⁹ and polychloroprene rubber CR by Subramaniam.^{229,231} However, according to the existing literature, there have been no studies on the effect of TFSI-based ionic liquid on the ionically crosslinked systems. The presence of the hydrophobic IL in the XNBR/LDH compounds did not substantially alter the high temperature relaxation T_i peak (**Figure 44 d**).

5.2.4. Mechanical properties of XNBR/IL-LDH composites

The influence of ionic liquids on the physical properties of the XNBR/LDH composites at 0, 2.5, 5, 10 and 15 phr concentrations is given in **Table 38**. In general, the incorporation of small quantities of ILs led to a slight improvement in tensile strength (TS) of XNBR/LDH composites. A clear effect of the types of ionic liquid on the mechanical parameters of elastomer material can be seen at concentrations of ILs greater than 5 phr in the elastomer matrix.

The composites with increasing levels of tetrachloroaluminate imidazolium salt exhibited lower tensile strength (TS) and elongation at break (EB) but higher hardness Shore A (H) and increased stress at 100, 200 and 300 % elongation (SE_{100} , SE_{200} and SE_{300}) in comparison with reference sample. This is due to the reduced mobility of the backbone chains (reduced flexibility) and the higher number of crosslinks in the XNBR/[BMIM][AlCl₄]-LDH. In this case, the increase in SE_{300} correlated well with already reported increment in the torque and the crosslink density of the rubber network.

Nevertheless, more commonly observed trend is when the excess of IL acts as a plasticizer and affects the mechanical properties of the resulting composites by increasing the flexibility of rubber material. The stretching stress at 300 %, (SE_{300}) and hardness (H) of the XNBR/[EMIM][SCN]-LDH clearly display an upward trend when 5 phr of [EMIM][SCN] is added and a downward trend upon further addition of hydrophilic IL. An increase in [EMIM][SCN] and TFSI-based ILs contents yielded poorer mechanical properties due to the softening of the polymer matrix and higher elasticity of the rubber materials.

The incorporation of small quantities (2.5 or 5 phr) of TFSI-based IL resulted in a slight increase in the tensile strength (TS) and elongation at break (EB) of the XNBR/LDH composite however, increasing the quantity to 10 or 15 phr slightly decreased stress at break and yielded a rubber material of higher elasticity.

Table 38 Mechanical properties of XNBR/IL-LDH composites crosslinked at 160 °C.

Sample name and IL content [phr]	SE ₁₀₀ [MPa]	SE ₂₀₀ [MPa]	SE ₃₀₀ [MPa]	TS [MPa]	EB [%]	H [°Sh]
XNBR/LDH	3.0 ± 0.1	5.3 ± 0.1	6.3 ± 0.2	17.6 ± 1.0	634 ± 20	62
[BMIM][AlCl ₄] 2.5	3.2 ± 0.2	5.2 ± 0.3	6.9 ± 0.3	17.3 ± 0.8	600 ± 10	67
[BMIM][AlCl ₄] 5	4.0 ± 0.1	6.3 ± 0.2	8.4 ± 0.4	13.5 ± 0.5	468 ± 20	70
[BMIM][AlCl ₄] 10	4.2 ± 0.1	6.5 ± 0.2	8.8 ± 0.3	10.4 ± 0.6	382 ± 20	71
[BMIM][AlCl ₄] 15	4.3 ± 1.0	7.1 ± 1.7	9.4 ± 1.7	9.4 ± 1.6	301 ± 50	71
[EMIM][SCN] 2.5	2.3 ± 0.1	4.2 ± 0.2	6.0 ± 0.2	18.1 ± 0.8	653 ± 40	63
[EMIM][SCN] 5	2.6 ± 0.2	4.9 ± 0.3	6.8 ± 0.3	17.4 ± 0.6	678 ± 27	65
[EMIM][SCN] 10	2.6 ± 0.2	4.6 ± 0.3	6.5 ± 0.4	16.2 ± 1.4	645 ± 24	61
[EMIM][SCN] 15	2.1 ± 0.2	3.3 ± 0.3	4.3 ± 0.4	6.4 ± 0.7	488 ± 25	59
[EMIM][TFSI] 2.5	2.6 ± 0.2	4.5 ± 0.4	6.0 ± 0.5	19.4 ± 1.3	665 ± 20	62
[EMIM][TFSI] 5	2.5 ± 0.1	4.3 ± 0.2	5.9 ± 0.3	18.8 ± 0.6	677 ± 30	62
[EMIM][TFSI] 10	2.2 ± 0.1	3.7 ± 0.2	5.1 ± 0.3	16.8 ± 0.6	690 ± 30	61
[EMIM][TFSI] 15	1.9 ± 0.1	3.3 ± 0.3	4.6 ± 0.4	14.1 ± 1.0	700 ± 30	60
[AMIM][TFSI] 2.5	2.6 ± 0.1	4.5 ± 0.2	6.2 ± 0.3	20.7 ± 0.5	660 ± 10	62
[AMIM][TFSI] 5	2.5 ± 0.2	4.3 ± 0.3	5.8 ± 0.3	19.3 ± 1.5	679 ± 30	61
[AMIM][TFSI] 10	2.2 ± 0.1	3.8 ± 0.1	5.2 ± 0.2	18.1 ± 0.5	700 ± 10	59
[AMIM][TFSI] 15	2.0 ± 0.1	3.4 ± 0.1	4.7 ± 0.1	15.1 ± 1.0	710 ± 30	59
[BMIM][TFSI] 2.5	2.3 ± 0.1	4.0 ± 0.2	5.5 ± 0.2	18.2 ± 1.0	665 ± 20	63
[BMIM][TFSI] 5	2.2 ± 0.1	3.8 ± 0.1	5.2 ± 0.1	18.0 ± 0.5	677 ± 15	62
[BMIM][TFSI] 10	2.2 ± 0.2	3.7 ± 0.4	5.1 ± 0.5	17.5 ± 0.8	705 ± 30	62
[BMIM][TFSI] 15	1.7 ± 0.1	2.8 ± 0.1	3.9 ± 0.1	13.5 ± 0.5	727 ± 30	59
[HMIM][TFSI] 2.5	2.1 ± 0.1	3.5 ± 0.1	4.7 ± 0.1	15.0 ± 1.0	717 ± 30	61
[HMIM][TFSI] 5	2.1 ± 0.1	3.5 ± 0.3	4.8 ± 0.4	15.1 ± 0.6	719 ± 30	60
[HMIM][TFSI] 10	2.0 ± 0.1	3.5 ± 0.2	4.8 ± 0.2	14.7 ± 0.3	725 ± 30	59
[HMIM][TFSI] 15	1.7 ± 0.1	2.8 ± 0.1	3.9 ± 0.1	13.5 ± 1.0	741 ± 50	58

This finding agrees with previous results, where it was shown that [TFSI]-based imidazolium salts do not increase the network density of XNBR/LDH composites, but rather act as a plasticizing agent in such systems thus increases elongation at break of the rubber material (**Figure 45**).

The presence of 1-hexyl-3-methylimidazolium *bis*(trifluoromethylsulfonyl)imide had the greatest impact in increasing the elongation at break (EB) and reducing the tensile strength (TS) of the XNBR/LDH composite. The plasticizing effect from extending the alkyl chain length on the imidazolium ring is evident even at the low concentration of 2.5 phr in the rubber matrix, due to the low value of $SE_{300\%}$ and high value of EB .

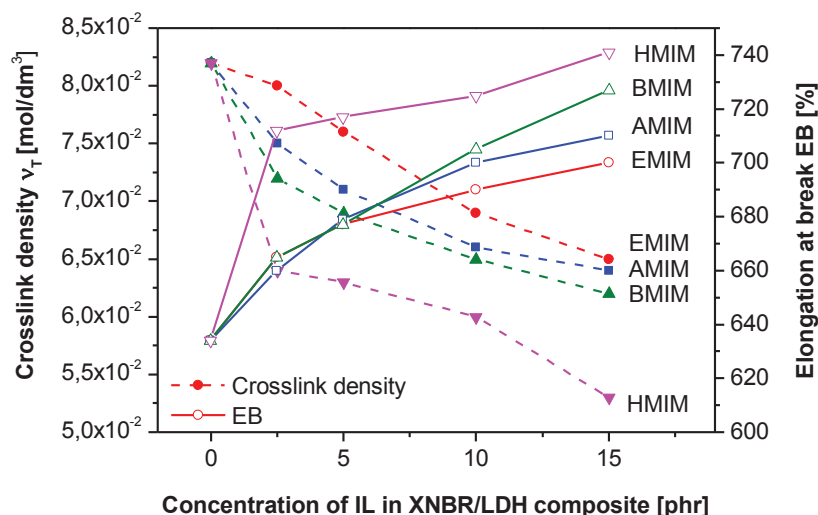


Figure 45 Effects of ILs cation type of TFSI-based IL and IL loading on the network density v_T and elongation at break EB of XNBR/LDH composites.

5.2.5. Ionic conductivity of XNBR/IL-LDH composites

Doping rubbers with highly conductive ionic liquids is a simple way to prepare composites with enhanced ionic conductivity and good elasticity. Because ionic liquids are composed of only ions, they show very high ionic conductivity and typical values of IL conductivity measured at 25 °C range from 10^{-3} to over 10^{-2} S/cm at room temperature. The hydrophilic [BMIM][AlCl₄] and [EMIM][SCN] show conductivities of 9.2×10^{-3} and 21×10^{-3} S/cm (20 °C), respectively whereas the hydrophobic [BMIM][TFSI] has conductivity of 3.5×10^{-3} S/cm (20 °C). As anticipated, increasing the amount of ionic liquid in the XNBR/IL-LDH resulted in an enhancement in the ionic conductivity of the elastomer composites which is based on the contribution of charge carriers. However, the improved conductivity of the rubber materials is a function not only of the number of IL ions and the conductivity of the pure IL but also may be influenced by the plasticizing effect of the ILs on the rubber matrix. The relationship between the plasticization effect and the increased conductivity of the polymer/IL material is presented in **Table 39**.

Table 39 Effect of ionic liquids on the XNBR/IL-LDH glass transition temperature T_g and ionic conductivity σ' .

Sample name and IL content [phr]	T_g from DSC [°C]	ΔT_g [°C]	σ' (1 Hz, 25 °C) [S/cm]	σ' (1 kHz, 25 °C) [S/cm]
XNBR Pure	-25	-	1.2×10^{-10}	2.5×10^{-10}
XNBR/LDH	-23	-	1.4×10^{-10}	4.6×10^{-10}
[BMIM][AlCl ₄] 2.5	-23	0	2.1×10^{-9}	4.9×10^{-9}
[BMIM][AlCl ₄] 5	-23	0	7.7×10^{-9}	1.7×10^{-8}
[BMIM][AlCl ₄] 10	-23	0	8.8×10^{-9}	1.4×10^{-8}
[BMIM][AlCl ₄] 15	-23	0	1.5×10^{-8}	2.3×10^{-8}
[EMIM][SCN] 2.5	-20	5	5.6×10^{-9}	8.7×10^{-9}
[EMIM][SCN] 5	-23	0	1.9×10^{-8}	2.4×10^{-8}
[EMIM][SCN] 10	-23	0	1.8×10^{-8}	2.4×10^{-8}
[EMIM][SCN] 15	-23	0	2.7×10^{-8}	3.2×10^{-8}
[EMIM][TFSI] 2.5	-24	1	7.1×10^{-9}	1.1×10^{-8}
[EMIM][TFSI] 5	-26	3	2.8×10^{-8}	3.4×10^{-8}
[EMIM][TFSI] 10	-28	5	8.0×10^{-8}	9.1×10^{-8}
[EMIM][TFSI] 15	-31	8	1.0×10^{-7}	1.1×10^{-7}
[AMIM][TFSI] 2.5	-24	1	7.4×10^{-9}	1.2×10^{-8}
[AMIM][TFSI] 5	-26	3	3.5×10^{-8}	3.9×10^{-8}
[AMIM][TFSI] 10	-29	6	7.2×10^{-8}	8.4×10^{-8}
[AMIM][TFSI] 15	-31	8	1.6×10^{-7}	1.7×10^{-7}
[BMIM][TFSI] 2.5	-24	1	1.1×10^{-8}	1.7×10^{-8}
[BMIM][TFSI] 5	-26	3	2.5×10^{-8}	2.9×10^{-8}
[BMIM][TFSI] 10	-28	5	1.2×10^{-7}	1.7×10^{-7}
[BMIM][TFSI] 15	-33	10	1.6×10^{-7}	2.4×10^{-7}
[HMIM][TFSI] 2.5	-24	1	9.4×10^{-9}	1.4×10^{-8}
[HMIM][TFSI] 5	-26	3	7.0×10^{-8}	8.2×10^{-8}
[HMIM][TFSI] 10	-29	6	1.3×10^{-7}	2.1×10^{-7}
[HMIM][TFSI] 15	-33	10	1.7×10^{-7}	3.5×10^{-7}

As it was already reported, the hydrophilic [BMIM][AlCl₄] and [EMIM][SCN] displayed a much less plasticizing effect by lowering the T_g of XNBR matrix in comparison to the hydrophobic TFSI-based ILs. This trend is in accordance with conductivity (σ') values reported for the corresponding samples. The incorporation of [TFSI]⁻ ions into XNBR/LDH matrix produced composites with higher ionic conductivity in comparison to that of those containing hydrophilic tetrachloroaluminate and thiocyanate salts. According to the data summarized in **Table 39**, the presence of 2.5 phr of [EMIM][SCN] and [BMIM][AlCl₄]

induced an order of magnitude increase in σ' from 4.6×10^{-10} (XNBR/LDH) to 8.7×10^{-9} and 4.9×10^{-9} S/cm respectively, however further increases in the hydrophilic ILs levels up to 15 phr had less significant impact on the composites' σ' than it was anticipated.

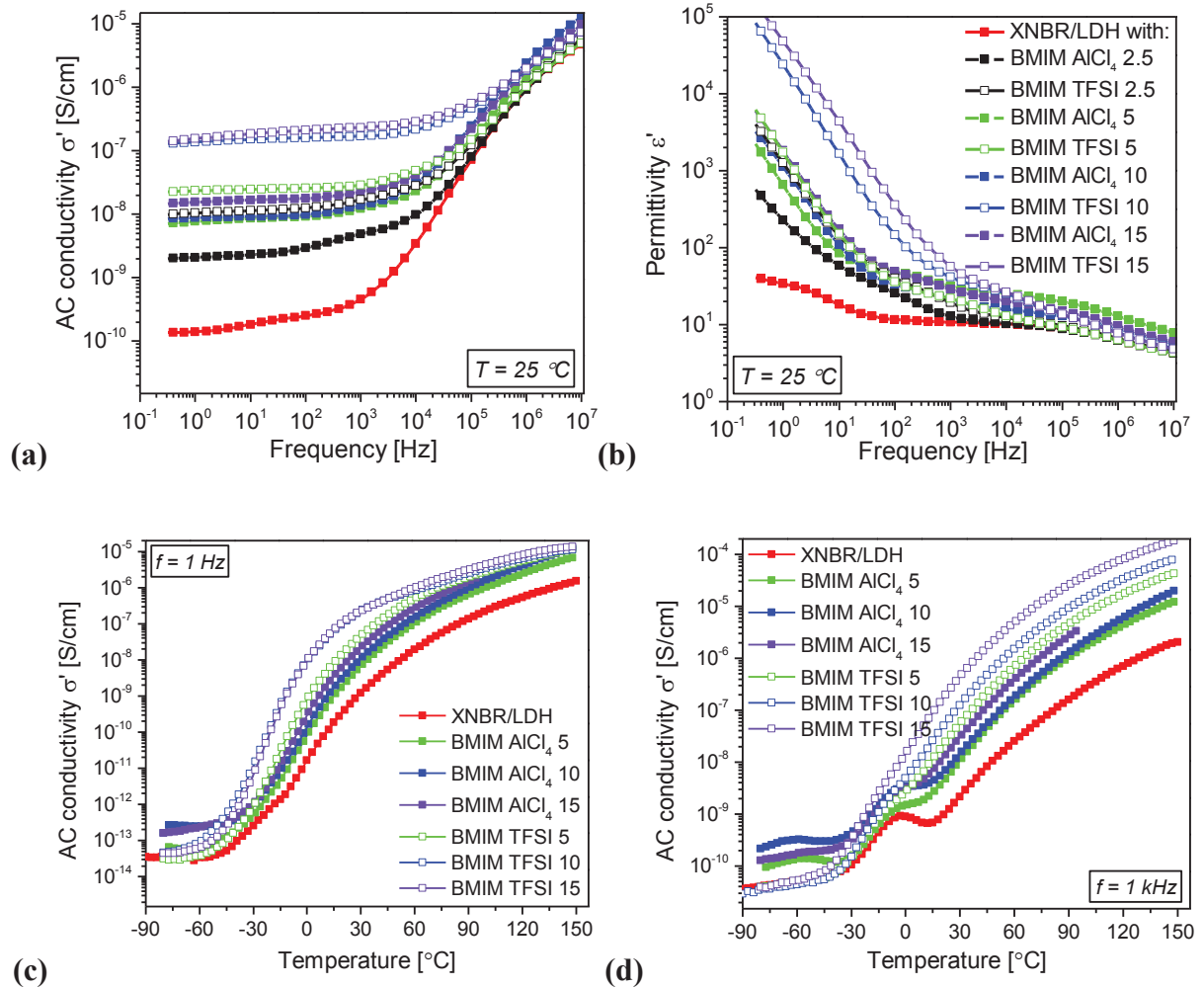


Figure 46 Plots of (a) AC conductivity σ' versus frequency at $25\text{ }^{\circ}\text{C}$, (b) permittivity ϵ' versus frequency at $25\text{ }^{\circ}\text{C}$, (c) AC conductivity σ' versus temperature at 1 Hz , (d) AC conductivity σ' versus temperature at 1 kHz of compounds XNBR containing [BMIM][AlCl_4] and [BMIM][TFSI].

Compared to hydrophilic ionic liquids, the use of hydrophobic TFSI-based ILs more efficiently enhanced the σ' of XNBR/LDH, resulting in a gradual increase to 10^{-7} S/cm at 15 phr content of imidazolium salt. Such a trend is in accordance with the hypothesis that the ionic conductivity of rubber material is dependent not only on the number of imidazolium salt ions and its conductivity, but is also influenced by the plasticizing effect of the IL. Remarkably increased mobility of the rubber chain segment of the XNBR/[TFSI]-LDH is

surely one of the main reasons for the enhancement of ionic conductivity of the composite. Another reason for this increase is that the TFSI-based IL acts as a reservoir for effective carrier ions and raised level of these ions in the composite resulted in higher values of σ' . As assumed, the conductivity increases steadily with an increase in the length of the alkyl backbone of the imidazolium ring and is highest for the XNBR/LDH sample containing 1-hexyl-3-methylimidazolium TFSI salt.

