

Mechanistic understanding of high strain rate impact behavior of ultra-high molecular weight polyethylene and the mechanism of coating formation during cold spraying

Kesavan Ravi

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Mechanistic Understanding of High Strain Rate Impact Behavior of Ultra-High Molecular Weight Polyethylene and the Mechanism of Coating Formation During Cold Spraying

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Analyse mécanique du comportement du polyéthylène à ultra haut poids moléculaire lors d'impact à haute vitesse et mécanismes de formation d'un revêtement en "cold-spray"

Devant le jury composé de :

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Mechanistic Understanding of High Strain Rate Impact Behavior of Ultra-High Molecular Weight Polyethylene and the Mechanism of Coating Formation During Cold Spraying

Abstract

Recent developments showed polymer coatings to be feasible by downstream injection cold spray technique on different surfaces (process known as Cold-Spray). This is especially important for Ultra-High Molecular Weight Polyethylene (UHMWPE), which cannot be classically processed from the molten state or in solution. Its deposition on various substrate materials was demonstrated in which it was seen to be able to deposit due to the control of three major parameters; particle surface activity (by addition of hydrophilic polar alumina nanoparticles like fumed nanoalumina (FNA) to the particle surface), particle temperature and particle velocity. But the mechanisms behind deposition was not largely understood due to the complexities of the physical and chemical nature of the polymers at high strain-rates and high heating rates. Further, discussions on the criteria and effect of FNA particles in the buildup of UHMWPE coatings have not been made vet. Systematic comparisons are performed with materials obtained by classical sintering under various pressure, temperature and time. The thesis presents a detailed mechanistic understanding of high strain rate impact behavior of UHMWPE and the mechanism of coating formation on Al substrate during cold Spraving. The coating formation is first broken down in to two major categories; 1. Interaction of UHMWPE with Al substrate (impacting particle-substrate interaction) during a high-speed impact and interaction of UHMWPE with already deposited UHMWPE particles (impacting particle-deposited particles) leading to a buildup in the coating. Then, a general idea of high-strain rate mechanism specific to UHMWPE material used in this study and an introduction to the strain-rate dependence of a UHMWPE-FNA composite material is presented.

First stage of coating formation was understood from a technique specially developed for this work and called Isolated Particle Deposition (IPD) method and its theoretical simulation. In the experimental IPD process, effects of gas temperature and FNA content were carefully calibrated empirically by depositing UHMWPE particles in an isolated manner on an Al substrate. The Deposition efficiency was seen to show a distinctly unique increasing trends when gas temperature and FNA content in the feedstock were increased. Thanks to the use of an ultrafast videocamera, it was then possible to determine the particle velocity, and through theoretical calculations to evaluate the temperature of UHMWPE particles before and during the impact process. Mechanical response of UHMWPE at different temperatures were understood by calculating elastic strain energy of UHMWPE which decreased with increasing material temperature and increased with the strain rate. Rebound of UHMWPE particles on Al surface depended upon whether UHMWPE particles after impact furnished a contact area with an interfacial bond stronger than elastic strain energy of the particle. The bonding of UHMWPE depended upon the extent of wetting at the particle-substrate interface. External contributions like H-bonds on the FNA surface provide sufficiently strong extra bonds at the contact surface to increase the window of deposition at higher temperatures, which was otherwise very low. Second stage of coating formation was understood from the mechanism of welding of UHMWPE grains at different interfacial loading conditions and at varying FNA contents. The morphological and mechanical characterization showed that when UHMWPE was processed under high loading conditions (using classical sintering technique), FNA particles reinforced the UHMWPE interface. On the contrary, when UHMWPE was processed under low loading conditions, FNA particles weakened the interface. Last to be discussed in the thesis is the strain rate effect of UHMWPE using Split-Hopkinson Pressure Bar (SHPB) experiments, in order to approach comparable conditions to what happens during particle impacts. This part of the study discussed in detail the effects a high strain-rate compression has on UHMWPE by analyzing its stress-strain curves, with and without FNA. Thus, the mechanical response data with the inclusion 0%, 4% and 10% FNA to UHMWPE is also presented and discussed.

Finally, this thesis presents a first approach understanding of coating formation of UHMWPE on Al substrate and provides a foundation to further developing polymer coatings for structural and functional applications.

KEYWORDS : Cold spray, UHMWPE, polymer

Mechanistic Understanding of High Strain Rate Impact Behavior of Ultra-High Molecular Weight Polyethylene and the Mechanism of Coating Formation During Cold Spraying

Résumé

Des travaux récents ont montré que des revêtements polymères étaient réalisables par une technique de pulvérisation à froid de particules sur différentes surfaces (procédé connu sous le nom de Cold-Spray). Ces travaux sont particulièrement importants pour les polymères de très hautes masses molaires qui ne peuvent pas être mis en forme par les méthodes conventionnelles (liquide fondu ou solution), comme pour le polyéthylène de très haute masse molaire (UHMWPE). Ainsi, on a montré que la qualité des dépôts d'UHMWPE sur divers substrats dépend essentiellement de trois paramètres majeurs, (i) la modification de la surface des particules (par l'ajout de nanoparticules d'alumine polaire hydrophile telle que "nanoalumine pyrogénée" ou FNA), (ii) la température des particules polymères et (iii) leur vitesse. Mais les mécanismes d'obtention des dépôts n'avaient pas été analysés, notamment en raison de leur complexité : en effet, ces mécanismes dépendent du comportement des polymères à des vitesses de déformation très élevées, soumis de plus à un échauffement ultra rapide. De plus, le rôle des nanoparticules FNA restait à comprendre. Cette thèse présente une analyse expérimentale mécanique détaillée du comportement à l'impact de particules d'UHMWPE et des mécanismes de formation du revêtement polymère sur un substrat en aluminium (Al) sous l'effet de la pulvérisation à froid de ces particules. La formation du revêtement se décompose en deux étapes : la première (1) se rapporte à la formation de la première couche de particules (interaction polymère-substrat), la deuxième (2) à la croissance (par ajout de couches successives) du revêtement polymère (interaction polymère-polymère). Un troisième aspect traité ici se rapporte au rôle des nanoparticules FNA. Le comportement de l'UHMWPE sous vitesse très élevée, avec et sans FNA est pris en compte pour comprendre les phénomènes observés.

La première étape de la formation du revêtement a été étudiée grâce à une technique expérimentale développée dans le cadre de cette thèse et appelée "Méthode de dépôt de particules isolées" (IPD), adossée à une modélisation théorique. Il s'agit de déposer des particules isolées de UHMWPE sur un substrat en Al, en utilisant la même machine Cold-Spray, tout en contrôlant de manière précise la température du gaz et la teneur en FNA. Grâce à l'utilisation d'une caméra rapide, il a été possible de déterminer la vitesse des particules d'UHMWPE et par le calcul d'évaluer leur température avant et pendant leur impact. L'efficacité (particules déposées / particules ayant rebondi) augmente avec d'une part la température et d'autre part la fraction de FNA. Cette efficacité dépend de la compétition entre l'énergie cinétique stockée sous forme d'énergie élastique Eel et l'énergie d'adhésion Ead du polymère à la surface du substrat. Ces deux termes dépendent des propriétés thermo-viscoélastiques de l'UHMWPE, le premier par la fraction d'énergie transformée en chaleur au cours de leur déformation plastique, et le deuxième par la surface de contact lors du choc, augmentant avec la température. Pour que le film polymère se forme, il faut que Ead > Eel. Par ailleurs, Ead dépend de l'interface entre polyéthylène et aluminium, et de la présence de FNA. Les liaisons H disponibles sur la surface des FNA contribuent à l'adhésion, ce qui augmente le domaine de température favorable à la réalisation du dépôt. Concernant la croissance du revêtement, il s'agit cette fois-ci de l'adhésion polyéthylènepolyéthylène, avec toujours l'effet des nanoparticules FNA. Les études microstructurales et mécanique ont montré qu'en frittage conventionnel du UHMWPE sous forte pression, l'ajout de FNA renforce la cohésion des matériaux obtenus, mais que l'effet inverse est observé pour un frittage incomplet (sous faible pression). Enfin, afin d'explorer l'effet de vitesse de sollicitation de l'UHMWPE comparable à celles observées pour le Cold-Spray, des expériences utilisant des barres dites de Split-Hopkinson (SHPB) ont été menées. Les courbes obtenues permettent de disposer d'une cartographie complète du comportement thermo-viscoélasto-plastique de ce polymère, pur ou additionné de FNA.

Ce travail constitue une première approche pour comprendre les mécanismes de la formation de revêtements polymères par Cold-Spray, ce qui ouvre de nombreuses perspectives pour concevoir de nouveaux revêtements (fonctionnels, à porosité contrôlée, etc.), sur des surfaces variées (au contraire du frittage conventionnel).

MOTS-CLÉS : Cold spray, UHMWPE, polymer

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Nomenclature

Symbol	Name	Unit
η_o	Melt viscosity	Pa.s
M	Molecular Weight	kg mol ⁻¹
C _p	Specific heat capacity	J kg ⁻¹ °C ⁻¹
Tg	Glass transition temperature	°C
ΔH_m	Melting Enthalpy	
$T_{m,nascent}$	Melting temperature of nascent powder UHMWPE	°C
$T_{m,melt-crystallized}$	Melting temperature of melt-crystallized UHMWPE	°C
$X_{c,nascent}$	Crystallinity of nascent UHMWPE	
$X_{c,melt}$ -crystallized	Crystallinity of melt-crystallized UHMWE	
d_P	Particle diameter	m
rp	Particle radius	m
ρ_P	Particle Density	kg m ⁻³
m_P	Mass of particle	kg
<i>V_{critical}</i>	Critical velocity	$m s^{-1}$
VP	Velocity of particle	$m s^{-1}$
C _D	Drag coefficient	
A _P	Cross sectional area of particle	m^2
A_s	Surface area of particle	m^2
$ ho_p$	Density of the particle	kg m ⁻³
$ ho_{ m g}$	Density of the gas	kg m ⁻³
Vg	Velocity of gas	m s ⁻¹
Q	Heat transferred	J
h	Heat transfer coefficient	$W m^{-2} K^{-1}$
T_i	Initial Temperature of particle	°C
T_p	Temperature of particle	°C
T_{gas}	Temperature of gas	°C
Nu	Nusselt number	

Re	Reynold's number	
Pr	Prandlt number	
k_g	thermal conductivity of gas	$W m^{-1} K^{-1}$
k_P	thermal conductivity of particle	$W m^{-1} K^{-1}$
v_R	Relative velocity between gas and UHMWPE	$m s^{-1}$
	particle	
μ_g	Dynamic viscosity of gas	kg m ⁻¹ s ⁻¹
$c_{p,p}$	specific heat of UHMWPE particle	J kg ⁻¹ °C ⁻¹
$c_{p,g}$	Specific heat of gas	J kg ⁻¹ °C ⁻¹
α	thermal diffusivity of UHMWPE particle	$m^2 s^{-1}$
Bi	Biot's number	
τ	Fourier number	
T(r,t)	Temperature inside the particle at a distance	°C
	$0 < r \leq r_P (^{\circ}C)$	
β	Heating rate	°C s ⁻¹
σ	Stress	N m ⁻²
σ_Y	Yield stress	N m ⁻²
ε	Strain	
Ė	Strain-rate	s ⁻¹
E_{H-bond}	Energy stored in H-bonds	J
Tprocessing	Processing temperature	
v_f	Volume fraction	
m_f	Mass fraction	
$ ho_{bulk}$	Bulk density of UHMWPE	kg m ⁻³
$ ho_s$	Density of the sintered product	kg m ⁻³
$ ho_{FNA}$	Density of fumed nano alumina (FNA)	
$ ho_r$	Relative density	
f	Frequency of a statistical distribution	
у	Class mid-point	
E_{porous}	Elastic modulus of porous material	$N m^{-2}$
E _{bulk}	Elastic modulus of fully dense bulk material	N m ⁻²
σ_n	nominal stress	$N m^{-2}$

σ_t	True stress	$N m^{-2}$
ε_n	Nominal strain	
ε_t	True strain	
$\dot{arepsilon}_n$	Nominal strain rate	s^{-1}
$\dot{arepsilon}_t$	True strain rate	s^{-1}
ε_R	Reflected strain	
ε_T	Transmitted strain	
v	Poisson's ratio	
C_b	Elastic wave speed propagating through the incident	$m s^{-1}$
	and the transmitted bar	
E_{bar}	Young's modulus of the transmitted and incident bar	$N m^{-2}$
L	Initial thickness of the specimen	М
A _{bar}	Cross sectional area of the transmitted and incident	m^2
	bar	
A _{specimen}	Cross sectional area of the specimen	m^2
$C_{p,Composite}$	Specific heat capacity of composite	J kg ⁻¹ °C ⁻¹
$C_{p,FNA}$	Specific heat capacity of FNA	J kg ⁻¹ °C ⁻¹
$C_{p,UHMWPE}$	Specific heat capacity of UHMWPE	J kg ⁻¹ °C ⁻¹
W	Weight fraction	

List of Figures

No.

Caption

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INTRODUCTION

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1.1 Ultra-High Molecular Weight Polyethylene (UHMWPE)

1.1.1 General Idea

UHMWPE is a unique high molecular weight polymer with outstanding physical and mechanical properties [1][2]. It belongs to a polymer family of polyethylene, which has a deceptively simple chemical composition consisting of only hydrogen and carbon. However, such simple chemical compositions give rise to complex organizational structures at molecular and super-molecular scales depending upon the chain conformations and architecture.

Essentially, UHMWPE is a linear homopolymer, which contains monomers of (C_2H_4) bonded together by chemical covalent bonds to form $(C_2H_4)_n$, where n is the degree of polymerization. Figure 1.1 represents the chemical composition of ethylene and polyethylene. Its simple chemical structure leads an easy crystallization during its polymerization, or from its melt state at decreasing temperature: thus, at room temperature it appears to be always partly crystalline, and belong to the class of "semi-crystalline polymers". The amorphous part is made of entangled coils of chains, much like a bowl of spaghetti. The crystalline region on the other hand a network of compactly arranged chains with a long-range order.

The semi-crystalline polyethylene polymers are structured in several scales. At angstrom scales, PE chain is in an extended planar zigzag conformation. At nano-meter scales, the structure consists of crystalline lamellae and amorphous zones in between the lamellae. And finally, at the micrometer scales, the structure is a super-structure, which depend upon the mode of crystallization. Figure 1.2 shows the illustration of the different structure at different scales. In general, there are several kinds of polyethylene with almost the same chemical compositions, as their chains contain some defects allowing the presence of lateral branches. The presence of such branches limits the crystal growth, which in turn the global crystallinity and crystal size. The higher the branch density, the lower the crystallinity and thus the specific weight (the crystalline phase is denser than the amorphous phase). Corresponding PE are therefore so-called LDPE (Low-density polyethylene), LLDPE (Linear Low-density polyethylene, with short lateral branches), HDPE (High-density polyethylene), etc. Moreover, they behave differently owing to the fundamental difference in the molecular weight and chain architecture. LDPE and HDPE usually have molecular weights of 50,000 g mol⁻¹ and 200,000 g mol⁻¹ respectively [1]. In contrast, UHMWPE has molecular weights of >3 million

g mol⁻¹. Hence, the properties exhibited by UHMWPE also differs significantly from its low molecular counterparts.

Table 1.1 shows different molecular weights of UHMWPE and its general mechanical and thermal properties of UHMWPE. The data is obtained from Ticona website.



Figure 1.1 Chemical structures of ethylene and polyethylene. n indicates the number of monomers in the chain

Table 1.1 UHMWPE with different molecular weights and their mechanical and thermal properties (data from Ticona Website).

Properties		Values		
Molecular Weight ($\times 10^6$ g mol ⁻¹)	3.9	6.8	10.5	
Density (g cm ⁻³)	0.94	0.93	0.93	
Yield stress (MPa)	≥17	≥17	≥17	
Shore hardness D	62	60	60	
Thermal Conductivity at 23°C (Wm^{-1} . K^{-1})	0.41	0.41	0.41	
Specific Heat at 23°C ($kJ. kg^{-1}. K^{-1}$)	1.84	1.84	1.84	



Figure 1.2 PE structures at different scales partly reproduced from Bowder et al. [3].

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1.1.2 Application

The high molecular weight of the Ultra High Molecular Weight Polyethylene (UHMWPE) makes it known to have exceptional physical and mechanical properties like wear resistance, impact resistance, and cavitation erosion resistance. Although most of semi-crystalline polymers exhibit the same ductility, UHMWPE (with molecular weight above 4 Mg mol⁻¹) is the only one to propagate deformation without necking probably due to an extremely high content of tie molecules [4] [5]. The tie molecules act as Stress Transmitters (ST) due to mechanical coupling between the crystalline and the amorphous phase during the yielding. The experimental quantification of the density of tie molecules are typically evaluated using indicators like natural draw ratio or strain hardening [6] [7] [8]. Hence, unlike most semi-crystalline polymers, the outstanding mechanical properties of UHMWPE is attributed to its large strain to failure (typically several hundred percent) [9].

1.1.2.1 Wear Resistance

In particular, it has an excellent wear resistance [10] [11] and is commonly used for total joint implants. In the case of the prosthetic joints, the durability of the slide member is the critical issue. Therefore, it is an important limiting factor which decides the longevity of the prosthetic joints [1] [10]. UHMWPE has been a choice for lining on the acetabular shell. The lining applied to such prosthetic joints are shown in Figure 1.3(a).

1.1.2.2 Impact Resistance

It also has an excellent resistance to impacts [2] [12] [13] and is a material of choice for body armors. Its unusual wear and impact resistance are related to its high ductility. It has a significant elongation at break (typically several hundred percents) and, as a result, a great ability to absorb energy before fracture. Figure 1.3(b) shows an illustration, which illustrates the advantage of a better impact resistant coating like UHMWPE over acrylic on the body armor.



Figure 1.3 Examples of applications where UHMWPE is used (a) A schematic of a prosthetic joint. (b) Illustration showing the UHMWPE coating on a body armor resisting the impact more efficiently than acrylic coating on the same

1.1.2.3 Cavitation Erosion Resistance

Experiments by INSA (Lyon, France) and LEGI lab (Grenoble, France) [14] showed that certain compression sintered UHMWPE (as shown in Figure 1.4) can exhibit an outstanding resistance to cavitation erosion (impacts). Cavitation tests were conducted in a hydrodynamic tunnel designed for a maximum operating pressure of 4MPa. This relatively high pressure provides high velocities, and consequently, high erosive potential for the cavitating flow. The samples to be tested are mounted on a holder of 100mm in diameter facing the nozzle at a distance of 2.5mm. Cavitation takes the form of an axisymmetric cavity attached to the nozzle outlet.



Figure 1.4 (a) The cavitation erosion tested samples of UHMWPE and a schematic of the testing setup. (b) Cavitation erosion depth of various materials compared with UHMWPE.

UHMWPE with molecular weight 10.5 Mg mol⁻¹ shows negligible mass loss significantly smaller than that of stainless steel A2205 after an exposure time of 98 hrs [14]. Figure 1.4 (a) shows the six cavitation erosion tested samples of UHMWPE for 98 hrs. Figure 1.4 (b) shows the erosion depth of various materials compared with UHMWPE.

1.1.3 Crystallinity

UHMWPE is essentially semi-crystalline in structure. At the melt, which is typically at approximately 137°C, it is entirely disordered amorphous in structure with its long molecules communicating with each other via entanglements. When it is brought below the melting point, the chains which can rotate about the C-C bonds [1], creates folds which form a locally ordered region called crystalline lamellae. Hence, below the melting point, UHMWPE is a structure comprising of crystalline lamellae embedded within an amorphous matrix. Figure 1.5 shows a schematic of a UHMWPE microstructure below and above its melting point. The crystalline structure of UHMWPE is predominantly orthorhombic [15].



Figure 1.5 Schematic of UHMWPE microstructure below and above the melting point

1.1.4 Thermal Characteristics

1.1.4.1 Thermal Transitions in UHMWPE

Polymers, in general, are extremely temperature sensitive when compared with other class of materials like metals and ceramics. Fundamentally, thermal transitions in UHMWPE are a direct consequence of how the chain conformations respond to the temperature. UHMWPE,

like many other polymers, generally undergo the following thermal transformations: the glass transition temperature (T_g) , the melt temperature (T_m) and unlike others, does not have the flow temperature due to the high entanglement network of polymer chains which prevents it from flowing.

Below the glass transition temperature, UHMWPE chains have an insufficient energy to slide past each other, hence responds by breaking/rupture of bonds when mechanically loaded. The T_g for UHMWPE is typically around -150°C to -160°C [1]. A temperature increase above T_g facilitates a mobility increase in the amorphous regions leading to an ease of deformability. Figure 1.6 shows the variations of the elastic shear modulus of UHMWPE (10⁶ g mol⁻¹) (f=1Hz) and polyethylene (10⁵ g mol⁻¹) versus temperature. At temperatures around 60°C-90°C [1] the crystallites begin to exhibit crystalline relaxations which softens the crystals and leads to an increase in its plasticity. Finally, around 137°C-141°C (depending on the heating rate, chain conformations, etc.) complete crystal melting occurs. The transition is shown in a typical DSC curve of UHMWPE in figure 1.7.

This transition is denoted by a drop in the modulus value as shown in figure 1.6. After this transition zone, the modulus stabilizes over a certain temperature range where the movements of the chains relative to each other are allowed, but hampered by the entanglements between chains. At this juncture, UHMWPE is a network of entanglements within an amorphous matrix. This zone which is called the rubbery plateau, because the more the material is entangled, the more its resistance to the application of a stress will be important. Therefore, higher the modulus, the entanglement density depends on the stiffness of a chain, i.e. the nature of the monomers and the length of the chains. Therefore, the number chain entanglements will strongly influence the length of the plateau whether it is a function of the temperature. In fact, the higher the number of entanglements per chain, the greater the temperature required for disentangling and thus the flow of the material. For UHMWPE, such high entanglement networks form due to the long chains unique to the material. When the temperature becomes too high, the polymer flows in the manner of a viscous liquid. The flow may also be non-existent when the chains are cross-linking consists of chemical nodes between the chains. In the case of polymers with very short chains, the rubbery plateu may be non-existent, polymer then flows after Tg.



Figure 1.6 Relationship between strength of polyethylene and temperature [9].

In a polymer in the amorphous or molten state, the chains are linked together by physical nodes called entanglements. These nodes have the peculiarity of being able to be created and destroyed throughout the movements of the chains. Nevertheless, for a material at equilibrium, the entanglement density remains generally constant without application of external stress. Several models have been developed to describe the way in which the chains will be able to move with respect to the others, particularly the models of Rouse [16] and de Gennes [17]. These two models describe the movements of the chains in a molten polymer differentiated by the length of the chains studied. The model of Rouse model describes the diffusion of the macromolecular chains for the case of short chains. The thermal motion of long chains, on the other hand, in the polymer melts is generally described by reptation model which was introduced to study rubbers [18]. According to the model, the motion of an entangled polymer molecule is represented as the motion of polymer in a tube. The virtual tube is formed by the surrounding and entwining polymer molecules. Although each molecule is constantly moving, the virtual tube stays about the same for the entire time it

takes the molecules to pass through it. The time required for the chain to completely exit its initial tube and thus to completely lose the memory of its initial conformation is given by the reptation time, τ_{rep} .

$$\tau_{\rm rep} = \frac{\zeta N^3 b^4}{\pi^2 k_{\rm B} T \alpha^2}$$
 (Equation 1.1)

Where ζ is the coefficient of friction of the chain, N is the number of Kuhn segment, b is the length of Kuhn segment, k_b is the Boltzmann's constant, T is the temperature, and α is the tube diameter. Since the reptation time determines the melt viscosity (η_o), the reptation time and the flowability of the polymer, or the melt viscosity, is directly related to the entanglement and the relationship relating melt viscosity and molecular weight, *M*, can be described by a power law [19] [20] [21] shown as follows;



$$\tau_{\rm rep} \propto \eta_o \propto M^{3.4}$$
 (Equation 1.2)

Figure 1.7 The DSC curve of a typical UHMWPE powder.

1.1.4.2 Melting Kinetics in UHMWPE

Melting in semi-crystalline polymers, especially in the case of UHMWPE is highly complicated. In this case, melting phenomenon is a time-dependent process and is a function of heating rate. The measured melting temperature increases with the increase in heating rate and this is called superheating [22] [23] [24]. Primarily, in situations where the chain reorganization during heating is infeasible, the super-heating is seen to occur. Lippits et al. [23] give a relationship between the variation of melting point vs. heating rate for entangled and disentangled structures of UHMWPE with a molecular weight of 4 Mg mol⁻¹. Figure 1.8 shows the change in the melting temperature with the heating rate for entangled and disentangled UHMWPE with molecular weight 4Mg mol⁻¹.



Figure 1.8 Dependence of melting temperature of entangled and disentangled nascent UHMWPE with the heating rate shown by Lippits et al. [23].

1.1.5 UHMWPE Processing

Owing to the large rubbery plateau as shown in Figure 1.6, unlike other polymers, it is difficult to process UHMWPE using conventional techniques such as injection molding, extrusion, etc. Such behavior is primarily due to its inability to flow at temperatures above its melting point and below its degradation temperatures (which becomes detectable at 350°C under nitrogen atmosphere [25]). One of the methods used for processing is by using solution

process, which proved to be a satisfactory processing method while addressing the issue of viscosity. But they are a time-consuming and an economically non-viable process. Further, in the context of being environmentally unfriendly, they have started to become increasingly unacceptable. Hence, one of the ways it is processed is via powder sintering process. Deplancke et al. detail the procedure used in processing via compression sintering process as shown in Figure 1.9.



Figure 1.9 Compression sintering procedure used in the study of Deplancke et al.

1.1.5.1 Interface Welding Mechanism during compression sintering

While processing UHMWPE via compression sintering, from powder to a bulk product, the interfaces should sinter perfectly to obtain a dense near-dense material. UHMWPE sintering is broadly divided in three stages: densification of the interface to promote wetting of the grains, diffusion of chains across the interface, and crystallization of the polymer [9] [25]. The diffusion of chains across the interface is generally described by reptation theory [26]. At interface temperature higher than the melting point, diffusion of chains occurs due to the random molecular motion. The chain segment diffusion across the interface leads to an
interpenetration of chains and to the formation of physical links between molecules from different sides of the interface forming reentanglements. The interface vanishes both optically and mechanically, when the interpenetration is sufficiently strong, so that static and dynamic forces can be transmitted across the interface. In addition, mechanical strength of the interface is reinforced by co-crystallization after the interdiffusion for semicrystalline polymers [27] [28]. Cocrystallization involves the formation of new crystallites across the interface helping to bind the initial powder particles.

However, in the case of sintering of nascent disentangled UHMWPE, the interface healing occurred much faster than predicted by reptation theory, as shown by Deplancke et al. [9] [25]. The work describes the mechanism of diffusion of chains via "melting-explosion" through the grain interfaces during heating and cocrystallization during cooling following which bulk products with excellent mechanical properties are obtained. The research work emphasizes the feasibility of short time sintering via a phenomenon called melting explosion which helps in rapid interdiffusion of chain segments when nascent UHMWPE reactor powder was compression sintered. Nascent UHMWPE powder, at room temperature, has a highly disentangled and a compact non-equilibrium state. Such conformations, above the melting point, can reach an equilibrium state in a very short duration of time by huge increase in the volume occupied by chains and rapidity of the process [29] [30]. This compact nonequilibrium state is characterized by a higher melting point of $\approx 141^{\circ}$ C. But, DSC ramp for a melt-crystallized UHMWPE shows a lower melting point of $\approx 137^{\circ}$ C, because of the change in the chain conformation to an equilibrium state. Importantly, it has to be noted that this transition in the non-equilibrium to equilibrium conformation and the subsequent decrease in the melting point is a handy tool in knowing whether nascent UHMWPE has been meltcrystallized during the process. Figure 1.10 shows the DSC curves of the nascent UHMWPE powder and a melt-crystallized UHWMPE indicating the decrease in the melting point and crystallinity when nascent UHMWPE is melt crystallized.



