# Ceramic and Polymeric Composite Materials used in Reinforcing UHMWPE for Improved Mechanical and Tribological Properties in Orthopedic Applications

Santosh K. Balivada<sup>\*</sup>, Gayathri Nayak, Chelsea Johnson, Syed J. Ahmed, Sathvik S. Appagana

Andhra Pradesh Medtech Zone, Visakhapatnam, Andhra Pradesh, India

# Received: 15th July, 2021; Revised: 08th November, 2022; Accepted: 26th November, 2022; Available Online: 10th December, 2022

# ABSTRACT

UHMWPE is a popular choice of biomaterial for joint replacements, particularly in hip, knee, and shoulder replacement procedures, notably as sliding material in between the load bearing surfaces due to its superior biocompatibility, tensile yield, impact strength, and high crystallinity. Even though it has good mechanical qualities, it has a relatively low wear resistance, which causes wear particles to shred and trigger immunological reactions and possibly osteolysis. This also has an impact on the implant's lifetime. The wear issue can be solved using a variety of approaches, including thermal therapy and antioxidant infusion. The mechanical qualities suffer as a result of these methods' efficacy in addressing tribological problems. One such way of reducing wear and oxidation rates while preserving mechanical characteristics is reinforcing the conventional UHMWPE with various composite materials. In this review the tensile and tribological properties of such ceramic and polymeric materials like zirconia, hydroxyapatite, carbon nanotube and graphene are evaluated. This review will investigate several ceramic and polymer-based fillers as an alternative to currently used methods such as improved radiation cross-linking and antioxidant treatment. CNT reinforced UHMWPE is still in the testing stage and is not yet on the market due to biocompatibility concerns. However, when compared to their competitors, their tribological properties are adequate but not exceptional. The best tensile properties are found in hydroxyapatite reinforced UHMWPE (but only at high concentrations such as 30wt%), followed by CNT. They do not have biocompatibility issues like CNT because of their structural similarity to natural bone. They also outperform CNT and ATZ composites in terms of tribological properties. As a result, they are best suited for reinforcement (with UHMWPE).

**Keywords:** Biomaterials, UHMWPE, Alumina, Zirconia, Hydroxyapatite, Carbon nanotube, graphene, composite materials, reinforcing materials, mechanical properties, tribological properties, orthopaedic applications.

International Journal of Health Technology and Innovation (2022)

**How to cite this article:** Balivada SK, Nayak G, Johnson C, Ahmed SJ, Appagana SS. Ceramic and Polymeric Composite Materials used in Reinforcing UHMWPE for Improved Mechanical and Tribological Properties in Orthopedic Applications. International Journal of Health Technology and Innovation. 2022;1(3):33-41.

Source of support: Nil.

Conflict of interest: None

# INTRODUCTION

Orthopaedic joint replacement surgeries around the world have a market share of around 20 billion USD as of 2019 and its usage is projected to increase rapidly at a rate of 7.6% annually. Out of which knee replacement alone constitutes 9.45 billion making hip, knee and shoulder most common among joint replacement surgeries. There is a wide choice of biomaterials used in the joints ranging from metals, bio-ceramics to synthetic polymers. However, synthetic polymers are usually preferred over others (like metals and bio ceramics) because unlike metals they have relatively lower wear and they are not as brittle as bio ceramics. Teflon was initially introduced as the choice of femoral head and acetabular cup in hip implants but was later proven to be ineffective.<sup>1</sup> Since, then many alternatives have been explored as bearing materials but UHMWPE stands out among the rest because of its excellent mechanical properties. Researchers have studied UHMWPE extensively over years to understand its properties of UHMWPE and figure 1 depicts the number of publications over years done on this topic.

A thermoplastic polymer with a molecular weight of 2-6 million g/mol ( $2-6*10^6$  g/mol), UHMWPE is made up of linearly branching ethylene units. It is produced utilizing the Zeigler process, which involves the massive polymerization of ethylene gas into UHMWPE resin powder. Later, a RAM extruder (to create rods) or a compress mould (into a sheet) are used to solidify this resin powder. Later, this prepared rod is machined by either milling (multi-point cutting) or turning into the desired shape (single-point cutting). After being machined, it is sterilized using gamma radiation in an inert environment, an electron beam, ethylene oxide, or gas



Publications on UHMWPE over the past 2 decades

Figure 1: Publications in total on UHMWPE from the year 2000

plasma, and it is then packed in an inert environment.<sup>2,3,4</sup> Therefore, the UHMWPE rod that was obtained is known as conventional or virgin UHMWPE.

It wasn't until the late 20th century until it became evident that osteolysis in individuals who had undergone implantation was caused by wear debris/particles created from the bearing materials. Although it has been demonstrated that crosslinking the polymer chains in virgin UHMWPE increases wear resistance in the bearing material, the results were unsatisfactory. By increasing density and using radiation cross linking to do so, the wear rate can be further decreased. During the irradiation process, C-C and C-H bonds are broken, causing the creation of free radicals. These radicals are then aggregated to provide an increased cross-linking density. A small number of the free radicals produced in the crystalline domains remain unbonded because not all of them are mobile enough to form bonds with other radicals. These free radicals (unbonded) result in early oxidation. Hence, they are either imparted with enough kinetic energy to make them mobile enough and bond to other free radical species or treated with radical scavengers like antioxidants (Vitamin E, PBHP, OBHC, IBHC) to eliminate them.