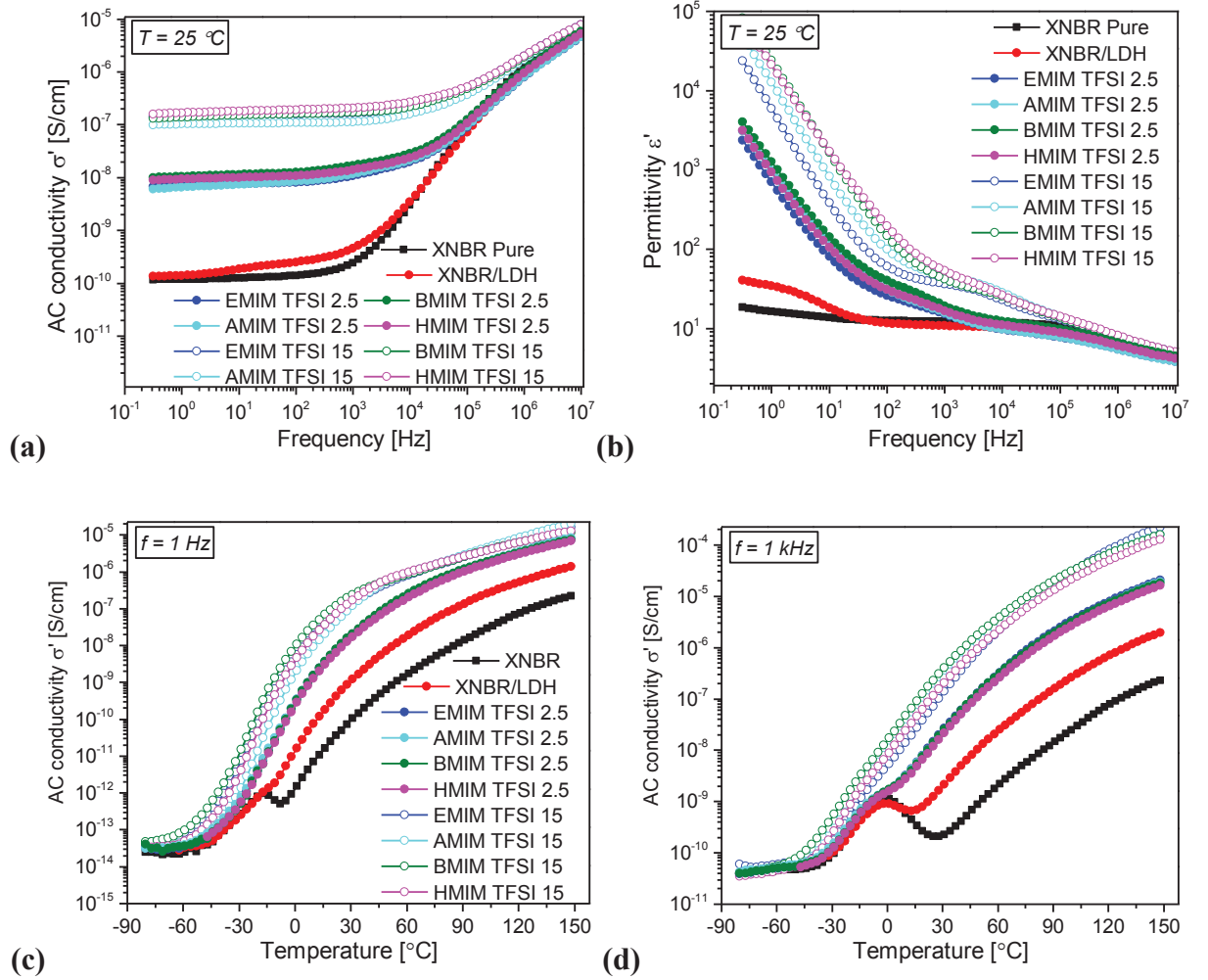


Figure 47 Plots of (a) AC conductivity σ' versus frequency at 25 $^{\circ}\text{C}$, (b) permittivity ϵ' versus frequency at 25 $^{\circ}\text{C}$, (c) AC conductivity σ' versus temperature at 1 Hz, (d) AC conductivity σ' versus temperature at 1kHz of compounds XNBR containing 2.5 and 15 phr of TFSI-based IL.

As shown in **Figure 46 a** and **Figure 47 a**, the conductivity σ' spectra of the XNBR/IL-LDH composites is characterized on the low frequency f side by the plateau the value of which directly yields the DC conductivity, σ_0 , and the characteristic radial frequency ω_C ($\omega=2\pi f$) at which dispersion sets in and turns into a power law at higher frequencies f .²⁸³

In the low frequencies range (10^{-1} Hz to 10^4 Hz), a frequency independent plateau is developed, related to long range diffusion of charge carriers giving rise to a direct current corresponding, by extrapolation, to a the DC-conductivity of the material. At high frequencies (10^4 Hz to 10^7 Hz) an increase in the values of σ' is observed for all samples, due to local fluctuations of charge carriers giving rise to a displacement current characteristic of a capacitive regime. The transition between these two spectral regions is marked by a characteristic frequency f_e related to the hoping time of the charge carriers $\tau_e = 1/2\pi f_e$. It is observed that this characteristic frequency is shifted to higher values with increasing the concentration of the ionic liquid, which corresponds to an enhancement in the charge mobility.

As shown in **Figure 46 b** and **Figure 47 b**, in the frequency range between 10 and 10^5 Hz, the permittivity (ϵ') of rubber materials decreased rapidly with the increasing frequency at the temperature 25 °C what is attributed to the mobile ions, which is particularly evident at higher concentrations IL of 15 phr and is not observed in the case of the pure XNBR and XNBR/LDH composite. A constant value of the permittivity ϵ' was obtained at a frequency higher than 10^6 Hz.

According to the **Figure 46 c, d** and **Figure 47 c, d**, with an increase in temperature, the conductivity σ' of rubber materials filled with ILs increased. The conductivity varied from 2×10^{-14} S/cm at -60 °C to 2×10^{-10} S/cm for the pure XNBR, 3×10^{-9} S/cm for XNBR./LDH and 10^{-6} S/cm for the composites containing 15 phr of [TFSI]-based ILs at 50 °C.

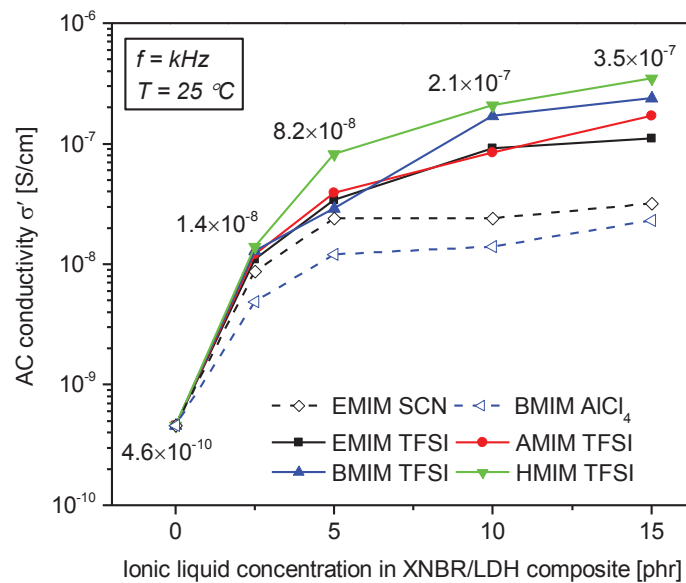


Figure 48 AC conductivity σ' in function of IL amount in the XNBR/LDH composite.

Figure 48 shows the effect of the concentration of ILs on ionic conductivity of the rubber composites. The sharpest jump in σ' value is observed in the presence of 2.5 phr of the ionic liquid in XNBR/LDH composite. Increasing the number of ions of the hydrophilic [EMIM][SCN] and [BMIM][AlCl₄] led to a slighter increase in σ' parameter in comparison to the hydrophobic TFSI-based ILs.

5.2.6. Thermal stability of XNBR/IL-LDH composites

The ILs used as components in rubber composites should be characterized by sufficient thermal stability to allow them to withstand the high temperatures used during both the melt-blending and curing processes of the composites. Ionic liquids are generally well-known for their high thermal stability. The types of anions are controlling the overall thermal stability of ILs. For example, TFSI-based ionic liquids are thermally stable up to 300 °C (what makes them useful additives during rubber processing at higher temperatures).

Table 40 Thermal properties of XNBR/IL-LDH composites investigated by TGA (under nitrogen).

Sample name and IL content [phr]	T ₂ [°C]	T ₅ [°C]	T ₁₀ [°C]	T ₅₀ [°C]	Char residue [wt%]
XNBR/LDH	207	291	391	445	13.45
[EMIM][SCN] 15	155	220	256	436	14.92
[EMIM][TFSI] 15	212	274	348	439	18.23
[BMIM][TFSI] 15	211	265	340	439	18.20
[HMIM][TFSI] 15	211	264	339	438	18.18
[BMIM][AlCl ₄]					
5	186	287	362	440	16.25
10	144	246	336	439	16.23
15	119	187	299	436	16.36
[BMIM][TFSI]					
5	212	284	364	441	16.81
10	212	278	350	439	17.87
15	211	265	340	439	18.20

The thermal properties of the XNBR/IL-LDH composites characterized by a thermogravimetric technique are summarized in **Table 40**. The TGA/DTG profiles are shown in **Figure 49 a-d**. The decomposition temperature of the imidazolium ionic liquids is below that of the control sample, therefore, the T_5 , T_{10} and T_{50} shift toward lower temperatures is observed (**Table 40**). It can be seen from **Figure 49 c**, that TGA profiles of the sample with

tetrachloroaluminate and thiocyanate imidazolium salt showed no thermal changes before 100 °C, and over 100 °C, the mass loss is most likely due to evaporation of water or impurities because both are highly hygroscopic compounds.

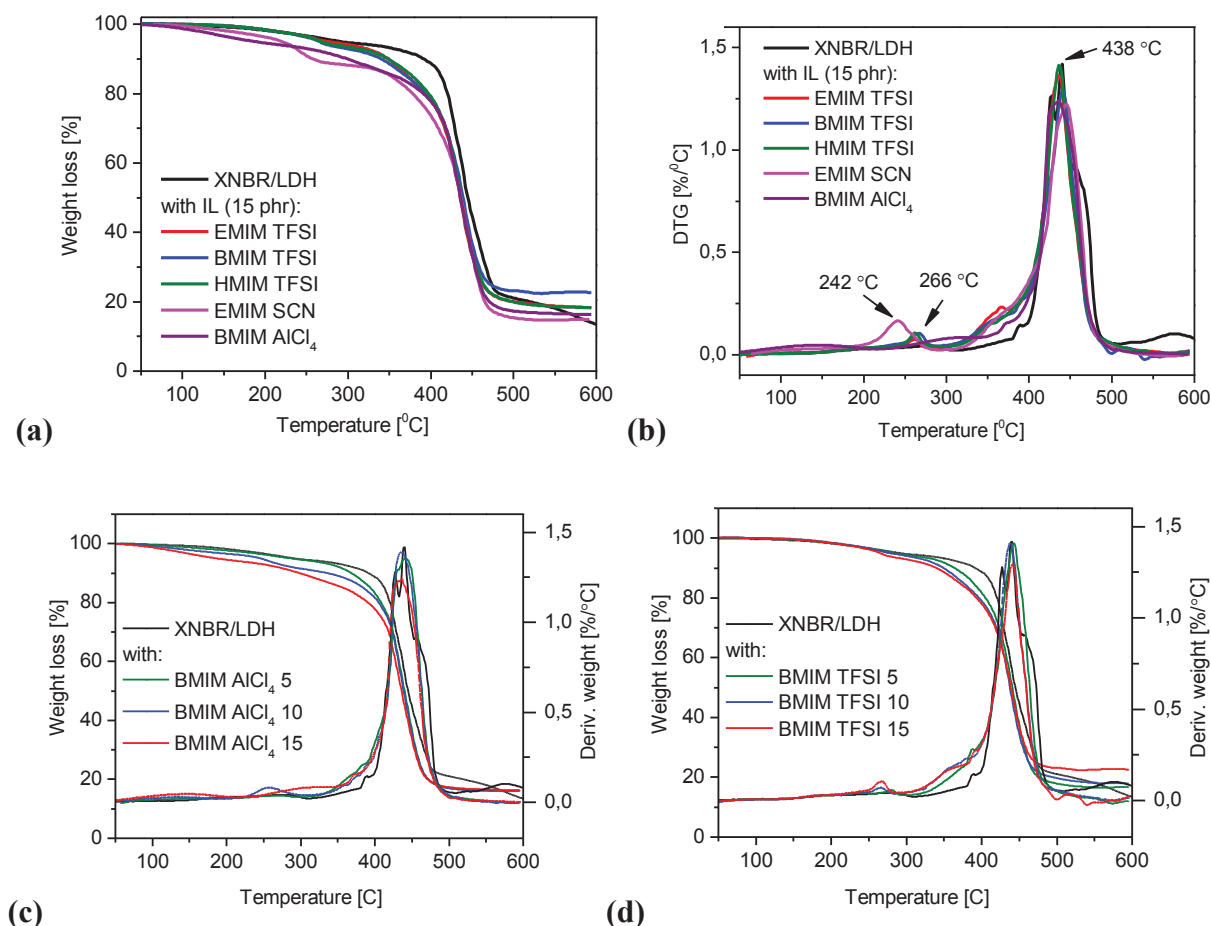


Figure 49 Thermal stability properties of XNBR/LDH composites (a) TGA profiles of composites with 15 phr of IL, (b) DTG profiles of composites with 15 phr of IL, (c) TGA/DTG profiles of composites with [BMIM][AlCl₄], (d) TGA/DTG profiles of composites with [BMIM][TFSI], (under nitrogen).

The addition of 15 phr IL with [TFSI]⁻ anion increased the decomposition temperature at 2 % mass loss (T_2) of XNBR/LDH and the TGA/DTG curves exhibited no thermal changes below 266 °C (Figure 49 a-b), which confirmed that the hydrophobic TFSI-based ILs are thermally stable in the temperature range of 25 – 250 °C. At higher temperatures, the TGA/DTG showed a significant mass loss between 309 °C and 480 °C ($\Delta m=72$ %), and a similar loss is observed in the control sample form 380 °C to 480 °C ($\Delta m=69$ %). The *bis*(trifluoromethylsulfonyl)imide imidazolium salt exhibits superior thermal stability for

elastomer processing compared to the less thermally stable hydrophilic tetrachloroaluminate and thiocyanate imidazolium salts.

The observed higher thermal stability of XNBR/LDH/[EMIM][TFSI] composite in comparison to the others is due to the higher stability of pure [EMIM][TFSI]. The thermal stability decrease with increasing number of carbon atoms in the alkyl chain from methyl to butyl of 1-*n*-alkyl-3-methylimidazolium *bis*(trifluoromethylsulfonyl)imide, after which no noticeable change in the decomposition temperature T_d can be seen.²²⁶

5.2.7. Microstructure and morphological analysis of XNBR/LDH/IL composites

Magnesium-aluminum layered double hydroxide is a highly active filler which interacts well with -COOH functionalities of XNBR macromolecules, as it was discussed in the **Chapter 5.1.3**. Nevertheless, a large quantity of layered double hydroxide needed for the preparation of high performance rubber material might provoke difficulties in obtaining a homogenous composite structure. The melt-mixing method used for the rubbers compounding is very economical, ecological and allows for the selection of the optimal processing parameters such as temperature and shear during the melt mixing, therefore is the most commonly used in the rubber industry. In the technological process, introduction of large amounts of filler to rubber is widely supported by the addition of plasticizers such as mineral oils and paraffins for the improved filler dispersion, improvement of compounding and rubbers processing, which are quite essential factors influencing the final properties of the product. The main functions performed by plasticizers are: viscosity reduction, dispersion aid for solid additives and modification of rheological properties. The filler dispersion in elastomer composites is of great importance in governing their performance and recently the ionic liquids have been found as useful aids for the improvement of filler distribution in the rubbery matrix. It was anticipated that the incorporation of ILs may help decrease the size of the LDH filler aggregates and agglomerates formed in the XNBR matrix.

Scanning electron microscopy (SEM) equipped with an energy dispersive spectrometer (EDS) was used to investigate the influence of hydrophilic and hydrophobic ionic liquids on the rubber composites morphology and the dispersion state of LDHs particles in the XNBR matrix. Hydrophilic [BMIM][AlCl₄] and hydrophobic [BMIM][TFSI] were selected as representative ionic liquids to demonstrate the effects of their different chemical natures on the composites morphology. The SEM-EDS micrographs of the reference sample of XNBR/LDH are shown in **Figure 50 a-b**. It is evident that LDH particles form agglomerates

with an average size of about 5 μm . It can be said that the melt mixing method used for LDH and XNBR compounding under high shear forces and elevated temperature conditions did not provide good enough dispersion, as some agglomerates were detected. In this case, the incorporation of a dispersing agent to improve distribution of such a high filler amount and facilitate the compounding step seems to be reasonable.

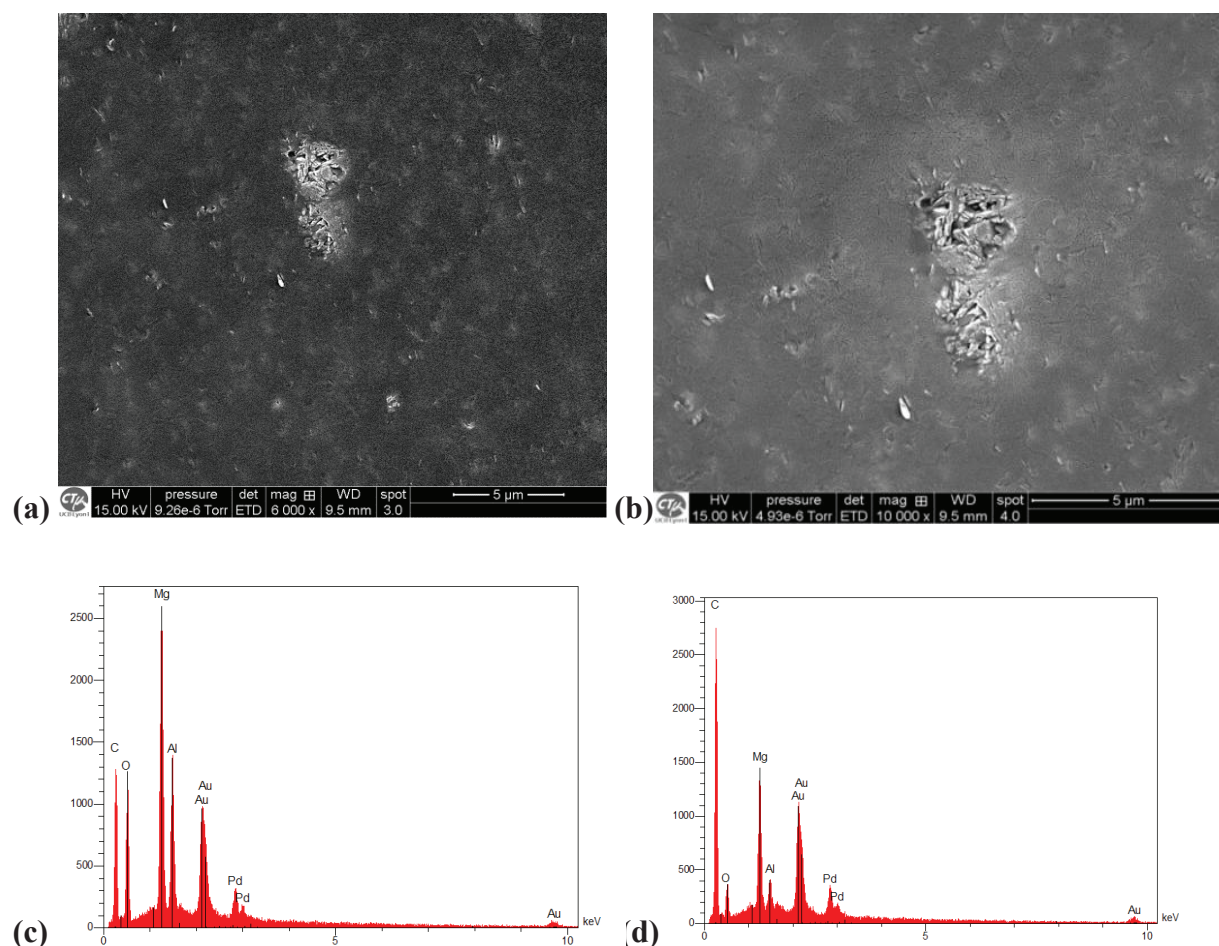


Figure 50 SEM-EDS of (a), (b) XNBR loaded with 30 phr of LDH, (c) filler point, (d) matrix point.