Figure 1.10 DSC curves of the nascent powder and the melt-crystallized UHMWPE [31].

Further, during the cooling the inter-diffused chains of adjacent grains co-crystallize to form a strongly welded interface. Hence rapid sintering via melting explosion phenomenon was possible primarily due to the choice of nascent UHMWPE.

However, the origin of the mechanical properties and the role of melting explosion is not yet entirely understood.

1.1.5.2 High-Velocity Compaction

In addition to sintering UHMWPE above its melting point, several kinds of literature [32] [33] [34] show the possibility of UHMWPE process ability below its melting point via High-Velocity Compaction (HVC) technique. The protocol followed in this process is as represented in the Figure 1.11 where a polymer powder is compacted and sintered by multiple impacts using a preheated die (below the melting point).



Figure 1.11 Schematic representation of the High-Velocity compaction process.

The general idea behind the sintering mechanism, in this case, is described in the literature by Jauffrès et al. The research discusses the non-possibility of sintering without localized melting and recrystallization/co-crystallization at the grain interfaces where the energy for fusion comes from the plastic work done by the multiple impacts by the punch. The localized melting leads to an inter-diffusion of chains across grain interfaces and co-crystallization during cooling helps to provide links between particles. It was deduced from this research work that the localized melting is a consequence of the large energy dissipation caused by confined elastic and plastic deformation during the impacts. This research work emphasizes the possibility of obtaining a welded interface when processed under the melting point of UHMWPE under high impacts loads to only create localized molten interfaces without melting the whole grain.

1.1.5.3 Possibility of a newer processing route

Because UHMWPE could be processed via powder sintering to obtain near perfect bulk products and the possibility of HVC techniques to sinter UHMWPE interfaces below its melting point gave rise to the option of using a method called cold-spray. Cold- spray is a coating technique where fine powder particles are impacted on a substrate surface at high velocities to obtain consolidated coating adhered to the substrate surface. Further, the requirement of a polymer-metal integrated system demands the use of a coating technique like cold-spray be used. Cold-spray can be especially advantageous in generating coating on large non-planar surfaces like in the case for protection of large ship rudders from cavitation erosion. The subsequent section below (1.2) details the cold-spray process and its application to obtain UHMWPE surface on a metallic surface. Thus, the goal of the present work is to analyze the mechanisms of thick coating formation relevant to the cold-spray process.

1.2 COLD-SPRAY

1.2.1. History

The process known as cold-spraying (CS) involves ballistic impact and a subsequent impingement of fine powder particles of the order 10-100µm on to a target surface at very high velocities (500 to 1500 m s⁻¹) to form coatings or solid components. Initially, the process was developed in the mid-1980s at the Institute of Applied Mechanics of the Siberian Branch of the Russian Academy of Science (ITAM SB RAS) in Novosibirsk by Papyrin and co-workers [35]). The technology gained prominence as it was able to produce components and coatings of several metallic materials successfully.

A typical cold-spray apparatus is arranged in the following manner; The accelerating gas is first generated which is then heated using electrical coils. The powder particles, usually in the particle size range from 5 to 100µm are accelerated when injected into a high-velocity stream of gas. The high-velocity gas is generated through the expansion of a pressurized preheated gas, which is accelerated to supersonic velocity, with an accompanying decrease in pressure and temperature, through a converging-diverging nozzle [36-38]. The accelerated particles are then impacted onto the substrate after exiting the nozzle. The final temperature and the

velocity of the powder particle, with a specific microstructure, is heavily dependent upon the gas pressure and gas temperature which in turn depends upon the nozzle geometry.

Cold-spray, is in fact, a type of thermal spray technique. It varies from a conventional thermal spray technique in a manner that there is an emphasis on increasing particle velocity and minimal increase in particle temperature. Figure 1.12 shows a comparison of approximate process temperature and particle velocities for cold-spray and several traditional thermal spray processes. As it is evident from the comparison, cold-spray employs shallow process temperatures combined with high particle velocities. It is clear, indeed, that cold-spray occupies a relatively unique position concerning other spray technologies.



Figure 1.12 Comparison of approximate process gas temperature and particle velocity ranges for several conventional thermal spray processes and cold-spray.

1.2.2 Types of Cold-spray equipment

Typically, there are two different types of cold-spray system available today; high-pressure cold-spray (HPCS) in which the powder particles are fed/injected before the spray nozzle throat from a highly pressurized gas supply [39]. The apparatus of an HPCS system is as

shown in Figure 1.13. The HPCS typically is used to achieve particle velocities of 800-1400 m s⁻¹.



Figure 1.13 A schematic of a typical high-pressure cold-spray system.

The second type of cold-spray system is called low-pressure cold-spray (LPCS) in which the particles are injected within the diverging section of the nozzle [40]. LPCS systems are used to achieve relatively low particle velocities limiting to 300-600 m s⁻¹ as the inlet pressure applied in this case is usually <1MPa. Figure 1.14 represents a typical downstream injection low-pressure cold-spray system.



Figure 1.14 A Schematic of a typical low-pressure cold-spray system.

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1.2.3 Cold-spray advantages for metals

The primary advantage of the cold-spray process is that it is a solid-state process, which results in many unique and high quality-coating characteristics. The deposition on the surface is purely attributed to the plastic deformation of the particles. The particles are not melted in the process, thought the surface softening of the particles occurs in the case of polymeric particles.

Some of the other significant advantages are discussed below.

a) High deposition efficiency and deposition rate

Very high deposition efficiencies and deposition rates have been achieved with the cold-spray process for most metals, alloys, and composites. Experiments have shown that, by minimizing stress distribution, oxygen content and optimizing the spray parameters, it is possible to obtain high deposition efficiencies for most of the materials. A narrow spray beam with a good powder feed rate ensures a very high deposition rate values. A single pass is sufficient to produce a coating thickness of 1-2mm [41].

b) No or little masking

A typical spray beam is about 10mm in diameter, which is sufficiently narrow and well defined with sharp edges.

c) High density

Cold-spray can be viewed as a combination of particulate and microscopic vapor deposition [42] which ensures a high-density coating with minimal pores and cracks. The loosely bound particles are sputtered away, and deposited particles are micropeened and finally each layer of coating 'shot peens' the underlying layer thereby increasing density.

d) Flexibility of substrate-coating selection

Unlike the thermal spray process, it is possible to select materials by design requirements in cold-spray. For example, Al/Cu interfaces are often unacceptable interfaces when thermal sprayed due to the brittle Cu-Al intermetallic phase being formed. In cold-spray, as the particles are not melted, the formation of such weak interfaces are avoided.

e) Minimum oxidation

Since the cold-spray employs low-temperature gas, there is no risk of oxidation, thermal degradation, grain growth or phase transformation [43]. Additionally, the high-temperature effects on the substrate are also avoided

1.2.4 Cold-spray limitations

Although over the traditional thermal spray process, the cold-spray process has a unique upper hand, it also has its limitations and disadvantages. The cold-spray process, today, is limited to depositing ductile metals onto metals. It is largely because the mechanisms involved in the cold-spray of other materials (ceramics/polymers) are not yet well understood. Cold-spray also uses a larger volume of gas as compared to traditional thermal spray processes. It becomes uneconomical especially when gas like Helium is used in the process. Otherwise, it is not a serious issue when the employed carrier gas is relatively inexpensive like air or nitrogen.

1.2.5 Material Systems

1.2.5.1 Metals

Several experimental studies and computational modeling have been performed to have a better understanding of the bonding process of metallic systems during CS [44]. It was understood that the two opposite phenomena took place during a high-velocity impact; i) grain structures were distorted, and generation and glide of dislocation occurred which resulted in work hardening. ii) The rest of the plastic work (almost 90%) is dissipated as heat, which results in thermal softening. At a certain velocity for particle, the thermal softening dominates over the work hardening effect, which leads to a drop in stress levels. This leads to localized instability and subsequently a large shear straining, which is called adiabatic shear instability. [45] [46]. It can be clearly seen that the bonding mechanism is heavily dependent on both mechanical and thermal properties of the powder material are essential in particle-substrate bonding.Further, critical velocity is a function of the yield strength, melting point and heat capacity of the material under consideration. Figure 1.15 shows the variation of calculated strain, temperature and stress for Cu with respect to time by Assadi et al. [45]. The critical velocity at which adiabatic shear instability occurs is shown in the Figure 1.15 when then temperature increases, stress drops, and the strain increases.



Figure 1.15 The calculated strain, temperature and stress of an impacting Cu particle at various velocities [45].

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1.2.5.2 Ceramics

As ceramic materials have high yield strength and are not plastically deformable, CS application remains extremely limited to obtaining single layered coatings owing to the presence of a deformable substrate. The first layer is often formed due to embedment of ceramic particles into the deformable substrate. Bonding mechanism observed in such ceramic coatings was mainly due to the destruction of a relatively large size agglomeration of feedstock powder particles upon impact on the substrate. As a result, very fine secondary particles were present in the microstructure and a surface with high roughness was formed. Surface roughness provided proper interlocking and voids reduction among the particles in the coating. High-resolution images showed that excellent adhesion was obtained between coating and substrate and particles had proper interlocking. Therefore, particle impact onto the first layer of the coating can improve adherence to the substrate mechanically and/or chemically [47]. Figure 1.16 shows an Illustration of SiC particle deposition on Inconel 625 substrate by cold-spray describing the mechanism of SiC deposition as follows; a) before SiC particle impingement onto the substrate, b) after first SiC particle impingement, the substrate deformed by SiC particles covers around the crushed particle. c) Second SiC particle impingement and d) the substrate deforms plastically and covers around SiC fragments and subsequently SiC coating forms on the substrate surface matrix.



Figure 1.16 Illustration of SiC particle deposition on Inconel 625 substrate by cold-spray; a)
before SiC particle impingement onto the substrate, b) after first SiC particle impingement,
the substrate deformed by SiC particles covers around the crushed particle. c) Second SiC
particle impingement and d) the substrate deforms plastically and covers around SiC
fragments and subsequently SiC coating forms on the substrate surface matrix [47].

1.2.5.3 Polymers

Although polymers have a wide variety of applications that far exceeds that of any other class of available materials ranging from packaging materials, textile materials, industrial fibers, composites, electronic devices, biomedical devices, optical devices, etc., there are only a handful of studies performed on cold-spray of polymeric powders. Just a few research works discuss the high-velocity deformation and deposition mechanism. Polymer deposition mechanism might be one of the poorly understood processes in cold-spray. There are a few works such as that of Xu et al. [48] where LPCS deposition of polyolefin powder has been

discussed, at substantially lower velocities (up to 135 m s⁻¹) than those used in the CS process for metals. Cylindrical nozzle instead of the conventional convergent-divergent nozzle was used. The deposition was performed at room temperature, and the air was used as the carrier gas. Both metallic and polymer substrates were experimentally investigated (polyethylene and aluminum). The critical impact velocity for coating build up was 100 m s⁻¹. Other works about cold-sprayed polymer depositions were conducted by Alhulaifi et al. [49] which dealt with the design of nozzles to achieve lower particle velocities for depositions. It was important to be noted that none of the research works above about polymer depositions by cold-spray discussed a structure-property co-relationship in detail during the impact process. The mechanism of deposition including adhesion on to the substrate is also largely ignored and not understood in detail.

Further works on polymer coatings by cold-spray was performed by our group [31] [50] which worked on development and characterization of UHMWPE coatings on several substrate materials. Details on these papers and their results will be discussed in section 1.3.

1.3 UHMWPE depositions with COLD-SPRAY- Previous Research works

Ultra-high molecular weight polyethylene (UHMWPE) is a challenging material to coat with, because of its viscoelastic behavior and chemical inertness. The cold-spray process appeared to be a promising alternative processing technique, but polymers are in general difficult to deposit using this method. So, attempts to develop UHMWPE coatings were made using a downstream injection cold-spray technique incorporating a few modifications. UHMWPE used in the study by us [31] [50] was obtained from Ticona (Oberhausen, Germany). It was in the form of powder with an average size distribution of 60 µm. Figure 1.17 shows the SEM image of the UHMWPE powder used in this study. The molecular mass deduced from viscosity measurements is 10.5 Mg mol⁻¹. The crystallinity ratio was measured by differential scanning calorimetry (DSC) using a Rigaku apparatus at a heating rate of 10 °C min⁻¹. The DSC curve of this polymer corresponds to that of nascent UHMWPE is discussed in the Figure 1.10. The temperature and heat flow scales were calibrated using high purity alumina.



Figure 1.17 SEM image of the UHMWPE feedstock.

1.3.1 Coatings with UHMWPE

A conventional downstream injection cold-spray, when used with the nozzle of length 200mm as shown in Figure 1.18 was seen to yield a thin-layered UHMWPE coating of approximately 45 μ m on Al substrate at a gas temperature and pressure range of 350-380 °C and 0.3-0.4 MPa, respectively. Since the average particle size of the UHMWPE was 60 μ m; it was understood that the coating obtained is a mono-particle layer. Figure 1.19 shows the image of UHMWPE coated Al surface. A major difficulty in this was seen to be the absence of buildup during coating even after a multiple number of passes.



Figure 1.18 Schematic of a low-pressure cold-spray system attached with a 200mm long nozzle.



Figure 1.19 UHMWPE coating on Al substrate

1.3.2 Coatings with fumed nano-alumina particles added to UHMWPE feedstock

As reported in the research work performed by us [31] [50], the addition of fumed nanoalumina particles increased the deposition efficiency of UHMWPE coating on Aluminum surface. Figure 1.20 shows a photograph of the UHMWPE coating on Al surface with the addition of fumed nano-alumina (FNA).



Figure 1.20 Photographs of UHMWPE coating on Al surface

The fumed nano-particles were present on the grain interfaces possible forming a bridge bond between grains of UHMWPE and between UHMWPE-A1 interface. Figure 1.21 shows the SEM and its corresponding EDX image of the nano-alumina particles settled around the UHMWPE grains. Although not experimentally proven, the literature discusses the possibility of the –OH groups on the fumed nano alumina surface providing extra bonds to reinforce the polymer-polymer and polymer-metal interfaces.



Figure 1.21 SEM and EDX image of cross section of UHMWPE-fumed nano-alumina coating, respectively.

Possible mechanism discussed in the literature is as shown in Figure 1.22 where the composite particles forming a loose aggregate during the flight and consequently depositing on the substrate surface.



Figure 1.22 Possible mechanism of deposition discussed in the literature [31] [50].

Further, while looking into the thermal state of the coating, it was observed that the deposits were melt-crystallized due to which it shows a lower melting point in comparison to that of nascent powder. This suggests the fact that UHMWPE melts during the process, although the juncture at which melting occurs was not discussed. The discussion on whether UHMWPE melts during the flight, during the impact or post-impact was not discussed. On the contrary, it was also observed that the particles which were not melt-crystallized rebounded. The paper addressed the fact that during the particle flight, it is possible for two or more particles to be in the close vicinity for heat transfer to occur non-uniformly. The work concluded one of the essential criteria for UHMWPE particle deposition is the extent of particle heating during the flight. Figure 1.23 (a) shows the DSC curves for the rebound particles compared with the DSC of nascent UHMWPE particles indicating that the curves for both are very close to each other. Figure 1.23 (b) shows the DSC curves for the deposited particles indicating that they are melt-crystallized.



Figure 1.23 (a) DSC curves of the rebounded particles at various gas temperatures. (b) DSC curves of the deposited particles

1.4. Present scenario

Cold-spray technology has been a very successful technique in coating various metallic powders on to metallic substrates. The understanding of the deposition mechanism of such metal/metal coatings is apparent today. However, this is not the case for polymer/polymer and polymer/metal deposition.

It was understood from research works [31] [50] that demonstrated the possibility of UHMWPE deposition on various substrate materials by downstream injection cold-spray technique. UHMWPE was seen to be able to deposit due to the control of three significant parameters; particle surface activity (by addition of hydrophilic polar nano-alumina particles like fumed nano-alumina (FNA) to the particle surface), particle temperature and particle velocity.

But there are several aspects of UHMWPE deposition which are yet unclear;

- 1. UHMWPE exhibits extremely low deposition efficiency when cold-sprayed.
 - Insufficiency in understanding the thermal response during the flight of the particle.
 - Insufficiency in the data about the extent of acceleration during the cold-spray of UHMWPE and subsequently the particle velocity before impact.
 - Insufficiency in understanding the visco-elasto-plastic response at high strain-rates (during the impact).
 - Insufficiency in understanding the sinterability between UHMWPE interfaces at different local loads at the interface.
- 2. The exact role of fumed nano-alumina particles in strengthening interfaces.
 - Effect of fumed nano-alumina during UHMWPE-substrate impact.
 - Effect of fumed nano-alumina during the sintering of UHMWPE grains.

But the exact role of mechanism due to the complexities of the physical and chemical nature of the polymers, the concept and the mechanism behind the deposition is much less understood as compared to metals. Further, discussions on the criteria and effect of fumed nano-alumina particles in the build-up of UHMWPE coatings have not been made yet.

1.5 Objectives of the Research Work

The goal of this research work is to understand the mechanism of UHMWPE coating formation on Aluminium substrates. Figure 1.24 provides the illustration of the basic flow of the thesis work and its contents. For the better understanding of coating formation, it is primarily divided into two broad categories.

Firstly, a coating process starts with the impact of UHMWPE on Al substrate. Hence, the first part of the study focusses on the high-velocity impact of UHMWPE particles on Al substrate.

Chapter 2 in this research work aims to "visualize" the deposition process by a technique of isolated particle deposition (IPD) method where particles are deposited on a suitable target surface in an isolated manner, and the individual particle impact behavior is characterized and analyzed. The experimental visualization includes identifying the particle velocities during impact, the microstructural analysis of the impacted particles at different gas temperatures, recording the deposition efficiency of UHMWPE with and without the inclusion of fumed nano-alumina particles in the feedstock.

Then, Chapter 3 proceeds to theoretically model the isolated particle deposition (IPD) method to predict the fundamental parameters like particle velocity and temperature. This section aims to calculate the particle temperature and velocity at nozzle outlet, during the impact and post impact. This part of the study tries to discuss the subtle nuances of thermal and mechanical responses of UHMWPE during the flight, impact, and post-impact from the calculated parameters and corroborate with the experimental results. The effect of FNA in enhancing the adhesion is also discussed in this section giving a perspective of how fumed nano-alumina is involved in the mechanism of deposition.

From the next section of the study, we proceed to the 2nd stage of the mechanism of coating formation- coating buildup. In Chapter 4, research focusses on the interaction of UHMWPE particles with other particles. This part of the study specifically focuses on understanding the mechanism of welding of UHMWPE grains. Three different sintering protocols namely; full sintering; half sintering and free sintering; were designed to analyze the weldability of UHMWPE grain under different local interfacial loads. Further, the effect of fumed nano-alumina particles in affecting the weldability is also discussed in details. Characterization

techniques like X-Ray tomography was used to identify the porosity ratio and relative densities in such samples. Finally, the mechanical characterization was performed to identify the fundamental parameters involved in affecting the strength of the interface.

Chapter 5, finally discusses the strain-rate effect of UHMWPE ranging from low strain rate to high strain rate tests. This part of the study explains in detail the possible effects a high strain-rate compression has on UHMWPE by analyzing the stress-strain curves of the same. This section also comments on the high strain-rate effects of fumed nano-alumina filled UHMWPE matrices.

Chapter 6 gives the final conclusion of this research work.



Figure 1.24 Flow Chart of the thesis progression.

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CHAPTER 2

ISOLATED PARTICLE DEPOSITION (IPD)

Method and Analysis

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2.1 Introduction

Identification of the dominant parameters and their independent effect on the morphology and mechano-thermal response of UHMWPE during coating formation will help in understanding the deposition mechanism in detail. Understanding of mechanism will not only help in the production of good quality polymer coatings via cold-spray but also assist in generalizing the technique to be applied to various other polymers as well. However, to understand the mechanism, it is essential to recognize and individually characterize the independent effects of each parameter, which is difficult using a traditional cold-spray apparatus. In the case of UHMWPE coating formation during the cold-spray, the mechanism can be broadly divided into two major phases.

1. UHMWPE-Substrate interaction

During the first phase of the coating formation, UHMWPE particle impacts the substrate material to form a deposition.

2. UHMWPE-UHMWPE interaction

A subsequent step involves the impact of UHMWPE particles on the already deposited UHMWPE layer on the substrate material.

2.1.1 Deposition behavior characterization- Limitations

This chapter is dedicated to understanding the first phase of the coating process, i.e., UHMWPE-Substrate interaction. Analyzing the impact behavior of individual UHMWPE particles requires an accurate record of the particle velocity, particle temperature, particle shape and size and particle surface conditions. But, there are difficulties in procuring such data experimentally because of several interdependent parameters operating simultaneously. Some of the significant hurdles observed are the following;

- 1. When the particle flux is high, there are numerous particles having various sizes, shapes, and velocities. Hence, at high flux densities, a dilute 2-phase flow assumption cannot be used for calculations for particle acceleration and heat transfer because of the particle interactions during the flight.
- For particle velocity and particle temperature measurements, the size of the particles should be high enough for it to be adequately resolved by a recording device such as High-Speed camera or IR (Infra-red) camera. Experimental verification for particle velocities is almost impossible for microscopic spray particles.

3. High-velocity single particle impact systems, where a particle of the desired material is scaled-up to dimensions from 1 mm-20 mm is used to study the deformation mechanism involved in high-velocity impacts. Typical examples like that used by Ito et al. [1], Schmidt et al. [2] and Nishida et al. [3], have been shown to be useful in understanding the deposition behavior of metallic materials at room temperature. Figure 2.1 shows the schematic of such a setup designed by Ito et al. for studying impact dynamics of single particles. The logistics to include a particle heating set up for a 1-20mm sized polymeric particle (low thermal conductivity and high specific heat capacity, C_p) to achieve a uniform spatial heating of a polymeric particle can prove to be a costly affair. Hence, such systems can be less efficient for studying the effects of particle temperature on deposition behavior for polymeric materials especially UHMWPE.



Figure 2.1 Schematic illustration of single particle impact testing system (SPITS) developed by Ito et al. [1].

2.1.2 Deposition behavior characterization- Ideal setup

To experimentally verify deposition behaviors, experiments are essential to be performed under a well calibrated set up with well-defined conditions. Such a set up can help to test the effects of parameters independently and efficiently.

Hence, the set up involves:

 Particles of known dimensions (particle shape and size) and surface conditions were analyzed for deposition behavior under accurately measurable spray conditions such as gas temperature and gas pressure.

- For accurate corroboration of theoretical calculation of particle temperature and velocity to the experimentally determined values, it is also required that the flow is a dilute 2 phase flow (gas and particle). This is to avoid the particle-particle interaction during the flow.
- 3. Lastly to accurately measure the mechanical response of the individual impacted particle, the impacting/depositing particles must be sufficiently isolated to negate the effects of particle/particle interaction during the impact.

Hence, the fundamental structure of the Isolated Particle Deposition method is based on a downstream injection cold-spray apparatus as shown in Figure 1.18. Additionally, several accessories were used in conjunction with the equipment to measure the spray parameters before the impact. The deposition data were analyzed post-deposition using image analysis software ImageJ. The powder required for the process, ultra-high molecular weight polyethylene (UHMWPE) was obtained from INSA Lyon, and the coating by cold-spray was performed at Tohoku University.

Hence, the main idea behind this research work is to understand the behavior of UHMWPE particles in conjunction with fumed nano-alumina particles in obtaining a successful deposition by cold-spray. This research work aims to "visualize" the deposition process by a technique of isolated particle deposition (IPD) method where particles are deposited on a suitable target surface in an isolated manner, and the individual particle impact behavior is characterized and analyzed.

2.2 Materials used

2.2.1 UHMWPE Feedstock

The UHMWPE used in this study is obtained from Ticona (Oberhausen, Germany) in the form of powder. Figure 2.2(a) depicts an SEM image of the UHMWPE powder particles used in this study. Figure 2.2 (b) shows the magnified image if UHMWPE surface in detail. The particles are almost spherical in nature. The molecular mass obtained from the viscosity measurements is 10.5 Mg mol⁻¹. The crystallinity ratio was measured by DSC using a PerkinElmer Pyris apparatus with a heating rate of 10 °C min⁻¹. The melting enthalpy of perfect PE crystal is ΔH_m =290 J g⁻¹. Table 2.1 gives the necessary information regarding the melting behavior of UHMWPE used in this study.

Table 2.1 The melting temperature and the crystallinity of the Nascent powder and the melt-
crystallized powder.

Properties	Values
Molecular weight, M (g mol ⁻¹)	10.5 X 10 ⁶
Melting temperature of nascent powder, $T_{m, nascent} \pm 1^{\circ}$ C	145
Crystallinity of nascent powder, $X_{c, nascent} \pm 2\%$	56
Melting temperature of melt-crystallized material, $T_{m, melt-crystallized} \pm 1^{\circ}$ C	136
Crystallinity of melt-crystallized material, $X_{c, melt-crystallized} \pm 2\%$	38



Figure 2.2 (a) SEM image of UHMWPE feedstock (b) Magnified image of the particle surface.

2.2.2 Fumed nano-alumina (FNA) Additive

Fumed nano-alumina (FNA), used in this study as an additive to UHMWPE, was obtained from Evonik under the product name of AEROXIDE[®] Alu 130. These FNA particles have a primary particle size of approximately 13nm and agglomerate size of 90nm. Furthermore, it has a BET surface of $130 \pm 20 \text{ m}^2 \text{ g}^{-1}$ and a tapped density of 50g L⁻¹. Additionally, based on the way it is processed, FNA is manufactured to be hydrophilic and positively charged [4] [5]. Figure 2.3 (a) shows the TEM image of FNA used in the study. Figure 2.3 (b) shows the electron diffraction pattern of FNA and Figure 2.3 (c) illustrates the surface of an FNA particle according to the literature.

Table 2.2 Basic physical data of FNA particles used in this study [4] [5].

Properties	Values
Primary particle size	13nm
Agglomerate size	90nm
Specific surface area $(m^2 g^{-1})$	130±20
Al_2O_3 content (wt. %)	≥99.8
Specific Gravity (g cm ⁻³)	≈3.2
Refractive Index	1.69
Character	Hydrophilic
Surface charge	Positive
Moisture, 2hrs at 105°C (wt. %)	≤5.0
pH, 4% dispersion	4.4-5.4



Figure 2.3 (a) TEM image of FNA (b) Electron diffraction pattern of FNA (c) Illustration of the surface of an FNA particle.

FNA powder is manufactured by flame hydrolysis of aluminum chloride in a hydrogen/oxygen flame. The particles obtained are in the form of aggregated primary particles. The primary particles are free from pores and contain hydroxyl groups on their surface [6] [7] [8]. Table 2.2 provides the underlying physical data about FNA particle used in this study.

2.2.3 Aluminum Substrate

The target surface/substrate used in this study is 1100 grade Aluminum. The substrate surface was polished and ultra-sonicated before it was used in experiments. The substrate samples of Al were prepared in dimensions of $10 \times 10 \times 5$ mm³.

2.3 Experimental

2.3.1 Feedstock Preparation

In this study, for accurate experimental verification of particle velocity and the corroboration of the theoretical model, feedstock was prepared with a very narrow size distribution. Such size distribution was ensured by sieving the as-received UHMWPE feedstock powder to a size distribution ranging from $+44\mu$ m to 60μ m. The feedstock was sieved multiple times to ensure the least dispersion in the particle sizes.


Figure 2.4 SEM image of (a) 2% UHMWPE-FNA composite particle (b) 4% UHMWPE-FNA composite particle (c) 10% UHMWPE-FNA composite particle (inset for each image shows the magnified SEM image of a single particle surface).

After the procurement of the sieved powder, FNA particles were mixed with it in an ethanol bath. The mixture is then ultra-sonicated to ensure that the loose agglomerates of FNA are broken down and settle on the UHMWPE surface. The ultra-sonication process was performed for 30mins. The mixture was then put to dry for 4-5 hours to dry out ethanol completely. Mixtures with 0%, 2%, 4% and 10% by weight of FNA were prepared for spraying.

An approximate calculation to determine the number of layers formed by FNA on the UHMWPE surface for the percentage of FNA added was performed by considering an *ABAB*... type of stacking of FNA on the UHMWPE surface. UHMWPE and FNA particles can be assumed to be spherical particles of average diameter 50µm and 13nm respectively. Hence, an addition of 2%, 4%, and 10% FNA yields approximately a 4, 8 and 20-layered FNA shell on the UHMWPE surface.

Figures 2.4(a), 2.4(b) and 2.4(c) show the SEM images of the UHMWPE-FNA composite powder particles. FNA particles can be seen loosely adhering to the porous UHMWPE surface with a flaky appearance. The nature of the bond between UHMWPE and FNA, at this juncture, is expected to be weak Van der Waals forces.

2.3.2 Isolated Particle Deposition Method

Isolated Particle Deposition (IPD) experiments were carried out using a downstream injection low-pressure cold-spray system. It is a conventional low-pressure cold-spray system available under the name Dymet 403K (Obninsk Centre for Powder Spraying, Russia). Figure 2.5 (a) represents a schematic of the downstream injection cold-spray apparatus used in the experiment. Pressurized air (0.2-0.8MPa) was supplied from a compressor, meets the powder particles after passing through converging-diverging section (de Laval region) of the nozzle. Gas temperature of the pressurized air can be varied from room temperature to 500°C (5 levels). A vibratory feeder was used to feed the powder particles at a steady, controllable rate. The powder particles go through the diverging nozzle before impacting the target surface. Table 2.3 specifies the unit specification of the system.

To control the standoff distance between the nozzle and substrate surface and also to control the traverse parameters, the cold-spray unit was mounted on an XYZ stage manipulated by a personal computer.



Figure 2.5 Images of the cold-spray system control unit and the gun.

Parameter	Description
Power	220 V, 3.3 kW
Pressure of consumed air	0.2-1.0 MPa
Consumption of compressed air	$0.4 \text{ m}^3 \text{ min}^{-1}$
Temperature range	Room temperature – 500°C (5 modes)
Number of powder feeders	2



Figure 2.6 Illustration of the process of Isolated Particle Deposition Method.

For isolated deposition of powder particles, following technicalities were taken into consideration:

- 1. Firstly, the nozzle was held right angles to the target surface with the end of the nozzle at a standoff distance of 5mm from the target;
- 2. Feed rate of the powder particles was controlled to ensure a low-density flux of particles within the spray plume to achieve a dilute 2 phase flow;

3. The traverse velocity/scan speed of the nozzle parallel to the substrate surface was adjusted to ensure isolated deposition of particles;

Figure 2.6 illustrates the intended deposition method.

2.3.3 High-Speed Camera Setup

A FASTCAM SA 1.1 model 675-M2 (high-speed camera) was set up to calculate the flightvelocity of particles and to observe the spray process during cold-spray. The high-speed camera was set up perpendicular to the spray direction. Figure 2.7 shows the recording set-up used in the study. The lens focus was set on an X-Y plane as shown in the Figure 2.7. The particles moving in this X-Y plane was taken into consideration, and the particles which had a Z-component to its direction of motion were discarded. Further, a 10mm calibration stick was used within the plane of focus to calibrate the distance traveled by particles.

The frame rate and shutter speed were adjusted to 40000 fps and 1/551000 s for an optimal view-ability of the spray process. Since the increase in the fps leads to lowering of resolution/quality of the footage, 40000 fps was the choice of the limit. Due to this restriction, fast-moving particles appeared as streaks in each of the time frames. Hence, for the measurement of the distance traveled by the particle in a unit time, the geometrical center of the particle is assumed to be the center of the particle taken into consideration in the way shown in Figure 2.8.



Figure 2.7 Schematic of the high-speed camera setup.



Figure 2.8 Illustration of the determination of particle center during high-speed camera observation.

2.3.4 Image Processing Software

The image processing software used to analyze the statistics of deposition, in this study, was done using public domain software called ImageJ [9]. Particle analysis is performed on the SEM images of the coated surface. The software is used to map the area covered by the particle on the surface to understand the size distribution of the deposited particles. Figure 2.9 shows the example of image processing for calculating area covered by the deposited particles.



Figure 2.9 Example of the protocol followed for image processing using ImageJ.

2.3.5 Morphological Studies

2.3.5.1 SEM

The morphological investigations were performed using a field emission scanning electron microscope (FE-SEM, Hitachi SU-70, available at Tohoku University, Japan), operated at 20 kV. A thin Platinum coating was applied before SEM observation by ion sputtering. Inspections were performed quick to not damage polymer by the electron beam.

2.3.5.2 FIB

The deposited particles were micro-machined along a plane normal to the particle-substrate interface plane to reveal the cross-section of the particle and to understand the degree of deformation using Focused Ion Beam technique (FIB). FIB system of model FB2200, Hitachi, available at Tohoku University, Japan was used in this study.

FIB, in this study, uses a finely focused beam of gallium ions that operated at low beam currents and high beam currents. The low beam currents were used for imaging and high beam currents for site-specific sectioning of deposited particles in a precise, controlled manner. Figure 2.10 shows an illustration of the FIB technique of sectioning and observation of deposited particle-substrate interface.

Successive thin slices of the deposited particle from its periphery were performed to have a smooth section. Finally, for observation, the interface was carefully polished by using successively lower intensity ion-beams currents.



Figure 2.10 Illustration of FIB technique.

2.4 Results and Discussion

2.4.1 High-Speed Camera Measurements

The high-speed camera was used to observe the deposition process of 0% and 4% UHMWPE-FNA composite particles at room temperature (R.T.) and 380°C carrier gas temperatures and gas pressure was adjusted to 0.4MPa. Particles were located from each time frame, and the velocity was calculated from the distance it travels with the increase in each time frames. Figure 2.11 shows one such example where a particle motion is recorded during its incidence and rebound.

Figure 2.12 shows the variations in the particle velocities at R.T. and 380° C gas temperatures. The respective incident velocities at R.T with 0% and 4% FNA were 190 ± 10 m s⁻¹ and 185 ± 10 m s⁻¹. Further, the incident particle velocities at the gas temperature of 380° C were recorded to be 210 ± 10 m s⁻¹ and 195 ± 10 m s for 0% and 4% FNA respectively. It was observed that the nanoparticle addition to the UHMWPE particle did not significantly alter its velocity. However, a small decrease in velocity of the FNA added UHMWPE particle was seen. A reduction in velocity due to the increase of the particle mass can be suspected either because of the added FNA particles or inflight agglomeration of particles. Also, a slight

increase in the particle velocity was recorded with the increase in the gas temperature since the velocity of the gas was also expected to increase with the rise in the gas temperature. This increase in velocity is primarily due to the decrease in the density of carrier gas as the temperature increases.



Figure 2.11 The timeframes showing the motion of a particle (circled) during its incidence and rebound.



Figure 2.12 Distribution of incident velocities and rebound velocities of 0% and 4% UHMWPE-FNA composite particles at gas temperatures corresponding to R.T. and 380°C.

In addition to the incident impact of the particles leading to deposition, there were also particles, which rebounded upon impact depending on the particle velocity and temperature. Hence, rebound velocities were also recorded from the high-speed camera footage, which showed that there was a significant loss of the incident kinetic energy (KE) on impact. Rebound velocities for the entire scenario tested were 40 ± 5 m s⁻¹. The loss in the KE for an average UHMWPE particle of 50µm, expended for plastic deformation and heat generation, approximately amounts to the order of 10^{-6} J. This loss in KE can potentially cause $\approx 10^{\circ}$ C increase the particle temperature if 100% plastic work converts into heat.

2.4.2 Effect of Gas Temperature/Particle Temperature

2.4.2.1 Deposition Behavior-Microscopy

To analyze the effect of particle temperature on its deposition behavior, the temperature of the carrier gas was varied as follows: T1(190°C), T2(275°C), T3(380°C), T4(460°C) and T5(500°C). The deposition volume was analyzed for 0%, 2%, 4% and 10% in weight of FNA for UHMWPE-FNA composite particles of 44-60 μ m particle size distribution. As the purpose of this set of experiments was to independently analyze the effect of particle temperature, the gas pressure was kept constant at 0.4MPa. It was interesting to note that even though the feedstock particles were of the distribution [44-60 μ m], depending upon the

temperature and % FNA, the size range of depositions varied from 10µm to as large as 100µm. Figure 2.13 shows the SEM images of the deposited particles depicting the small particles and agglomerated particles. During the sieving of UHMWPE powder, it is possible that some trace amounts of particles smaller than 45µm ended up in the feedstock.

2.4.2.2 Size Distribution of Deposited particles

The SEM images of the depositions were analyzed by ImageJ where the area covered by the deposited particle on the surface was mapped when viewed perpendicular to the deposited surface. Figure 2.14 depicts the size distribution of deposited particles for depositions with UHMWPE and UHMWPE+10% FNA as a feedstock when sprayed at gas temperatures $T1(190^{\circ}C)$, $T3(380^{\circ}C)$ and $T5(500^{\circ}C)$.

Firstly, it was seen that cold-spray with UHMWPE at 190°C showed meager numbers of depositions. Additionally, the deposited particles were observed to be small in size. But, the number of such small-sized deposited particles increased in number as the gas temperature was increased. At 500°C gas temperature, the size distribution of the deposited particles shifted to a more significant value.

For the depositions with UHMWPE-FNA feedstock, the presence of FNA on the surface allowed a broader size distribution of deposits for the same temperature when compared with depositions of UHMWPE without nano-particles. Observations showed that addition of FNA not only increased the overall number of depositions but also significantly shifted the size distribution towards the right as shown in Figure 2.14. Further, when the high FNA concentration was coupled with high temperature, the deposited particles were observed to be agglomerated (deposits as large as 100 μ m in diameter). Since FNA allows higher number and larger sized particles to be deposited, it is clear that it helps in the UHMWPE-substrate adhesion. Hence, it is likely that agglomerate formation is due to small particles attaching to an already deposited particle.



Figure 2.13(a) SEM images of UHMWPE feedstock deposited at different gas temperatures.



Figure 2.13(b) SEM images of UHMWPE+2% FNA feedstock deposited at different gas temperatures.



Figure 2.13(c) SEM images of UHMWPE+4% FNA feedstock deposited at different gas temperatures.



Figure 2.13(d) SEM images of UHMWPE+10% FNA feedstock deposited at different gas temperatures.



Figure 2.14 Size distribution of deposited particles for UHMWPE and UHMWPE+10% FNA feedstock at T1 (190°C), T3 (380°C) and T5 (500°C) gas temperatures. The y-axis of each graph represents the area covered by the particle when viewed normal to the deposited surface. Interval start from 0-50 and end at 4850-5000 and x-axis represents the number of particles in those intervals.

2.4.2.3 Deposition Efficiency

Deposition Efficiency (DE) is represented here as the ratio of deposited volume to spray volume. The deposited volume on a unit mm² surface area of the substrate surface was calculated from SEM images of the deposited surface. The deposited particle was assumed to be a spherical cap with volume $V_{cap} = \frac{1}{6}\pi h_{cap}(3a_{cap}^2 + h_{cap}^2)$. The radius of the base of the cap, a_{cap} , was measured from the images normal to the viewing line. The height of the cap, h_{cap} , on the other hand, was calculated from the apparent height measured from SEM images when the sample stage was tilted 50° to the viewing line.

The total sprayed volume on a unit mm^2 area was calculated from spray parameters like feed rate and traverse speed of nozzle scan parallel to the substrate surface. Linear approximation on the deposition data was made to identify the trend line as shown in Figure 2.15.

Without the nano-particles on the surface, UHMWPE showed little or no deposition at low gas temperatures. The deposited particles were mostly a few particles of size around 10 μ m. As the gas temperature was increased, a slight increase in the deposited volume was observed which could be attributed to decreasing strength of UHMWPE as an effect of temperature, which will be explained in later section.

Further, as the FNA percentage was increased, there was a detectable increase in the volume of deposition where UHMWPE with 10% FNA showed almost 10 times the deposited volume without FNA. Successive increase in the FNA content reflected a progressive increase in the deposition volume and deposition efficiency. Deposition volume was lowest at a 190°C gas temperature and 0% FNA and highest at a 500°C gas temperature and 10% FNA. There was an increase (lowest to highest deposition efficiency) from 10^{-2} % to 1.4%.



Figure 2.15 Evolution of number of particles deposited with an increase in gas temperature for different percentages of FNA.

Deposition of a particle largely depends upon the thermal energy transferred to the particle along the nozzle. Although feed rates were kept sufficiently low to allow a certain interparticle distance during the flow, in reality, there can be instances of two or more particles in proximity to each other. Such cases may lead to a difference in particle temperatures and hence, a dispersion in the deposited volume data as represented in Figure 2.15 as error bars. As commented earlier, the gas velocity is bound to increase by a small amount due to increase in the gas temperature. Hence, since the feed rate (or flux density of the flow) would

increase with gas velocity, the dispersion in the data also increases by a small amount. The error bars are thus the highest and the lowest recorded value for each deposition condition.

2.4.2.4 FIB Analysis

The deposited particles were cut along the particle-substrate cross-section to evaluate their degree of deformation after impact when deposited under the above conditions. This degree of deformation is represented as the aspect ratio, L_1/L_2 , as shown in Figure 2.16. The aspect ratio (L_1/L_2) of the initial spray particle is approximately equal to 1 as they are spherical and that of a deformed particle will be less than 1 depending upon the extent of deformation. The degree of deformation can also be interpreted as the degree of the surface area contributed by a particle of a given volume. Hence, a particle with a higher degree of deformation can lend a larger surface area for contact than a particle, of the same volume, with a lower degree of deformation. Thus, the aspect ratio of the deformed particles was plotted for 0%, 2%, 4% and 10% UHMWPE-FNA composite particles at the temperatures 190°C, 380°C, and 500°C as shown in Figure 2.17. Aspect ratio of UHMWPE (0% FNA) deposits at T1 and T3 were difficult to record as they were minimal in size and the energy of FIB ions were too high to make precise cuts along the cross-section of the particle. At T5, the deposits of UHMWPE were observed to be heavily deformed.

The deposits showed the effects of temperature and FNA quite distinctly. The increase in temperature led to a progressive increase in the degree of deformation of the deposits. At the same time, growth in the FNA content also resulted in the deposition of particles, which offered a lower surface area for contact. Hence, in addition to the particles that were splash deposited, there were also additional particles deposited with a smaller degree of deformation bringing the average L_1/L_2 ratio higher than the one without FNA. This phenomenon is one of the first clues that suggested that FNA covered impacting surfaces provide stronger adhesion with the substrate. A detailed explanation of the extra interfacial bonding by FNA is given in the next chapter. The illustration shown in Figure 2.18, explains the interpretation of the data from the FIB.



Figure 2.16 SEM image depicting the lengths L_1 and L_2 introduced in this study.



Figure 2.17 Degree of deformation of the deposited particles at different FNA content and gas temperatures T1 (190°C), T3 (380°C) and T5 (500°C).



Figure 2.18 An illustration showing the effect of FNA in allowing particles with a lower contact area to get stuck on the surface.

2.5 Summary

The Chapter attempts to explain the general observation and empirical understanding of the cold-spray deposition of UHMWPE in conjunction with FNA particles.

- 1. The motion of UHMWPE particles was observed using a high-speed camera to calculate its velocity before impact. It was found out that the particles moved at an incident velocity of 188 ± 10 m s⁻¹ and 212 ± 10 m s⁻¹ at gas temperatures at R.T and 380° C.
- 2. Significant parameters that influence UHMWPE deposition is the gas temperature and the surface content of FNA on UHMWPE particle surface.
- It was seen that increase in the gas temperature allowed larger particles to deposit and also increase the deposition numbers of similarly sized particles. The overall deposition volume also rose for UHMWPE with the increase in the operating gas temperature.
- 4. Addition of FNA particles, firstly, increased the number of similarly sized deposit for the same operating gas temperature. Further, it helped in the deposition of large-sized deposits. FNA nano-alumina particles also enhanced the overall deposition volume and deposition efficiency.
- 5. FIB sectioning of the deposited particles indicated heavy degree of deformation of UHMWPE particles at high gas temperatures. The observation of the sectioned deposits with different percentages of FNA showed that in addition to heavily deformed deposits at high gas temperatures, FNA also helps in the deposition of particles which contribute a lower contact area during impact.

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CHAPTER 3

ISOLATED PARTICLE DEPOSITION (IPD)

Theoretical Model and

Interpretation

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3.1 Introduction

The Isolated Particle Deposition (IPD) Method as discussed in the previous chapter provides an experimental overview and empirical understanding of the deposition process. It was helpful in understanding the "macro-effects" such as the overall effect of the gas temperature, gas pressure and % FNA on the deposition process by presenting a detailed causative effect of the gas temperature and FNA content at which depositions occur and their deposition efficiencies. But, for a micro-structural understanding of the response of UHMWPE, regarding its probability of successful deposition, during impact, it is essential to understand the variation of the particle material property like particle temperature, particle velocity and the bonds formed during the process by modeling the gas dynamics of the process. Hence, the essential parameters that are to be evaluated to accurately predict the mechanical response of UHMWPE during the impact are;

- Particle temperature;
- Particle velocity;
- Interfacial bonding energy

3.1.1 General impact dynamics

The discussion about this chapter is an impact study which involves the collision of UHMWPE particle to an Aluminum substrate. Essential parameters involved in this phenomenon include striking velocity, geometry, material chemistry, strain-rate, plastic flow, the coefficient of friction. Further, this chapter also analyses the impact response of the UHMWPE particle from the knowledge of geometry if impacting bodies, visco-elasto-plastic deformation effects, strain-rate effects, work hardening, thermal effects and the propagation of failure in the impacting material.

It is quite clear and evident for any deposition process that the success of a deposition is primarily because of a net zero rebound energy of the impacting material. Rebound energy, on the other hand, is, in fact, its stored elastic strain energy. Hence, the amount of rebound energy/stored elastic energy primarily depends upon the proportion of elasticity and plasticity of the material which in turn is affected due to work hardening of the material and its temperature during impact. Hence, this chapter attempts to theoretically model the IPD process in detail to calculate the particle velocity and temperature during the to evaluate and understand rebound energy post-impact.

3.1.2 Particle temperature and Velocity

Firstly, the parameters, especially particle temperature and particle velocity, essential for deposition, vary mainly depending upon the type of materials and target surfaces [1]. Although, the high-speed elasto-plastic deformation mechanism involved in metals by coldspray have been understood quite well and documented [2-5], the literature on polymers are very scarce in comparison [6-9]. In the case of ductile metals, the phenomenon referred to as "adiabatic shear instability" explains the primary reason behind its deposition. High-pressure field due to the high-velocity impact generates plastic deformation and work hardening in the material. But, the deposition occurs beyond a certain velocity, defined as critical velocity $(V_{critical})$, after which the decrease in the yield stress due to temperature increase, because of the dissipation of heat generated by plastic work, dominates the increase in yield stress due to work hardening. In the case of UHMWPE, the visco-elasto-plastic response [10] mechanism at higher stain rates and heating rates, which is markedly different from the elasto-plastic responses seen in metals when a finite strain is imposed on these solids, has to be discussed in detail. In addition, unlike the melting kinetic observed in metals, the kinetics seen in the case of UHMWPE is very slow. Further, there is a strong time-dependency in the melting of UHMWPE [11-13].

3.1.3 Interfacial Bonding Energy

Secondly, adhesion energy between a particle and substrate is signified by the value of bond energy (BE) of the possible bonds created during the impact. In the case of ductile metalsmetal systems, metallic bonding between particle and substrate takes place due to intimate contacts at atomic scales [14-16]. Figure 3.1 shows the Scanning Transmission Electron Microscopy (STEM) image and High Resolution (HR) lattice images near the interfaces of titanium particles deposited of aluminum by cold-spray.



Figure 3.1 STEM image and HR lattice images near the interfaces of titanium particles deposited on aluminum (a, b) (P: Particle, S: Substrate) [14].

Unlike the metals, bonding within polymer-metal systems often relies on bonds like Donoracceptor bonds, Hydrogen bonds (H-bonds) and Van der Waals bonds. Further, enhancements in the bonding quality are usually achieved by macroscopic or microscopic mechanical anchorage.

The previous chapter showed the deposition behavior of UHMWPE particles on Al substrate by IPD method in which UHMWPE was seen to be able to deposit due to the control of three significant parameters; particle surface activity (by addition of hydrophilic polar nanoalumina particles like fumed nano-alumina (FNA) to the particle surface), particle temperature and particle velocity. Hence the chapter presents the following;

- 1. A theoretical model will be shown in this chapter to first calculate the velocity and the temperature of the particle before and during the impact process.
- 2. Secondly, a mechanical characterization of UHMWPE is presented to understand temperature and strain-rate dependence on its stress-strain behavior.
- 3. Thirdly, the bond energy between UHMWPE-Al is discussed, and the effect of FNA particles is explained. The approach to calculating particle bonding is simplified as the information on friction and the adhesion at the scale and time resolution during the cold-spray phenomena is difficult to procure.

Information from all the three above is used to interpret the final response of a UHMWPE particle to the impact. Figure 3.2 provides a detailed flowchart of the intended way to understand the process.



Figure 3.2 An illustration representing the objective of this chapter.

3.2 Isolated Particle Deposition Process Model

3.2.1 Model Assumptions

Firstly, the underlying gas flow assumptions are explained in this section. The following are the assumption used in the IPD model to a reasonable accuracy:

- 1. The gas flow is first assumed to be isentropic (adiabatic and frictionless) and onedimensional.
- 2. The process gas considered here is approximated to be a perfect gas with constant specific heats.
- 3. The 1D analysis in this particular study ignores the gas flow boundary along the walls of the nozzle where the gas velocity is lower than the average. Hence, the rate of the gas flow will be slightly over-estimated value than the real value.
- 4. It is also noted here that as the particle flux is assumed to be two-phase flow (gas and particles), which is dilute, the heat transfer between the particles and gas is considered not to violate the adiabatic gas flow assumption.
- 5. Gas temperatures mentioned in the study are the temperature from the throat of the nozzle to its exit. It is assumed to be constant throughout the nozzle traverse.

3.2.2 Model Description

The Isolated Particle Deposition, or IPD process, as described in the previous chapter, was modeled for UHMWPE particles. The model is described in the following section. As in a typical case, the cold-spray geometry involves a converging/diverging nozzle. The gas and the particle dynamics during cold-spray performed using a converging-diverging type nozzle was theoretically evaluated. Based on the assumptions described in section 3.2.1, the gas conditions become a function of nozzle geometry, total gas temperature, and stagnation (chamber) pressure [18]. The acceleration and deceleration of the gas flow are decided by the changing flow areas inside the nozzle. The total gas temperature and stagnant pressure are the temperature and pressure of the gas at the source of the nozzle.

The gas flow is assumed to originate from a chamber with stagnation pressure (P_o), the temperature is the total temperature (T_{total}), and the velocity of the gas is zero. Assuming the throat condition is sonic, the gas temperature at the throat, T^* , is equated to the T_{total} , by the following relation:

$$\frac{T_{total}}{T^*} = 1 + \frac{\gamma - 1}{2}$$
(Equation 3.1)

Where γ is the ratio of specific heats. For monoatomic gases, it is 1.66 [19] and for diatomic gases, it is typically 1.4 [20]. Under sonic conditions at the throat, Mach number, M, is unity and the velocity of the gas at the throat, V_{gas}^* is obtained from [18] [21] [22]:

$$V_{gas}^* = \sqrt{\gamma R T^*}$$
 (Equation 3.2)

Where

R- Specific gas constant (the universal gas constant divided by the gas molecular weight). The throat density can be calculated via mass balance [18] [21] [22]:

$$\rho^* = \frac{\dot{m}}{V_{gas}^* A^*}$$
(Equation 3.3)

Where

 \dot{m} - Mass flow rate

*A**- Throat area

From perfect gas law, the throat pressure is calculated as follows [18] [21] [22]:

$$P^* = \rho^* R T^*$$
 (Equation 3.4)

Next, the exit Mach number is calculated when the exit area is given [18] [21] [22]:

$$\frac{A_e}{A^*} = \left(\frac{1}{M}\right) \left[\left(\frac{2}{\gamma+1}\right) \left(1 + \frac{\gamma-1}{2} M^2\right) \right]^{(\gamma+1)/[2(\gamma-1)]}$$
(Equation 3.5)

Other gas conditions, namely pressure, temperature, and velocity of the gas, are calculated once the exit Mach number is known from isentropic relations [18] [21] [22]:

$$\frac{P}{P^*} = \left(\frac{\gamma+1}{2+(\gamma-1)M^2}\right)^{\frac{\gamma}{\gamma-1}}$$
(Equation 3.6)

$$\frac{T_{total}}{T} = 1 + \frac{\gamma - 1}{2}M^2$$
 (Equation 3.7)

$$V_{gas} = M \sqrt{\gamma RT}$$
 (Equation 3.8)

In this study, air is modeled as a diatomic gas as it is a mixture of mostly nitrogen and oxygen. The nozzle consists of diverging part of 200 mm and the ratio of exit area to throat area (A_e/A^*) equal to 4.9. Propellant gas with a pressure of $P_o=0.4$ MPa and four different total temperatures (T_{total}) of 200°C, 300°C, 400°C, and 500°C was used in the model. The process gas is approximated as a perfect gas with constant specific heats. The gas flow conditions, gas velocity (V_{gas}) and gas temperature (T_{gas}), along the converging-diverging nozzle was computed using a Java applet developed by Devenport et al. [15]. The applet employs the isentropic flow relationships for a perfect gas (as described earlier in the section

3.2.2) and plots the relationship of velocity and temperature of the gas along the nozzle length.

Hence, the 1D model is designed to explain the IPD process in detail. The stages are illustrated in detail as shown in Figure 3.3.

Table 3.1 and 3.2 gives the details of the gas and particle used in the model respectively.

Table 3.1 Specifications of the gas used in the 1D calculations

Gas	GasFlowGas Temperatures (T _{total})	
Air	Isentropic	200°C, 300°C, 400°C and 500°C

Table 3.2 Specifications of the particle used in the 1D calculations

Particle	Shape	Molecular Weight	Diameter,	Density pp	Specific Heat
		(Mg mol ⁻¹)	d _P (μm)	(kg m ⁻³)	$(J g^{-1} K^{-1})$
UHMWPE	Sphere	10.5	52	930	2.22

The moving heated gas accelerates and heats up the UHMWPE particles and subsequently imparts a certain velocity and temperature to the particle before it impacts the substrate. Hence, from an energy standpoint, in IPD process, there are 3 distinct stages;

- 1. Inflight stage: in this step, the powder particles are heated up and accelerated by the carrier gas through the nozzle.
- 2. Impact stage: the particles impact the substrate at strain-rates according to particle velocity and particle temperature.
- 3. Post-Impact stage: according to mechanical response to the impact, particle deposits or rebounds



Figure 3.3 Illustration showing the different stages of model.