The SEM-EDS micrographs of XNBR/IL-LDH containing 5 and 15 phr of hydrophobic *bis*(trifluoromethylsulfonyl)imide and hydrophilic tetrachloroaluminate [BMIM]s are presented in **Figure 51 a-d** and **Figure 52 a-d**, respectively. The incorporation of LDH particles which surface was covered with hydrophobic TFSI-based imidazolium salt to XNBR matrix allowed to reduce the size of filler agglomerates and obtaining a quite uniform dispersion of LDHs particles in the composites (containing 5 phr or 15 phr of IL), which can be clearly seen in **Figure 51 a-b**. The domain size of dispersed phase was remarkably decreased in comparison with the reference sample (**Figure 50 a-b**) in which agglomeration

within 5 μm was observed. Moreover, the plasticizing effect of TFSI-based IL on the XNBR matrix might facilitate the orientation of the layers of filler in the direction of the shear force during compounding.

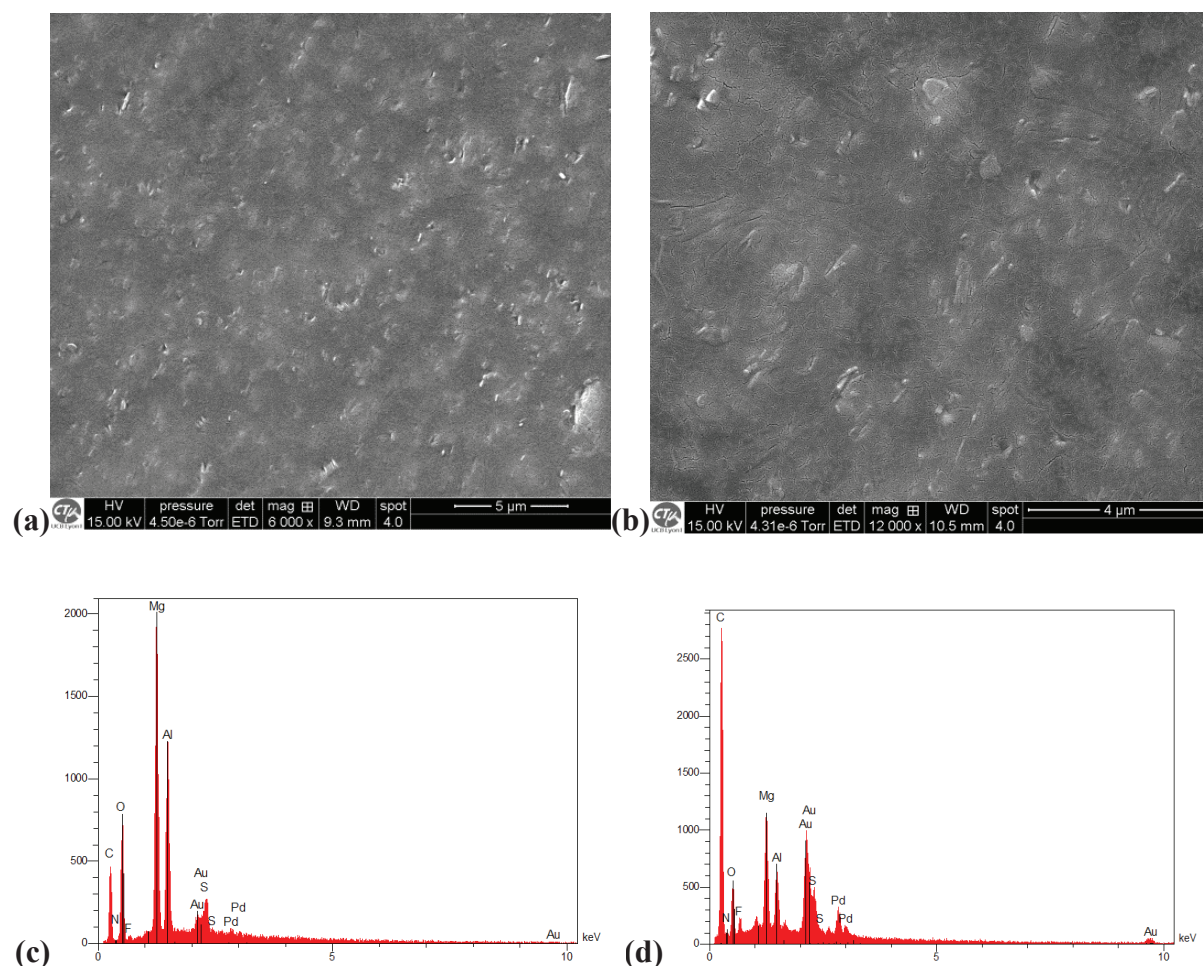


Figure 51 SEM-EDS of XNBR/LDH containing [BMIM][TFSI] in amount of (a) 5 phr, (b) 15 phr, (c) filler point, (d) matrix point.

Additionally, the distribution of the TFSI-based ionic liquid in the XNBR/LDH composite was also investigated using EDS technique. A higher imidazolium salt concentration (reflected in the intensity of the signal originating from the sulfur and fluorine) was detected in the XNBR matrix (**Figure 51 d**) than at that so-called “filler point” (**Figure 51 c**), where it was originally applied. Moreover, during processing of IL-rubber compounds, hydrophobic TFSI-based imidazolium salt was easily mixed with nitrile rubber material, what confirms good miscibility and compatibility between both components. Hydrophobicity is valuable advantage of TFSI-based imidazolium ILs making them more compatible with hydrophobic

rubber matrices, preventing leakage (migration within the polymer matrix), facilitating rubber processing and improving filler dispersion throughout the elastomer matrix.

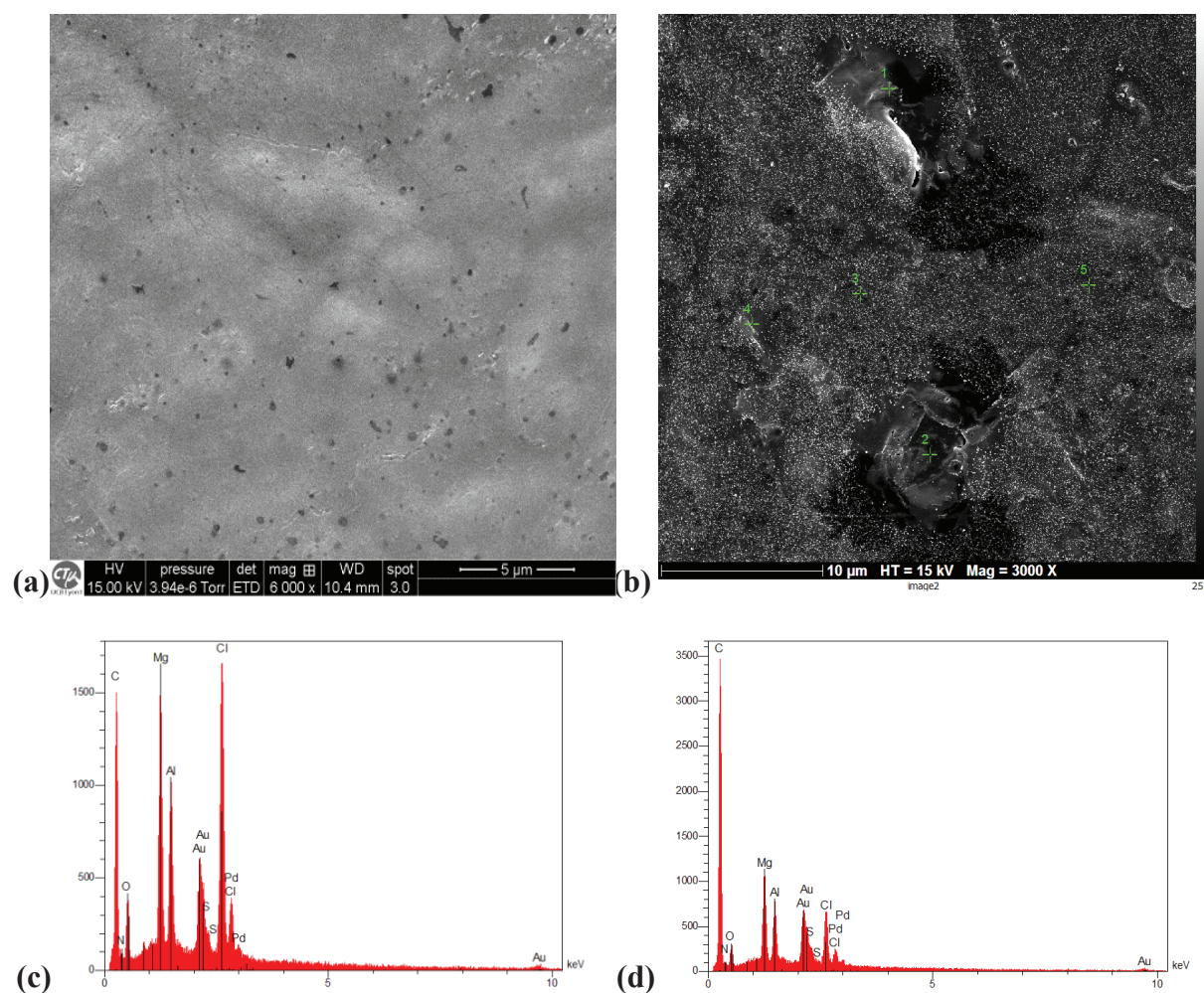


Figure 52 SEM-EDS of XNBR/LDH containing [BMIM][AlCl₄] in amount of (a) 5 phr, (b) 15 phr, (c) filler point, (d) matrix point.

Similarly, SEM studies showed that there is an improvement in the morphology of the XNBR/LDH with the addition of hydrophilic [BMIM][AlCl₄] which contributed to the reduction of the filler agglomerates size and more uniform composite structure as it is shown in **Figure 52 a-b**. However, the opposite effect of hydrophilic IL distribution in the XNBR/LDH material was found. The IL concentration was detected to be the highest in the “filler point” (**Figure 52 c**) and very low in the XNBR matrix (**Figure 52 d**). Moreover, the miscibility between hydrophilic IL and nitrile rubber was limited and incorporation of filler coated with higher loadings of IL during compounding was a time-consuming process in comparison to the LDH with hydrophobic [BMIM][TFSI] which was easily introduced into the elastomer matrix. Comparing both ionic liquids, the hydrophobic one containing a

bis(trifluoromethylsulfonyl)imide anion is much more suitable than a hydrophilic IL with a tetrachloroaluminate anion for use as a dispersion agent. This is not only because of its higher thermal and chemical stability, but also due to its better compatibility and miscibility with nitrile rubber.

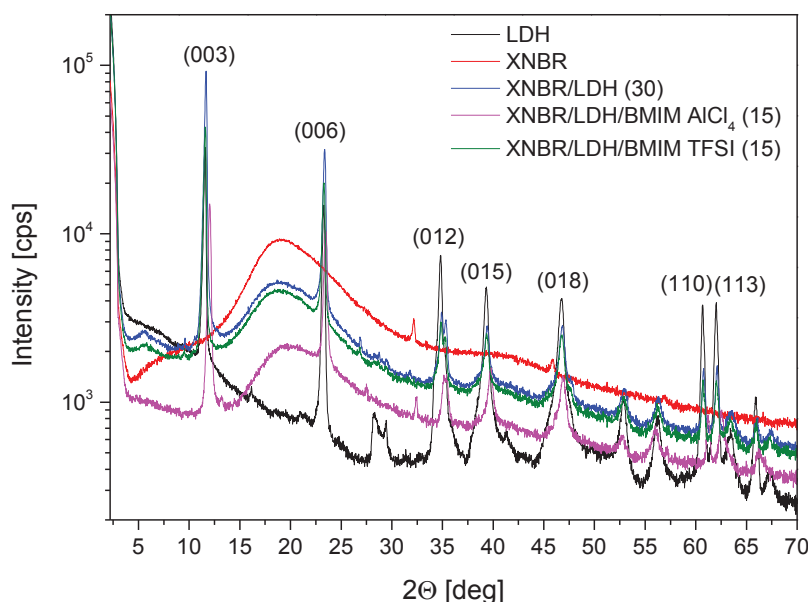


Figure 53 XRD patterns of XNBR composites.

The XRD study was carried out in order to provide some information about any changes in the XNBR/LDH microstructure which could occur due to the presence of ionic liquids. The effect of high loadings (15 phr) of hydrophobic [BMIM][TFSI] and hydrophilic [BMIM][AlCl₄] on the XNBR/LDH composite microstructure was investigated via XRD and the results are presented in **Figure 53**. For the XNBR/LDH and XNBR/IL-LDH composites the positions of the 2θ values remained unchanged from those of the pristine LDH, which shows the basal reflections (003), (006), (012), and so forth, observed in the crystalline structure. The LDH particles used herein at the substantial concentration of 30 phr, are rather dispersed as aggregates in rubber matrix, also in the presence of 15 phr IL. The intensities of the reflection peaks for the composite containing IL are below those of the control sample, which may be explained through the dilution effect of crystalline phase (30 phr LDH and 15 phr of IL) or may result from the orientation of the LDH particles in the rubber matrix under the influence of the ionic liquid.

5.2.8. Accelerated UV aging of XNBR/IL-LDH composites

Table 41 summarizes the mechanical properties of XNBR/IL-LDH samples subjected to the UV aging. The presence of increasing concentrations of TFSI-based ILs had no significant effect on the UV stability of rubber composites as the aging factor K_{UV} remained almost unchanged and oscillated around the value of 0.5. The increase in modulus at 300 % of elongation SE_{300} is observed for the composites containing [BMIM][AlCl₄], which showed a trend to increase the crosslink density of XNBR/LDH compound as it has been previously demonstrated. In this case, exposition to UV radiation and high temperature conditions may induce intensification of crosslinking process which consequently leads to a significant reduction in elasticity of the material.

Table 41 Mechanical properties of XNBR/IL-LDH composites subjected to UV aging.

Sample name and IL content [phr]	SE ₁₀₀ [MPa]	SE ₂₀₀ [MPa]	SE ₃₀₀ [MPa]	TS [MPa]	EB [%]	K _{UV} [-]
XNBR/LDH	2.9 ± 0.1	4.3 ± 0.1	5.5 ± 0.1	9.6 ± 0.7	530 ± 10	0.5
[BMIM][AlCl ₄] 2.5	3.7 ± 0.1	5.8 ± 0.2	7.4 ± 0.2	10.6 ± 0.3	459 ± 20	0.5
[BMIM][AlCl ₄] 5	4.4 ± 0.2	6.7 ± 0.2	8.8 ± 0.2	13.8 ± 0.8	463 ± 20	1.0
[BMIM][AlCl ₄] 10	4.2 ± 0.3	6.5 ± 0.3	8.7 ± 0.2	10.2 ± 2.0	384 ± 20	1.0
[BMIM][AlCl ₄] 15	4.2 ± 0.1	6.6 ± 0.2	9.1 ± 0.4	8.9 ± 1.0	308 ± 30	1.0
[EMIM][SCN] 2.5	2.8 ± 0.1	4.5 ± 0.1	6.0 ± 0.1	10.4 ± 0.2	522 ± 10	0.5
[EMIM][SCN] 5	2.5 ± 0.1	4.3 ± 0.2	5.7 ± 0.2	10.7 ± 0.4	542 ± 10	0.5
[EMIM][SCN] 10	2.7 ± 0.1	4.5 ± 0.1	6.0 ± 0.1	10.1 ± 0.6	522 ± 10	0.5
[EMIM][SCN] 15	2.3 ± 0.1	3.4 ± 0.2	7.3 ± 0.1	4.7 ± 0.9	397 ± 30	0.5
[EMIM][TFSI] 2.5	3.0 ± 0.1	4.7 ± 0.1	6.0 ± 0.1	10.6 ± 0.1	520 ± 10	0.4
[EMIM][TFSI] 5	2.7 ± 0.1	4.1 ± 0.1	5.2 ± 0.1	10.5 ± 0.1	571 ± 10	0.5
[EMIM][TFSI] 10	2.5 ± 0.1	3.8 ± 0.1	5.0 ± 0.1	9.1 ± 0.7	550 ± 20	0.4
[EMIM][TFSI] 15	2.3 ± 0.1	3.3 ± 0.1	4.1 ± 0.1	8.4 ± 0.4	540 ± 10	0.4
[AMIM][TFSI] 2.5	2.9 ± 0.1	4.4 ± 0.1	5.7 ± 0.1	10.4 ± 0.2	510 ± 10	0.4
[AMIM][TFSI] 5	2.9 ± 0.1	4.1 ± 0.1	5.3 ± 0.1	10.2 ± 0.7	530 ± 20	0.4
[AMIM][TFSI] 10	2.6 ± 0.1	3.9 ± 0.1	5.0 ± 0.1	9.2 ± 0.2	564 ± 10	0.4
[AMIM][TFSI] 15	2.2 ± 0.2	3.2 ± 0.2	4.2 ± 0.2	9.3 ± 0.5	620 ± 20	0.5
[BMIM][TFSI] 2.5	2.8 ± 0.1	4.4 ± 0.2	5.7 ± 0.2	10.6 ± 0.5	507 ± 10	0.4
[BMIM][TFSI] 5	2.9 ± 0.1	4.2 ± 0.1	5.3 ± 0.4	10.2 ± 0.4	550 ± 10	0.5
[BMIM][TFSI] 10	2.8 ± 0.1	4.2 ± 0.1	5.2 ± 0.1	9.9 ± 0.6	574 ± 10	0.5
[BMIM][TFSI] 15	2.6 ± 0.1	4.0 ± 0.1	5.3 ± 0.2	9.0 ± 0.4	528 ± 10	0.5
[HMIM][TFSI] 2.5	2.8 ± 0.1	4.3 ± 0.1	5.6 ± 0.1	8.7 ± 0.1	504 ± 10	0.4
[HMIM][TFSI] 5	2.7 ± 0.1	4.1 ± 0.1	5.2 ± 0.1	8.9 ± 1.0	550 ± 20	0.5
[HMIM][TFSI] 10	2.6 ± 0.1	3.9 ± 0.2	5.0 ± 0.2	8.3 ± 1.0	555 ± 10	0.4
[HMIM][TFSI] 15	2.1 ± 0.1	3.2 ± 0.1	4.2 ± 0.1	7.3 ± 0.6	552 ± 10	0.4

5.2.9. Conclusions

This study considered the effects of hydrophilic and hydrophobic imidazolium ionic liquids on the curing behavior, cure degree, mechano-dynamical, morphological and ionic conductivity properties of XNBR/LDH composites. The hydrophilic imidazolium salt [BMIM][AlCl₄] was found to be reactive toward XNBR by increasing the network density of the rubber composites and significantly accelerating the curing process. Despite its own high ionic conductivity of 10 mS/cm, tetrachloroaluminate salt did not induce a significant increase in the ionic conductivity of rubber composites even when added at high concentration as the conductivity increased only about two orders of magnitude. Similarly, the other hydrophilic ionic liquid – thiocyanate imidazolium salt, which is also characterized by high ionic conductivity of 27 mS/cm, displayed a moderated influence on the enhancement in the ionic conductivity of the XNBR/LDH composite.