3.2.2.1 Stage 1: In-flight Process

UHMWPE particle is accelerated to a certain velocity in a heated carrier gas (in this case dry air), before impact. The particle hence possesses a specific Kinetic Energy (KE) from its velocity and a particular Thermal Energy (TE) from its exposure to the high-temperature gas.

3.2.2.1.1 Particle Acceleration Model

In this section, particle acceleration due to the gas flow is calculated. Flow is assumed to be two-phase flow (gas and particles) which is dilute enough so that the drag equations hold considering it has been proved to be a reasonable assumption in some earlier studies [16] [17]. The total gas temperatures of 200°C, 300°C, 400°C, and 500°C are considered for the calculations below. The acceleration of the particle velocity can be calculated by equating it to the drag force on the particle [18] [23], which is given by

$$m_{\rm P} \frac{dV_{\rm P}}{dt} = m_{\rm P} V_{\rm P} \frac{dV_{\rm P}}{dx} = \frac{C_{\rm D} A_{\rm P} \rho_{\rm g} (V_{\rm g} - V_{\rm P})^2}{2}$$
(Equation 3.9)

where,

x- Distance travelled by the particle within the nozzle m_P -Mass of particle V_P -Velocity of particle, C_D -Drag coefficient A_P -Cross sectional area of particle ρ_g -Density of the gas (air) V_g -Velocity of gas

Integrating equation 3.9 with respect to distance traveled by particle inside the nozzle, x, the following equation is obtained:

$$log(\frac{V_g - V_P}{V_g}) + (\frac{V_P}{V_g - V_P}) - 1 = \frac{C_D A_P \rho_g x}{2m_P}$$
(Equation 3.10)

The particle velocity, v_p , under the above spraying conditions, was calculated roughly from equation 3.10 thanks to one-dimensional isentropic theory [18] [24].

$$v_p = V_{gas} \sqrt{\frac{c_D A_p \rho_g x}{m_p}}$$
(Equation 3.11)

Where C_D is the drag coefficient, A_p is the cross-sectional area of the particle, ρ_g is the density of the gas, *x* is the distance covered by the particle inside the nozzle and m_p is the mass of the particle. The variation of C_D for a smooth spherical particle is given by Morsi and Alexander [25]:

$$C_D = a_1 + a_2/Re + a_3/Re^2$$
 (Equation 3.12)

Where a_1 , a_2 and a_3 are constants (appendix A) that apply over different ranges of Reynolds number (*Re*). *Re* is given by:

$$Re = (2\rho_g r_p (V_{gas} - v_p))/\mu_g$$
 (Equation 3.13)

During the spray process, gas flows through the converging-diverging nozzle, and the powder particles are injected after the throat of the nozzle. Figure 3.4 (a) shows the evolution of gas temperature and velocity over the nozzle length at different T_{total} (200°C, 300°C, 400°C, and 500°C). As can be seen from the figure 3.4 (a), the gas flow inside the nozzle can be described as a choked flow. The gas is understood to be accelerating through the nozzle reaching a super-sonic velocity at the throat, while the temperature decreases. It has to be noted that the flow rates calculated are slightly higher than seen in reality as the analysis ignores aspects like gas-flow boundary layers along the nozzle walls where the gas flow would be smaller than the average.

Next, the evolution of the particle velocity for a spherical UHMWPE particle with diameter 50 μ m during the 2-phase flow is calculated from equations 3.9-3.13 as shown in Figure 3.4 (b). The particle velocities calculated were significantly lower than the gas velocities. The strong change in the slope seen in the evolution of particle velocity can be explained by the decreasing drag coefficient and the density of the gas. The particle velocities for all the conditions from the calculations were quite close to each other numerically as the drag coefficients, and density of the gas for each instance was also numerically close to each other.





3.2.2.1.2 Heating Model

The heating model utilized in this study for UHMWPE, assuming the particle is a perfect sphere, takes into account the convective heat-transfer between the carrier gas and particle and conduction within the particle to predict the final particle temperature. Figure 3.5 shows an illustration of the heat transfer dynamics in the particle during the flight.

Convective heat transfer

The heat transfer, in this case, is considered to be a case of forced convection in a two-phase system (gas and particle), which are moving relative to each other. Figure 3.5 shows a schematic of the particle geometry and the heating model. The rate of heat transfer by convection is given below [26]:

$$dQ/dt = hA_s(T_i - T_{gas})$$
(Equation 3.14)

where,

h- heat transfer coefficient A_s -Surface area of the particle T_i -Initial Temperature of particle T_{gas} - Temperature of gas

Heat transfer coefficient, h, Nusselt number, Nu (that accounts for forced convection heat transfer) [27], Reynold's number, Re, and Prandtl number, Pr, [28] are given by the relationships shown below:

$$h = (k_g N u)/(2r_p); N_u = 2 + 0.6 \times Re_p^{0.5} \times Pr^{0.33}; Re = (2\rho_g v_R r_p)/\mu_g; Pr = (c_{p,g} \mu_g)/k_g$$

where,

 k_g - thermal conductivity of gas (air) v_R -Relative velocity between gas and particle μ_g -dynamic viscosity of gas (air) $c_{p,g}$ -specific heat of gas (air)
Substituting h in equation 3.14 gives the following relationship,

$$\frac{dQ}{dt} = r_p \Delta T (C_1 + C_2 (v_R r_P)^{0.5})$$
 (Equation 3.15)

where,

$$C_1 = 4\pi k_g$$

$$C_2 = \frac{2.82\pi (k_g)^{0.67} (\rho_g)^{0.5} (c_{p,g})^{0.33}}{(\mu_g)^{0.17}}$$

 C_1, C_2 are constants for a constant gas temperature. It is interesting to note that when $v_R = 0$, the equation of forced convective heat transfer rate (dQ/dt) essentially becomes an equation of free convection considering the free convective heat transfer to be by simple conduction and mass transfer by simple diffusion (but in reality, density differences within the heat transfer path and apparent fluid velocity causes the free convection rate to behave differently) [19].



Figure 3.5 Illustration of heat transfer dynamics during the flight.

In the present study, heating of the particle is assumed to be symmetrical. But, in reality, due to the high-speed nature of the process, the particles in the flow would be asymmetrically heated more along the surface pushed by the carrier gas. Table 3.3 lists the values of temperature dependent parameters used in this study [28]. A corollary to the Equation 3.15 shown in Equation 3.7 shows that for a particular energy transferred (dQ) in an instant of

time (dt) at a constant relative velocity, a smaller particle will have a higher surface temperature.

$$\Delta T \propto \frac{1}{r_p(c_1 + c_2(v_R r_P)^{0.5})}$$
(Equation 3.16)

Temperature	$ \rho_g \ (kg \ m^{-3}) $	k_g	μ_g	$c_{p,g}$
(°C)		$(10^{-2}W m^{-1} K^{-1})$	$(10^{-5} kg m^{-1} s^{-1})$	$(kJ \ kg^{-1} \ K^{-1})$
200	0.75	3.71	2.49	1.02
300	0.64	4.37	2.84	1.04
400	0.54	4.95	3.18	1.06
500	0.47	5.51	3.48	1.08

Table 3.3 List of temperature dependent parameters used in the study [28].

Conductive heat transfer

The heat transferred into the particle by convection during time dt is used to increase the overall energy of the body in the same duration. Since the particle has a finite size, spatial effects were to be analyzed, and a one-dimensional transient heat conduction solution was used to solve the problem. The particle was assumed already as a sphere with geometric and thermal symmetry about its center point (r=0). Further, radiation heat transfer or radiation effect between the spherical particle and the gas is neglected or incorporated into the convection heat transfer coefficient. The entire particle is at the initial temperature, T_i when it is first exposed to the heated gas at a temperature, $T_{gas} > T_i$. As time progresses, temperatures near the surface rise increase early and cause a temperature gradient to appear in the temperature profile of the particle.

The representative problem to be discussed here in the simplest form is the Laplace equation as shown below;

$$\frac{d^2T}{dr^2} = \frac{1}{\alpha} \frac{\partial T}{\partial t}$$
(Equation 3.17)

where,

 α - thermal diffusivity of UHMWPE particle; $\alpha = \frac{k_p}{\rho_P c_{p,p}}$

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 k_p -thermal conductivity of UHMWPE particle.

 $c_{p,p}$ -specific heat capacity of UHMWPE particle.

And the general solution of the problem takes the form of the dimensional functional equation as follows;

$$T(r,t) - T_{gas} = f[(T_i - T_{gas}), r, r_p, t, \alpha, h, k_p]$$
(Equation 3.18)

For the problem involving the parameters mentioned in equation 3.18 is solved by nondimensionalising the parameters as follows;

Biot's number,
$$Bi = \frac{hr_P}{k_P}$$
; and

Fourier number,
$$\tau = \frac{k_P t}{(r_P^2 \rho_P c_{p,p})}$$
 (Equation 3.19) [29]

Biot's number is a dimensionless quantity to represent the ease of a body to conduct the heat supplied by transferred convective heat from the surrounding. Similarly, Fourier number at time t is the ratio of the rate of heat conducted to the ratio of heat stored at the time t.

For UHMWPE particle of 52 µm diameter during the passage along the nozzle, for a constant gas temperature, the heat transfer coefficient varies with relative velocity between gas and particle. Thus, when the gas temperature is 200°C, *h* value varies from, $5.8 \times 10^3 < h < 9.4 \times 10^3$ Which implies, *Bi* ranges from 0.3 < Bi < 0.6. The analytical solution for a 1D transient heat conduction in a sphere of radius r_P is given by;

$$\frac{T(r,t) - T_{gas}}{T_i - T_{gas}} = A_1 e^{-\lambda_1^2 \tau} \frac{\sin(\lambda_1 r/r_P)}{\lambda_1 r/r_P}, \tau > 0.2$$
 (Equation 3.20) [29]

where,

 T_{gas} -Gas temperature

 T_i -Initial temperature of particle

T(r, t)-Temperature inside the particle at a distance $0 < r \le r_p$

 A_1 , λ_1 -Constants which are functions of Biot's Number. Their values are listed in table 3.4 against the Biot's number for a spherical geometry.

So, at the center of the particle, since $r \to 0$, $\sin(\lambda_1 r/r_p)/(\lambda_1 r/r_p) = 1$

$$\frac{T(r,t) - T_{gas}}{T_i - T_{gas}} = A_1 e^{-\lambda_1^2 \tau}$$
(Equation 3.21)

From the Equations 3.20 and 3.21, the temperature at r=0 and $r=r_p$ can be calculated at the nozzle outlet and subsequently temperature difference, ΔT , between center and surface of the particle can be calculated. Figure 3.6 shows the calculated temperature profile of a 52µm diameter particle, along the particle radius, at t=1.4ms and gas temperature 200°C (473K) for different values of *Bi*. The calculated temperature difference was observed to be low. Further, the gradient is calculated when *Bi* (or *h*) is assumed to be constant throughout the duration of exposure. But in fact, *h*, reduces rapidly as the gas accelerates the particle. Thus, in reality, the temperature gradient will be much less steep than calculated. Hence, it is reasonable to assume a uniform temperature instead of a gradient temperature distribution inside the particle for the sake of simplification further. This generalization can be extended to other gas temperatures as well, as the value of convective heat transfer coefficient, *h*, is not much different (hence the value of *Bi*) for 300°C, 400°C and 500°C gas temperatures.

Bi	Sphere		
	λ_1	A ₁	
0.01	0.1730	1.0030	
0.02	0.2445	1.0060	
0.04	0.3450	1.0120	
0.06	0.4217	1.0179	
0.08	0.4860	1.0239	
0.1	0.5423	1.0298	
0.2	0.7593	1.0592	
0.3	0.9208	1.0880	
0.4	1.0528	1.1164	
0.5	1.1656	1.1441	
0.6	1.2644	1.1713	

 Table 3.4 Coefficients used in the one-term approximation of 1D transient heat conduction in a spherical particle.



Figure 3.6 Calculated temperature profile of a 52 μ m diameter UHMWPE particle, along with the particle radius, at the outlet of the nozzle and gas temperature 200°C (473K) for different values of *Bi*.

Now, by the reasonable assumption that during the heating of UHMWPE particle, increase in the temperature dT occurs uniformly along its volume. The heating rate of a particle is calculated from the energy input by convection.

$$dQ = m_p c_{p,p} dT + \Delta H m_p X_c \qquad (Equation 3.22)$$

Where ΔH is the melting enthalpy of the crystal (290 J g⁻¹), X_c is the crystallinity of the nascent powder deduced from DSC (%), $c_{p,p}$ the average heat capacity (2.22 J g⁻¹ K⁻¹) over [35°C - 135°C] temperature range of UHMWPE with 56% of crystallinity [30]. Hence dT/dt is calculated for each time step dt and the final temperature of UHMWPE particle is obtained before its impact on the target surface.

From the calculations, it can be shown that the heating rates experienced by UHMWPE particles during the flight are of the order of 10^{40} C s⁻¹. Normally, at a slow and steady heating rate, melting peak in nascent reactor UHMWPE is observed at $\approx 141^{\circ}C$ [12][31][32]. This melting point value is higher than a conventional PE ($\approx 137^{\circ}C$) because of its chain conformation out of equilibrium. Below the melting point, the C-C bonds rotate and form folds to create local ordered regions, which forms the crystalline regions. As the temperature is increased, at low heating rates (10 °C min⁻¹), the chains become mobile due to increase in thermal energy and the crystallites begin to melt [33].

According to the literature by Wang et al. [34], an increase in the heating rate shifts the melting peak towards a higher melting temperature. Further, Lippit et al. [12] suggest that in situations where chain reorganization is not feasible, like in this case where nascent disentangled UHMWPE is heated at an extremely high heating rates for a concise time frame, measured melting peak temperature increases with increasing heating rates (see Figure 1.8). The same research work suggests a non-linear relationship between the melting peak temperature and the rate of heating for nascent disentangled UHMWPE. This indicates a tendency of crystallite melting to show super-heating when the heating rate is increased. The superheating is primarily due to the time dependence of the melting process.

Hence, when the heating rates are incredibly high, the "superheating" in this case might be so high that a definite melting transition might not take place. The high heating rates result in an immediate increase in the entropy. In this time frame, it is highly unlikely for the chains to escape the crystallite. Hence, the chains are highly likely to be in an intermediate non-equilibrium state with an insufficient mobility with the possibility for chains in the crystalline lamellae to slide against each other. Figure 3.7 illustrates the possible chain movement at different heating rates. At extremely high heating rates, Figure 3.7 shows the possibility of crystalline lamellae to slide against each other contrary to the low heating rates allowing the possibility to "reel-out" the chains from the crystalline phase.

The recent research works by Toda et al. [35] [36] explains the non-linear dependence of the melting process, on the heating rate of polymers, to be governed by an activation process such as nucleation. The research work discusses a possible mechanism of activation barrier for the melting. Further, the work also addresses the heating rate dependence of the endothermic peak on the melting of PE crystals at different heating rates. However, until further validation, the concept of nucleation for melting remains only a possible explanation for the effect of heating rate on the melting phenomena.



Figure 3.7 Illustration of the melting behavior of UHMWPE chains at a low and a high heating rate.

Previous research, which dealt with the thermal state of cold-sprayed UHMWPE showed DSC measurements performed on rebounded particles to be keeping their native crystalline features and deposited particles melt-crystallizing [8-9]. It can be considered as an evidence of the superheating as a rebound UHMWPE particle, after experiencing a high heating rate before the impact and a high quenching rate after the rebound is shown to be keeping its crystalline state. The deposited particles, in contrast, melts as it gets sufficient time to shift back to an equilibrium state (as the particle, after the impact, would be still at a temperature higher than its melting point).

Hence, it can be reasonably assumed that at heating rates $10^{4\circ}$ C s⁻¹, the melting transition might not be apparent and for further calculations, the term ΔHm_pX_c is neglected. Based on the above assumption, the temperature rise of a 50 µm size UHMWPE particle during the flow is calculated using equations 3.14-3.16. This evolution of the particle temperature at different T_{total} (200°C, 300°C, 400°C, and 500°C) is plotted in figure 3.4(b).

3.2.2.2 Stage 2: Impact process

During the impact process, the available energy in the form of Q_{tot} is utilized to increase the particle temperature and the energy in the form of *KE* utilized in the plastic deformation of the particle. At high strain-rates, the plastic work will lead to an *in-situ* increase in the temperature of the particle. As it is difficult to measure the exact contribution of *KE* to the

temperature increase, the final temperature of the particle after the impact is represented in Table 3.5 as the particle temperature with 0% contribution of *KE* to thermal energy to 100% contribution of *KE*. As can be seen from the table 3.5, the energy contributed by KE (which essentially becomes plastic work) does not translate to a large ΔT even with a 100% translation of the energy in to dissipated heat. This is an extremely important point to be noted because when compared with metals like Zn, Al etc., the specific heat, $c_{p,p}$ of UHMWPE is very large. The $c_{p,p}$ for UHMWPE is $\approx 2.22 \text{ J g}^{-1} \text{ K}^{-1}$ whereas for Al and Zn it is $\approx 0.9 \text{ J g}^{-1} \text{ K}^{-1}$ and $\approx 0.3 \text{ J g}^{-1} \text{ K}^{-1}$. Hence, it is more difficult to raise the temperature of an UHMWPE particle as compared to its metallic counterparts for an equal amount of heat supplied.

Table 3.5 The value of the expected temperature of the particles at different gas temperatures.

T _{gas} (°C)	Particle Temperature (°C)
200	85< <i>T</i> _p <95
300	$125 < T_p < 135$
400	$160 < T_p < 170$
500	200< <i>T</i> _p <210

As can be seen from Table 3.5, the thermal energy, Q_{tot} , carried by the particles is comparatively much higher than the *KE*.

3.2.2.3 Stage 3: Post Impact

After calculating the particle temperature and particle velocity during the impact, the mechanical response of the UHMWPE is analyzed in this section. In this section, the post-impact behavior is the most crucial part to predict from the analysis whether a particle would rebound after the impact.

A deformation, in general, for a polymer, requires an adequate flexibility of the chain segments to ensure plastic flow on the molecular level. It has been well researched upon that mobility of the macromolecular chains is a crucial factor in determining the brittle or ductile behavior of a polymer [37-39]. A decrease in the yield stress of a polymer with an increase of

the temperature is caused by the rise in macromolecular chain mobility. Yield stress can serve as a good measure of macromolecular chain mobility.

In crystalline polymers above their glass transition temperature, the yield stress is determined by the yield stress of crystals, and not by the amorphous phase. The behavior of crystals differs from that of the amorphous phase because the possibilities of motion of macromolecular chains within the crystals are subjected to severe constraints.

Now, when a typical impact of UHMWPE is considered, KE energy is consumed in deforming UHMWPE upon impact, in the form of plastic energy, which is utilized to deform permanently, and elastic energy, which is stored in the chains. The plastic energy is used to irreversibly deform the particle, and most of it is dissipated in the form of heat. On the other hand, the stored elastic energy gets released when the load is removed, and the material has an elastic recovery. But unlike a complete elastic recovery, in the case of metals, polymers have a visco-elastic recovery which is signified by a time-dependent recovery. This recovery is predominantly responsible for contributing to rebound and is exhibited, in the form of rebound energy.

Hence, after impact, the net rebound energy of the particle determines whether the particles should remain stuck to the surface or bounce off. In the previous section, due to the influence of extremely high rates during the heating phase, it was reasonably assumed that it is highly unlikely for UHMWPE to melt. Hence, in this section, the behavior of elastic strain energy of UHMWPE will be investigated with a temperature below the standard melting point.

3.2.2.3.1 Elastic rebound- Experimental understanding

Sample Preparation

Dumbbell-shaped specimens of 10.5 Mg mol⁻¹ UHMWPE samples were cut using a punch from cylindrically shaped specimens from full sintered samples, which were made using the protocol shown in Figure 1.8 [31] and also in chapter 4, section 4.2.2.1 for tensile tests. The thickness (=2 mm) for all the samples were kept same. Full sintered materials were the choice because the bulk samples have the same density and molecular weight as that of a cold-sprayed UHMWPE particle. The results obtained with a full sintered UHMWPE can be used to explain the mechanical behavior of cold-sprayed UHMWPE to a large extent.

Mechanical Characterization

Tensile tests were carried out have been carried out at 25°C, 50°C, 80°C, and 120°C. The primary interest of this mechanical approach is to understand the mechanical behavior of the crystalline phase at temperatures close to melting point. All tensile tests were performed using a tensile machine MTS 1/ME equipped with an oven MTS CE412. The tensile machine was fitted with two kinds of load cells, one having a 5 kN range for tensile tests at RT and the other one having a 100 N range for tensile tests at 50°C, 80°C, and 120°C. For all the tensile, the cross-head speed was 2 mm min⁻¹; thus, the initial strain-rate evaluated was 3.5×10^{-3} s⁻¹. The sample temperature was checked using a thermocouple glued to the head of the tensile specimen. Careful calibrations were done to ensure the temperature gradient over the sample length to not exceed 3 °C. The time necessary for heating the tensile grips and sample was 15 min, the holding period of the sample above T_f being about 5 min. These conditions were reasonably repeatable so that the results from different sintering treatments can be compared. Tensile tests were repeated four times for every sintering conditions.

These tensile tests were aimed at calculating the elastic strain energy of UHMWPE specimen at 50% deformation. Hence, the tensile sample was loaded at a strain-rate of $3.5 \times 10^{-3} \text{ s}^{-1}$ until 50% deformation and unloaded at the same rate. Thus, Figure 3.8 (a) shows the stress-strain graph of 10M UHMWPE at different temperatures. It can be seen that as the temperature is increased, Young's modulus and the yield stress reduces accordingly. Further, to map the variation in elastic strain energy, as shown in the Figure, it is evaluated by calculating the area under the unloading section of the curve.

Hence, elastic strain energy per unit volume is evaluated as below:

$$\frac{elastic strain energy}{unit volume} = \int_{\varepsilon_{50\%}}^{\varepsilon_{recovery}} \sigma d\varepsilon$$
 (Equation 3.23)



Figure 3.8 (a)Stress-strain curve for 10.5 Mg mol⁻¹ UHMWPE at different specimen temperatures. (b) Variation in elastic energy/volume of UHMWPE vs specimen temperature at different strain-rates.

Figure 3.8 (b) shows the variation in the elastic energy per unit volume of UHMWPE with respect to specimen temperature. To understand the evolution at strain-rates close to a realistic value seen in cold-spray $(10^4-10^5 \text{ s}^{-1})$, the stored elastic energy was approximately evaluated for strain-rates 0.01 to 2600 s⁻¹ at 25°C from the literature by Brown et al. [40]. Several types of research suggest an increase in the stored elastic energy due to a rise in its Young's modulus and tensile strength [40] [41] at higher strain-rates. The elastic energy decay of UHMWPE with temperature for two strain-rates 0.003 s⁻¹ (experimental) and 0.1 s⁻¹ [40] was compared, and a linear fit is assumed in these cases based on the work by Brown et al. [40] where a linear fit was considered appropriate. As can be seen from the Figure 3.8 (b), the data points fit well within the error bars for a linear regression.

It is almost impossible to record the elastic strain energy at extremely high strain-rates comparable to that seen in the case of cold-spray (~10⁵ s⁻¹). It is quite known that, in the case of polymers, the increase in temperature causes a same effect on the yield strength as a decrease in the strain-rate [42]. According to the established Eyring plots [43] representing $\sigma_y/_T$ versus $log\dot{\mathcal{E}}$, the relationship that governs the variation in yield stress with temperature and strain-rate is the following;

$$\Delta(\log \dot{\varepsilon}) = \log \dot{\varepsilon}(T_{ref}) - \log \dot{\varepsilon}(T)$$

$$\Delta\binom{\sigma_y}{T} = \frac{\sigma_y}{T_{ref}} (T_{ref}) - \frac{\sigma_y}{T} (T)$$
(Equation 3.24)

Hence, by applying this time-temperature superposition principle to the experimentally collected values and the values used from the reference, the nature of the decay with respect to temperature for higher strain-rates can be evaluated and plotted as shown in Figure 3.8. From the Figure, and from calculations, it can be demonstrated approximately that the yield stress will reach a near-zero value at a temperature ~200°C for strain-rates corresponding to 10^5 s^{-1} .



Figure 3.9 Evaluated temperature at which the $\sigma_y/_T$ value of UHMWPE becomes near zero at strain-rate 10^5 s^{-1} .

Discussion

It can be seen that from the Figure 3.8 (b) elastic energy per unit volume decreases as the temperature increases. This result, in fact, corroborates with the experimental results seen in the case of IPD experiments with UHMWPE (Figure 2.15, section 2.4.2.3, chapter 2) where the deposition volume shows an increase in accordance to the decrease in the elastic energy per unit volume. It can be seen that initial temperature increases showed a steady increase of almost \approx 400% increase in the deposition efficiency until 380°C (T_p \approx 170°C). After 380°C, the increase of \approx 500% of the deposition efficiency at 380°C was observed for depositions where the T_p is evaluated from table 3.5 to be typically around 200°C-210°C.

These results are consistent with the elastic energy decrease with increase in temperature. As can be seen from the Figure 3.8 (b) and Figure 3.9, the value of stored elastic energy becomes almost zero at UHMWPE temperature $\approx 200^{\circ}$ C for strain-rates 10^{5} s⁻¹. Also, from the table 3.5, the particle temperature reaches $\approx 170^{\circ}$ C (depending upon the %KE transferred as heat) at a gas temperature >400°C from which point elastic energy possessed by the particle can be considered negligible. This shows that for a successful deposition of UHMWPE particle, its elastic strain energy must have an "almost" net zero value.

When considering a distribution of differently sized particles being sprayed, the smaller particles firstly reaches a higher temperature as Equation 3.16 suggests an inverse relationship between ΔT and r_p , which essentially means that the elastic energy for smaller particles would be much lower than the larger particles. Similarly, vice versa is applicable for higher sized particles. This effect is seen in the Figure 2.14 where the size distribution always leans towards the smaller size distribution.

3.3 Interfacial Bonding and their evaluation

It has to be understood that a net zero rebound energy doesn't necessarily mean a deposition. It signifies whether a particle would rebound upon impact. Hence, for a deposition in the "real sense," the particle-substrate interface must also possess a certain bond energy. In case of metallic systems, the bond energies are often very high compared to that of polymer-metal systems. Hence, a lower value of bond energy should be compensated with a more substantial wetted surface by the grains on the substrate. It was observed that the wetting of grains was better when there was a high degree of deformation (low L_1/L_2 ratio) upon impact. Figure 3.10 (a), (b) and (c) below shows a FIB section of a UHMWPE interface depicting the wetting of the UHMWPE grains of different L_1/L_2 ratios on Al surface and their interfacial bonding and gaps bonding and gaps. The wettability of the grains is increased due to the increase in the particle temperature and a subsequent decrease of its strength, thereby accelerating the lateral strain of the particle and giving a newly available surface for contact. The sections below discuss the availability of bonds on the surface of a virgin UHMWPE and the surface of a UHMWPE-FNA composite particle.

3.3.1 UHMWPE-metal bonding

UHMWPE-metal bonding is inherently weak because of the primary reason of having a low surface energy [44]. This is as a result of UHMWPE or PE not having any functional groups attached which can potentially form bonds. The low surface energy can lead to further issues like low wettability which, to obtain good adhesion it is necessary, but not necessarily sufficient. The criteria most important for an excellent adhesion is the availability of active groups to potentially bond with other surfaces [45].

In the case of the high-speed impact of UHMWPE on Al surface at room temperature, neither a low elastic strain energy or a presence of any functional groups can be expected. But when the gas temperature/particle temperature increases, small-scale thermal oxidation is inevitable which can introduce groups mainly keto, aldehyde and some acid groups [46]. But again, the extent of such thermal oxidation would be minimal considering the low flight time of UHMWPE particle in the heated gas (\approx 1.4ms). Additionally, the rebound energy decreases and wettability increases. Hence, the deposition of UHMWPE is formed from a delicate balance of a decrease in elastic energy coupled with Vander Waals forces (at intimate interfaces) and a possible increase in the surface energy of UHMWPE due to the functional groups.



Figure 3.10 FIB sections of UHMWPE interfaces depicting the wetting of the UHMWPE grains of (a) 0.49 (b) 0.34 (c) 0.24 L_1/L_2 ratios on Al surface.

3.3.2 Effect of FNA

3.3.2.1 Relevance to Cold-spray

It was interesting to note that FNA on the surface of UHMWPE particles played a critical role in increasing the volume of deposition to a great extent. The reason for such a phenomenon is investigated in this section. From the high-speed camera data, it was clear that impact time of UHMWPE particles was of the order $\sim 10^{-4}$ s. Hence, firstly, effects like recrystallization, induced nucleation by FNA (if any) can be considered highly unlikely as their kinetics are too slow within the time frame of impact. The most likely phenomenon that is possible in this particular time-frame is adhesion via H-bonds. Fumed nano-alumina (FNA in this case) is known to have hydroxyl groups on its surface [47]. Weston et al. estimate 8 hydroxyl groups nm⁻² on the surface of FNA.

Energy stored by hydrogen bonds are estimated to be around 1-5kcal/mole or 4184-20920J/mole [48]. A spherical 52µm in diameter particle with a monolayer of FNA having 8 hydroxyl groups/nm² is considered to be deforming to a hemisphere of the same volume. Hence, contact surface area available for adhesion is $7 \times 10^{-9} m^2$. If we consider 8 hydroxyl groups/nm² on the contact surface, then the total number of hydroxyl groups on its surface can be estimated to be 6×10^{10} . Total energy stored by the hydrogen bonds in the hydroxyl groups is $4 \times 10^{-10} J < E_{H-bond} < 2 \times 10^{-9} J$. Hence, if the rebound energy of the particle is lower than or equal to the energy stored by the hydrogen bonds, the particle will stick to the surface. For UHMWPE particle without the FNA (or H-bonds), the elastic energy/unit volume has to be zero to obtain a successful deposition. But, in the presence of FNA, the deposition window is increased as the H-bonds can overcome the non-zero net rebound energy by a value of $\approx 2 \times 10^4 I m^{-3}$ by "pinning" incoming particles with elastic energy/volume lower than this value. If the 52µm particle upon impact can furnish a surface larger surface area than $7.2 \times 10^{-9} m^2$ as in the calculation above, it will have more H-bonds available for adhesion. Also, if the FNA layer on UHMWPE is multilayered, the contact surface would have more H-bonds for adhesion. In the above two cases, deposition of particles with higher rebound energy/volume can adhere on to substrate as the total energy stored by H-bonds can overcome its rebound energy. Figure 3.11 illustrates the deposition criteria in general and the effect of FNA on the enhancing the deposition efficiency.

While considering the IPD process, this is fundamentally significant because while spraying at high temperatures, the larger sized particles would have a relatively higher elastic energy due to the lower ΔT (as explained before). Hence, they don't deposit when UHMWPE feedstock is sprayed. But on the other hand, the deposition of large-sized particles is observed in the case when UHMWPE-FNA feedstock is sprayed which can be seen in Figure 2.14.



Figure 3.11 Illustration of criteria of particle deposition and the effect of FNA layer.

3.3.2.2 Possible Sites for H-bonds and their interactions

Now, firstly, H-bonds can be assumed as a bridge bond between UHMWPE and oxide layer on Al substrate. Sufficient literature suggests the formation of stable hydroxide layers active to form hydrogen bonds when moisture is adsorbed by the oxide layer [49-51]. Even in the case of dehydrated Al₂O₃, exposed oxygen ions can also potentially form hydrogen bonds [50] [52]. Hence, bond between fumed nano-alumina (FNA) and an oxide layer on Al substrate can be a network of H-bonds by the –OH groups at the hydrated oxide layer and – OH groups at FNA surface or between oxygen ions on the dehydrated oxide layer and –OH groups at FNA surface. The illustration shown in Figure 3.12 depicts potential sites for hydrogen bonding on a vertical section of a hydrated and a dehydrated Al₂O₃ surface.

But the bond between FNA particles and UHMWPE is highly unlikely via H-bonds as UHMWPE is made of predominantly non-polar C-C covalent bonds. Hence, the FNA-UHMWPE should be visualized as more of a mechanical bond, which forms as the particle impacts the substrate. FNA particles can be visualized as piercing into the UHMWPE interface creating a mechanical interlock and at the same time establishing H-bonds with the Al₂O₃ layer on the substrate. The interlocking mechanism can be visualized in the illustration shown in the Figure 3.13.

Hence, the reason for an increased deposition volume depending upon the temperature of particle and FNA on the surface can be attributed to the "pinning" effect of hydrogen bonds.



(a)



Figure 3.12 Illustration showing a vertical section through an ideal Al₂O₃ surface (a) hydrated surface, (b) dehydrated surface [52].



Figure 3.13 Illustration depicting a mechanical interlock by FNA penetrating inside UHMWPE matrix after the impact.

3.4 Conclusions

The present study has attempted to understand the fundamental mechanism of cold-sprayed UHMWPE-FNA particle deposition in detail by modeling the Isolated Particle Deposition Method and identifying the parameters responsible for adhesion of UHMWPE particle and Al surface. The model helped to explain the individual and independent causative effects of these parameters and helped to explain the empirical data from IPD in detail. The following conclusions can be drawn from the study.

- 1. UHMWPE experiences heating rates of the order 10⁴ K s⁻¹, they are assumed to remain at an intermediate non-equilibrium crystalline state before impact.
- Elastic energy/rebound energy of UHMWPE decreases at increasing gas temperature and increases with the strain-rate. At the same time, a temperature-strain-rate equivalence principle is seen which is used to calculate the temperature at which stored elastic energy within the particle can be shown to be near-zero.
- 3. Rebound of UHMWPE particles on Al surface depends upon whether UHMWPE particles after impact can furnish a contact area with an interfacial bond stronger than elastic strain energy of the particle.
- 4. The bonding of UHMWPE depends upon the extent of wetting at the particle-substrate interface. External agents like H-bonds on the FNA surface provide sufficiently strong extra bonds at the contact surface to increase the window of deposition at higher temperatures, which was otherwise very low.
- 5. Significant parameters that influence significantly the UHMWPE deposition efficiency is the particle temperature and velocity, elastic strain energy and the amount of FNA (or density of H-bonds). Increase in particle temperature radically decreases its elastic energy and density of –OH bonds help in withstanding the rebound energy to a certain extent, thereby increasing the window of deposition.

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CHAPTER 4

INTER-PARTICLE SINTERING

Microstructural and

Mechanical Characterization

Contents

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4.1 Introduction

One of the aims of Cold-Spray is to be able to sinter powders, avoiding the traditional tools, such as monitored temperature presses, to process coating over large and not plane surfaces. Thus, the comparison between conventional sintering and Cold-Spray is highly relevant.

This chapter discusses the next critical stage of coating formation, namely, the buildup of the coating. This stage involves formation of the second distinct type of bonding, which is particle-to-particle bonding, which primarily concerns the nature of build-up of the cold-sprayed deposit. Hence, the study is relevant for the cohesive strength and physical properties of the deposited material.

The bonding nature, ability to bond and the extent of binding during the stage of particle-todeposit is still a big question mark.

4.1.1 Coating Buildup- A Perspective

Coating buildup process, in a general sense, is an unconfined ultra-high velocity consolidation process to obtain tight interfaces at high interfacial loads. Hence, the significant hurdles in understanding the way the buildup progresses are:

• Bond strength of first deposit and substrate

Although the gas dynamics during cold-spray is reasonably symmetric, the impact process on an already deposited particle/layer is not. Hence, from a simulation perspective, there are a lot of complications associated with the direction of stress on the spray particle, deposited particle, adjacent deposited particles and the substrate surface. Further, as the process is not confined along the direction parallel to the substrate surface and due to the irregularity in the surface of the already deposited layer, the progression of coating buildup relies on the strength of deposit-substrate bonds. Figure 4.1 (a) illustrates the limiting factor in the first stage of coating buildup.

Inter-particle sinterability (Interface strength)
 Coating buildup progresses once the integrity of a deposited layer with the substrate is ensured. At this juncture, the major issue for the second layer to adhere to the deposited layer is the strength of interface it generates with the depositions. As explained before, this stage is comparable to an ultra-high velocity consolidation process where the strength of the interface depends upon the extent of wetted interface

coupled with a strong local load normal to the interface [1][2][3]. Finally, it is a consequence of thermally active adhesion process to facilitate proximal contacts between particles. Figure 4.1 (b) illustrates the limiting factor in the second stage of coating buildup.

4.1.2 UHMWPE Coating Buildup

4.1.2.1 Understanding the Stages During the Coating

As discussed before, the progression of a buildup is limited by several factors. In the case of UHMWPE buildup, unlike the metallic buildup, is equally affected by the two limiting factors described above. Firstly, as UHMWPE-metal bond strengths are not inherently strong, hence the probability of an incoming particle knocking-off an already deposited particle is extremely high. But, when UHMWPE is sprayed with FNA particles, the bond strength was seen to increase which substantially increased the probability of the next spray particle to deposit on an already deposited particle without knocking it off. An inter-particle sintering scenario was seen, in the form of large deposits (larger than the feedstock particle size distribution) in IPD process when UHMWPE was sprayed with 10% FNA feedstock at 500°C gas temperature. Further, coating buildup was seen for UHMWPE coatings. Previous works on the UHMWPE coatings also reported that buildup of the coating was not observed when UHMWPE feedstock was cold-sprayed with nano-alumina particles without R-OH bonds (in contrast to FNA particles having R-OH on its surface) on its surface. The absence of such groups strongly suggested a decrease of the bond strength between the UHMWPE particles with the substrate [4][5] which impeded the buildup. It was seen that when $\sim 4\%$ by weight of each kind of nano-alumina particles were mixed with UHMWPE feedstock and sprayed at same spray parameters, the feedstock with FNA showed deposition thickness of almost 4mm in contrast to other which showed a coating thickness of around 100µm. Figure 4.2 shows the values of coating thickness for each nano-alumina particle used.



Figure 4.1 An illustration showing the (a) first stage and the (b) second stage of coating buildup process during cold-spray coating.



Figure 4.2 Coating thickness values reported by the previous study by our group when UHMWPE was cold-sprayed with two different kinds of nano-alumina particles [4].

Another interesting result to note was that UHMWPE sprayed with 0-10% FNA showed coating build up only when the concentration was \sim 4%. This was in contrast to what was observed in the IPD process, where the deposition efficiency increases with the increase in the FNA concentration. Growth in the deposition efficiency from 0-4% FNA was expected as the FNA content increased, the average density of –OH bonds also increased which means that with the successive increase in FNA, a successively stronger anchorage is possible by the particles deposited first. But a decrease in the ability for a coating buildup was not understood even with the successively stronger anchorage contributed by the particles depositing first by increasing FNA. Hence, the buildup, in this case, is limited by a factor that affects the inter-particle sinterability as discussed in the previous section.

4.1.2.2 Load Distribution and Wetting

To understand the UHMWPE sinterability and its mechanism during coating buildup, it is essential to first understand the load distribution during the coating formation. Several kinds of literature on cold-spray indicate a presence of a gradient porosity distribution along the section of the cold-sprayed coating [6] [7] [8] [9]. This gradient is also observed in UHMWPE coatings.



Figure 4.3 SEM images showing the porosities distributed within the cross-section of coldsprayed UHMWPE +4% FNA deposit, from the coating substrate to its free surface.

Figure 4.3 shows the porosities distributed within the cross-section of UHMWPE +4% FNA deposit. The image shows a dense microstructure at the region near the substrate and the presence of porosity as when traversed to the top portion of the cross-section. It is very clear from the literature that, the reason for such a formation is due to an apparent shot peening of deposited layer by the next layer. Hence, there is a gradient of shot peening intensity along the cross-section. Essentially the layer below experiences a higher interface load relative to the layer above leading to good wetted interfaces (less porosity) near the substrate and interfaces wetted partially as you go up the distance from the substrate. It is important to be noted that this section discusses only the wetting efficiency due to the interfacial load and not the strength of the welded joint. Figure 4.4 shows the magnified SEM images of the periphery of coating (i.e., close to the free surface) where there is no apparent interfacial load on the particle, and the particles are wetted and welded at point contacts and of the bulk of the coating where partial welding of the particles can be seen.



Figure 4.4 SEM image of the periphery of a coating showing welding at point contacts (left) and partially welded connections in the bulk of the coating.

It is also important to be noted that, the load distribution will also vary along each particle boundary depending upon the extent of wetting of particles by each other. There are points along interfaces at different proximities to each other and high and low localized loads.

Figure 4.5 shows the welding possibility only along close conformal contacts along the interface.



Figure 4.5 An illustration showing the welding possibility of UHMWPE grain along interfaces at close contacts and local loads.

4.1.3 Inter-particle Sintering in UHMWPE and the relevance to Cold-spray

In the case of semi-crystalline polymers in general, sintering occurs due to two distinct phenomena (also see section 1.1.5.1 and 1.1.5.2):

- i. Diffusion of chains across the interfaces of adjacent grains to facilitate chain entanglements. [10] [2].
- ii. Cocrystallization, where the chains of adjacent grains re-crystallize along the interface, strengthening the interface [11] [12].

Inter-particle sintering in the case of polymers has to be discussed in detail in relevance to cold-spray because strong inter-particle adhesion of same polymers occurs via diffusion of chains (large scale molecular motions), unlike metals. In metals, the strong adhesions are seen with the generation of atomistic contacts [13] within the timescale of cold-spray impacts $(10^{-5}-10^{-6}s)$. But the kinetics of polymer sintering is very slow in comparison to interparticle sintering in metals.



Figure 4.6 Schematic showing the chain diffusion by "melting explosion".

When it comes to nascent UHMWPE, used in this study, studies have shown uniqueness in its ability to sinter when compared with other semi-crystalline polymers. Figure 4.6 illustrates the chain diffusion of nascent UHMWPE at the interface.
- i. Firstly, nascent UHMWPE exhibits a phenomenon called "melting explosion" when the material is brought above its melting point. This event is characterized by a fast migration of chain loops and chain ends through the interface. This helps in a fast intertwining of chains from neighboring grains [14] [15].
- Secondly, when such high entanglement density and intertwined chains from the neighboring chains in the interface zone co-crystallize, they lead to a strong interface. Thanks to the high entanglement density, the inter-diffusion depth requirements for a strong interface is much less for nascent UHMWPE.

Literature like that of Jauffres et al. provided significant information on the ability of nascent UHMWPE to consolidate below its melting point by high-velocity compaction [16] [17]. Although majority fraction of the grain remains below the melting point, sintering at the interfaces is still facilitated by local interfacial melting from the impact energy supplied by the compacting punch.

From the knowledge regarding the nascent UHMWPE from previous works, it is clear that for UHMWPE to have a mechanically strong interface; (i) temperature of the interfacial area should be above the melting point; (ii) the interface should be under a load to facilitate the proximity of the two sintering faces.

To understand the sintering mechanism and the effects of FNA particles relevant to coldspray, it is imperative first to recognize the thermal and physical condition of UHMWPE before impacting a deposited particle and lead to a subsequent welding. In a cold-spray deposition, firstly, UHMWPE particles are at a temperature much higher than the melting point during the impact in an apparently non-equilibrium crystalline state due to the high heating rates experienced by the particle (see chapter 3, IPD Model). But, once it impacts, it no longer experiences the high heating rates and is at a temperature higher than its melting point. Hence, now, the particle can be assumed to have sufficient time to come to an equilibrium melt state as its temperature is still above its melting point.

Now, in fact, the coated deposit is a consolidate with an interfacial load distribution varying along the cross-section of the coating and the interfaces as shown in Figures 4.3 and 4.4. Based on the coating structure, experiments were designed to have UHMWPE grains have their interfaces welded/sintered under different interfacial loads. Hence, it is possible to find fully welded, partially welded and interfaces welded at point contact in the cold-sprayed coating.

Further, the effect of FNA particles on the mechanical properties of the sintered product was also analyzed (it was otherwise impossible to characterize its effect for >4% and <4% FNA

as the cold-sprayed deposits with the feedstock didn't allow buildup in the coating). Although it was understood from the cold-sprayed deposits that interfacial loads affected the weldability, this effect was not quantified.

Hence, the samples were prepared by compression sintering under different interfacial loads. They are as follows:

- i. Full sintering: Welded interface with a high interfacial load.
- ii. Half sintering: Welded interface with a low interfacial load.
- iii. Free sintering: Welded interface with no interfacial loads.

The nomenclature for the naming different sintered samples were done according to its relative densities. The interfacial loading was adjusted empirically to obtain samples with different relative densities. The full sintered samples had a relative density of 100% with interfaces welded completely. Secondly, as the free sintered samples were prepared without any interfacial loading, they were expected to have a relative density of ~50% (free stacking of spheres). Lastly, half sintered samples were prepared under the sintering conditions to obtain an intermediate relative density (~75%) between full sintering and free sintering.

4.2 Experimental

4.2.1 Materials Used

The powder material used for the sintering protocol is UHMWPE of molecular weight 10.5 Mg mol⁻¹. The feedstock had an average grain size of 150 μ m, and the size distribution ranged from 50-500 μ m, as measured by laser scattering technique. Other characteristics of the powder are described in section 2.2.1.

The fumed nano-alumina particles used in this chapter, and the UHMWPE-FNA mixture feedstock preparation technique are also already described in section 2.2.2 and section 2.3.1 respectively. The prepared feedstocks were mixtures of UHMWPE and FNA mixed at different percentages ranging from 0-10% by weight.

4.2.2 Sintering Protocols

The compression load was provided by an Instron compressive testing machine, and the sample temperature was achieved using a Servatin Oven.

4.2.2.1 Full Sintering- Welded interface with a high interfacial load

Fabricating a fully sintered sample with strong welded interfaces and minimal porosities were performed by compressing the powder at a temperature higher than its T_m . This protocol was proved to be very effective in achieving the desired properties from the results of experiments performed by Deplancke et al. [14] [15].

The protocol consisted of 3 distinct stages and was carried out separately:

- Powder densification: Powder was applied a compressive stress of 80MPa and vacuum of ~10mbar after heating it up to a temperature of $80^{\circ}C$ ($T_{\text{processing}} < T_{\text{m}}$).
- Diffusion of chains: This particular stage was carried out at a temperature higher than the melting point of UHMWPE T_{processing}=200°C (T_{processing}>T_m) at a compressive stress of 5MPa for 1hr where the diffusion of chains through the grain interfaces was facilitated.
- Crystallization: This stage was performed under a compressive pressure of 20MPa, during cooling, to prevent shrinkage due to crystallization. The jig containing the sample was cooled in air.

The detailed illustration of the process is already described in Figure 1.9.

4.2.2.2 Half Sintering- Welded interface with a low interfacial load

Fabrication of a half-sintered sample of UHMWPE with partially welded particle interfaces was performed by compressing/consolidating the powder at a load (empirically optimized) at a temperature $T_{processing}>T_m$. Figure 4.7 illustrates the fabrication protocol for preparing samples of Half Sintered UHMWPE. The protocol, in this case, consists stages as described below:

- Partial Wetting: As the first objective of this sintering protocol is to provide partial wetting of the particles, a compressive stress of 0.05MPa was used at the beginning of the heating cycle for 20min.
- Chain Diffusion: The partially wetted grains were allowed to have chain diffusion along the wetted areas when sample temperature reaches T_{processing}=200°C (T_{processing}>T_m) for 1hr.
- Crystallization: This stage was performed under no apparent compressive stress. The sample was cooled in air.



Figure 4.7 An illustration describing the half sintering protocol.

4.2.2.3 Free Sintering- Welded interface with a no interfacial load

The sample fabrication of a free sintered UHMWPE was performed to analyze the fabricated material properties with particle welding taking place at point contacts. As the particles used in this study are reasonably spherical, the wetting of the grains with each other was only expected along point contacts. Such point contacts between particles were ensured throughout the sintering protocol by heating the powder with no compressive stress. This essentially leads to the wetting of particles only along the contact determined by the stacking

efficiency. The sample was allowed to crystallize at the same cooling rate as used in both full sintering and half sintering protocols. Figure 4.8 illustrates the process used in the protocol.



Figure 4.8 An illustration describing the half sintering protocol.

4.2.3 X-ray Tomography

4.2.3.1 Experiments

The X-ray tomography was used to characterize the relative density of the material, map the porosity distribution in the fully sintered, half sintered and the fully sintered UHMWPE samples and the result obtained is in the form of 3D images of the internal microstructure. The instrument was a standard tomograph made by Phoenix X-ray. Figure 4.9 shows the main components of the setup.

The X-ray source can be operated at accelerating voltages from 40 to 160kV. The transmission target hit by focused electrons is made of tungsten or molybdenum. The detector

is a Paxscan \mathbb{R} amorphous silicon flat panel. The voxel size used for the entirety of the analysis was 2.5 μ m.

A typical scan time at an accelerating voltage of 90 kV and a current of 200 μ A with 900 angular positions is of the order of 30 min. The reconstruction time (weighted filtered back projection, Feldkamp algorithm) on a Desktop computer with a bi Intel Xeon quad-core processor, 3 GHz CPU, 64 GBytes RAM, takes approximately 30 min for a 1,000 × 1,000 × 1,000 voxels 3D image. Scanning parameters specific to the samples tested are shown in table 4.1.



Figure 4.9 The lead protected casing of a standard tomograph showing the detector, rotating stage and the X-ray source [18].

Series of scans/slices were taken for the samples corresponding to the same number of angular positions of the sample and is recorded with a CCD detector. A reconstruction software is used, as described above, to obtain a 3D image with an elementary voxel size of 2.5 μ m. The FNA particles were easily detected and distinguishable within the matrix due to the difference in the radio-attenuation between UHMWPE and the nano-particles.

4.2.3.2 Data and Image processing

The image processing software used to analyze the internal structure of the sintered products, in this study, was done using public domain software called Fiji [19]. Phase contrast method

was used to characterize the images of different sintered products. Images generated by performing phase contrast method give a good representation of porous materials as it helps to define the boundary between UHMWPE particle and the voids. The image slices were 3D constructed, and the relative density of the sample was calculated by analyzing the fraction of porosity in each 2D slices.

Table 4.1 Scanning parameter for the tomograph available in MATEIS used in this study.

Filament	Tungsten
Tension (keV)	50
Intensity (μA)	110
Detector	CCD
Number of Images taken	1120
Voxel Size (µm)	2.5
Scan time (min)	45

4.2.4 Mechanical Characterization

Tensile tests of the sintered samples were carried out to understand the strength of the interfaces. A dual mechanical approach was used; (i) tensile testing at RT and (ii) tensile testing in the rubbery state at 150°C. This characterization technique was adopted from Xue et al. [12] and Deplancke et al. [14] [15] to differentiate the contribution of chain re-entanglement and co-crystallization.

The tensile tests were performed using MTS 1/ME equipped with an oven MTS CE412. The machine was equipped with interchangeable load cells, one having a 100N range and the other with a 5kN range. The tensile tests at 150°C and the for the brittle samples were performed using a 100N load cell, and for all the other samples, a 5kN cell was used.

The cross-head speed for all the tensile tests was 6 mm min⁻¹; hence, the initial strain-rate was calculated to be 10^{-2} s⁻¹. To ensure the uniform temperature of the sample inside the oven, thermocouples were fixed at two shoulders and the gauge region of the specimen and monitored. The temperature gradient over the length of the specimen was not seen to be over 3°C. The tensile grips and the sample heated up to the desired temperature in ~15mins. The

tensile tests under these conditions were repeatable and were repeated 4 times to ensure the same.

4.3 Results and Discussion

4.3.1 X-ray tomography- 2D and 3D Observations

X-ray tomography observations were performed on full sintered, half sintered and free sintered UHMWPE samples with 0%, 4%, and 10%.

4.3.1.1 Full Sintered

X-ray tomography for full sintered is shown in Figures 4.10 (a) and (b) which shows the slices for a full sintered UHMWPE and full sintered UHMWPE + 4% FNA. As intended from the sintering experiment, the interfaces of UHMWPE can be seen fully welded together, and the sample appears as a bulk sample as shown in the tomograph (Figure 4.10 (a)). Addition of FNA can be seen distinctly at the UHMWPE particle interfaces due to the difference in the radio-attenuation of UHMWPE and FNA particles as can be seen in Figure 4.10 (b). The samples with FNA addition showed no change in the density of the sample.

4.3.1.2 Half Sintered

The tomographs of the half-sintered samples show UHMWPE grains partially wetted and welded along the interfaces deformed plastically as shown in Figure 4.11 (a). Also, represented in Figure 4.11 (b) is the 3D porosity network within the sample reconstructed from the tomograph slices.

Figures 4.11 and 4.12 show the half-sintered UHMWPE + 4% FNA and UHMWPE + 10% FNA respectively along with their 3D porosity network reconstruction. Qualitative evidence shows some surfaces being restricted by FNA to successfully wet each other; thus, restrict in welding. Several contacts seem to look incomplete when compared with the contacts seen in the case of half-sintered samples without FNA.

4.3.1.3 Free Sintered

The tomographs of free-sintered UHMWPE is shown in Figure 4.14 (a) where the particles are indicated with having welded along point contacts. As this was intended and expected to be the case since the particles were reasonably spherical and the wetting occurs only along the point contacts. Further, the addition of FNA yielded free sintered samples as shown in Figures 4.15 and 4.16. Also, qualitative observations showed that the point contacts were significantly lowered with the addition of FNA particles.





Figure 4.10 (a) Slices of full sintered UHMWPE (b) Slices of full sintered UHMWPE + 4% FNA.



Figure 4.11 (a) Slices of half sintered UHMWPE and (b) 3D reconstruction of the porosity network inside the sample.



Figure 4.12 (a) Slices of half sintered UHMWPE + 4% FNA and (b) 3D reconstruction of the porosity network inside the sample



Figure 4.13 (a) Slices of half sintered UHMWPE + 10% FNA and (b) 3D reconstruction of the porosity network inside the sample.







Figure 4.14 (a) Slices of free sintered UHMWPE and (b) 3D reconstruction of the porosity network inside the sample.







Figure 4.15 (a) Slices of free sintered UHMWPE + 4% FNA and (b) 3D reconstruction of the porosity network inside the sample.







Figure 4.16 (a) Slices of free sintered UHMWPE + 10% FNA and (b) 3D reconstruction of the porosity network inside the sample.

4.3.2 X-ray tomography- Relative Density

Density of the sintered product, ρ_s can be calculated from the 3D reconstructed volumes. By considering a 3D volume, volume fraction of UHMWPE, v_f , in the overall volume, v_{total} was calculated from the tomography slices. Then, the total mass, m_f , of the volume fraction is calculated from the volume fraction multiplied by bulk density of UHMWPE, ρ_{bulk} . Hence, density is obtained by dividing the mass fraction of UHMWPE with the overall 3D volume considered. Further, relative density, ρ_r is calculated as the ration between the calculated density of the volume and the density of a bulk UHMWPE.

$$m_f = v_f \times \rho_{bulk} \tag{Equation 4.1}$$

$$\rho_s = \frac{m_f}{v_{total}} \tag{Equation 4.2}$$

$$\rho_r = \frac{\rho_s}{\rho_{bulk}}$$
(Equation 4.3)

Figure 4.17 shows the relative densities measured for full sintered, half sintered and free sintered UHMWPE with 0%, 4% and 10% FNA. As can be seen from the Figure, the relative densities of full sintered UHMWPE are equal to 1 which was quite expected as the sintering technique employed has ensured complete welding of the interfaces. Further, the addition of FNA particles also didn't alter the relative density of the material; hence, allowing a total healing of interfaces in the case of 4% and 10% FNA. It has to be noted that, the relative density calculation for UHMWPE-FNA composites accounts for the inclusion of density of FNA, ρ_{FNA} , in the calculation of both ρ_s and ρ_{bulk} . This suggests that when under high interfacial loads, a complete welding of the interface can be expected.