In contrast, the incorporation of a series of hydrophobic 1-n-alkyl-3-methylimidazolium *bis*(trifluoromethylsulfonyl)imide ILs into the XNBR/LDH matrix produced elastomer composites with a higher ionic conductivity than those containing hydrophilic tetrachloroaluminate or thiocyanate salt. For XNBR/LDH composites, the conductivity increased about three orders of magnitude (10^{-10} to 10^{-7} S/cm) at room temperature when 15 phr of TFSI-based IL was added. Advantageously, TFSI-based imidazolium salts exhibited sufficient thermal stability for elastomer processing. With the addition of hydrophobic TFSI-based imidazolium ILs, filler dispersion and ionic conductivity of the XNBR/LDH composites were effectively improved. Such ILs showed a plasticizing effect on the XNBR matrix, shifting the T_g towards lower temperatures with increasing concentrations. The 1-hexyl-3-methylimidazolium *bis*(trifluoromethylsulfonyl)imide displayed the highest plasticizing effect in the XNBR/LDH material and the most efficiently increased the ionic conductivity of the composite. However, the impact of the cation alkyl chain length on this parameter was found to be less significant as it was anticipated. The optimal amount of TFSI-based imidazolium IL for the preparation composites with enhanced conductivity and improved morphological and mechanical properties was found to be 2.5 – 5 phr.

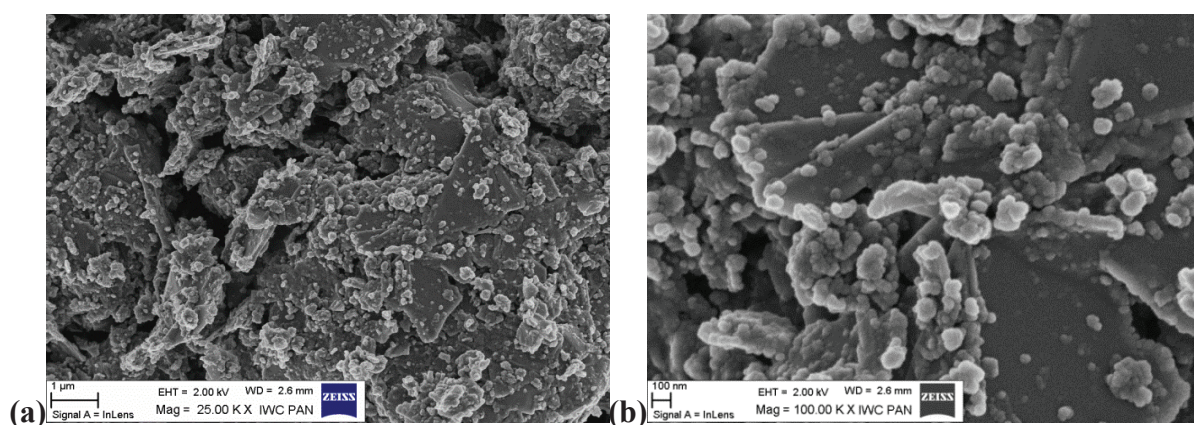
5.3. NITRILE RUBBER COMPOSITES CONTAINING GRAPHENE FILLERS

5.3.1. CHARACTERIZATION OF MORPHOLOGICAL, SURFACE AND THERMAL PROPERTIES OF GRAPHENE FILLERS

INTRODUCTION: This section focuses on the evaluation of morphological, surface and thermal properties of various types of graphene-based materials (xGnP-C-300, xGnP-C-500, xGnP-C-750, xGnP-M and exfoliated graphene (EG)) by following techniques: scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), N₂ adsorption measurements, thermogravimetric analysis (TGA).

5.3.1.1. SEM observations of graphene particles morphology

Graphene nanoplatelets were obtained as a bulk black powder. **Figure 54 a-j** shows the SEM images of the morphology of the graphene nanoplatelets xGnP-C-300, xGnP-C-500, xGnP-C-750, xGnP-M and EG. The electron micrographs of the graphene fillers revealed a large number of individual plate-like particles, which vary depending on the type of filler. In general, we may observe a standard shape of two-dimensional plates stacked one over the other with a high tendency for agglomeration, however, the layered structure and the largest aspect ratio of particles were the most pronounced for xGnP-M and EG and least pronounced for xGnP-C-750.



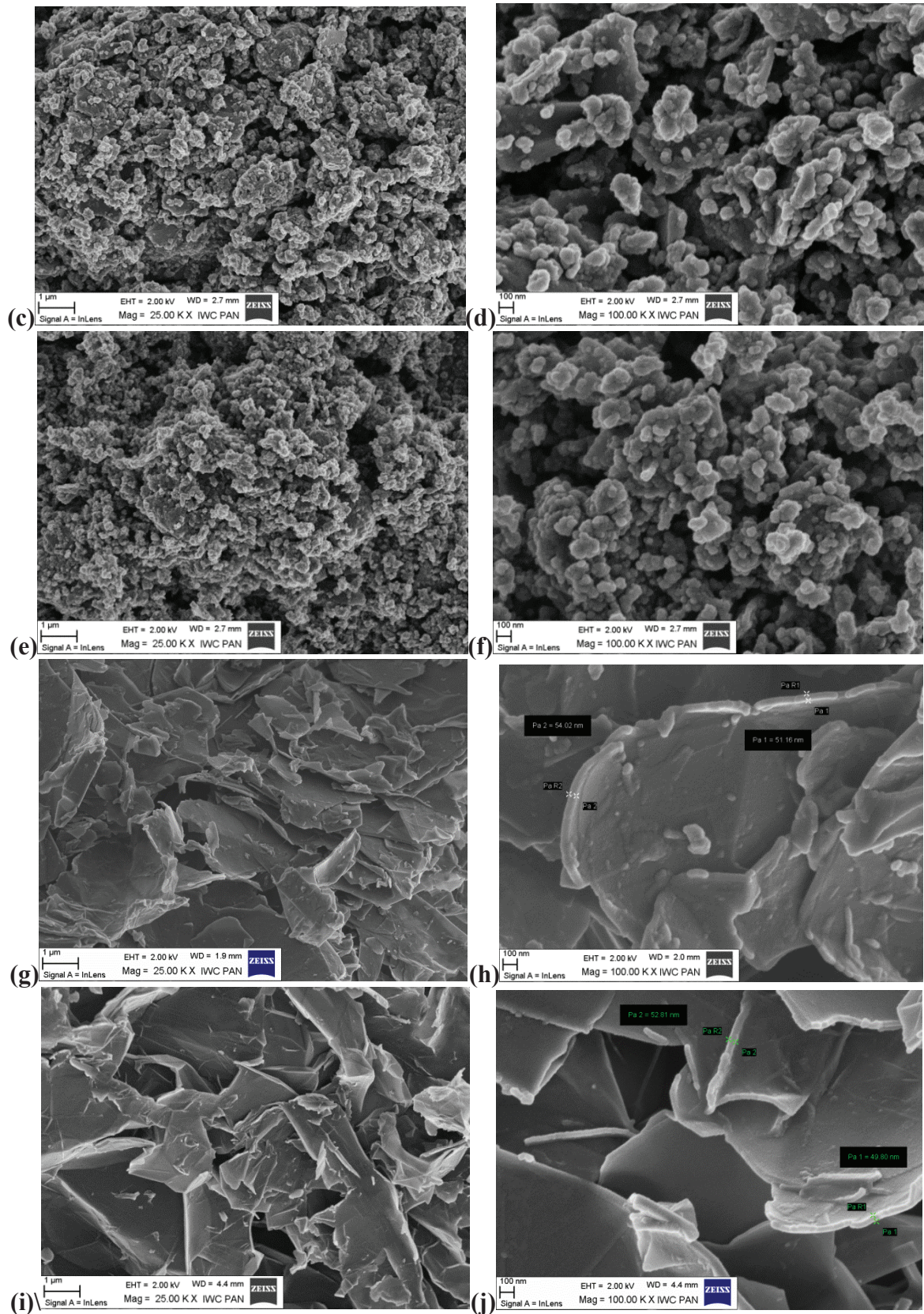


Figure 54 SEM images of (a, b) xGnP-C-300, (c, d) xGnP-C-500, (e, f) xGnP-C-750, (g, h) xGnP-M-5, and (i, j) exfoliated graphene (EG).

As shown in **Figure 54 g-j**, thin and exfoliated flakes are the most characteristic for xGnP-M-5 and EG. In the case of the filler with the highest specific surface area (xGnP-C-750), a more spherical particle shape is observed rather than a layered structure. Particles of the xGnP-C series (**Figure 54 a-f**) have irregular shapes with different dimensionalities and the layer diameter size decreased with increasing specific surface area. The SEM images revealed that the lateral dimensions of xGnP-M5 and EG particles ranged from 30 to 50 μm with a thickness of approximately 50 nm, whereas the average particle size of the xGnP-C series was much smaller and did not exceed 20 μm , 5 μm and 0.5 μm for xGnP-C-300, xGnP-C-500, and xGnP-C-750, respectively.

5.3.1.2. Specific surface area and structure of graphene fillers

The values of specific surface area (S_A) and oil absorption (DBPA) of the graphene fillers are presented in **Table 42**.

The N_2 adsorption measurements revealed that the graphene fillers with a high platelet aspect ratios were characterized by low specific surface areas ranging from 50 to 120 m^2/g . This result is in good agreement with their larger particle size compared to the xGnP-C series. A large specific surface area of xGnP-C-750 is advantageous because it provides a high-level contact area of the nanoparticles with the matrix. Exfoliated graphene (EG) exhibited a particularly high absorption capacity estimated based on dibutyl phthalate absorption, indicating large particle aggregation and structure.

Table 42 Surface properties of graphene fillers.

Sample name	Specific surface area S_A (BET) [m^2/g]	DBPA number [ml/100 g]
xGnP-C-300	294.8	150.0
xGnP-C-500	429.0	145.0
xGnP-C-750	609.3	156.0
xGnP-M-5	50.9	250.0
Exfoliated graphene (EG)	116.8	958.0

5.3.1.3. Examination of the surface chemical composition of graphenes by XPS

Numerous types of organic functional groups, including carboxylic acid groups at the edge and epoxy/hydroxyl groups on the basal planes, present on the graphene surface may contribute, along with the surface microstructure, to the filler surface activity, an important parameter for rubber reinforcement. The surface chemical compositions of the different types of graphene were analyzed by XPS, and the percentages of individual components in the spectra of C1s are presented.

The XPS spectra of the graphenes indicated a considerable degree of oxidation, with seven major signatures corresponding to carbon atoms in different functional groups, as shown in **Figure 55**. The carbon atoms are the non-oxygenated ring C at 284.5 eV, which corresponds to the mutual bonding of carbon atoms, *e.g.*, planes of graphite with sp^2 hybridization, the CH component with a binding energy at 285.0 eV, which corresponds to the carbon atoms of sp^3 hybridization, and the C–COH that appears at a binding energy of 285.5 eV and corresponds to the carbon atoms that are not bound directly to oxygen but are adjacent to atoms linked to carbon atoms.

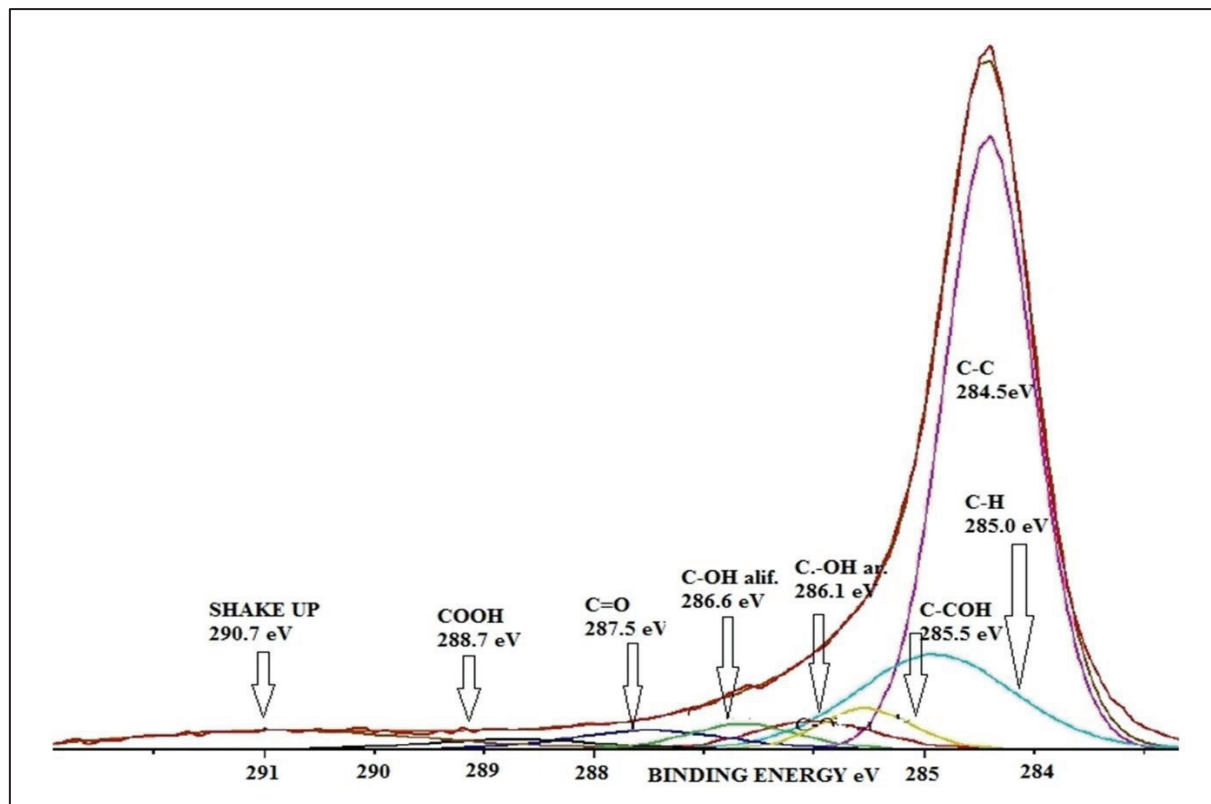


Figure 55 An example of the C1s XPS spectrum recorded for exfoliated graphene (EG).

The component designated as C–OH with a bond energy of 286.1 eV corresponds to the aromatic ring bound to the carbon atoms with hydroxyl groups. The component labeled C–OH with a binding energy of 286.6 eV corresponds to carbon atoms linked to the aliphatic hydroxyl groups. The component indicated by C=O with a binding energy of 287.5 eV corresponds to the carbon-oxygen double bond and the carbon atoms in the O–C–O groups. The COOH component with a binding energy of 288.7 eV corresponds to the carbon atoms in the carboxyl and COOR groups. The $\pi \rightarrow \pi^*$ signal, assigned as a "shake-up", with a binding energy of 290.7 eV corresponds to the satellite lines arising from electronic transitions between orbitals, which is characteristic of aromatic structures and dehydrated carbon structures (graphite, CB, carbon nanotubes, fullerenes).

Table 43 The percentage of individual components in the spectra of C 1s [%].

Sample name	The percentage of individual components in the spectra of C 1s [%]							
	C–C	C–H	C–COH	C–OH AR.	C–OH AL.	C= O	O–C=O	Shake up $\pi-\pi^*$
xGnP-C-300	52.5	17.4	6.3	5.3	4.0	4.0	2.6	7.9
xGnP-C-500	50.1	17.7	7.8	5.1	4.8	3.9	2.8	7.8
xGnP-C-750	46.9	18.6	10.6	4.0	4.7	4.7	3.3	7.2
xGnP-M-5	57.1	17.4	6.6	3.8	4.1	3.7	2.2	5.1
Exfoliated graphene (EG)	60.7	16.6	4.3	3.7	3.2	3.4	1.9	6.2

The C1s XPS spectra of the graphenes indicated some degree of oxidation. The concentration of oxygen-containing functional groups varied with the particle size of the carbon filler. Both exfoliated graphene and xGnP-M-5 were characterized by a higher content of C=O groups compared with the xGnP-C series. As the specific surface area represented by index x of the xGnP-C series increased, the degree of oxidation of graphene increased, with a substantial majority of groups of the type C–O–R. The content of acidic groups (carboxylic groups) on the graphene surface gradually increased with specific surface area and was highest for xGnP-C-750 and lowest for EG and xGnP-M-5.

Table 44 Elemental composition and the percentage of individual components of the model (neighborhoods chemicals) in the spectra of O1s.

Sample name	Elemental composition [% at.]		O1s spectra [%]	
	Carbon	Oxygen	C=O	C–O–R
xGnP-C-300	96.4	3.6	21.8	78.2
xGnP-C-500	95.1	4.9	20.2	79.8
xGnP-C-750	93.9	6.1	14.5	85.5
xGnP-M-5	94.1	5.9	60.2	39.8
Exfoliated graphene (EG)	94.5	5.5	43.5	56.5

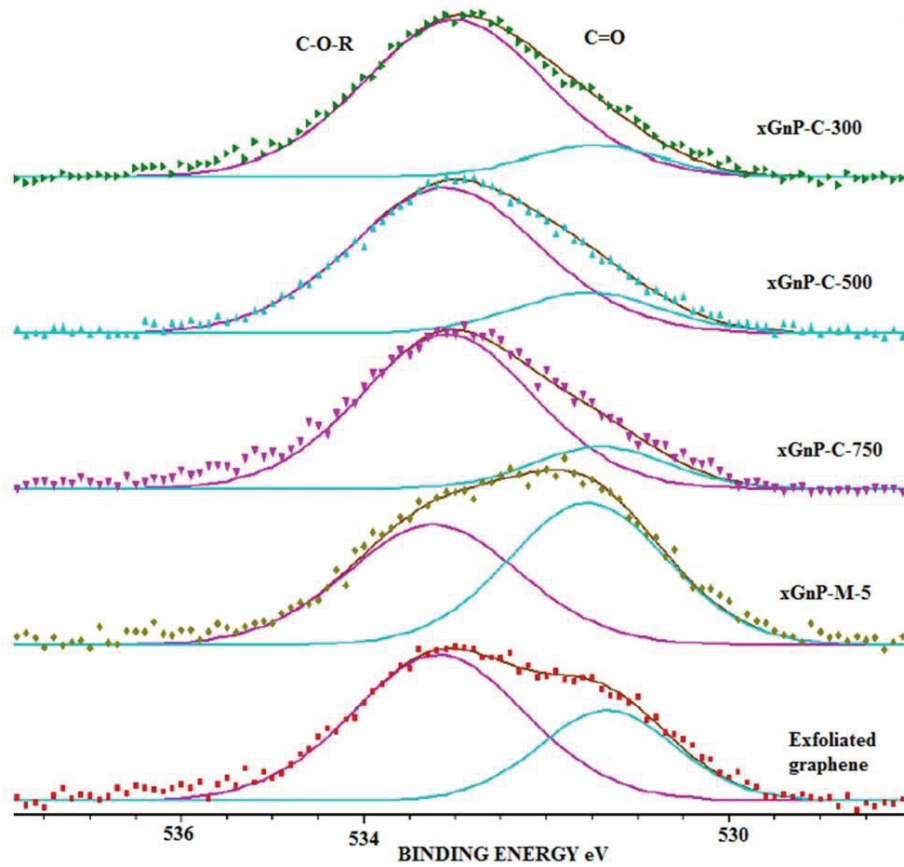


Figure 56 O1s XPS spectra of graphenes.