Figure 4.17 Relative densities for full sintered, half sintered and free sintered UHMWPE with 0%, 4% and 10% FNA.

In the case of half-sintered samples, an increase in the porosity, and hence a decrease in the relative density to 0.78 was expected, as the particles were not allowed to wet entirely during the process. But, it was interesting to note that when the FNA content was increased, the relative density decreased which suggests the importance of interfacial load during the sintering process. Considering this evidence, it seemed as if FNA particles on the interface acted as a defect which hindered an effective sintering between two UHMWPE particles at low interfacial loads and on the other hand a high interfacial load ensured to overcome the hindrance by FNA particles.

Finally, in the case of the free sintered sample, due to the complete lack of a compressive load during sintered and as the wetting occurred only along point contacts, the relative density of the product was more or less similar to the relative density of freely stacked UHMWPE powder. As seen in the case of evolution of relative densities half sintered samples with FNA particle, ρ_r for free sintered samples also showed a decreasing trend. Also, an interesting observation was the increase in its slope relative to that seen for the evolution of half sintered samples.

The error bars in the measurement is representative of the dispersion seen while calculating the relative densities of different volumes considered and the final value represented in the graph is the average of values from all the volumes considered.

4.3.3 X-ray tomography- Porosity distribution

Pore space the inside the sintered products were characterized to understand the porosity distribution of the same. Figures 4.18 and 4.19 represent the porosity distribution in a 1mmX1mmX0.5mm volume of half sintered and free sintered UHMWPE with 0%, 4% and 10% FNA samples respectively. Also, represented in each of the images is the mean pore size of the distribution. The mean pore size of the statistical distribution is calculated using the simple equation;

$$Mean = \frac{\Sigma(f \times y)}{\Sigma f}$$
(Equation 4.4)

where,

f: Frequency

y: Class mid-point

Half sintered volume of UHMWPE with 0%, 4%, and 10% show a very similar distribution with mean pore size slightly increasing. The distributions run from $\sim 2 \mu m$ to $\sim 30 \mu m$ and peaking at $\sim 7 \mu m$. On the other hand, the porosity distribution for free-sintered volume showed a presence of large-sized pores relative to that seen in half sintered. Also, worth noting was that there were significant variations in the form of large-sized pores at higher FNA content in the distribution. As it was understood from the previous section that FNA particles are detrimental to the progress of interface welding under low interfacial loads, the presence of such large-sized pores can be justified using the same argument.

The mean pore size for each percentage is plotted in Figure 4.20. The error bars in the plot represents the dispersion of the data as the mean pore size was calculated from several different randomly chosen 1mm×1mm×0.5mm volumes.

It has to be noted that the information from these graphs provides significant understanding of stacking inside a cold-sprayed-deposit.



Figure 4.18 Porosity Size distribution of a half-sintered sample.



Size of porosity (µm)

Figure 4.19 Porosity Size distribution of a free-sintered sample.



Figure 4.20 Mean Porosity Size evolution for a half-sintered and a free-sintered sample with the % FNA content.

4.3.4 Mechanical Characterization

The influence of the FNA particles on the mechanical properties of the composite material was investigated below and above the melting temperature, which is around 135-136°C (table 2.1, chapter 2). The characterization was performed for full sintered, and half sintered UHMWPE volumes with 0-10% FNA content. Free sintered samples were too brittle to be performed tensile tests.

4.3.4.1 Full Sintered

4.3.4.1.1 Tensile Tests below the melting temperature

The initial structure of the semi-crystalline UHMWPE can be visualized as shown in Figure 1.4 (chapter 1, Bibliography). Firstly, the initial behavior while stretching the polymer is mostly visco-elastic due to the straining of the amorphous domains between the crystalline lamellae [20]. At yield, "strain softening" is absent in the case of UHMWPE due to the high crystallinity as well as the inability of chains in amorphous phase to orient themselves. Prevalent theories of onset of plastic deformation are described by the chain slip mechanism in the crystalline where the crystalline lamellae experience intra-crystalline shear resulting in its subsequent fragmentation [21]. This is followed by these fragmented phases forming a

part of fibril network aligned along the direction of stretching, and further deformation leads to stretching of this aligned fibril network until its macro-failure.

Figure 4.21 shows the stress-strain curves at room temperature were procured for full sintered UHMWPE at different FNA content. Firstly, considering the elastic domain, it can be seen that modulus of elasticity positively evolves as shown in Figure 4.22 (a) with the increase in the FNA.



Figure 4.21 Stress-strain curve at room temperature for full-sintered UHMWPE with different FNA content.



Figure 4.22 Variation of (a) Elastic Modulus and (b) Yield stress with FNA content for tensile tests at RT for full sintered samples.

The increase in the elastic modulus during the first phase of FNA addition (0%-1%) was seen to be almost 38% per percentage increase in FNA whereas 4%-10% showed an increase of around 1.5%. It is highly likely that FNA by themselves would not be able to sharply alter the modulus of UHMWPE as they are spherical sized nano-particles they are not dispersed well

into the volume of polymers. However, if the fillers are wetted enough by the entanglement network near the grain interface, the interaction can lead to a formation of an interfacial zones of polymer-nano composite with high FNA content with good coupling with the core grains. This formation of such zones can have a large-scale effect due to the large interfacial area between nano-particles and polymer [22] [23] [24]. Also, due to high FNA content, the interfacial layer is expected to have a modulus higher than the core UHMWPE (without FNA).

When increasing the FNA content, the initial increase in the global modulus and yield stress indicates mechanical percolation of the interfacial zone (shell) so that the mechanical coupling between the core and the shell come close to a parallel coupling, inducing a measurable effect on the macroscopic modulus.

Figure 4.22 indicates the formation of such percolated interfacial zones at low contents of FNA in which case the mechanical coupling between the interfacial zones and the core is close to parallel. On the other hand, a further increase in the FNA content saturates the effect of percolation leading to a saturation of the modulus evolution. The schematic shown in figure 4.23 illustrates the formation of the interfacial zones with high FNA content induced by the wetting of nano particles by UHMWPE at the interface. Also shown is the increase in such interfacial zones to form a percolating network as the FNA content is increased.





UHMWPE cross-section with no FNA Boundaries with FNA

Interfacial zones consisting of wetted FNA by UHMWPE chains at the interface

Figure 4.23 Schematic of the evolution of the interfacial zones created by the wetting of FNA particles by the UHMWPE chains at the grain interfaces. The interfacial zones are illustrated to be starting to percolate at 4% FNA and saturate at 10% FNA.

At the moment, a detailed analysis of the fracture stress is futile, as the fracture stress for UHMWPE exhibits very high dispersion. Although, it is possible to draw viable statistical conclusions out of the same when number of data is high.

4.3.4.1.2 Tensile Tests above the melting temperature

Above the melting temperature, UHMWPE is typically an isotropic amorphous material with random chain orientations. Initial behavior is represented by a non-linear elastic response as can be seen from the tensile curves, the slope of the curve decreases with the increase in the strain. After it reaches a typical yield point, represented by an onset of plastic deformation, a phenomenon known as "strain softening" is exhibited where local structural changes in the chain orientation help it to rotate easier and thus stress value drops. This phase is succeeded by a strain-hardening phase where the chains get aligned in the direction of stress applied and gradually extension limit is reached after which the stress value increases.

It has to be understood that UHMWPE during the tensile test is at an equilibrium state. Chain relaxation due to disentanglement and chain extension is the two-competing phenomenon working against each other during tensile testing above the melting point [26]. Additionally, disentanglements occur according to the rapidity of the reptation phenomenon for 10.5 Mg mol⁻¹ UHMWPE. But, for UHMWPE in equilibrium, the reptation time can be as high as 45hrs [15], and the duration of tensile tests were barely 10-30mins (depending upon the elongation at failure).



Figure 4.24 Stress-strain curve at 150°C for full-sintered UHMWPE with different FNA content.



Figure 4.25 Variation of (a) Elastic Modulus and (b) Yield stress with FNA content for tensile tests above the melting point for full sintered samples.

The experiments above the melting point facilitate to look into the entanglement networks between UHMWPE polymer chains and between the chains and the FNA particles. Figure 4.24 shows the stress-strain curves of the tensile tests performed at 150°C for full sintered UHMWPE with 0%-10% content of FNA particles. From 0-10% of FNA, the curves show a

successive increase in the corresponding elastic modulus and the yield stress as shown in Figures 4.25 (a) and (b) respectively. Further, they can act as efficient cross-linking nodes which can explain the strain hardening aspect. Although reinforcement of strain hardening from 0-4% is quite negligible, 10% shows a significant increase in the strain hardening behavior and elongation at break. Detailed analysis of the mechanism of deformation of the material is discussed in the next section.

4.3.4.1.3 Morphological Characterization- Tensile Tests above melting point

Morphological observations were done on the samples undergone tensile testing above its melting point to understand the role of FNA particles within the entanglement network and its mechanism in reinforcing. Since only chain stretching is believed to be the prominent phenomenon active during the tensile testing above the melting point, the reinforcement due to FNA in increasing the yield stress is prominently in causing the nano-particles to share the load with the UHMWPE fibers during the stretching. Hence, to understand the same, the tensile specimens were stretched until (i) beginning of yield, (ii) intermediate stage, and (iii) before fracture and allowed to immediately crystallize at that position without unloading. This effectively preserves the morphological features of specimen fibrillary network at each of these loading positions. The positions are as shown in Figure 4.26.



Figure 4.26 The tensile test curve of UHMWPE performed above the melting temperature showing the loading positions at which the morphology was preserved.

UHMWPE Full Sinter



Figure 4.27 SEM images showing the preserved morphological features at (i) beginning of yield, (ii) intermediate stage, and (iii) before fracture of full sintered UHMWPE tensile tested above its melting point.



Figure 4.28 SEM images showing the preserved morphological features at (i) beginning of yield, (ii) intermediate stage, and (iii) before fracture of full sintered UHMWPE+4% FNA tensile tested above its melting point.

UHMWPE+10%FNA Full Sinter



Figure 4.29 SEM images showing the preserved morphological features at (i) beginning of yield, (ii) intermediate stage, and (iii) before fracture of full sintered UHMWPE+10% FNA tensile tested above its melting point.

Figures 4.27-4.29 show the SEM images of the stretched specimen at these locations. The fibril network between the particles/grain of UHMWPE is visible in the SEM images shown

in Figure 4.27. At the beginning of yield, the grains start separating out from each other, showing the apparent network of chains diffused into each other grains during sintering. As the stretching continues, the chain stretching leads to thinning of the fibril network, which can be seen at the intermediate stage and the stage before fracture.

The SEM images for tensile specimens at different loadings of full sintered UHMWPE+4% FNA material shows the presence of FNA particles within the re-entangled network. It was interesting to note that, FNA particles were wholly wetted by the entanglement network. Figure 4.30 shows a magnified image of an FNA particle within a set of individual fibers.

The reinforcement of the fibril network by the FNA particles is seen during the intermediate loading position and before fracture where the FNA particles seem to bind fibrils together, forming a thicker fibril network. The same effect, but much more pronounced, is seen with 10% FNA content as shown in Figure 4.29. In the case of FNA particles acting as cross-linking nodes can explain the reinforced strain hardening in case of 10% FNA content. Hence, as described before, the increase in the mechanical properties of the full sintered volume due to FNA inclusion can be attributed to the adequate wetting of the nano-particles by UHMWPE chains and the reinforcement of these chains by sharing their load.



Figure 4.30 Magnified SEM image of UHMWPE fibrils reinforced by FNA particle during stretching.

4.3.4.2 Half Sinter

4.3.4.2.1 Tensile Testing below melting point

Figure 4.31 shows the tensile test curves at room temperature of half-sintered UHMWPE with 0-10% FNA content. First look at the elastic part of the half-sintered UHMWPE show that the elastic modulus is significantly lower than its full sintered counterpart. This is primarily because since half sintered samples were fabricated under a very low compression load relative to full sintered samples, the total surface area under contact was significantly smaller than its full sintered counterpart.



Figure 4.31 Stress-strain curve at room temperature for half-sintered UHMWPE with different FNA content.


Figure 4.32 Variation of (a) Elastic Modulus and (b) Yield stress with FNA content for tensile tests at RT for half sintered samples.

The decrease in the mechanical properties can be attributed to the reduction in the relative density and increase in the porosity of the half-sintered material which can be verified using Kerner equation [27]. The Kerner equation is one of the most versatile and elaborate equations for a composite material consisting of soft spherical particles in a rigid matrix.

However, in this case, the porosities are assumed to very soft inclusions with a negligible value of its elastic modulus and when the modulus of elasticity of the inclusion, E_I , is much less than that of the rigid matrix, E_M , the ratio of Young's modulus of the porous solid, E_{porous} , to that of the bulk, E_{bulk} , can be directly predicted from the volume fraction of the porosity, V_I as shown in equation 3. The relationship is given below as following;

$$\frac{E_{porous}}{E_{bulk}} \approx \frac{1 - V_I}{1 + V_I}, \qquad \qquad \text{For } E_I \ll E_M \text{ (Equation 4.5)}$$

According to this model and considering the modulus value of bulk UHMWPE to be 137 MPa, the value of modulus can be calculated to be \approx 90 MPa. The experimental result, which is \approx 92 MPa is in good agreement with the Kerner model show that the continuity between contacts for a half-sintered volume is similar to that of a full-sintered one.

Next, the tensile curves for UHMWPE half-sintered with FNA show a decreasing trend with respect to the modulus and the yield stress value. Figure 4.32 and 4.34 shows the pattern set by elastic modulus and yield stress with the increase in the FNA content. This trend also is in contrast to the reinforcing effect seen in the case of full-sintering. Also, the elongation at break decreases with the increase in the FNA content.

Hence, both the tensile tests of half-sintered samples at room temperature and above melting point show that increase in the FNA content weakens the UHMWPE interface by acting as defects.

4.3.4.2.2 Tensile Testing above melting point

Similar to the previous protocols, tensile testing of half-sintered samples was performed above its melting point as represented in Figure 4.33. The decreasing trend of modulus and yield stress which is also seen here is apparently representative of the decreasing entanglement density between UHMWPE grains in the presence of FNA particles. The half-sintered UHMWPE without any FNA content represents the interface with highest entanglement density, and the one with 10% FNA represents the lowest. As seen in the tensile test below the melting point, here too, the elongation at break decreases with increase in FNA content which characteristic of a defect.



Figure 4.33 Stress-strain curve at 150°C for half-sintered UHMWPE with different FNA content.





Figure 4.34 Variation of (a) Elastic Modulus and (b) Yield stress with FNA content for tensile tests above the melting point for half sintered samples.

4.4 Summary

4.4.1 Sintering Mechanism- Effect of interfacial load and FNA

Considering the above results and discussion regarding the morphological and mechanical characterization performed on full sintered, half sintered and free sintered samples, it was quite clear that sintering is heavily influenced by the interfacial load and interfacial FNA particles.

Firstly, while looking into the sintering of any two interfaces of nascent UHMWPE particles, it was under understood that when the interface reaches melting point, primarily driven by the "melting-explosion" phenomenon, the chain diffusion and re-entanglement occurs through the interface. The consequential re-entanglement density per unit area of a virgin UHMWPE surface was seen to be not depending much on the interfacial load being applied, which was seen from the fact that modulus value of the half-sintered material obtained experimentally and using Kerner model was in good agreement with each other.

On the other hand, the results obtained with FNA content at high and low compressive loads contradicted each other. It showed that a sufficiently high interfacial load is necessary to embed FNA particles into the polymer matrix to promote wetting and continuity of polymer around FNA. Due to the consequential wetting of FNA particles by the UHMWPE chains (as can be seen in Figure 4.30), it was shown to reinforce the interfaces (from mechanical tests, Figures 4.21 and 4.23). Most likely phenomena for reinforcement is believed to be a percolating interfacial zone comprising of a co-continuous network of polymer chains and FNA particles wetted by polymer chains. In stark contrast, the low interfacial load was seen to be decreasing the mechanical property of the volume (from mechanical tests, Figures 4.31 and 4.33) with the increase in the FNA content. Considering the evidence based on the X-ray tomography, the relative density decreased with FNA content which suggests that interfacial load, during half-sintering, was not sufficient enough to provide the energy to press the interface against each other for a good wetting and a subsequent inter-diffusion. The illustration described in Figure 4.35 and Figure 4.36 explains the whole mechanism in short for full sintering and half sintering respectively with and without FNA content.

4.4.2 Sintering Mechanism- Cold-spray coating buildup

In a cold-sprayed deposit, UHMWPE deposits without FNA fails to build up as the impact energy is far higher than the bond energy generated at UHMWPE-substrate interface. Next, as the FNA content was increased, as previously explained in chapter 3, -OH bonds can help to raise the bond energy, and at ~3-4% FNA, the density of –OH bonds can probably support a buildup. Although, the reason why the deposition efficiency peaks at 4% FNA content and drops down after can be explained from the reasoning constructed from the sintering experiments designed.

In a cold-sprayed deposit, there are areas experiencing high, low and no interfacial load at all. Although the first layer formation was observed during UHMWPE depositions with >4% FNA, the buildup was not observed. It has to be noted that the interfacial load applied during full sintering experiment may not be numerically the same. Nevertheless, the sintering experiments were necessary to understand the general trend followed by the effect of the interfacial load on the sinterability of UHMWPE grains. Hence, the reason for the drop of deposition efficiency after 4% can be primarily because the interfacial load generated during the impact becomes insufficient to embed the FNA particles into the polymer matrix for obtaining a subsequently sufficient wetting and a chain diffusion and re-entanglements of the grain interfaces.







Figure 4.35 Illustration of full sintering mechanism without and with FNA content.



Figure 4.36 Illustration of half sintering mechanism without and with FNA content.

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CHAPTER 5

EFFECTS OF STRAIN-RATE ON UHMWPE Result and Analysis

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5.1 Introduction

Chapter 3, ISOLATED PARTICLE DEPOSITION (IPD) – Theoretical Model and Interpretation discussed the effect of high strain-rates on UHMWPE exhibited in the form of a higher elastic strain energy and a higher rebound energy. The discussion on the microstructural aspect of the increase in the yield-stress value was not done primarily because a microstructural analysis did not seem to be important in understanding that stage. Also, the topic of high-strain-rate deformation of UHMWPE, in itself, was a vast topic to discuss and is thus presented as a separate chapter.

In general, yield and flow in polymers are much more complicated and sophisticated than metals due to their dependency on time, temperature, strain, strain-rate and the history of the polymer. The two phenomena are different in the sense that, the yield is a homogenous and flow is more of a localized deformation process. Hence, essentially, while considering the high strain-rate process, it is quite important to discuss the yield and the flow stress.

5.1.1 Temperature and Strain-rate sensitivity of semi-crystalline polymers

The mechanical behavior of semicrystalline polymers is highly non-linear and sensitive to several external parameters (such as temperature, strain rate) and structural factors (crystallinity, molecular weight, physical entanglements and cross-linking). Semicrystalline polymers may be considered as nano-composite materials. Their structure comprises both amorphous and crystalline phases interconnected in a complex manner. For amorphous and semi-crystalline polymers, the increase in temperature usually leads to its decrease in Young's modulus and yield stress. Specific examples include of the sensitivity shown by UHMWPE, HDPE, and PEX in the research work by Brown et al. [1], Adiprene (urethane elastomer) by Gray et al. [2]. Also, a detailed account and analysis of the effect of temperature on UHMWPE are discussed in chapter 3 (see section 3.2.3.1.2). Figure 5.1 shows the mechanical response of HDPE and Adiprene with temperature.



Figure 5.1 Mechanical response of (a) HDPE [1] (b) Adiprene [2] as a function of temperature at different strain-rates.

Several kinds of literature have dwelled into understanding the change in the mechanical properties of the polymer under different strain-rates. The polymer is seen to show a sharp difference in sensitivity towards low and high strain-rates. Literature like Walley et al. [3] and Briscoe et al. [4], show that most semi-crystalline polymers exhibit a linear stress-logarithmic strain-rate dependence in the range of 10^{-2} - 10^3 s⁻¹. But a variety of semi-crystalline polymers like HDPE, and Nylatron, a nylon plastic, shows an increase in stress at strain-rates 7×10^3 s⁻¹ and 4×10^3 s⁻¹ respectively as reported by Al-Maliky et al. [5]. Further, some of the previous results showed an apparent maximum strain-rate after which the stress dropped [6]. Figure 5.2 (a) and (b) shows the cumulative stress-strain-rate evolution obtained by different research works on various materials tested.



Figure 5.2 (a) Stress at 5% strain vs. log of strain-rate for HDPE, UHMWPE, and Nylatron. [5] (b) Stress at 5% strain against log strain-rate for PEEK, HDPE, UHMWPE and Nylatron

[6].

5.1.2 High Strain-rate behavior-UHMWPE

Polyethylene is a well-studied semi-crystalline polymer for strain-rate response behavior, but complications arise out of complex molecular conformations with varying molecular weights. Research work by Brown et al. [7] [1] investigates several polymers including UHMWPE ($\sim 3.1-5.7 \times 10^6$), HDPE ($\sim 930-935$ kg m³) and PEX (cross-linked polyethylene). Although there are works extensively looking into the various polymers and their strain-rate response in detail, the high strain response of high molecular weight PE (~ 10.5 Mg mol⁻¹) have not been extensively studied. Moreover, the high strain response of UHMWPE is great in demand for applications involved in high-velocity impact testing, cold-spray etc. Further, it was quite clear from the previous analysis that nano-ceramic particles lead to changes within the chain structures and modify the property of the bulk system.

UHMWPE is also known to exhibit exceptional wear and impact resistance which was highlighted by the work of Deplancke et al. in which UHMWPE exhibited outstanding shock resistance in the case of hydrodynamic cavitation erosion [8]. However, it remains very difficult to predict the plastic deformation and the lifetime of the coatings in such conditions. Understanding the deformation behavior especially at high strain rates would be highly useful in modeling the cavitation erosion resistance behavior in the future.

To predict the behavior of UHMWPE, an experimental approach is employed in which the evolution of stress-stress behavior under progressive strain rates is tested. Hence, this chapter is dedicated to understanding the high strain-rate mechanical response of 10.5 Mg mol⁻¹ UHMWPE. Secondly, this chapter attempts to understand the mechanical response at high strain rates effect of FNA addition to the bulk UHMWPE.

5.2 Experimental

5.2.1 Materials Used

The sample used for the compression testing is full sintered UHMWPE (detailed protocol is described in chapter 4, section 4.2.2.1) of molecular weight 10.5 Mg mol⁻¹. Samples were cylindrically shaped and were cut using a circular punch to a diameter of 8 mm and a thickness of 4 mm. Sample shape and size used for both low-strain-rate and high strain-rate compressions were the same.

Full sintered UHMWPE-FNA nano-composites with 0-10% FNA by weight were prepared along the same lines and the dimensions of the same sample as described above. Full sintered materials were the choice because the bulk samples have the same density and molecular weight as that of a cold-sprayed UHMWPE particle. The results obtained with a full sintered UHMWPE can be used to explain the mechanical behavior of cold-sprayed UHMWPE to a large extent.

It has to be specifically kept in mind that, in this chapter here, full sintered UHMWPE is representative of a typical UHMWPE particle undergoing a high strain deformation during cold-spray unlike in chapter 4, where it was representative of a section of coating thickness. But, a full sintered UHMWPE with 0-10% FNA is not entirely representative of a UHMWPE particle with 0-10% FNA because a full sintered sample is a volume with FNA dispersed inside the matrix whereas FNA in cold-sprayed UHMWPE is essentially just attached to the UHMWPE surface by weak Van der Waals forces. Nevertheless, the information obtained from the mechanical testing of a full sintered UHMWPE and FNA sample can give insights into the thermo-mechanical interactions between UHMWPE and FNA particles during the cold-spray process.

5.2.2 Low strain-rate compression tests

Low strain-rate compression tests corresponding to strain-rates of 10^{-2} s⁻¹ and 10 s⁻¹ were carried out at room temperature using a servo-hydraulic compression testing apparatus (INSTRON). Samples were ensured to have a flat surface contact with the compressing platens. The frictional effects were avoided by lubricating the specimen ends.

5.2.3 High strain compression tests

High strain-rate testing corresponding to 970 s⁻¹ and 1160 s⁻¹ were carried out using a Split-Hopkinson Pressure Bar (SHPB) available at the facility provided by iCUBE laboratory, University of Strasbourg. A typical SHPB setup consists of a striker bar, an incident bar, and a transmitted bar. The incident bar and the transmitted bar are made of 316L steel with a length of 3m and a diameter of 22mm. The striker of 1m length was used in the experiments and was also made of 316L steel. The strain gauges are conveniently glued to the middle of both the incident beam and the transmitted beam.

Cylindrical UHMWPE specimens were sandwiched between the transmitted bar and the incident bar to measure the compressive stress-strain behavior under different strain-rates. The striker bar is propelled at a certain velocity by a propulsion system using pressurized gas during which two-speed sensors are used to calculate the velocity of the striker accurately. The energy of the striker bar is utilized to create a longitudinal compressive wave. This compressive wave and the corresponding strain, $\varepsilon_I(t)$, is recorded using the strain gauge mounted on the incident bar. The difference in the mechanical impedances at the specimenincident bar interface results in a part of the incident wave reflected back along the opposite direction. On the other hand, the rest of the wave is transmitted along the transmitted bar. The reflected wave, $\varepsilon_R(t)$, and the transmitted wave, $\varepsilon_T(t)$, are both measured by the strain gauges mounted on the incident bar and the transmitted bar respectively. Figure 5.3 (a) shows the setup and its schematic with its components labelled and Figure 5.3 (b) shows the nature of the signal obtained from a typical test representing the incident wave, reflected wave and the transmitted wave.

The values for the nominal stress (σ_n), nominal strain (ε_n) and nominal strain-rate ($\dot{\varepsilon}_n$) of UHMWPE samples tested are calculated using the following Equations [9]:

$$\dot{\varepsilon}_n = \frac{2C_b}{L} \varepsilon_R(t)$$
 (Equation 5.1)

$$\varepsilon_n = \frac{2C_b}{L} \int \varepsilon_R(t) dt$$
 (Equation 5.2)

$$\sigma_n = E_{bar} \cdot \left(\frac{A_{bar}}{A_{specimen}}\right) \cdot \varepsilon_T(t)$$
 (Equation 5.3)

where,

 C_b : Elastic wave speed propagating through the incident and the transmitted bar. It is the same for both the bars as they are made of the same material;

*E*_{bar}: Young's modulus of the bars;

L: Initial thickness of the specimen;

Abar and Aspecimen: Cross sectional area of the bars and specimen;

The true stress σ_t , true strain $\varepsilon_t(t)$ and true strain-rate $\dot{\varepsilon}_t(t)$ can be calculated using the already calculated nominal counterparts by the following expressions:

$$\dot{\varepsilon}_t(t) = \frac{\dot{\varepsilon}_n(t)}{1 - \varepsilon_n(t)}$$
(Equation 5.4)

$$\varepsilon_t(t) = -\ln\left(1 - \varepsilon_n(t)\right)$$
 (Equation 5.5)
$$\sigma_t(t) = \sigma_t(t) e^{-2v\varepsilon_t(t)}$$
 (Equation 5.6)

$$\sigma_t(t) = \sigma_n(t)e^{-2\nu \epsilon_t(t)}$$
(Equation 5.6)

Where,

v: Poisson's ratio of the specimen. In this case, the v = 0.5 is used for UHMWPE and UHMWPE-FNA composites, because they behave almost like rubber materials.