Different oxygen functionalities were detected on the surface of the graphene layers. This type of filler may interact well with nitrile rubbers, particularly XNBR, which contains polar groups ($-\text{COOH}$ (7 %), $-\text{CN}$ (27 %)). The large number of oxygen-containing functional groups existing on the graphene surface contributed to an increase in filler-rubber interactions. In addition to $-\text{CN}$, which may have some physical interactions with hydroxyl groups of the filler due to the existence of $-\text{COOH}$ groups in XNBR, chemical bonding of the $-\text{OH}$ onto the filler surface is possible.

5.3.1.4. Thermal stability of graphene fillers

The thermal behaviors of the graphene materials were investigated by TGA in an air atmosphere. As shown in **Table 45** and **Figure 57**, the most thermally stable graphene among the investigated series was xGnP-C-300, whereas the least thermally stable was exfoliated graphene (EG). EG exhibited three decreases in mass at 250, 423 and approximately 700 °C, which can be attributed to the removal of oxygen-functional groups and the combustion of the carbon skeleton. The thermal behaviors of xGnP-M-5 and graphene exfoliated were similar, however xGnP-M-5 showed only 2-step of mass loss and its decomposition temperatures at corresponding weight loss and the char residue at 800 °C are slightly higher comparing to those of exfoliated graphene (EG).

By contrast, the xGnP-C series exhibited only one main mass loss at 701 °C, corresponding to the combustion of the carbon skeleton. With the increased degree of sheet oxidation and increased specific surface area of the xGnP-C series, the degradation temperatures at 2 %, 5 %, 10 % and 50 % of weight loss shifted to relatively lower temperatures. xGnP-C-300 exhibited the highest thermal stability, possibly because it also contained the lowest number of oxygen-containing groups on its surface.

Table 45 Thermal stability behavior of graphene fillers (under air atmosphere).

Sample name	T _{2%} [°C]	T _{5%} [°C]	T _{10%} [°C]	T _{50%} [°C]	Char residue at 800 °C [wt. %]
xGnP-C-300	347	497	588	731	19
xGnP-C-500	261	413	522	691	1
xGnP-C-750	171	347	454	663	0.2
xGnP-M-5	248	351	408	715	13
Exfoliated graphene (EG)	176	289	391	663	8

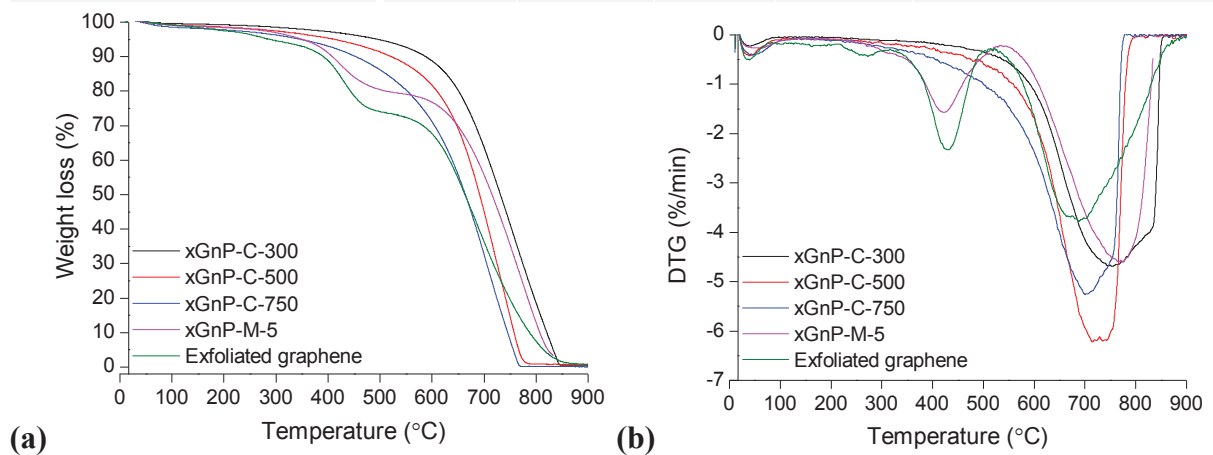


Figure 57 (a) TGA and (b) DTG profiles of graphene fillers (under air atmosphere).

5.3.1.5. Conclusions

Among the investigated types of graphene-based materials, xGnP-M-5 and EG were distinguished by the highest particle aspect ratio and the most typical graphene layered structure consisting of thin and highly exfoliated nanoplatelets. Due to the large particle dimensionalities of these fillers, they were characterized by lower specific surface areas (S_A) than the xGnP-C series, ranging from 50 to 120 m²/g. Exfoliated graphene (EG) exhibited exceptional absorption capacities reflected in a high DBPA number of 958.2 ml/100 g, which indicates large particle aggregation and a highly developed structure. The XPS analysis of the surface chemical composition revealed a high degree of oxidation of xGnP-M-5 and exfoliated graphene (EG) fillers in which a substantial majority were C=O groups. The thermal stability of these types of graphenes was lower than that of the xGnP-C series, most likely due to the higher percentages of oxygen-functional groups on their surfaces. By contrast, a series of xGnP-C graphenes varied in the content of oxygen-containing functional groups on their surfaces depending on the specific surface area. The highest oxidation degree was observed when a substantial majority of the functional groups were C–O–R groups, as observed for xGnP-C-750, which had the highest specific surface area (S_A) of 609 m²/g, and gradually decreased with decreasing S_A value. The xGnP-C series showed only 1 main step of mass loss at 701°C during thermal degradation in an air atmosphere, and the char residue decreased with the degree of surface oxidation. Morphological analysis by SEM revealed that xGnP-C-750 had the smallest particle size, the particles only slightly resembled plate-like structures. The particle size increased and the shape became more lamellar as the specific surface area of the xGnP-C graphenes decreased.

5.3.2. REINFORCEMENT OF ACRYLONITRILE-BUTADIENE RUBBER (NBR) AND CARBOXYLATED ACRYLONITRILE-BUTADIENE RUBBER (XNBR) WITH GRAPHENE NANOPATELETS WITH VARYING SURFACE AREAS AND MORPHOLOGIES

INTRODUCTION: Graphene fillers with various specific areas, surface chemistries and particle morphologies were investigated as novel reinforcing fillers for NBR and XNBR. The effects of different types of graphene nanoflakes on the rheometric characteristics, stress-strain behavior, crosslink density, resistance to thermo-oxidative aging and UV radiation of the NBR and XNBR composites were investigated.

5.3.2.1. Preparation of NBR and XNBR composites containing graphene fillers

The graphene nanoplatelets (5, 10 and 15 phr) were mixed with NBR and XNBR in a laboratory two roll mill at a temperature of approximately 40 °C. The total compounding cycle was less than 10 min. The friction ratio of the rolling mill was 1:1.1 during the mixing period. The raw rubber was masticated prior to the addition of filler and curative. Graphene was first mixed, and then the curing agents were incorporated.

5.3.2.2. Curing studies and crosslink densities of NBR and XNBR compounds

The rheometric characteristics of the NBR and XNBR compounds are shown in **Table 46** and **Table 47**. The addition of fillers caused variations in the torque (MH, ML) and scorch time values ($t_{\Delta 2}$). Generally, the presence of graphene filler resulted in an increase in the minimum torque (ML) and maximum torque (MH) compared with unfilled specimens of both types of rubbers. The ML is representative of the rubber mix viscosity, whereas the MH depends on the extent of crosslinking between rubber chains and the reinforcement by the filler particles. Increasing the amount of graphene and its specific surface area in the elastomer matrix contributed to an increase in the viscosity and the cure degree of compounds, as indicated by the ML and MH parameters. In addition, the reinforcing potential of graphene was reflected in the difference between the maximum and minimum torque (ΔM).

Table 46 Rheometric properties of NBR/graphene compounds crosslinked at 160 °C.

Sample name and filler loading [phr]	ML [dNm]	MH [dNm]	ΔM [dNm]	$t_{\Delta 2}$ [min]	t_{90} [min]	CRI [min ⁻¹]	α_f [°]	$v_T \cdot 10^{-5}$ [mol/cm ³]
NBR	0.4	8.6	8.2	1.1	6.7	17.9	-	5.92 ± 0.08
N/xGnP-C-300 5	0.5	9.8	9.3	2.0	8.6	15.2	2.7	6.18 ± 0.14
N/xGnP-C-300 10	0.7	11.0	10.3	2.6	16.3	7.3	2.6	5.74 ± 0.37
N/xGnP-C-300 15	0.9	12.8	11.9	2.3	15.8	7.4	3.0	5.67 ± 0.33
N/xGnP-C-500 5	0.6	9.9	9.3	2.5	9.7	13.9	2.7	5.82 ± 0.10
N/xGnP-C-500 10	0.7	11.1	10.4	2.9	16.3	7.5	2.7	6.23 ± 0.21
N/xGnP-C-500 15	1.0	13.4	12.4	2.7	19.2	6.1	3.4	5.44 ± 0.08
N/xGnP-C-750 5	0.6	10.1	9.5	2.6	13.7	9.0	3.2	5.81 ± 0.49
N/xGnP-C-750 10	0.8	11.6	10.8	3.4	18.0	6.9	3.2	5.91 ± 0.24
N/xGnP-C-750 15	1.2	13.8	12.6	3.3	21.3	5.6	3.6	5.86 ± 0.07
N/xGnP-M-5 5	0.5	10.6	10.1	2.0	8.0	16.7	4.6	5.96 ± 0.09
N/xGnP-M-5 10	0.6	11.1	10.5	2.0	9.6	13.2	2.8	6.17 ± 0.06
N/xGnP-M-5 15	0.9	12.9	12.0	2.1	10.0	12.7	3.1	6.28 ± 0.10
N/EG 5	0.5	10.5	10.0	2.4	8.1	17.5	4.4	6.22 ± 0.13
N/EG 10	0.7	11.3	10.6	3.0	12.7	10.3	2.9	5.74 ± 0.12
N/EG 15	0.8	13.3	12.5	2.3	11.5	10.9	3.5	5.05 ± 0.08

Table 47 Rheometric properties of XNBR/graphene compounds crosslinked at 160 °C.

Sample name and filler loading [phr]	ML [dNm]	MH [dNm]	ΔM [dNm]	$t_{\Delta 2}$ [min]	t_{90} [min]	CRI [min ⁻¹]	α_f [°]	$v_T \cdot 10^{-5}$ [mol/cm ³]
XNBR	0.5	4.6	4.1	1.9	35	3.0	-	1.81 ± 0.70
X/xGnP-C-300 5	0.6	5.3	4.7	1.9	35	3.0	2.9	1.83 ± 0.02
X/xGnP-C-300 10	0.7	6.6	5.9	1.8	29	3.7	4.4	2.22 ± 0.07
X/xGnP-C-300 15	0.8	7.5	6.7	1.7	31	3.4	4.2	2.58 ± 0.07
X/xGnP-C-500 5	0.6	5.6	5.0	1.7	30	3.5	4.4	1.98 ± 0.10
X/xGnP-C-500 10	0.8	7.0	6.2	1.4	29	3.6	5.1	2.26 ± 0.09
X/xGnP-C-500 15	1.0	8.8	7.8	1.4	29	3.6	6.0	2.63 ± 0.13
X/xGnP-C-750 5	0.6	5.5	4.9	1.8	30	3.6	3.9	1.85 ± 0.05
X/xGnP-C-750 10	0.8	6.8	6.0	1.6	30	3.5	4.6	2.64 ± 0.17
X/xGnP-C-750 15	1.1	9.2	8.1	1.4	30	3.5	6.5	4.25 ± 0.25
X/xGnP-M-5 5	0.6	5.1	4.5	2.2	35	3.0	1.9	1.60 ± 0.29
X/xGnP-M-5 10	0.7	7.5	6.8	2.0	31	3.4	6.6	2.26 ± 0.21
X/xGnP-M-5 15	0.8	8.2	7.4	1.7	30	3.5	5.4	2.53 ± 0.23
X/EG 5	0.6	4.9	4.3	4.3	29	4.0	1.0	1.75 ± 0.13
X/EG 10	0.7	7.4	6.7	2.1	21	5.3	6.3	1.80 ± 0.29
X/EG 15	0.8	8.6	7.8	1.9	20	5.5	6.0	2.24 ± 0.16

The torque difference (ΔM) increased with increased filler loading and its specific surface area. Generally, in all of the filled compounds, the torque or ΔM increased with filler loading because of the hydrodynamic forces and the formation of a stable filler network. ΔM is indirectly related to the crosslink density of the blends and can therefore be an approximation of the extent of cure degree in the rubber phase.

The rate of the vulcanization of NBR and the curing of XNBR is represented by the *CRI* parameter. A higher *CRI* value indicates a faster crosslinking process. By increasing the graphene loading in the rubber matrix, the NBR vulcanization process is gradually retarded, and the optimal cure time (t_{90}) is steadily extended in comparison with the reference sample. This result is the most likely due to the absorption of active ingredients of the sulfur vulcanizing system onto the graphene sheet surfaces. In contrast to NBR, the XNBR crosslinking reaction was slightly accelerated by the presence of graphene. The value of t_{90} was reduced to 30 min by the addition of 5 phr xGnP-C-500 and xGnP-C-750, whereas the scorch time ($t_{\Delta 2}$) was significantly decreased from 1.9 to 1.4 min in the presence of higher graphene loadings.

The presence of carbon filler in the NBR matrix did not have a significantly impact on the changes in the crosslink density (v_T) of the compounds, which remained almost unaltered at a value of approximately $6.0 \cdot 10^{-5} \text{ mol/cm}^3$. Only the sample containing exfoliated graphene (EG) exhibited a downward trend in the extent of network density with increasing filler content, possibly due to the absorption of vulcanizing agents by a larger amount of graphene layers.

The equilibrium swelling results indicated that the presence of graphene particles may affect the cure degree in XNBR. In contrast to the NBR compounds, the crosslink number (v_T) in the XNBR network was slightly impacted by increasing graphene filler content and its specific surface area. The highest crosslink density of $4.25 \cdot 10^{-5} \text{ mol/cm}^3$ was achieved for the XNBR composite filled with xGnP-C-750 at the highest filler loading of 15 phr. This observation is also supported by the highest torque value (MH) of 8.1 MPa obtained for the same sample, as measured using a moving die rheometer. Because many oxygen-containing functionalities are present on the graphene surface, as detected by XPS, some physical and chemical interactions between the graphene and XNBR macromolecular chains may occur during the curing process. Both high filler loadings and large specific surface areas provide more functional groups on the filler surface, which are potential sites for interaction with the –COOH functionalities of XNBR. The extent of equilibrium swelling may also be reduced due

to the adsorption of polymer chains onto the filler particle surfaces. In general, the increase in the crosslink density of XNBR in the presence of graphene filler may result from (a) the adsorption of rubber chains on the filler sheet surfaces and (b) the interactions between oxygen-containing groups of the filler and the –COOH functionalities of XNBR.

The changes in the rheometric studies with filler loading might be a measure of the filler-rubber interaction or reinforcement represented by the reinforcing factor (α_f). An increase in the α_f values with increasing graphene content was observed for both types of elastomers, however, this effect was more pronounced for the functionalized XNBR. The values of α_f were also higher when the composite contained fillers with large specific surface areas, in this case, xGnP-C-750 with $S_A = 750 \text{ m}^2/\text{g}$.

5.3.2.3. Mechanical properties of NBR and XNBR composites

The influence of graphene fillers with different specific surface areas and various particle aspect ratios on the physical properties of the NBR and XNBR compounds at 5, 10 and 15 phr is presented in **Table 48** and **Table 49**. Significant improvements in the tensile properties of the nitrile composites were achieved. The results of the tensile strength measurements clearly indicate that graphene reinforces both types of matrix, however, a higher level of reinforcement was observed in XNBR. The tensile strength (TS) of XNBR composites was superior even at small filler concentrations, such as 5 phr (xGnP-C-750), whereas the improvement in tensile strength of NBR/graphene composites exhibited a steady upward trend with increasing filler concentration from 5 to 15 phr. As expected, the stress at 100, 200 and 300 % elongation (SE_{100} , SE_{200} , and SE_{300}), the tensile strength (TS) and the hardness (H) of all loaded samples increased in all cases compared with unfilled rubbers. The stretching stress at 300 % (SE_{300}) is commonly related to the maximum torque (MH) and crosslink density (v_T). The results of the mechanical testing were in good agreement with the results of previous rheometric studies. The increased loading of graphene with high platelet aspect ratios, such as EG, xGnP-M-5 and xGnP-C-300, led to an essential increase in the *EB* of the NBR composites, most likely due to the absorption of vulcanizing agents on the filler surface. As the specific surface area of the fillers increased, the *EB* tended to decrease, particularly for those NBR samples loaded with xGnP-C-500 and xGnP-C-750. Some studies have reported a severe decrease in *EB* with the addition of graphene-based materials to polymers.²⁸⁴

Table 48 Mechanical properties of NBR/graphene composites.

Sample name and filler loading [phr]	SE ₁₀₀ [MPa]	SE ₂₀₀ [MPa]	SE ₃₀₀ (MPa)	TS [MPa]	EB [%]	H [°Sh]
NBR	1.2 ± 0.1	1.6 ± 0.1	1.9 ± 0.1	3.8 ± 0.7	499 ± 20	58
N/xGnP-C-300 5	1.5 ± 0.1	2.1 ± 0.1	3.0 ± 0.1	8.9 ± 0.6	533 ± 10	59
N/xGnP-C-300 10	1.5 ± 0.1	2.3 ± 0.1	3.5 ± 0.2	8.1 ± 1.0	526 ± 20	61
N/xGnP-C-300 15	1.9 ± 0.1	3.3 ± 0.1	5.2 ± 0.1	11.4 ± 1.3	543 ± 30	62
N/xGnP-C-500 5	1.3 ± 0.1	1.8 ± 0.1	2.5 ± 0.1	8.5 ± 0.4	568 ± 10	60
N/xGnP-C-500 10	1.5 ± 0.1	2.5 ± 0.2	4.1 ± 0.3	9.9 ± 0.7	530 ± 20	62
N/xGnP-C-500 15	1.7 ± 0.1	3.0 ± 0.1	5.1 ± 0.1	12.5 ± 0.7	505 ± 30	63
N/xGnP-C-750 5	1.4 ± 0.1	2.0 ± 0.1	3.0 ± 0.1	7.2 ± 0.3	473 ± 5	61
N/xGnP-C-750 10	1.3 ± 0.1	1.8 ± 0.1	2.7 ± 0.1	10.3 ± 0.5	541 ± 20	61
N/xGnP-C-750 15	1.9 ± 0.1	3.1 ± 0.1	6.3 ± 0.3	14.3 ± 0.6	491 ± 5	62
N/xGnP-M-5 5	1.5 ± 0.1	2.1 ± 0.1	2.5 ± 0.1	7.7 ± 1.0	597 ± 20	59
N/xGnP-M-5 10	1.9 ± 0.1	2.7 ± 0.1	3.3 ± 0.1	9.6 ± 0.3	609 ± 10	63
N/xGnP-M-5 15	2.5 ± 0.1	3.4 ± 0.1	4.0 ± 0.1	10.9 ± 1.1	658 ± 20	65
N/EG 5	1.7 ± 0.1	2.3 ± 0.1	2.8 ± 0.1	6.1 ± 1.0	553 ± 30	60
N/EG 10	1.9 ± 0.1	2.4 ± 0.1	2.8 ± 0.1	5.8 ± 0.5	606 ± 25	64
N/EG 15	2.1 ± 0.1	2.6 ± 0.1	2.9 ± 0.1	10.6 ± 0.7	807 ± 20	65

Table 49 Mechanical properties of XNBR/graphene composites.

Sample name and filler loading [phr]	SE ₁₀₀ [MPa]	SE ₂₀₀ [MPa]	SE ₃₀₀ (MPa)	TS [MPa]	EB [%]	H [°Sh]
XNBR (X/ZnO)	1.6 ± 0.3	2.3 ± 0.3	3.2 ± 0.6	19.6 ± 2.0	520 ± 20	60
X/xGnP-C-300 5	2.1 ± 0.3	3.7 ± 0.3	6.5 ± 0.4	24.7 ± 1.0	489 ± 20	61
X/xGnP-C-300 10	3.3 ± 0.1	6.5 ± 0.3	10.9 ± 0.7	30.3 ± 2.0	484 ± 25	63
X/xGnP-C-300 15	5.3 ± 0.1	10.6 ± 0.2	16.8 ± 0.4	31.7 ± 3.8	431 ± 17	65
X/xGnP-C-500 5	2.2 ± 0.1	3.7 ± 0.1	6.7 ± 0.4	27.2 ± 1.0	500 ± 15	61
X/xGnP-C-500 10	3.5 ± 0.2	7.7 ± 0.2	13.6 ± 0.2	31.1 ± 1.6	460 ± 10	63
X/xGnP-C-500 15	4.9 ± 0.2	11.0 ± 0.3	18.4 ± 0.8	30.4 ± 1.9	421 ± 10	65
X/xGnP-C-750 5	2.0 ± 0.1	4.1 ± 0.3	9.5 ± 1.0	31.0 ± 1.0	448 ± 10	63
X/xGnP-C-750 10	2.9 ± 0.1	6.6 ± 0.2	13.5 ± 0.5	28.7 ± 1.9	429 ± 14	65
X/xGnP-C-750 15	4.4 ± 0.2	10.6 ± 0.5	19.9 ± 0.9	28.1 ± 2.5	371 ± 20	67
X/xGnP-M-5 5	2.4 ± 0.1	3.7 ± 0.1	5.9 ± 0.3	18.4 ± 1.4	500 ± 15	62
X/xGnP-M-5 10	3.5 ± 0.4	6.0 ± 0.5	8.6 ± 0.7	22.7 ± 2.0	485 ± 15	63
X/xGnP-M-5 15	5.9 ± 0.3	8.6 ± 0.4	13.9 ± 1.0	30.0 ± 2.5	480 ± 20	66
X/EG 5	2.6 ± 0.1	3.7 ± 0.1	5.4 ± 0.1	19.3 ± 2.0	484 ± 15	61
X/EG 10	4.1 ± 0.4	5.9 ± 0.7	08.7 ± 1.1	27.8 ± 3.3	477 ± 15	64
X/EG 15	6.5 ± 0.2	8.8 ± 0.2	12.2 ± 0.6	31.0 ± 2.8	476 ± 20	65

In contrast to NBR, the XNBR samples containing graphene exhibited a gradual decrease in elongation at break (EB) with increasing filler content for all types of fillers. A decrease in EB may indicate an increase in the crosslinking density. This effect was the most pronounced for XNBR loaded with 15 phr of xGnP-C-750, in which a substantial reduction in EB from 598 to 371 % was reported. The best results in improving the tensile properties at small loadings were obtained when graphene with the highest specific surface area (750 m²/g) was employed. Because the xGnP-C-750 loading did not exceed 5 phr, the composite exhibited the highest value of stress at break (TS). When the concentration of xGnP-C-750 was increased from 5 to 15 phr, the tensile strength of XNBR slightly decreased from 31 to 28 MPa. This result can be attributed to the poor dispersion of filler incorporated in larger amounts, which increase the tendency of the particles to agglomerate. The opposite effect was observed for the XNBR compounds filled with other types of graphene, increased filler concentration resulted in a gradual enhancement of tensile strength. Thus, the specific surface area of the filler is one of the main factors influencing the effectiveness of rubber reinforcement. However, the improvement in the mechanical properties of XNBR by graphene fillers may be due to not only the high value of its specific surface area but also the high degree of oxidation and large number of oxygen-containing groups, which might promote physical and chemical interactions with XNBR functional groups, particularly –COOH.

The hardness of the filled NBR and XNBR materials steadily increased with the incorporation of higher filler loadings, however, EG and xGnP-M5, which possessed moderate specific surface areas of 150 m²/g but the highest particle aspect ratio compared to the other types of graphene fillers, had the greatest impact on the hardness of the NBR composites relative to these loaded with the xGnP-C series.

5.3.2.4. Dynamic mechanical analysis (DMA) of XNBR/xGnP-C-750 composites

The changes in the glass transition temperature (T_g) and the loss factor ($\tan \delta$) of XNBR due to the addition of xGnP-C-750 composites are illustrated in **Figure 58**. The height of the main $\tan \delta$ peak corresponding to the T_g declined after the addition of filler. The lower height of the $\tan \delta$ peak is due to the reduction of deformable polymer content under oscillatory strain and reflects the toughness or stiffness of the material at the relaxation temperature. The surface area of xGnP-C-750 was large, therefore, the interactions between the rubber chains and the graphene layers might have limited the conformations of the polymer molecules in the

composites. Greater polymer-filler interactions lead to a lower $\tan \delta$ peak height. The physical adsorption of chains on the xGnP-C filler surface reduced chain mobility, decreasing the height of the transition temperature peak.

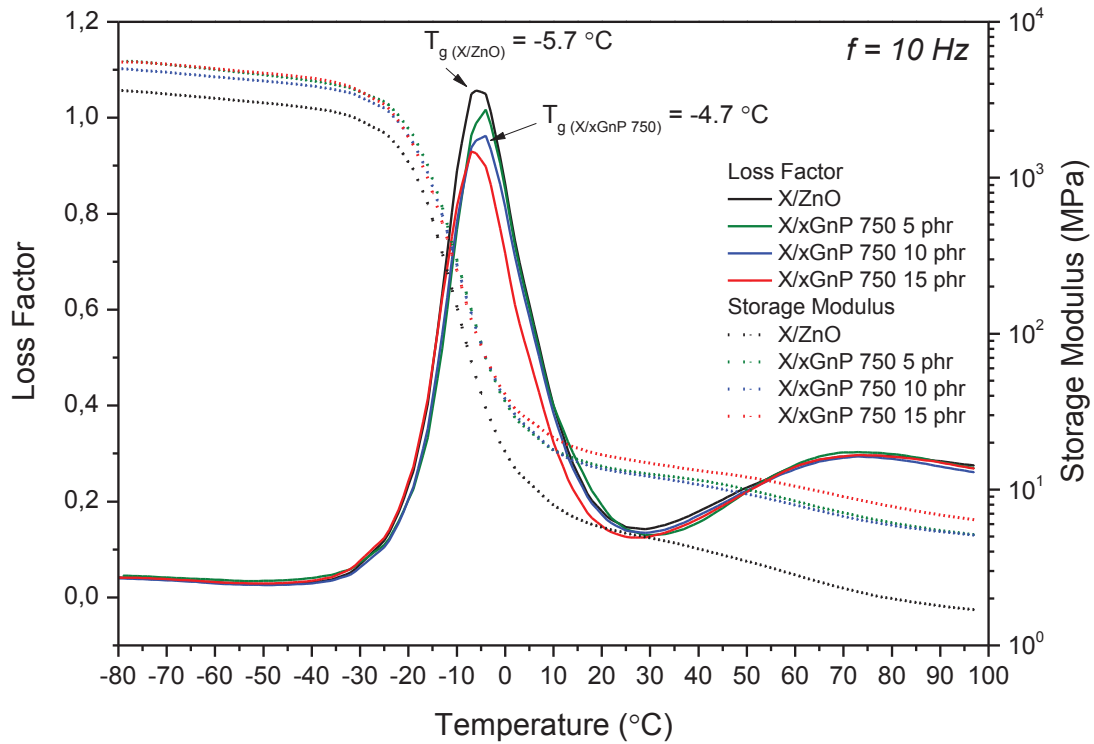


Figure 58 Plots of loss factor $\tan \delta$ and storage modulus E' versus temperature for XNBR system: effect of xGnP-C-750 loading.

The constraint imposed by the crosslinks typically manifests itself as an increase in T_g with increasing crosslink density. In the presence of xGnP-C, a very slight shift in T_g from -5.7 to -4.7 °C might be related to a slightly increased cure degree of the XNBR/graphene composite. In **Figure 58**, a high temperature transition, the so-called ionic transition, can be observed. This additional high temperature relaxation peak appeared due to the formation of ionic clusters in the XNBR-ZnO vulcanizates, as it was described in details in **Chapter 5.1.3**. Both unfilled XNBR and the composites exhibited two $\tan \delta$ peaks: T_g at -5.7 (-4.7) °C and another with a maximum at 75 °C. Measurement of the storage moduli at different temperatures demonstrated that E' significantly increased with increasing xGnP-C-750 content due to the reinforcing effect of the graphene filler. The presence of xGnP-C-750 in the XNBR composite enhanced E' in the entire temperature range from -60 to 100 °C.

Table 50 Dynamic mechanical measurements at 10 [Hz] of XNBR composites.

Sample name and filler loading [phr]	T _g from E'' [°C]	T _g from tan δ [°C]	Height of tan δ [-]	T _i from tan δ [°C]	E' at 25 °C [MPa]
XNBR (X/ZnO)	-18.2	-5.9	1.06	73.9	5.2
X/xGnP-C-750 5	-18.8	-3.8	0.97	73.2	13.1
X/xGnP-C-750 10	-18.8	-3.8	0.92	73.2	13.7
X/xGnP-C-750 15	-18.8	-5.8	0.90	73.2	15.7

5.3.2.5. Thermal stability of XNBR/xGnP-C-750 composites

The effect of the xGnP-C-750 concentration on the thermal stability of XNBR/ZnO composites is presented in **Figure 59** and **Table 51**. Both unfilled XNBR and the composites underwent one main degradation process. The initial degradation temperature (T_5 , at which 5 wt% mass loss occurs) for XNBR/ZnO started at 373 °C. The maximum mass loss temperature (T_{max}) (at which the maximum loss rate occurs) occurred at 444 °C. T_5 decreased to 373, 370 and 358 °C at concentrations of xGnP-C-750 in the rubber matrix of 5, 10, and 15 phr, respectively.

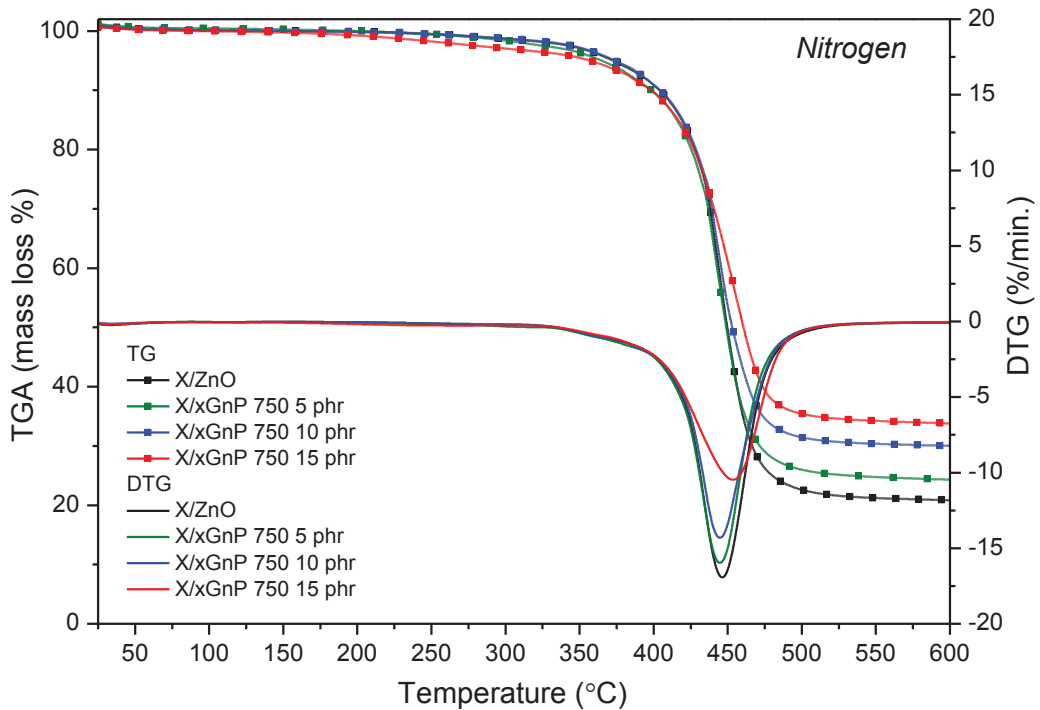


Figure 59 TGA and DTG curves of XNBR/xGnP-C-750 composites with various filler loadings (under nitrogen).

Table 51 Thermal behavior of XNBR composites containing various loadings of xGnP-C-750 (under nitrogen).

Sample name and loading [phr]	T _{5%} [°C]	T _{10%} [°C]	T _{50%} [°C]	T _{70%} [°C]
XNBR (X/ZnO)	373	400	450	465
X/xGnP-C-750 5	373	400	450	469
X/xGnP-C-750 10	370	400	452	511
X/xGnP-C-750 15	358	398	460	670

This decrease in T_5 with increasing filler concentration is likely due to the thermal behavior of pristine graphene, which may release absorbed water or large amounts of graphene that could act as heat sources and promote thermal degradation. However, the final degradation temperature was remarkably increased. The residue after the thermal decomposition of XNBR/ZnO/xGnP-C compounds was approximately 20, 24, 30, and 34 % for 0, 5, 10, and 15 phr xGnP-C-750 in the rubber matrix, respectively.

It could be assumed that the residue in the TGA data increases not only due to the presence of graphene but also due to (a) the presence of charred graphene layers, which inhibit further thermal degradation of the XNBR composite, and/or (b) the formation of a highly crosslinked XNBR structure during heating.

5.3.2.6. Microstructure and morphological analysis of NBR and XNBR composites

The incorporation of graphenes into the elastomer matrix was performed by a standard melt mixing method. The preparation technique was expected to separate the stacks to monolayer graphene under shear during the mixing process. The degree of distribution of various types of graphene particles in the NBR and XNBR matrices was analyzed using SEM. Micrographs of the corresponding composites loaded with 5 phr of filler are presented in **Figure 60 - Figure 63**. Achieving a stable and homogeneous dispersion of the graphene-based materials in an elastomer matrix is difficult due to the large surface area and strong van der Waals forces between layers, however, the compounding of the highly viscous rubber and layered filler under high shear stress and elevated temperature conditions may lead to the partial exfoliation of graphite nanoplatelets and separate the stack of the layers into single sheets, leading to their uniform distribution throughout the polymer matrix. XNBR is more polar than NBR because of the –COOH groups in the chain structure of XNBR, XNBR is also more viscous than NBR.

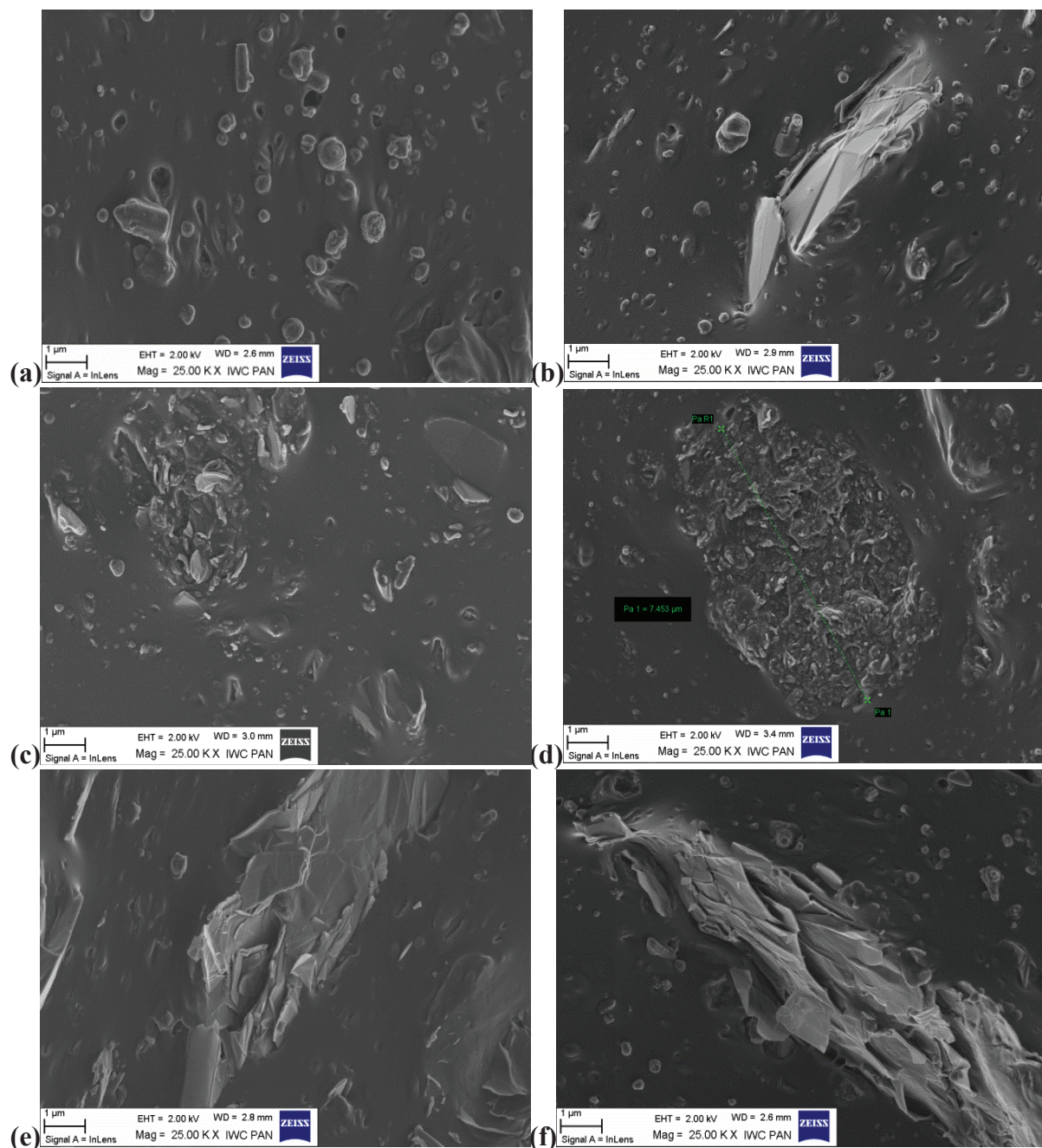


Figure 60 SEM micrographs of (a) NBR, (b) N/xGnP-C-300, (c) N/xGnP-C-500, (d) N/xGnP-C-750, (e) N/xGnP-M-5, (f) N/EG, at 5 phr of filler concentration.