(b)

Figure 5.3 (a) Photograph of the Split Hopkinson Pressure Bar setup and its corresponding components illustrated by a schematic. (b) Typical signals from the strain gauges on the incident bar and the transmitted bar representing the incident wave, reflected wave and the transmitted wave.

The technique of SHPB is primarily based on the assumptions as follows;

- 1. One dimensional wave propagation is assumed when incident wave is very high relative to the length of the sample [10] [11]
- Uniform stress-strain fields in the specimen are assumed by selecting thin samples.
 [12] [13]
- 3. Inertial effects on the specimen are neglected.
- 4. Interface friction effect between the bar and the sample is substantially minimized by adding petroleum jelly as lubrication to the contact surfaces.

In this study, the results and discussion for high strain-rate tests performed by an SHPB equipment for full sintered UHMWPE and UHMWPE-FNA (0-10% by weight) will be presented. The tests were carried out at different strain-rates, 760 s⁻¹, 970 s⁻¹ and 1160 s⁻¹ as shown in Figure 5.4 which represents the nominal strain-rate vs. nominal strain curve.



Figure 5.4 Nominal strain-rate vs. nominal strain curve for the SHPB testing.

5.3 Results and Discussion

5.3.1 High strain-rate response of 10.5 Mg mol⁻¹ UHMWPE

Figure 5.5 represents the experimental true stress-strain curves in compression of a full sintered UHMWPE at different strain-rates ranging from 10^{-2} s⁻¹ to 1160 s⁻¹. The whole of the testing regime can be separated into three stages, namely; pre-yield, yield point, and post-yield. Starting from the elastic region or the pre-yield and yield point region, 10.5 Mg mol⁻¹ UHMWPE exhibit an increase in the tangent modulus and the yield stress with an increase in strain-rate. Further, the post-yield phenomenon in UHMWPE shows no apparent post-yield softening and shows an increase in the strain-hardening with the rising strain-rate. The curves at increasingly higher strain-rates show an increasingly pronounced bi-linearity to its flow behavior with the rate of hardening increasing above 10~15% strain.



Figure 5.5 True stress-strain curves in compression for full sintered UHMWPE at different strain-rates obtained with SHPB testing.



Figure 5.6 True-stress at 7.5% and 20% strain in UHMWPE as a function of strain-rate.

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Because of several reasons like sample/bar impedance mismatch, sound speed in the sample, straightness of the bar, it is challenging to measure the elastic modulus of the curve accurately. In this study, yield stress at 7.5% strain is taken to quantify the strain-rate dependence. Flow behavior at 20% strain is included to explain the flow behaviors further. Figure 5.6 represents the stress levels at 7.5% and 20% strain in UHMWPE as a function of strain-rate. Stress as a function of strain-rate seems to be linear, hence under the domain tested, phase changes are highly unlikely. The mechanical properties are consistent with the literature where the increase in the both the strength and stiffness, due to a reduced mobility during strain hardening coupled with an increase in the rate of non-affine segmental displacements, is observed.

The most important aspect to note here is that a logarithmic fit can depict the strain-rate dependence for UHMWPE (i.e., linear in the space of log (strain-rate), $\sigma = D + E \log(\dot{\varepsilon})$). This aspect of strain-rate dependence with the temperature dependence was described in chapter 3 IPD model in the form of temperature-time superposition. This aspect of superposition is very unique to polymers and has been verified in many literatures, one of them being by Brown et al.

The mechanical behavior of UHMWPE is highly non-linear and sensitive to several structural factors like crystallinity, molecular weight, physical entanglements and cross-linking. UHMWPE being a semicrystalline polymer can be considered as a macromolecular network (a rubber when $T>T_g$) bridled by a crystalline network formed by lamellar stacking [14] [15] generally arranged in an isotropic spherulitic structure.

Firstly, the initial behavior while compressing the polymer at low strain rates is mostly viscoelastic due to the straining of the amorphous domains between the crystalline lamellae [16]. At yield, "strain softening" is absent in the case of UHMWPE due to the high crystallinity as well as the inability of chains in amorphous phase to orient themselves. The plasticity in semicrystalline polymers is known to be due to the motion of dislocations in the crystalline phase, which is a thermally activated phenomenon [17] [18]. It is also known that the energy barrier for dislocation motion is increasing with the crystalline thickness, and then with the crystallinity. At high strain, the crystalline network has collapsed and reorganized into small crystalline blocks that are positioned relatively regularly along a fibril. This collapse induces a large decrease of the material stiffness whereas a progressive mechanical hardening is simultaneously observed. When the strain rate is increased, the changes in the mechanical behavior are reflected from the macromolecular network, the tie-molecules and the crystalline networks.

One of the contributions to the strain hardening can be explained by a viscous contribution added to the entropic elasticity. This flow stress is related to the intermolecular frictions at a monomeric or segmental scale [19] [20]. The viscous flow stress is a function of the strain rate, $\dot{\varepsilon}$, which is described by an Eyring relation can be expressed as a function of the total deformation. Moreover, Tie Molecules (TM) which link adjacent crystallites are also partially responsible for affecting elastic and yielding behavior, as well as fibrillar formation and hardening [21].

Based on thermally activated mechanisms and defect mobility due to stress, the Eyring models can be used to describe the plastic behavior of UHMWPE used in the study.

Hence, the strain hardening in UHMWPE can be understood as a combination of the following steps:

- The decrease of the intra-cohesive lamellar forces of the crystal network due to the shear of the crystal lamellae and the destruction of the spherulitic structure in favor of a fibrillar structure.
- The strain hardening due to the entanglement network.
- The disentanglement of the macromolecular chains describing the slipping of the fibrils.

5.3.2 High strain-rate response of 10.5 Mg mol⁻¹ UHMWPE-FNA composite

5.3.2.1 Results

Strain-rate response was recorded for full sintered UHMWPE-FNA composite with 0-10% FNA content at two different strain-rates; (i) Intermediate strain-rate (\approx 760 s⁻¹) and (ii) High strain-rate (\approx 1300 s⁻¹). The major intention to perform these experiments was to analyze the evolution of the flow stress of UHMWPE with different FNA content at two different strain-rates as mentioned above.

Figure 5.7 represents the true stress-strain graph of full sintered UHMWPE with 0%, 4% and 10% FNA at an intermediate strain-rate of \approx 760 s⁻¹. As can be seen from the stress-strain diagram, for UHMWPE with 0%, 4%, and 10%, the pre-yield and yield seem to be quite similar. But, UHMWPE with 10% FNA shows an increase in the rate of strain hardening

relative to 0% and 4% FNA. As was seen earlier in chapter 4, where the reinforcing effect of FNA was quite clear. In the case seen in chapter 4, the tests showed an almost 33% increase in the stress near yield point of 0% and 10% FNA. On the other hand, an increase of around 17% was seen for the same increase in FNA content in the SHPB compression tests performed at strain-rate of 760 s⁻¹.

The effect described above can be extended to the mechanical behavior obtained at strainrates $\approx 1300 \text{ s}^{-1}$. In Figure 5.9, it can be seen that although there were no discernable differences in the pre-yield and yield region for UHMWPE with 0%, 4%, and 10% FNA, the post-yield hardening was seen to be reversed. At this strain-rate, the 10% FNA showed a lower rate of hardening in comparison to 4% and 0% FNA content. Figure 5.10 shows the true-stress levels at 7.5%, 30% and 70% strain in composites of UHMWPE as a function of % FNA content at a high strain-rate of $\approx 1300 \text{ s}^{-1}$. A larger ΔT for a composite due to a smaller C_p and a subsequent post yield softening can be probable reasoning for the mechanical response seen here.

5.3.2.2 Possible Explanations

A possible explanation that can put forward to explain the decrease in the reinforcement can be the temperature increase due to the plastic work to heat conversion during the high strainrate process and a subsequent drop in the stress value. The difference in temperature for UHMWPE will be different from the UHMWPE-FNA composite because of the difference in their overall specific heat capacity. Hence, composites with a lower C_p , has the possibility to heat up to a higher temperature relative to the virgin UHMWPE.

The specific heat capacity of a composite, $C_{p,Composite}$, is actually equal to the weighted average of each constituent heat capacities in the case of an isotropic composite with constant pressure and volume (negligible thermal expansion) [22].

$$C_{p,Composite} = w \times C_{p,FNA} + (1 - w) \times C_{p,UHMWPE}$$
(Equation 5.7)

At large increasing strain values seen during high strain-rate tests, the deformation of the polymers becomes more and more adiabatic, deviating from an isothermal heating. The internal heat generated during the inelastic deformation doesn't have time to dissipate and can lead to an increase in mean temperature of the specimen.

Since the dynamic behavior of the materials is based on the competition between strengthening at high strain-rates and softening with temperature increase under adiabatic loading conditions [23], FNA particles probably help to provide the propensity for thermal softening by lowering the overall C_p of the volume. The internal energy, ΔH generated during the inelastic deformation can be equated to the C_p of the material as follows (below its melting point):

$$\Delta H = mC_p \Delta T \qquad (Equation 5.8)$$

Hence, a lower C_p material will have a higher ΔT and thus, a greater deformability. Experiments measuring the temperature of the sample in-situ will, in the future, help to verify this hypothesis.



Figure 5.7 True stress-strain curves in compression obtained by SHPB testing for full sintered UHMWPE with 0%, 4% and 10% FNA content at an intermediate strain-rate of \approx 760 s⁻¹.



Figure 5.8 True-stress levels (SHPB testing) at 7.5% and 30% strain in composites of UHMWPE as a function of % FNA content at an intermediate strain-rate of \approx 760s⁻¹.



Figure 5.9 True stress-strain curves (SHPB testing) in compression for full sintered UHMWPE with 0%, 4% and 10% FNA content at a high strain-rate of $\approx 1300 \text{ s}^{-1}$.



Figure 5.10 True-stress levels at 7.5%, 30% and 70% strain in composites of UHMWPE as a function of % FNA content at a high strain-rate of \approx 1300 s⁻¹ (SHPB testing).

Another possibility mostly in conjunction with the above process can be due to a local interaction of FNA particles with the UHMWPE chains, as it was already seen in chapter 4. Also because FNA has a higher hardness than UHMWPE, the possibility of local chain scissioning around FNA particles during the high strain-rate impact process is high. This chain scissioning can induce a better mobility of chains, which can reduce the resistance to deformation. However, the above explanations need to be validated by performing further experiments in the future.

The phenomenon seen here can be beneficial during the cold-spray process if the impacting particles are similar to the full sintered UHMWPE-FNA composite because it seems to exhibit a higher ductility and deformability. The lower yield hardening as compared to a virgin can be helpful in creating a better wetting between the substrate and the particle.

5.4 Conclusions

This chapter presented a general picture of the mechanical response of UHMWPE under increasingly higher strain-rates. With the increase in strain-rate, UHMWPE exhibits a higher stress at the beginning of yield. Also, it was evident from the compression curves that, the rate of strain hardening was also seen to increase with an increase in the strain-rates. This phenomenon was taken into consideration in chapter 3, in addition to the effect of temperature (together called temperature-strain-rate superposition principle), to explain its deposition mechanism. This chapter provides the mechanical data relevant to the material under consideration for the elucidation of the mechanism, i.e., 10.5 Mg mol⁻¹ UHMWPE.

Further, the mechanical response data with the inclusion 0%, 4% and 10% FNA to UHMWPE was also presented. The increasing rate of post-yield softening phenomenon with 10% FNA is probably due to the lowering of the C_p value leading to a larger ΔT . While the exact molecular mechanism of involvement of FNA particle, which can explain the macromechanical behavior, cannot be derived from these results. The experimental results helps to speculate the origins and only a probable mechanism is explained for this phenomenon. For further elucidation of this mechanism, experiments with more set of strain-rates have to be included to prove the assumption.

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CHAPTER 6

CONCLUSIONS

Cette thèse est accessible à l'adresse : http://theses.insa-lyon.fr/publication/2018LYSEI008/these.pdf © [K. Ravi], [2018], INSA Lyon, tous droits réservés The thesis presented a detailed mechanistic understanding of high strain-rate impact behavior of Ultra-High Molecular Weight Polyethylene and the mechanism of coating formation on Al substrate during cold-spraying.

As for any coating formation, the cold-spray process of UHMWPE particles was broken down in to two major categories:

- (i) Interaction of UHMWPE with Al substrate during a high-speed impact.
- (ii) Interaction of UHMWPE with already deposited UHMWPE particles leading to a buildup in the coating.

Interaction of UHMWPE with Al substrate during a high-speed impact was covered in chapter 2 and chapter 3 in this research work. Chapter 4 covered the topic of interaction of UHMWPE with already deposited UHMWPE particles leading to a buildup in the coating. Chapter 5 presented the general idea of a high-strain-rate mechanism specific to UHMWPE material used in this study and a general introduction to the strain-rate dependence of a UHMWPE-FNA composite material.

In order to efficiently characterize the high velocity UHMWPE-Al interaction, a method called "Isolated Particle Deposition" (IPD) was developed. Using this method, UHMWPE particles were sprayed within a dilute 2-phase flow and were deposited on Al substrate in an isolated manner. This method was prepared on the assumption that such a spray configuration would lead to an undisturbed interaction of UHMWPE and carrier gas during the flow and individual deposition behavior of UHMWPE in consequence of the mechanical and thermal state of particle during the impact could be accurately analyzed. The experimental process included identifying the particle velocities during impact, the microstructural analysis of the impacted particles at different gas temperatures, recording the deposition efficiency of UHMWPE with and without the inclusion of fumed nano-alumina particles in the feedstock. The general observation and empirical understanding of the cold-spray deposition of UHMWPE in conjunction with FNA particles obtained from the IPD method are as follows:

- One of the major parameters that influenced UHMWPE deposition is the gas temperature. Deposition efficiency was seen to show a spike at a gas temperature greater than 380°C. Effect of increase in gas temperature was seen in following ways:
 - a. Increase in number of similar-sized particles deposits,
 - b. Increase in the size of deposits.
- 2. FNA particles addition to the feedstock was seen to be the second important parameter that affected the deposition efficiency. FNA nano-alumina particles also enhanced the
overall deposition volume and deposition efficiency. Effect of FNA addition was seen in the following ways:

- a. Increased in number of similarly sized deposit for the same operating gas temperature with successive increase in FNA content.
- b. Increase in size of deposits.
- 3. FIB sectioning of the deposited particles indicated heavy degree of deformation of UHMWPE particles at high gas temperatures. The observation of the sectioned deposits with different percentages of FNA showed that in addition to heavily deformed deposits at high gas temperatures, FNA also helps in the deposition of particles that contribute a lower contact area during impact.

In order to explain these empirical observations, IPD process was theoretically modeled in which thermal and the kinetic states, which are represented by particle temperature and particle velocity respectively, were calculated at nozzle outlet and during the impact. The final deposition characteristic that depended on the mechanical response of the impacting particle was predicted by calculating its stress–strain response at different temperatures and strain-rate relevant to cold-spray. This part of the study discussed the subtle nuances of thermal and mechanical responses of UHMWPE during the flight, impact and post-impact from the calculated parameters and corroborated with the experimental results. The effect of FNA in enhancing the adhesion was also discussed, giving a perspective of how fumed nano-alumina was involved in the mechanism of deposition.

The following conclusions were drawn from the study:

- 1. UHMWPE experiences heating rates of the order 10⁴ K s⁻¹, they are assumed to remain at an intermediate non-equilibrium crystalline state before impact.
- Elastic energy/rebound energy of UHMWPE decreases at increasing gas temperature and increases with the strain-rate. At the same time, a temperature-strain-rate equivalence principle is used to calculate the temperature at which stored elastic energy within the particle can be shown to be near zero.
- 3. Deposition of UHMWPE particles on Al surface depends upon whether UHMWPE particles after impact can furnish a contact area with an interfacial bond stronger than elastic strain energy of the particle.
- 4. The bonding of UHMWPE depends upon the extent of wetting at the particle-substrate interface. External agents like H-bonds on the FNA surface provide sufficiently strong extra bonds at the contact surface to increase the window of deposition at higher temperatures, which was otherwise very low.

Major parameters that influenced significantly the UHMWPE deposition behavior were the particle temperature and velocity, elastic strain energy and the amount of FNA (or density of H-bonds). Increase in particle temperature essentially decreases its rebound energy and density of –OH bonds help in withstanding the elastic energy to a certain extent, thereby increasing the window of deposition. Hence, a successful UHMWPE-Al deposition during cold-spray required UHMWPE to have a near-zero elastic strain energy. Additionally, for a strong bond with the substrate, UHMWPE have to rely on external agents like FNA particles which can provide hydrogen bonds to increase the interfacial bond energy.

In chapter 4, research focused on the interaction of impacting UHMWPE particles with the already deposited UHMWPE layer. This part of the study specifically focused on understanding the mechanism of welding of UHMWPE grains relevant to cold spray technique. Two important parameters; interfacial load and % FNA; were identified playing important role during cold-spray process. Hence, to find out their interdependence, welding mechanisms and to account for the presence of porosity in the cold-sprayed samples, a new set of samples were prepared by classical sintering, using three different protocols namely; full sintering; half sintering and free sintering; to analyze the weldability of UHMWPE grain under different local interfacial loads. Among the characterization used in this work, X-Ray tomography was used to identify the porosity ratio and relative densities in such samples and mechanical characterization was performed to identify the fundamental parameters involved in the strength of the interface.

The morphological and mechanical characterization performed on full sintered, half sintered and free sintered samples showed that sintering is heavily influenced by the interfacial load and interfacial FNA particles.

Firstly, while looking into the sintering of any two interface of nascent UHMWPE particles, it was under understood that when the interface reaches melting point, largely driven by the "melting-explosion" phenomenon, the chain diffusion and re-entanglement occurs through the interface. The consequential re-entanglement density per unit area of a virgin UHMWPE surface was seen to be not depending much on the interfacial load being applied, which was seen from the fact that modulus value of the half-sintered material obtained experimentally and using Kerner model were both in good agreement with each other.

On the other hand, the results obtained with FNA

at high and low compressive loads contradicted each other. It showed that a sufficiently high interfacial load is necessary to embed FNA particles in to the polymer matrix to promote wetting and a continuity of polymer around FNA by letting chains go around the particles.

Thanks to this wetting of FNA particles during the re-entanglement, it was shown to contribute to the reinforcement of these interfaces. Most likely phenomena for reinforcement is believed to be a percolating interfacial zone comprising of a co-continuous network of polymer chains and FNA particles wetted by polymer chains. By stark contrast, the low interfacial load was seen to be decreasing the mechanical property of the volume with the increase in the FNA content. Considering the evidences based on the X-ray tomography, the relative density decreased with FNA content which suggested that interfacial load, during half-sintering, was not sufficient enough to provide the energy to press the interface against each other for a good wetting and a subsequent inter-diffusion.

A cold-sprayed UHMWPE fails to build up as the impact energy is far greater than the bond energy generated at UHMWPE-substrate interface. Next, as the FNA content was successively increased, -OH bonds can help to increase the bond energy and at ~3-4% FNA, the density of –OH bonds can probably support a buildup. Although, the reason why the deposition efficiency peaks at 4% FNA content and drops down after was explained from the reasoning constructed from the sintering experiments designed.

In a cold-sprayed deposit, there are areas experiencing high, low and no interfacial load at all. The sintering experiments were necessary to understand the general trend followed by the effect of the interfacial load on the sintering of UHMWPE grains. Hence, the reason for the drop of deposition efficiency after 4% was explained primarily due to the fact that the interfacial load generated during the impact becomes insufficient to embed the FNA particles in to the polymer matrix for obtaining a subsequently sufficient wetting and a chain diffusion and re-entanglements of the grain interfaces.

Chapter 5, finally discusses the strain-rate effect of UHMWPE by comparing the mechanical response of UHMWPE from low strain rates to high strain rates. This part of the study discusses in detail the possible effects a high strain-rate compression has on UHMWPE by analyzing the stress-strain curves of the same. This section also comments on the high strain-rate effects of fumed nano-alumina strengthened UHMWPE matrices. This chapter presented a general picture of the mechanical response of UHMWPE under increasingly higher strain-rates. With the increase in strain-rate, UHMWPE exhibited a higher stress at beginning of yield. Also, it was evident from the compression curves that, rate of strain hardening was also seen to increase with increase in the strain-rates. This phenomenon was taken in to consideration in chapter 3, in addition to the effect of temperature (together called temperature-strain-rate superposition principle), to explain its deposition mechanism. This chapter, provides the mechanical data relevant to the material under consideration for the

elucidation of the mechanism i.e. 10.5 Mg mol⁻¹ UHMWPE. Further, the mechanical response data with the inclusion 0%, 4% and 10% FNA to UHMWPE was also presented. The increasing rate of post yield softening phenomenon seen with 10% FNA was seen which is probably due to the lowering of the total C_p value of the composite because of a lower C_p FNA as compared to UHMWPE. This subsequently leads to a larger specimen temperature. While the exact molecular mechanism of involvement of FNA particle, which can explain the macro-mechanical behavior, cannot be derived from these results, the experimental results helped to speculate the origins. Only a probable mechanism was explained for this phenomenon. For further elucidation of this mechanism, experiments with more set of strain-rates have to be included.

The thesis identifies the fundamental parameters responsible for the deposition and coating buildup and attempts to elucidate the independent effect of each of those parameters. The thesis attempts to be instrumental in clarifying polymer deposition mechanism for cold spray process, which was quite less explored successfully connecting the macroscopic mechanical behavior of UHMWPE to its intrinsic material behavior. Finally, this study has been helpful in uncovering the mechanism behind the role of FNA particles in enhancing the deposition behavior of UHMWPE. Finally, this thesis presents a first approach understanding the coating formation of UHMWPE on Al substrate and provides a foundation to further developing polymer coatings for structural and functional applications.

As a future perspective, the understanding of the coating behavior of UHMWPE can largely be used to attempt in understanding how to obtain a better coating by the optimization of parameters whose effects are known. Primarily one can attempt to spray the polymeric particles at high particle velocities and temperature at the same time to have an optimal flow of the particles and also attain a large impact area with the substrate. Another area that can be exploited is the optimization of FNA content to rightly figure out the exact content required to balance the interfacial bonding effect, particle-particle reinforcing and weakening effect during the coating process. Also, a future attempt towards understanding the usage of other bonding agents will also potentially help in obtaining industrial standard coatings of polymers via cold spray.

The first approach study presented in this thesis can be extended to a more detailed understanding by performing simulation studies based on FEM modeling/MD simulations to understand the effect of the gas dynamics on the in-flight particle, UHMWPE impact behavior and UHMWPE-FNA interactions.

Appendix A

Abbreviations

UHMWPE	Ultra-high molecular weight polyethylene
PE	Polyethylene
LDPE	Low density polyethylene
LLDPE	Linear Low-density polyethylene
HDPE	High density polyethylene
DSC	Differential scanning calorimetry
HVC	High Velocity Compaction
CS	Cold spray
HVOF	High velocity oxy-fuel
HPCS	High pressure cold-spray
LPCS	Low pressure cold-spray
SEM	Scanning electron microscopy
FNA	Fumed nano-alumina
EDX	Energy-dispersive X-ray spectroscopy
IPD	Isolated particle deposition
IR	Infra-red
FIB	Focused ion beam
RT	Room temperature
KE	Kinetic energy
BE	Bond energy
TE	Thermal energy
STEM	Scanning transmission electron microscopy
H-bonds	Hydrogen bonds
YS	Yield stress
CCD	Charge coupled device

PEX	Cross-linked polyethylene
SHPB	Split-Hopkinson Pressure Bar

Abstract

UHMWPE is a unique high molecular weight polymer (>3 million g/mol) with outstanding physical and mechanical properties like high wear resistance, impact resistance and cavitation erosion resistance. It is a linear homopolymer belonging to a polymer family of polyethylene having monomers of (C_2H_4) bonded together by chemical covalent bonds to form $(C_2H_4)_n$. Considering the fact that UHMWPE could be processed via powder sintering to obtain near perfect bulk products and the possibility of High Velocity Compaction (HVC) techniques to sinter UHMWPE interfaces gave rise to the possibility of using a technique called cold-spray. Cold-spray is a coating technique where fine powder particles are impacted on a substrate surface at high velocities to obtain consolidated coating adhered to the substrate surface. The process involves high strain rate impact and a subsequent impingement of fine powder particles of the order 10-100µm on to a target surface at very high velocities (500 to 1500 m/s) to form coatings or solid components. Cold-spray can be especially advantageous in generating coating on large non-planar surfaces like in the case for protection of large ship rudders from cavitation erosion. Processing UHMWPE coatings via cold-spray rendered thick coatings on Al substrates thanks to the careful control of three major parameters; particle surface activity (by addition of hydrophilic polar nano-alumina particles like fumed nano-alumina (FNA) to the particle surface), particle temperature and particle velocity. But the detailed understanding of the UHMWPE deposition process was largely unclear.

The thesis presents a detailed mechanistic understanding of high strain-rate impact behavior of Ultra-High Molecular Weight Polyethylene and the mechanism of coating formation on Al substrate during cold-spraying.

As for any coating formation, the cold-spray process of UHMWPE particles was broken down in to two major categories:

- (iii) Interaction of UHMWPE with Al substrate during the first layer formation.
- (iv) Interaction of UHMWPE with already deposited UHMWPE particles leading to a buildup in the coating.

Interaction of UHMWPE with Al substrate during a high-speed impact was covered in chapter 2 and chapter 3 in this research work. Chapter 4 covered the topic of interaction of UHMWPE with already deposited UHMWPE particles leading to a buildup in the coating. Chapter 5 presented the general idea of a high-strain-rate mechanism specific to UHMWPE

material used in this study and a general introduction to the strain-rate dependence of a UHMWPE-FNA composite material.

In order to efficiently characterize the high velocity UHMWPE-Al interaction, a method called "Isolated Particle Deposition" (IPD) was developed. Using this method, UHMWPE particles were sprayed within a dilute 2 phase flow and was deposited on Al substrate in an isolated manner. This method was prepared on the assumption that such a spray configuration would lead to an accurate application of isentropic equation and individual deposition behavior of UHMWPE in consequence of the mechanical and thermal state of particle during the impact could be accurately analyzed. The experimental process included identifying the particle velocities during impact, the microstructural analysis of the impacted particles at different gas temperatures, recording the deposition efficiency of UHMWPE with and without the inclusion of fumed nano-alumina particles in the feedstock.

The general observation and empirical understanding of the cold-spray deposition of UHMWPE in conjunction with FNA particles obtained from the IPD method are as follows:

- 4. One of the major parameters that influenced UHMWPE deposition is the gas temperature. Deposition efficiency was seen to show a faint bi-linear behavior with an increase in gas temperature. Effect of increase in gas temperature was seen in following ways:
 - c. Increase in number of similar-sized particles deposits,
 - d. Increase in the size of deposits.
 - e. Increase in the degree of deformation
- 5. FNA particles addition to the feedstock was seen to be the second important parameter that affected the deposition efficiency. FNA nano-alumina particles also enhanced the overall deposition volume and deposition efficiency. Effect of FNA addition was seen in the following ways:
 - a. Increased in number of similarly sized deposit for the same operating gas temperature with successive increase in FNA content.
 - b. Increase in size of deposits.
 - c. Allowing the deposition of particles with lower contact surface area

In order to explain these empirical observations, IPD process was theoretically modeled in which thermal and the kinetic state which are represented by particle temperature and particle velocity respectively were calculated at nozzle outlet and during the impact. The final deposition characteristic which depended on the mechanical response of the impacting particle, was predicted by calculating its stress–strain response at different temperatures and strain-rate relevant to cold-spray. This part of the study discussed the subtle nuances of thermal and mechanical responses of UHMWPE during the flight, impact and post-impact from the calculated parameters and corroborated with the experimental results. The effect of FNA in enhancing the adhesion was also discussed, giving a perspective of how fumed nanoalumina was involved in the mechanism of deposition.