The dispersion of graphene nanoplatelets (at 5 phr) in both types of nitrile rubber was dependent at some points on the filler aspect ratio. Due to the plate-shaped particles of xGnP-C-300, xGnP-M-5 and EG, these fillers predominantly existed in the elastomer matrix as micro-sized agglomerates formed by stacking of several filler layers, as shown in **Figure 60** and **Figure 62**. However, the highly anisotropic graphene layers tend to orient in the rubber matrix under a high mechanical shear force. Consequently, the rubber composites loaded with

5 phr of graphene exhibited partially exfoliated/intercalated structures, as illustrated in **Figure 61** and **Figure 63**.

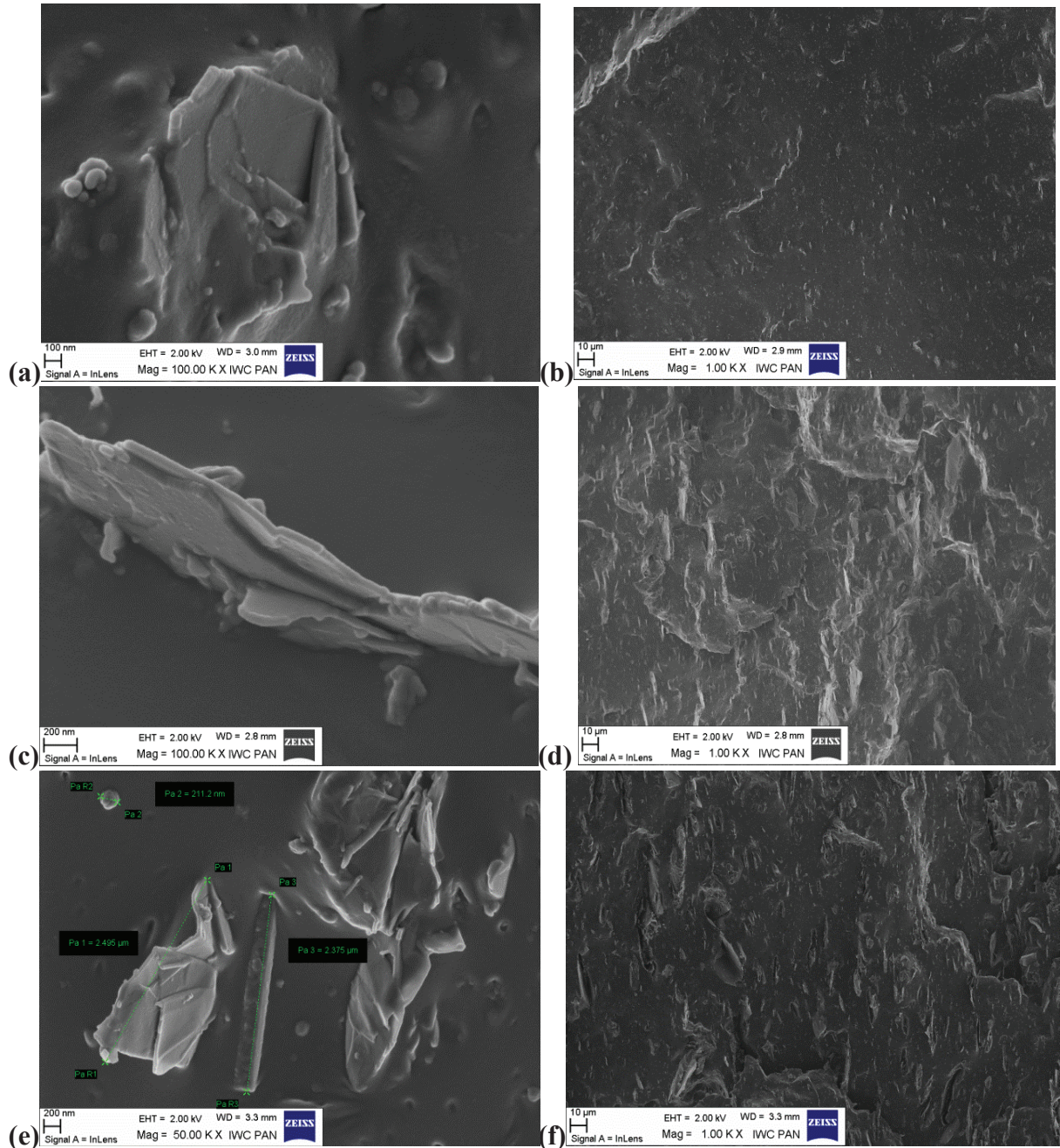


Figure 61 SEM micrographs of XNBR/graphene composites presenting the partially exfoliated structures and the orientation of graphene sheets under the high shear forces of composites: (a, b) N/GnP-C-300 (5 phr), (c, d) N/GnP-M-5 (5 phr), (f, g) N/EG (5 phr).

In contrast to the highly anisotropic graphenes, both xGnP-C-500 and xGnP-C-750 were characterized by a less-lamellar shape of the particles and high specific surface areas. The

elastomer composites filled with these types of graphenes exhibited microstructures consisting of randomly distributed micro-sized agglomerates. The size of the filler agglomerates was dependent on the specific surface area (particle size) and the type of rubber. In the XNBR matrix, agglomerates were larger than 10 μm , approximately 5 μm and approximately 1 – 2 μm in the presence of xGnP-C-300, xGnP-C-500, xGnP-C-750, respectively. In the case of NBR composites filled with xGnP-C-750, large agglomerates greater than 10 microns in size were detected, as shown in **Figure 60 d**.

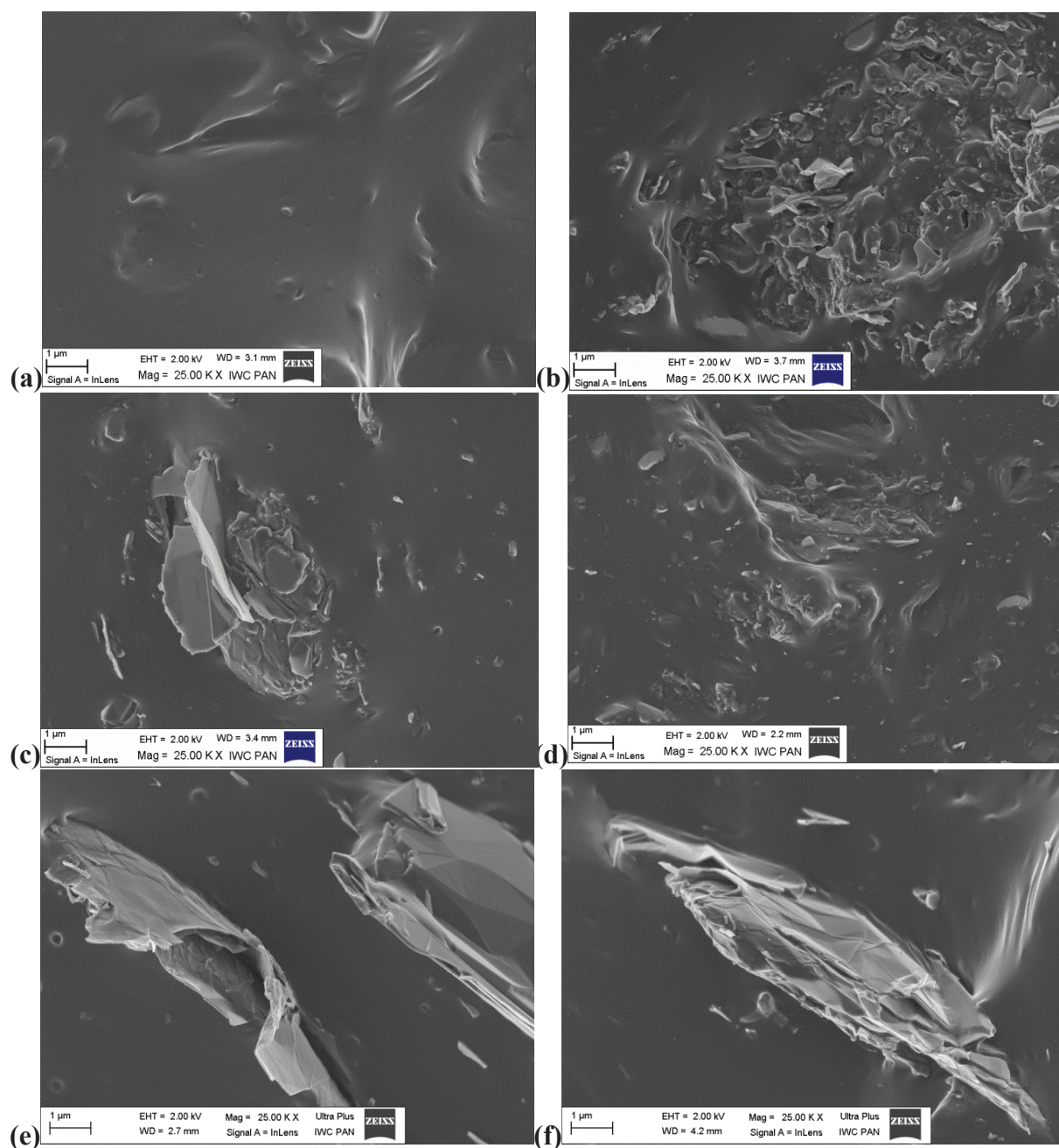


Figure 62 SEM micrographs of (a) X/ZnO, (b) X/xGnP-C-300, (c) X/xGnP-C-500, (d) X/xGnP-C-750, (e) X/xGnP-M-5, (f) X/EG, at 5 phr of filler concentration.

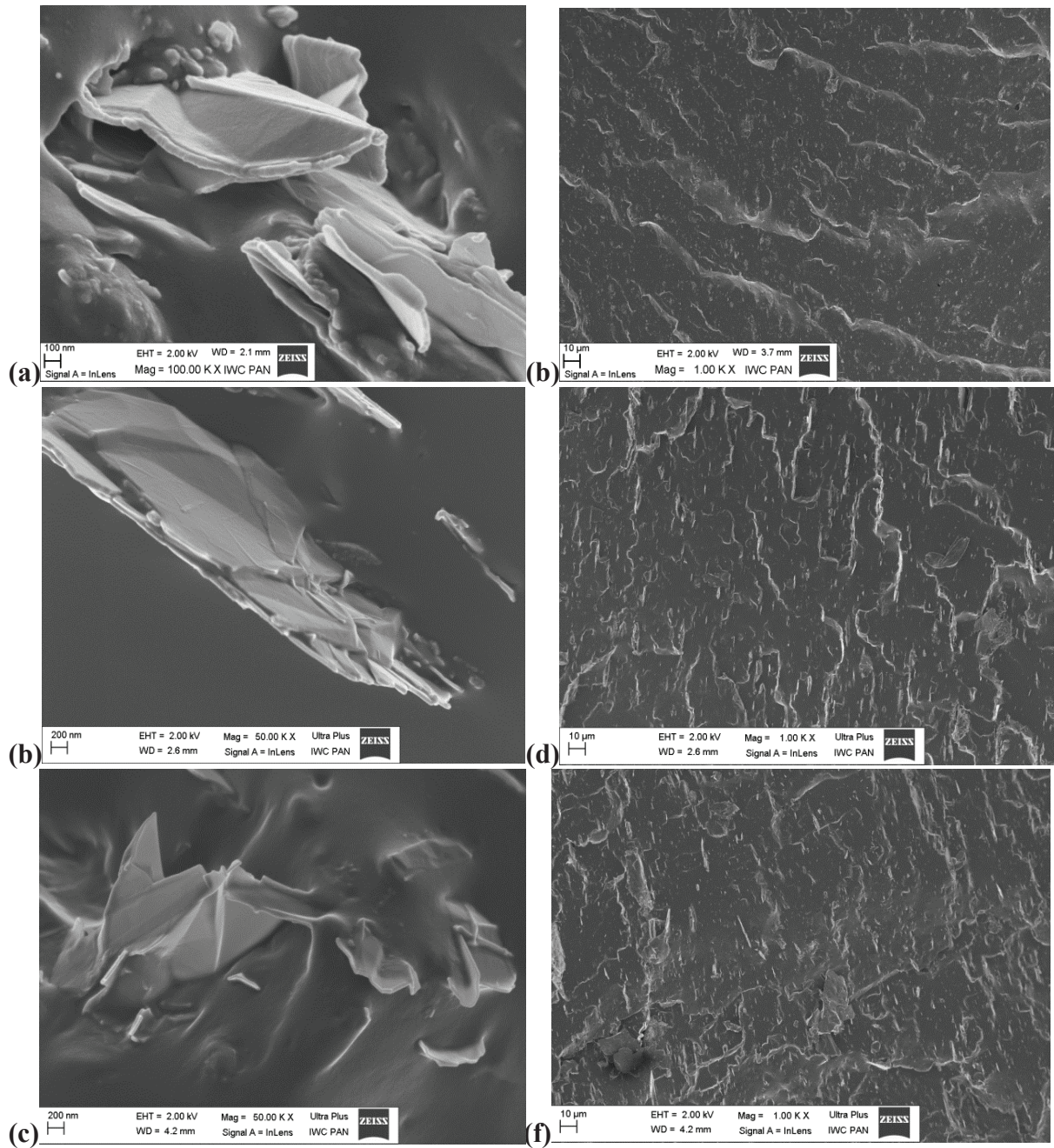


Figure 63 SEM micrographs of XNBR/graphene composites presenting the partially exfoliated structures and the orientation of graphene sheets under the high shear forces of composites: (a, b) X/GnP-C-300 (5 phr), (c, d) X/GnP-M-5 (5 phr), (f, g) X/EG (5 phr).

5.3.2.7. Thermo-oxidative aging of nitrile rubber composites

Table 52 and **Table 53** summarize the influence of accelerated thermo-oxidative aging on the mechanical properties of the NBR and XNBR composites loaded with increasing amounts of different types of graphene fillers. Based on the data presented in **Table 52**, increasing

levels of graphene did not markedly protect NBR against the effects of thermo-oxidative aging conditions, the aging coefficient (K_T) of the NBR/graphene composites remained nearly unchanged, with low values ranging from 0.2 to 0.4. The thermally aged NBR materials became more brittle and exhibited significantly reduced percentages of *EB*, particularly at higher graphene concentrations. All of the graphenes investigated exhibited a similar effect on the mechanical properties of NBR exposed to thermo-oxidative aging conditions, however, a clear impact of increasing specific surface area of the fillers and their concentration on the gradual reduction in *EB* was observed.

Table 52 Mechanical properties and crosslink densities of NBR composites subjected to thermo-oxidative aging.

Sample name and filler loading [phr]	SE ₁₀₀ [MPa]	SE ₂₀₀ [MPa]	SE ₃₀₀ [MPa]	TS [MPa]	EB [%]	K _T [-]
NBR	1.1 ± 0.1	1.5 ± 0.1	-	2.7 ± 0.7	282 ± 30	0.4
N/xGnP-C-300 5	2.1 ± 0.1	4.3 ± 0.1	-	5.2 ± 0.1	227 ± 5	0.3
N/xGnP-C-300 10	2.9 ± 0.1	6.4 ± 0.1	-	7.6 ± 0.1	224 ± 20	0.3
N/xGnP-C-300 15	4.6 ± 0.1	9.8 ± 0.1	-	10.7 ± 2.0	187 ± 20	0.4
N/xGnP-C-500 5	2.1 ± 0.1	4.4 ± 0.1	-	5.5 ± 0.1	228 ± 5	0.3
N/xGnP-C-500 10	4.5 ± 0.9	-	-	8.7 ± 0.1	193 ± 5	0.3
N/xGnP-C-500 15	5.8 ± 0.1	-	-	12.2 ± 0.1	174 ± 5	0.3
N/xGnP-C-750 5	2.7 ± 0.1	7.1 ± 0.1	-	7.4 ± 0.1	209 ± 7	0.4
N/xGnP-C-750 10	3.5 ± 0.1	9.8 ± 0.2	-	10.6 ± 0.1	197 ± 5	0.4
N/xGnP-C-750 15	9.2 ± 0.5	-	-	12.9 ± 1.5	125 ± 15	0.2
N/xGnP-M-5	2.1 ± 0.1	3.3 ± 0.1	-	4.3 ± 0.4	253 ± 17	0.2
N/xGnP-M-10	3.4 ± 0.1	5.4 ± 0.1	-	6.0 ± 0.5	218 ± 14	0.2
N/xGnP-M-15	3.6 ± 0.1	5.6 ± 0.1	-	6.7 ± 0.6	205 ± 10	0.2
N/EG 5	2.1 ± 0.1	3.0 ± 0.1	-	3.9 ± 0.1	270 ± 5	0.3
N/EG 10	2.7 ± 0.1	3.6 ± 0.1	-	4.4 ± 0.1	274 ± 1	0.3
N/EG 15	3.0 ± 0.1	4.0 ± 0.1	-	5.2 ± 0.2	253 ± 5	0.2

In contrast to the NBR composites, the XNBR compounds exposed to oxygen and high temperature (100 °C) exhibited significantly increased stiffness, as reflected in higher modulus values at 100, 200 and 300 % elongation and higher crosslink densities (ν_T) compared with the corresponding unaged samples (**Figure 64**). The coefficient K_T reported for the XNBR/graphene composites was very high and corresponds to a value of approximately 1 or more. This result indicates that the thermo-oxidative aging conditions promoted further crosslinking, as confirmed by the nearly twofold increase in crosslink density values for the thermally aged samples compared with the unaged samples. The crosslink density in the XNBR/graphene compounds tended to increase with increasing filler

content and specific surface area. Based on the data presented in **Table 53**, the tensile properties of the XNBR samples improved by up to 40 MPa for the sample containing 5 phr of graphene xGnP-C-750, which had the highest specific surface area.

Table 53 Mechanical properties and crosslink densities of XNBR composites subjected to thermo-oxidative aging.

Sample name and filler loading [phr]	SE ₁₀₀ [MPa]	SE ₂₀₀ [MPa]	SE ₃₀₀ [MPa]	TS [MPa]	EB [%]	K _T [-]
XNBR	2.0 ± 0.1	2.8 ± 0.1	4.6 ± 0.1	22.7 ± 2.0	458 ± 10	0.8
X/xGnP-C-300 5	3.1 ± 0.1	5.5 ± 0.2	9.7 ± 0.2	30.5 ± 2.2	450 ± 10	1.1
X/xGnP-C-300 10	5.2 ± 0.1	10.4 ± 0.3	17.0 ± 0.5	35.3 ± 3.9	410 ± 10	1.0
X/xGnP-C-300 15	8.6 ± 0.3	15.5 ± 0.5	23.4 ± 0.8	39.0 ± 1.6	395 ± 5	1.1
X/xGnP-C-500 5	3.3 ± 0.1	6.7 ± 0.1	12.9 ± 0.1	35.2 ± 2.1	430 ± 5	1.1
X/xGnP-C-500 10	5.9 ± 0.1	13.5 ± 0.1	23.7 ± 0.4	33.0 ± 2.0	364 ± 5	1.0
X/xGnP-C-500 15	7.3 ± 0.2	15.9 ± 0.2	26.1 ± 0.4	33.1 ± 1.2	359 ± 5	0.9
X/xGnP-C-750 5	3.1 ± 0.1	6.5 ± 0.1	13.9 ± 0.1	40.5 ± 1.0	430 ± 5	1.1
X/xGnP-C-750 10	5.4 ± 0.1	13.9 ± 0.4	27.2 ± 1.0	38.1 ± 1.8	361 ± 10	1.0
X/xGnP-C-750 15	8.4 ± 0.1	20.2 ± 0.1	33.2 ± 2.2	33.5 ± 2.7	305 ± 20	1.0

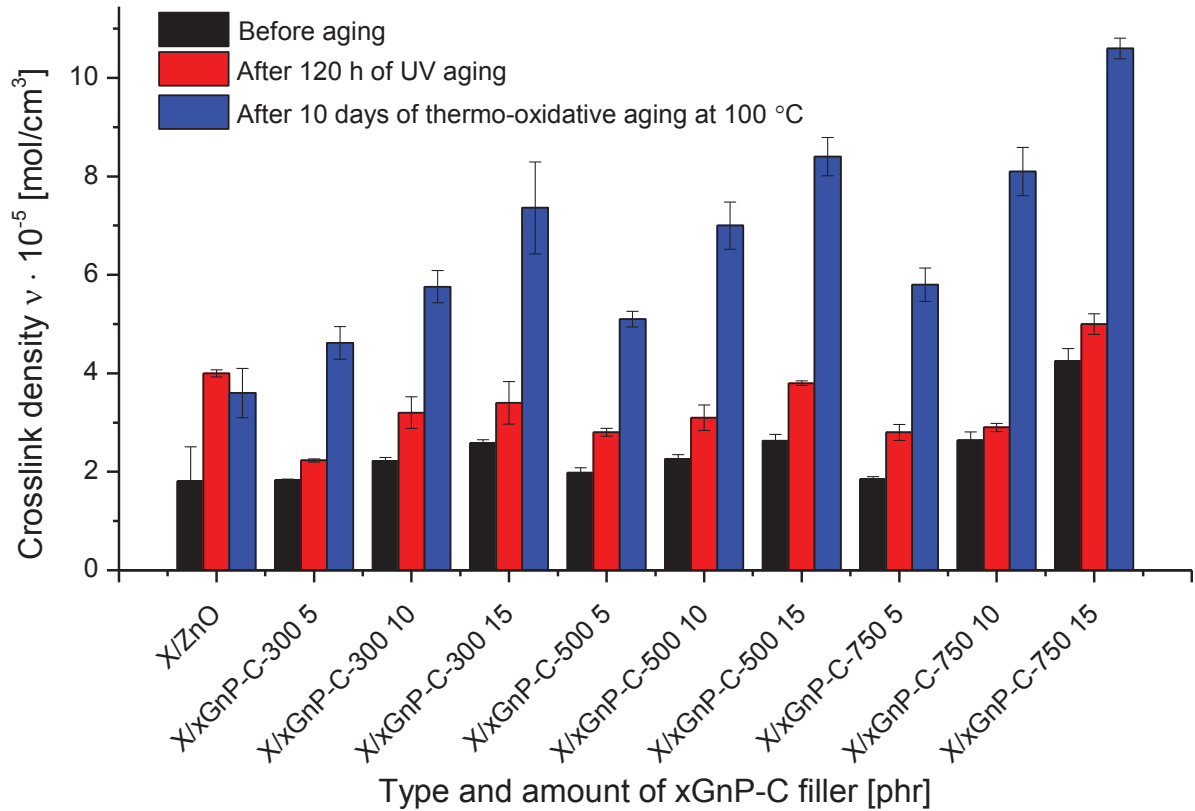


Figure 64 Crosslink densities of XNBR/ZnO and XNBR/ZnO/xGnP-C composites before aging, after UV-aging and after thermo-oxidative aging.

5.3.2.8. Accelerated UV aging of nitrile rubber composites

Graphene similarly to carbon black (CB), due to its color it is an excellent absorber of light. It therefore absorbs most of the ultraviolet components of sunlight, which can otherwise initiate oxidative degradation of the rubber. All types of graphenes significantly enhanced the UV stability of the NBR and XNBR compounds. The results presented in **Table 54** and **Table 55** indicate a steady upward trend in the values of the UV aging coefficient (K_{UV}) with increasing carbon filler content. This effect is most pronounced for samples containing xGnP-C-750, which had the highest specific surface area ($750 \text{ m}^2/\text{g}$), at higher concentrations, whereas xGnP-C-750 was the most effective UV absorber. Notably, the incorporation of a series of xGnP-C into XNBR increased the UV stability of the composites, contributing to the maintenance of a very good performance material compared to unfilled rubber. For XNBR, the crosslinking reactions still occurred, most likely due to the elevated temperature. Thus, higher values of network densities after UV aging were reported after conducting equilibrium swelling of the UV-aged samples (**Figure 64**).

Table 54 Mechanical properties and crosslink densities of NBR composites subjected to UV radiation.

Sample name and filler loading [phr]	SE ₁₀₀ [MPa]	SE ₂₀₀ [MPa]	SE ₃₀₀ [MPa]	TS [MPa]	EB [%]	K _{UV} [-]
NBR	1.5 ± 0.1	-	-	1.5 ± 0.1	189 ± 20	0.2
N/xGnP-C-300 5	1.6 ± 0.1	2.2 ± 0.1	3.2 ± 0.1	4.5 ± 0.3	399 ± 20	0.4
N/xGnP-C-300 10	1.6 ± 0.1	2.4 ± 0.1	3.6 ± 0.1	7.9 ± 1.3	505 ± 10	0.9
N/xGnP-C-300 15	2.1 ± 0.1	3.7 ± 0.1	5.8 ± 0.2	10.4 ± 1.2	474 ± 5	0.8
N/xGnP-C-500 5	1.4 ± 0.1	1.9 ± 0.1	2.5 ± 0.3	5.9 ± 0.5	528 ± 54	0.6
N/xGnP-C-500 10	1.6 ± 0.1	2.5 ± 0.1	4.1 ± 0.2	8.2 ± 0.8	451 ± 10	0.7
N/xGnP-C-500 15	1.9 ± 0.1	3.4 ± 0.1	5.9 ± 0.1	10.3 ± 1.4	422 ± 20	0.7
N/xGnP-C-750 5	1.5 ± 0.1	2.2 ± 0.1	3.2 ± 0.1	5.6 ± 0.4	424 ± 15	0.7
N/xGnP-C-750 10	1.7 ± 0.1	2.5 ± 0.1	4.4 ± 0.2	8.9 ± 0.4	442 ± 20	0.7
N/xGnP-C-750 15	2.1 ± 0.1	3.9 ± 0.1	7.2 ± 0.4	12.6 ± 0.6	424 ± 10	0.8
N/xGnP-M-5 5	1.7 ± 0.1	2.3 ± 0.1	2.8 ± 0.1	3.2 ± 0.1	367 ± 30	0.3
N/xGnP-M-5 10	2.1 ± 0.1	2.9 ± 0.1	3.5 ± 0.2	5.8 ± 0.7	516 ± 20	0.5
N/xGnP-M-5 15	2.6 ± 0.1	3.5 ± 0.1	4.1 ± 0.1	8.4 ± 1.0	581 ± 17	0.7
N/EG 5	1.7 ± 0.1	2.3 ± 0.1	2.8 ± 0.1	3.2 ± 0.1	374 ± 20	0.4
N/EG 10	2.1 ± 0.1	2.7 ± 0.1	3.1 ± 0.1	4.0 ± 0.1	478 ± 5	0.5
N/EG 15	2.5 ± 0.1	3.1 ± 0.1	3.5 ± 0.1	7.8 ± 1.4	577 ± 20	0.5

Table 55 Mechanical properties and crosslink densities of XNBR composites subjected to UV radiation.

Sample name and filler loading [phr]	SE ₁₀₀ [MPa]	SE ₂₀₀ [MPa]	SE ₃₀₀ (MPa)	TS [MPa]	EB [%]	K _{UV} [-]
XNBR	2.1 ± 0.1	2.6 ± 0.2	3.5 ± 0.2	6.0 ± 0.4	400 ± 20	0.2
X/xGnP-C-300 5	2.4 ± 0.1	4.0 ± 0.1	6.4 ± 0.2	11.6 ± 0.3	410 ± 10	0.4
X/xGnP-C-300 10	3.6 ± 0.1	7.1 ± 0.1	11.5 ± 0.1	22.2 ± 0.8	430 ± 10	0.7
X/xGnP-C-300 15	5.6 ± 0.3	10.5 ± 0.4	15.6 ± 0.8	26.0 ± 2.0	429 ± 5	0.8
X/xGnP-C-500 5	2.8 ± 0.1	4.8 ± 0.2	8.4 ± 0.4	14.9 ± 0.1	394 ± 5	0.4
X/xGnP-C-500 10	4.0 ± 0.2	8.0 ± 0.4	14.0 ± 0.5	26.6 ± 3.0	437 ± 30	0.8
X/xGnP-C-500 15	4.9 ± 0.1	10.6 ± 0.2	17.5 ± 0.4	28.1 ± 2.0	419 ± 25	0.9
X/xGnP-C-750 5	2.6 ± 0.1	4.7 ± 0.1	8.7 ± 0.1	17.4 ± 1.5	407 ± 10	0.5
X/xGnP-C-750 10	3.1 ± 0.1	6.3 ± 0.1	12.1 ± 0.4	23.1 ± 1.5	421 ± 10	0.8
X/xGnP-C-750 15	4.8 ± 0.2	11.1 ± 0.6	20.0 ± 1.0	27.9 ± 2.2	381 ± 27	1.0

5.3.2.9. Conclusions

The technological potential of graphenes as a reinforcing nanofiller in elastomers was analyzed. Incorporation of graphene-based materials with high specific surface areas (300, 500 and 750 m²/g) or large aspect ratios into a rubber matrix led to significant increases in stress at 100, 200 and 300 % elongation and increases in the tensile strength and hardness of the composites and efficiently protected the acrylonitrile-butadiene rubbers against degradation by UV radiation. Both types of rubbers, NBR and XNBR, exhibited substantial improvements in their mechanical properties and UV stability in the presence of all types of graphene investigated. However, a higher level of reinforcement by graphene nanoplatelets was observed in the XNBR matrix compared with the NBR matrix. This result may be due to strong filler-rubber interactions, physical interactions and chemical bonding between the carboxylic functionalities of the XNBR chain structure and the remaining oxygen-containing functional groups present on the graphene surface. A high degree of oxidation of the graphene surface along with a larger specific surface area caused an increase in the rubber-filler bonding in the XNBR composites. In this context, graphene also functions as an absorber of UV radiation, and its UV protection capability is dependent on the magnitude of the specific surface area.

6. CONCLUSIONS

The aim of this thesis was the fabrication and study of elastomer composites produced by a simple melt-mixing method and containing layered fillers and ionic liquids. These elastomer materials were expected to exhibit improved mechanical properties, decreased swelling in solvents, enhanced gas barrier properties and increased ionic conductivity. The layered fillers were investigated with respect to their morphological, structural, thermal and surface properties using the following techniques: SEM, XRD, N₂ adsorption measurements, FTIR, TGA, XPS and IGC. A detailed determination of the characteristic features of the layered fillers, such as particle morphology and dimensionality, specific surface area, thermal stability, surface chemical composition and surface acid-base characteristics, facilitated the elucidation of the effects of fillers in the rubber matrices and their impact on the extent of reinforcement. Natural hectorite, which was characterized by a large aspect ratio of lamellar particles, may be useful for the production of eco-friendly rubber composites with reduced gas permeability. However, due to the presence of mixtures of other mineral phases, a high dispersive component of the surface free energy and acidic surface properties, the hectorite particle distribution in the rubber matrix is heterogeneous. Rubbers filled with natural hectorite did not exhibit any substantial improvements in mechanical properties, thus, this type of filler could be regarded as non-reinforcing. By contrast, synthetic silicate, which exhibited particle morphologies and surface chemical compositions similar to those of natural hectorite, was much more suitable for the preparation of reinforced rubber composites. Its reinforcing effect was the most pronounced in the XNBR matrix, in which the additional –COOH functional groups in the rubber chain may contribute to rubber reinforcement due to enhanced rubber-filler interactions. The anisotropic layers of synthetic hectorite were well-oriented in the direction of the high shear stress applied during rubber and filler melt compounding, resulting in further improvement of the mechanical properties of the composite material. SYN HEC influenced the cure degree of XNBR, indicating the existence of some interaction between its surface and the carboxylic rubber macromolecules. Similarly, the incorporation of increased loadings of the synthetic anionic clay HT resulted in remarkable increases in the network density of XNBR, which gave rise to the expectation that this layered filler might be applied not only as a filler but also as a curative for the functionalized carboxylic elastomer. Therefore, subsequent research aimed to simultaneously apply

MgAl-LDH as a filler and crosslinking agent in XNBR, for these experiments, the composite components were mixed in an internal mixer under high shear forces and elevated temperature. Mechanically strong and transparent elastomer composites were fabricated in the absence of standard curatives, such as zinc oxide, or a sulfur cure system, enabling the production of eco-friendly materials due to the decrease in toxic ZnO, the reduction of ingredients in the rubber formulation, the use of non-toxic and easily synthesized fillers and the reduction of proportion of rubber by incorporating significant amounts of filler, an important economic advantage. The optical properties of the XNBR/LDH composites were reversible depending on the temperature and type of MgAl-LDH. The use of high levels of LDH with a Mg/Al ratio $\approx 2:1$ in the XNBR matrix produced composites with thermoreversible transparency. Moreover, LDHs effectively participated in the crosslinking reaction of XNBR and contributed to the production of strong, stiff elastomeric composites. The high aspect ratio of the layers and the high magnesium content in the LDH structure led to significant improvements in the mechanical and barrier properties and promoted the formation of a higher number of ionic crosslinks between the XNBR and the filler. The parallel orientation of highly anisotropic filler layers in the rubber matrix under the high shear force in the internal mixer is advantageous and produces elastomer composites with improved physical properties. The dynamic mechanical analysis revealed a remarkable enhancement in the storage moduli and an increase in the glass transition temperature when LDH was present in the XNBR matrix. The increase in crosslink density and the improvement in the mechanical properties of the XNBR/HT composites may be due to the interactions between (a) the acidic functionalities of XNBR and the basic hydroxyl groups on the filler sheets, (b) the polar functional groups of XNBR and the polar surface of the filler, and (c) $-\text{COOH}$ and the metal ions provided by HT (ionic bonds). The incorporation of LDH delivers not only an environmentally friendly, zinc oxide-free rubber product but also an ionic elastomer composite with excellent mechanical, barrier and transparent properties. However, obtaining a material with the aforementioned parameters requires quite high loadings of the layered mineral. The application of large amounts of an inexpensive and easily synthesized filler is economically beneficial due to the reduction of the cost of the final product.

The effects of anion type (tetrachloroaluminate $[\text{AlCl}_4]^-$, thiocyanate $[\text{SCN}]^-$ and *bis*(trifluoromethylsulfonyl)imide $[\text{TFSI}]^-$) of imidazolium ionic liquid and the impacts of the length of alkyl chain of 1-*n*-alkyl-3-methylimidazolium salt consisting with *bis*(trifluoromethylsulfonyl)imide anion $[\text{Cn-MIM}][\text{TFSI}]$ on the properties of XNBR/LDH compounds were analyzed. The hydrophilic imidazolium salt $[\text{BMIM}][\text{AlCl}_4]$ was found to

be reactive toward XNBR by increasing the network density of the rubber composites and significantly accelerating the curing process. The incorporation of a series of hydrophobic 1-n-alkyl-3-methylimidazolium *bis*(trifluoromethylsulfonyl)imide ILs into the XNBR/LDH matrix produced elastomer composites with higher ionic conductivity than those containing hydrophilic tetrachloroaluminate or thiocyanate salt. For XNBR/LDH composites, the conductivity increased by approximately three orders of magnitude (10^{-10} to 10^{-7} S/cm) when 15 phr of TFSI-based IL was added. In addition, [TFSI] imidazolium salts exhibited sufficient thermal stability for elastomer processing. With the addition of hydrophobic TFSI-based imidazolium ILs, the filler dispersion and ionic conductivity of the XNBR/LDH composites were effectively improved. These ILs exerted a plasticizing effect on the XNBR matrix, shifting the T_g toward lower temperatures at increasing concentrations. 1-Hexyl-3-methylimidazolium *bis*(trifluoromethylsulfonyl)imide displayed the highest plasticizing effect in the XNBR/LDH material and most efficiently increased the ionic conductivity of the composite. However, the impact of the cation alkyl chain length on this parameter was less significant than anticipated. The optimal amount of TFSI-based imidazolium IL for the preparation of composites with enhanced conductivity and improved morphological and mechanical properties was 2.5 – 5 phr. The most important advantages of 1-n-alkyl-3-methylimidazolium *bis*(trifluoromethylsulfonyl)imide ionic liquids making them useful as melt processing aids in the XNBR/filler composites are following,

- 1. Good compatibility and miscibility with carboxylated acrylonitrile-butadiene rubber XNBR prevents against leaking form elastomer matrix,**
- 2. Sufficient thermal stability which allows to withstand high temperatures during rubber processing and vulcanization,**
- 3. Colorless and chemical stability,**
- 4. Enhanced ionic conductivity of the rubber composites in the order of 10^{-8} S/cm at low ionic liquid concentration,**
- 5. Improvement of filler dispersion and mechanical properties of XNBR/filler composites.**

The NBR and XNBR exhibited a substantial improvement in mechanical properties even when a small amount (approximately 5 phr) of graphene nanoplatelets was incorporated. Graphene fillers with high specific surface areas (300, 500 and 750 m²/g) increased the tensile strength and stress at 100, 200 and 300% elongation of the rubber composites and efficiently protected XNBR against degradation by UV radiation. In this case, graphene acted as a perfect absorber of UV radiation.

7. LIST OF PUBLICATIONS

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ACHIEVMENTS

1. **Lodz Marshall Scholarship for PhD students 2013. Financed project:** "Elastomeric nanocomposites with enhanced functional properties containing layered fillers".

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