The following conclusions were drawn from the study:

- 5. UHMWPE experiences heating rates of the order 10⁴K/s, they are assumed to remain at an intermediate non-equilibrium crystalline state before impact.
- 6. Elastic energy of UHMWPE decreased at increasing gas temperature and increased with the strain-rate.
- 7. Rebound of UHMWPE particles on Al surface depended upon whether UHMWPE particles after impact can furnish a contact area with an interfacial bond stronger than elastic strain energy of the particle.
- 8. The bonding of UHMWPE depended upon the extent of wetting at the particle-substrate interface. External agents like H-bonds on the FNA surface provided sufficiently strong extra bonds at the contact surface to increase the window of deposition at higher temperatures, which was otherwise very low.

Next part of the research focused on the interaction of impacting UHMWPE particles with the already deposited UHMWPE layer. This part of the study specifically focused on understanding the mechanism of welding of UHMWPE grains relevant to cold spray technique. Two important parameters, interfacial load and percentage of FNA content were identified playing important role during cold-spray process. Hence, to find out their interdependence, welding mechanism and to account for the presence of porosity in the cold-sprayed samples, a new set of samples were prepared at different interfacial loading conditions and FNA content by classical sintering, using three different protocols namely; full sintering; half sintering and free sintering. Among the characterization used in this work, X-Ray tomography was used to identify the porosity ratio and relative densities in such samples and mechanical characterization was performed to identify the fundamental parameters involved in the strength of the interface.

The morphological and mechanical characterization performed on full sintered, half sintered and free sintered samples showed that sintering is heavily influenced by the interfacial load and interfacial FNA particles.

Firstly, while looking into the sintering of any two interface of nascent UHMWPE particles, it was understood that when the interface reaches melting point, largely driven by the "melting-explosion" phenomenon, the chain diffusion and re-entanglement occurs through

the interface. The interfacial loading affected the porosity and the relative density of the sintered material. Lower interfacial loading during the processing led to a lower relative density of the sintered volume. The decrease in the strength of the interface of the porous volume depended on the extent of pore volume fraction. The experimental elastic modulus and the calculated modulus via Kerner equation were in good agreement with each other.

On the other hand, the results obtained with FNA content when processed under high and low compressive loads contradicted each other. It showed that a sufficiently high interfacial load is necessary to embed FNA particles in to the polymer matrix to promote wetting and a subsequent re-entanglement by letting chains go around the FNA particles. Thanks to this wetting of FNA particles during the re-entanglement, it was shown to contribute to the reinforcement of these interfaces. By stark contrast, the low interfacial load was seen to be decreasing the mechanical property of the volume with the increase in the FNA content. Considering the evidences based on the X-ray tomography, the relative density decreased with FNA content which suggested that interfacial load, during half-sintering, was not sufficient enough to provide the energy to press the interface against each other for a good wetting and a subsequent inter-diffusion.

A cold-sprayed UHMWPE fails to build up as the impact energy is far greater than the bond energy generated at UHMWPE-substrate interface. Next, as the FNA content was successively increased, -OH bonds can help to increase the bond energy and at ~3-4% FNA, the density of –OH bonds can probably support a buildup. Although, the reason why the deposition efficiency peaks at 4% FNA content and drops down after was explained from the reasoning constructed from the sintering experiments designed.

In a cold-sprayed deposit, there are areas experiencing high, low and no interfacial load at all. The sintering experiments were necessary to understand the general trend followed by the effect of the interfacial load on the sintering of UHMWPE grains. Hence, the reason for the drop of deposition efficiency after 4% was explained primarily due to the fact that the interfacial load generated during the impact becomes insufficient to embed the FNA particles in to the polymer matrix for obtaining a subsequently sufficient wetting and a chain diffusion and re-entanglements of the grain interfaces.

Finally, the lqst section of the thesis discusses the strain-rate effect of UHMWPE using Split-Hopkinson Pressure Bar (SHPB) experiments. This part of the study discusses in detail the possible effects high strain-rate compression has on UHMWPE by analyzing the stress-strain curves of the same. This section also comments on the high strain-rate effects of fumed nanoalumina strengthened UHMWPE matrices. This chapter presents a general picture of the mechanical response of UHMWPE under increasingly higher strain-rates. With the increase in strain-rate, UHMWPE exhibited a higher stress at beginning of yield. Also, it was evident from the compression curves that, rate of strain hardening was also seen to increase with increase in the strain-rates. This phenomenon was taken in to consideration in chapter 3, in addition to the effect of temperature (together called temperature-strain-rate superposition principle), to explain its deposition mechanism. This chapter, provides the mechanical data relevant to the material under consideration for the elucidation of the mechanism i.e. 10.5Mg/mol UHMWPE. Further, the mechanical response data with the inclusion 0%, 4% and 10% FNA to UHMWPE was also presented. The increasing rate of post yield softening phenomenon seen with 10% FNA was seen which is probably due to the lowering of the total C_p value of the composite because of a lower C_p FNA as compared to UHMWPE. This subsequently leads to a larger specimen temperature. While the exact molecular mechanism of involvement of FNA particle which can explain the macro-mechanical behavior cannot be derived from these results, the experimental results helped to speculate the origins. Only a probable mechanism was explained for this phenomenon. For further elucidation of this mechanism, experiments with more set of strain-rates have to be included.

Résumé

Les polyéthylènes étudiés ici, de masse molaire très élevée (> 3 millions g/mol), ou UHMWPE sont des polymères ayant d'excellentes propriétés physiques et mécaniques, telles qu'une très grande résistance à l'usure, ainsi qu'aux chocs et à l'érosion par cavitation hydraulique. C'est un homopolymère linéaire appartenant à une famille de polyéthylène constitués des monomères (C_2H_4) reliés par des liaisons covalentes chimiques pour former (C_2H_4)_n.

Partant du fait que l'UHMWPE ne peut être mis en forme que par frittage de poudre pour obtenir des produits massifs presque parfaits, ou encore par des techniques de compactage à haute vitesse (HVC), ce travail explore la possibilité d'utiliser une technique de pulvérisation à froid, appelée Cold-Spray.

Le Cold-Spray est une technique de revêtement dans laquelle des particules de poudre sont projetées sur la surface d'un substrat à des vitesses élevées pour obtenir un revêtement compact adhérant à la surface du substrat. Plus précisément, le procédé repose sur la mise en œuvre de vitesses de déformation plastique très élevées de particules de l'ordre de 10-100 µm de diamètre, lors de leur impact sur une surface cible à des vitesses de l'ordre de 500 à 1500 m/s. Le but est d'obtenir des revêtements compacts plus ou moins épais. Le Cold-Spray peut être particulièrement avantageux pour générer des revêtements sur de grandes surfaces non planes, comme dans le cas de la protection des hélices de navires contre l'érosion par cavitation.

Dans un travail précédent, on a montré que l'ajout de nanoparticules d'alumine jouait un rôle majeur dans la formation du revêtement. Ainsi, cette formation sur un substrat, ici en aluminium (Al), apparait dépendre principalement de trois paramètres majeurs : (i) l'état de surface des particules polymères (par l'addition de nanoparticules d'alumine polaire hydrophile telle que l'alumine fumée (FNA) à la surface des particules), (ii) la température des particules et (iii) leur vitesse. Mais la compréhension détaillée des mécanismes de dépôt de l'UHMWPE était loin d'être aboutie.

Ce travail de thèse présente une analyse détaillée du comportement mécanique lors du choc à haute vitesse de déformation de l'UHMWPE et des mécanismes de formation du revêtement sur le substrat pendant la projection à froid. La formation d'un revêtement est naturellement décomposée en deux étapes principales :

- La formation de la première couche de particules d'UHMWPE sur le substrat, qui conduit à l'analyse des interactions polymère-aluminium ;
- (ii) La formation des couches polymère sur polymère (croissance du revêtement).

L'interaction de l'UHMWPE avec le substrat Al au cours d'un impact à grande vitesse est traitée dans le chapitre 2 et le chapitre 3 de ce travail de recherche. Le chapitre 4 couvre le sujet de l'interaction des particules d'UHMWPE avec l'UHMWPE déjà déposé, lors de la croissance du revêtement. Le chapitre 5 présente les grandes lignes des mécanismes de déformation à haute vitesse, spécifiques au matériau UHMWPE utilisé dans cette étude et une introduction générale à la dépendance à la vitesse de déformation de matériaux nanocomposites UHMWPE-FNA.

Afin de caractériser précisément l'interaction entre UHMWPE et Al lors des chocs à grande vitesse, une méthode appelée "Isolated Particle Deposition" (IPD) a été développée. En utilisant cette méthode, des particules d'UHMWPE ont été pulvérisées en petit nombre (écoulement dilué) et ont été déposées sur un substrat en Al de telle sorte qu'elles demeurent isolées les unes des autres. Cette méthode a été conçue en supposant que dans de telles conditions, le comportement des particules soit isentropique (durant le parcours des particules, avant leur contact avec la cible) et que le comportement des particules au cours du choc pourrait être analysé avec précision, connaissant les paramètres thermomécaniques de l'UHMWPE. Le procédé expérimental comprend (i) la mesure des vitesses des particules pendant l'impact, (ii) l'analyse microstructurale des particules impactées pour différentes températures du gaz de transport, et (iii) l'observation des dépôts de UHMWPE avec et sans addition de nanoparticules FNA.

L'observation générale et la compréhension empirique du dépôt par Cold-Spray de UHMWPE avec et sans nanoparticules FNA découlant de la méthode IPD sont les suivantes :

- L'un des principaux paramètres qui influence le dépôt d'UHMWPE est la température du gaz vecteur. Le taux de polymère déposé augmente linéairement avec la température du gaz. L'augmentation de la température du gaz conduit aux observations suivantes :
 - a) Augmentation du nombre de dépôts de taille similaire,
 - b) Augmentation de la taille des dépôts,
 - c) Augmentation du taux de déformation ;
- 2. l'ajout de nanoparticules FNA constitue le second paramètre important qui affecte l'efficacité du dépôt. Les nanoparticules FNA améliorent également la fraction de polymère déposé (les autres particules de polymère n'ayant pas adhéré). L'effet des nanoparticules FNA se traduit de la manière suivante :
 - a) Augmentation du nombre de dépôts de même taille, liée à l'augmentation de la teneur en FNA (pour la même température du gaz vecteur),
 - b) Augmentation de la taille des dépôts,

c) Possibilité de réaliser le dépôt de particules ayant une faible surface de contact.

Afin d'expliquer ces observations empiriques, le procédé IPD a été modélisé théoriquement. Il s'agit de déterminer la température des particules et la vitesse des particules à la sortie de la buse et pendant l'impact, à partir de leur histoire thermique et de leur évolution cinétique.

Le rendement du dépôt (fraction des particules adhérentes) et ses caractéristiques, qui dépendent notamment des propriétés mécaniques des particules polymères est évalué en extrapolant leur réponse contrainte-déformation à différentes températures et vitesse de déformation correspondant au procédé Cold-Spray. Dans cette partie l'évolution du comportement de l'UHMWPE pendant le temps de vol et au cours de l'impact est évaluée par le calcul et discutée sur la base des résultats expérimentaux.

L'effet des nanoparticules FNA sur l'adhésion des particules polymères est également discuté, en proposant un mécanisme d'interaction polymère-substrat et polymère-polymère. Les conclusions suivantes ont été tirées de l'étude :

- Les particules d'UHMWPE sont soumises à des vitesse d'échauffement de l'ordre de 10⁴ K/s, ce qui ne leur laisse pas le temps de fondre (elles restent dans un état cristallin hors-équilibre avant l'impact),
- 2. L'énergie élastique des particules UHMWPE diminue avec l'augmentation de la température du gaz et augmente à la vitesse croissante de déformation,
- Le rebond des particules d'UHMWPE sur la surface d'Al vient du fait qu'après impact, elles présentent une énergie d'adhésion (liaison interfaciale) plus faible que leur énergie de déformation élastique,
- 4. L'énergie d'adhésion des particules UHMWPE sur le substrat dépend de la surface de contact (mouillage) à l'interface particule-substrat. Des contributions supplémentaires telles que des liaisons H disponibles sur la surface les nanoparticules FNA sont suffisamment fortes au niveau de la surface de contact pour élargir la fenêtre "température vitesse" de dépôt à des températures plus faibles, fenêtre initialement (c'est-à-dire sans FNA) très réduite.

La partie suivante de ce travail se focalise sur l'interaction des particules UHMWPE avec la couche UHMWPE déjà déposée. Cette partie de l'étude porte spécifiquement sur la compréhension du mécanisme de soudage des grains UHMWPE, indispensable pour mener à bien la mise en œuvre par Cold-Spray. Deux paramètres importants, la pression interfaciale et la fraction en nanoparticules FNA sont considérées ici. Dans ce but, pour analyser leurs rôles respectifs sur d'une part les mécanismes de soudage et d'autre part l'obtention de porosité

dans les échantillons pulvérisés à froid, un nouvel ensemble d'échantillons a été préparé par frittage conventionnel dans une matrice de type piston-cylindre.

En faisant varier la contrainte interfaciale et la fraction de nanoparticules FNA, suivant trois protocoles différents : (i) frittage complet, (ii) "demi-frittage" (sous faible contrainte de compression) et (iii) "frittage libre" (c'est-à-dire sans contrainte appliquée). Parmi les outils de caractérisation utilisés dans ce travail, la tomographie par rayons X a permis d'identifier la fraction de porosité et les densités relatives des échantillons. Leur caractérisation mécanique a été effectuée pour identifier les paramètres fondamentaux impliqués dans la création des interfaces particules - particules.

La caractérisation morphologique et mécanique effectuée sur des échantillons frittés, "semifrittés" et "frittés-libres" confirme que le frittage est fortement influencé par la pression interfaciale et par la présence des nanoparticules FNA aux interfaces.

Tout d'abord, en examinant l'interface créée lors du frittage de deux particules UHMWPE naissantes (c'est-à-dire obtenue juste après polymérisation, telles qu'elles sont fournies par le fabriquant), il apparait clairement que lorsqu'elles atteignent leur point de fusion, qui s'accompagne du phénomène connu sous le nom de "fusion-explosion", l'interdiffusion des chaînes et leur enchevêtrement se produit à l'interface, permettant une forte adhésion entre particules en contact. La pression interfaciale lors du frittage diminue la porosité et augmente donc la densité relative du matériau fritté : une pression interfaciale plus faible conduit à une densité plus faible du matériau fritté. Le module d'élasticité expérimental macroscopique peut être prédit en utilisant un modèle de couplage mécanique (modèle de champ moyen) sur la base d'inclusions (vide) dans une matrice continue : le module calculé par l'équation de Kerner est en bon accord avec les données expérimentales.

D'autre part, les résultats obtenus sur des matériaux frittés et comportant des nanoparticules FNA indiquent des tendances opposées selon lorsqu'ils sont obtenus sous contraintes de compression élevées ou faibles. Il apparait qu'une pression interfaciale élevée est nécessaire pour incorporer les nanoparticules FNA dans la matrice polymère, ce qui favorise leur mouillage et un enchevêtrement plus complet aux interfaces particule - particule : ce phénomène contribue efficacement au renforcement de ces interfaces. Tout au contraire, une faible contrainte de compression lors du frittage conduit à la diminution des propriétés mécaniques du matériau (module et contrainte à la rupture) lorsqu'on augmente la teneur en FNA. A partir des résultats obtenus en tomographie aux rayons X, la densité relative diminue avec la teneur en FNA, ce qui suggère que la pression interfaciale, pendant le "demi-frittage", n'est pas suffisante pour permettre l'interdiffusion à l'interface entre particules polymères voisines.

De manière générale, une particule UHMWPE projetée n'adhère pas car son énergie cinétique est bien supérieure à l'énergie d'adhésion générée à l'interface UHMWPE - substrat ou UHMWPE - UHMWPE. A mesure qu'on ajoute des nanoparticules de FNA, des liaisons -OH

peuvent se former entre nanoparticules et contribuer à augmenter l'énergie de liaison. Pour environ 3 à 4% de FNA, la densité des liaisons -OH favorise la croissance du revêtement. On observe que l'efficacité du procédé Cold-Spray atteint son maximum pour 4% de FNA puis diminue : ce phénomène est expliqué à partir des expériences de frittage conventionnel.

Lors d'un dépôt effectué par Cold-Spray, il y a des zones où la pression interfaciale est élevée, faible ou nulle. Les expériences de frittage ont permis de comprendre la tendance générale induite par la pression interfaciale sur le frittage des grains de UHMWPE. Ainsi, la raison de la baisse de l'efficacité du dépôt au-delà de 4% s'explique principalement par le fait que la pression interfaciale générée par l'impact devient insuffisante pour incorporer les particules de FNA dans la matrice polymère et leur présence devient un frein à l'interdiffusion des chaines polymères à l'interface entre particules polymères en contact.

Enfin, le dernier chapitre de la thèse traite de l'effet de vitesses de déformation élevées de l'UHMWPE en utilisant des expériences de barre de compression de Split-Hopkinson (SHPB). Cette partie de l'étude discute en détail les effets possibles d'une compression à haute vitesse de déformation sur l'UHMWPE en analysant les courbes contrainte-déformation de celui-ci. L'étude porte sur les polymères purs ainsi que sur les formulations contenant des nanoparticules FNA. Ce chapitre présente une image générale de la réponse mécanique de l'UHMWPE sous des contraintes de plus en plus élevées. A vitesse croissante de déformation, l'UHMWPE montre une contrainte croissante au seuil de plasticité plus élevée. De plus, il est clair, au vu des courbes de compression que le taux de durcissement augmente également à vitesse de déformation croissante. Ce phénomène a d'ailleurs été pris en compte dans le chapitre 3, en plus de l'effet de la température (principe de superposition temps-température). Ce chapitre fournit les données mécaniques pertinentes pour le matériau considéré ici, l'UHMWPE ayant une masse molaire moyenne de 10,5 Mg/mol. De même, les réponses mécaniques des formulations contenant 0%, 4% et 10% de FNA sont également présentées.

La diminution du durcissement au-delà du seuil de plasticité observée pour 10% de FNA est probablement due à une température du nanocomposite plus élevée, toute chose égale par ailleurs.

Ce pourrait être la conséquence de l'abaissement de la valeur de la chaleur spécifique globale C_p du nanocomposite, due à la faible valeur de C_p des FNA comparée à celle de l'UHMWPE. Bien que les mécanismes moléculaires exacts du rôle des nanoparticules FNA, pouvant expliquer le comportement macroscopique de nos matériaux, ne peuvent être précisément décrits, l'ensemble des données expérimentales permet de spéculer sur leur rôle. Pour aller plus loin dans cette analyse, des expériences complémentaires doivent être menées, faisant varier le taux de déformation et de nanoparticules de FNA.



FOLIO ADMINISTRATIF

THESE DE L'UNIVERSITE DE LYON OPEREE AU SEIN DE L'INSA LYON

NOM : Ravi Prénoms : Kesavan

DATE de SOUTENANCE : 22/01/2018

TITRE : Mechanistic Understanding of High Strain Rate Impact Behavior of Ultra-High Molecular Weight Polyethylene and the Mechanism of Coating Formation During Cold Spraying

NATURE : Doctorat

Numéro d'ordre : 2018LYSEI008

Ecole doctorale : Ecole Doctorale Matériaux de Lyon

Spécialité : Science des Matériaux

RESUME :

Recent developments showed polymer coatings to be feasible by downstream injection cold spray technique on different surfaces (process known as Cold-Spray). This is especially important for ultrahigh molecular weight polymers which cannot be classically processed i.e. in the molten state or in solution, like Ultra-High Molecular Weight Polyethylene (UHMWPE). Its deposition on various substrate materials was demonstrated in which it was seen to be able to deposit due to the control of three major parameters; particle surface activity (by addition of hydrophilic polar alumina nanoparticles like fumed nanoalumina (FNA) to the particle surface), particle temperature and particle velocity. But the mechanisms behind deposition was not largely understood due to the complexities of the physical and chemical nature of the polymers at high strain-rates and high heating rates. Further, discussions on the criteria and effect of fumed nano alumina particles in the build-up of UHMWPE coatings have not been made yet. Systematic comparisons are performed with materials obtained by classical sintering under various pressure, temperature and time. The thesis presents a detailed mechanistic understanding of high strain rate impact behavior of Ultra-High Molecular Weight Polyethylene and the mechanism of coating formation on Al substrate during cold Spraying. The coating formation is first broken down in to two major categories: 1. Interaction of UHMWPE with Al substrate (impacting particle-deposited particles) leading to a buildup in the coating. Then, a general idea of high-strain rate mechanism specific to UHMWPE with already deposited UHMWPE particles (impacting particle-deposited particles) leading to a buildup in the coating. Then, a general idea of high-strain rate mechanism specific to UHMWPE material used in this study and an introduction to the strain-rate dependence of a UHMWPE FNA composite material is presented.

First stage of coating formation was understood from a technique specially developed for this work and called Isolated Particle Deposition (IPD) method and its theoretical simulation. In the experimental IPD process, effects of gas temperature and FNA content were carefully calibrated empirically by depositing UHMWPE particles in an isolated manner on an AI substrate. The Deposition efficiency was seen to show a distinctly unique increasing trends when gas temperature and FNA content in the feedstock were increased. Thanks to the use of an ultrafast video-camera, it was then possible to determine the particle velocity, and through theoretical calculations to evaluate the temperatures were understood by calculating elastic strain energy of UHMWPE which decreased with increasing material temperature and increased with the strain rate. Rebound of UHMWPE particles on AI surface depended upon whether UHMWPE particles after impact furnished a contact area with an interfacial bond stronger than elastic strain energy of the particle. The bonding of UHMWPE depended upon the extent of wetting at the particle-substrate interface. External contributions like H-bonds on the FNA surface provide sufficiently strong extra bonds at the contact surface to increase the window of deposition at higher temperatures, which was otherwise very low.

contact surface to increase the window of deposition at higher temperatures, which was otherwise very low. Second stage of coating formation was understood from the mechanism of welding of UHMWPE grains at different interfacial loading conditions and at varying FNA contents. The morphological and mechanical characterization showed that when UHMWPE was processed under high loading conditions (using classical sintering technique), FNA particles reinforced the UHMWPE interface. On the contrary, when UHMWPE was processed under low loading conditions, FNA particles weakened the interface.Last to be discussed in the thesis is the strain rate effect of UHMWPE using Split-Hopkinson Pressure Bar (SHPB) experiments, in order to approach comparable conditions to what happens during particle impacts. This part of the study discussed in detail the effects a high strain-rate compression has on UHMWPE by analyzing its stress-strain curves, with and without FNA. Thus, the mechanical response data with the inclusion 0%, 4% and 10% FNA to UHMWPE is also presented and discussed. Finally, this thesis presents a first approach understanding of high- strain rate deposition of UHMWPE on Al substrate and provides a foundation to further developing polymer coatings for structural and functional applications.

MOTS-CLÉS : Cold spray, UHMWPE, polymer

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RESUME :

Des travaux récents ont montré que des revêtements polymères étaient réalisables par une technique de pulvérisation à froid de particules sur différentes surfaces (procédé connu sous le nom de Cold-Spray). Ces travaux sont particulièrement importants pour les polymères de très hautes masses molaires qui ne peuvent pas être mis en forme par les méthodes conventionnelles (liquide fondu ou solution), comme pour le polyéthylène de très haute masse molaire (UHMWPE). Ainsi, on a montré que la qualité des dépôts d'UHMWPE sur divers substrats dépend essentiellement de trois paramètres majeurs, (i) la modification de la surface des particules (par l'ajout de nanoparticules d'alumine polaire hydrophile telle que "nanoalumine pyrogénée" ou FNA), (ii) la température des particules polymères et (iii) leur vitesse. Mais les mécanismes d'obtention des dépôts n'avaient pas été analysés, notamment en raison de leur complexité : en effet, ces mécanismes dépendent du comportement des polymères à des vitesses de déformation très élevées, soumis de plus à un échauffement ultra rapide. De plus, le rôle des nanoparticules FNA restait à comprendre. Cette thèse présente une analyse expérimentale mécanique détaillée du comportement à l'impact de particules d'UHMWPE et des mécanismes de formation du revêtement polymère sur un substrat en aluminium (AI) sous l'effet de la pulvérisation à froid de ces particules. La formation du revêtement se décompose en deux étapes : la première (1) se rapporte à la formation de la première couche de particules (interaction polymère-substrat), la deuxième (2) à la croissance (par ajout de couches successives) du revêtement polymère (interaction polymère-substrat), la deuxième (2) à la croissance (par ajout de couches successives) du revêtement polymèrement de polymère-polymère). Un troisième aspect traité ici se rapporte au rôle des nanoparticules FNA. Le comportement de l'UHMWPE sous vitesse très élevée, avec et sans FNA est pris en compte pour comprendre les phénomènes observés. La première étape de la formation du revêtement a été étudiée grâce à une technique expérimentale développée dans le cadre de cette thèse et appelée "Méthode de dépôt de particules isolées" (IPD), adossée à une modélisation théorique. Il s'agit de déposer des particules isolées de UHMWPE sur un substrat en Al, en utilisant la même machine Cold-Spray, tout en contrôlant de manière précise la température du gaz et la teneur en FNA. Grâce à l'utilisation d'une caméra rapide, il a été possible de déterminer la vitesse des particules d'UHMWPE et par le calcul d'évaluer leur température avant et pendant leur impact. L'efficacité (particules déposées / particules ayant rebondi) augmente avec d'une part la température et d'autre part la fraction de FNA. Cette efficacité dépend de la compétition entre l'énergie cinétique stockée sous forme d'énergie élastique Eel et l'énergie d'adhésion Ead du polymère à la surface du substrat. Ces deux termes dépendent des propriétés thermo-viscoélastiques de l'UHMWPE, le premier par la fraction d'énergie transformée en chaleur au cours de leur déformation plastique, et le deuxième par la surface de contact lors du choc, augmentant avec la température. Pour que le film polymère se forme, il faut que Ead > Eel. Par ailleurs, Ead dépend de l'interface entre polyéthylène et aluminium, et de la présence de FNA. Les liaisons H disponibles sur la surface des FNA contribuent à l'adhésion, ce qui augmente le domaine de température favorable à la réalisation du dépôt. Concernant la croissance du revêtement, il s'agit cette fois-ci de l'adhésion polyéthylènepolyéthylène, avec toujours l'effet des nanoparticules FNA. Les études microstructurales et mécanique ont montré qu'en frittage conventionnel du UHMWPE sous forte pression, l'ajout de FNA renforce la cohésion des matériaux obtenus, mais que l'effet inverse est observé pour un frittage incomplet (sous faible pression). Enfin, afin d'explorer l'effet de vitesse de sollicitation de l'UHMWPE comparable à celles observées pour le Cold-Spray, des expériences utilisant des barres dites de Split-Hopkinson (SHPB) ont été menées. Les courbes obtenues permettent de disposer d'une cartographie complète du comportement thermoviscoélasto-plastique de ce polymère, pur ou additionné de FNA.

Ce travail constitue une première approche pour comprendre les mécanismes de la formation de revêtements polymères par Cold-Spray, ce qui ouvre de nombreuses perspectives pour concevoir de nouveaux revêtements (fonctionnels, à porosité contrôlée, etc.), sur des surfaces variées (au contraire du frittage conventionnel).

MOTS-CLÉS : Cold spray, UHMWPE, polymer

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