In this review, we will investigate several ceramic and polymer-based fillers as an alternative to currently used methods such as improved radiation cross-linking and antioxidant treatment. Composite materials are a heterogeneous combination of several components. The majority of naturally occurring biomaterials are composites, such as cartilage, bone, and dentin. The volume of the filler, the filler's shape, and the manufacturing conditions used to create the composite material all have an impact on the tensile and tribological properties of the material. They are made utilizing a variety of processes, including injection moulding, gel casting, compression moulding, and extrusion (ram & screw). A variety of techniques, including TEM (tunneling electron microscope), SEM (scanning electron microscope), DSC (differential scanning calorimetry), FTIR (Fourier Transform Infrared Spectroscopy), and others are used to characterize the composite once it has been created.<sup>5</sup> Utilizing a universal testing equipment, bend testing and small punch testing are performed in order to evaluate various mechanical qualities. To measure tribological parameters including wear volume and coefficient of friction, tribometers like pin on disc, pin on plate, and ball on disc are typically employed (which is calculated during the wear test as a function of sliding distance against different materials).

## **Orthopaedic Applications**

Numerous studies have found that UHMWPE offers an environment that is favourable for the development of cells including fibroblasts, osteoblasts, and macrophages. UHMWPE is employed in load-bearing applications in orthopaedics because to its superior tensile qualities and biocompatibility. Total hip arthroplasty (THA), Total knee arthroplasty (TKA), and Total shoulder replacement are the three most popular types of joint replacement (TSR). UHMWPE is employed as a plastic liner at the bone's articulation junction in each of these instances. Joint replacements are frequently redone due to wear particles ripped from the bearing material, even if they can be successful in some circumstances. Hips are ball-andsocket joints (acetabulum and femur) morphologically (where the hip has a concave socket at the pelvis called acetabulum). In THA, the damaged cartilage or bone is surgically replaced with artificial biomaterial, such as a metal or ceramic ball, a metal or titanium alloy stem, and a plastic liner that typically contains a low-friction and highly wear-resistant polymer (like UHMWPE). The humeral head is fitted into a glenoid cavity at the shoulder's ball and socket joint. In TSR surgery, the diseased cartilage or bone is surgically replaced with artificial biomaterial, such as a plastic liner typically made of polymer (like UHMWPE) with a low coefficient of friction and high wear resistance, and metal/ceramic-based ball and metal-based stem (steel and titanium alloys). Speaking of the knee, it is a hinge joint made up of the femur at the lower end, the tibia on top, and the patella on the back. In TKA, a diseased or damaged portion of the knee is replaced with an artificial biomaterial. Round, finished implants are attached to the femur to imitate the normal state of the bone, and the tibia component contains a stem that is inserted inside the bone.

### **Ceramic Based Fillers**

Ceramics are non-metallic powders of an inorganic type that are created from fine powdered ingredients, water, and a binder, then dried out using thermal treatment and thereafter subjected to sintering. Due to bad production practices, ceramics were fragile, but the development of current, cutting-edge fabrication techniques made them sturdy. A variety of ceramic materials, including mixed-oxide ceramics, bioactive ceramics, bioactive glasses, and bioactive bone cements, are employed in arthroplasty.<sup>6,7</sup> Because of their exceptional biocompatibility which results from their non-toxicity, non-inflammatory, and non-carcinogenic nature—they are employed in orthopaedics. They can be further divided into comparatively inert ceramics, which are nonabsorbable like alumina and zirconia, semiinert ceramics, which are bioactive like hydroxyapatite, and non-inert ceramics, which are biodegradable like calcium

Material Properties of Orthoplastics for Implant Manufacturing

Table 1. Comparison of incentanceal properties of various of twi with 2-ATZ composites							
Composite & concentration material	Mixing technique	Youngs modulus (E), Mpa	Strain at yield point, (Mpa)	Stress at the break, (Mpa)	Hardness (D)	Plasticity index (D/E)	Ref.
2.5 w.t% ATZ-UHMWPE	Ball milling	$620\pm47$	$20.2\pm2.7$	$42.2\pm2.4$	$69\pm1$	0.111	[9]
2.5 w.t% ATZ-UHMWPE	Turbula mixer	$537\pm36$	$20.2\pm1.8$	$49.2\pm5.0$	$65\pm1$	0.121	[10]
10 w.t% ATZ-UHMWPE	Turbula mixer	$541\pm23$	$17.0\pm0.1$	$35.5\pm1.4$	$67\pm2$	0.123	[10]
20 w.t% ATZ-UHMWPE	Turbula mixer	$636\pm37$	$19.5\pm1.0$	$36.0\pm3.1$	$66 \pm 1$	0.103	[10]

Table 1:	Com	parison	of mee	hanical	pro	perties	of	various	UHM	WPE-	ATZ	com	posite
			01 11100		P. 0	0010100	~.	10000	· · · · · ·			• • • • • •	000100

phosphate, depending on how inert they are.

# *(i). Relatively inert ceramics*

They are generally used for structural support in implants since they are wear resistant and corrosion resistant, hence their name inert ceramics. Examples include aluminum oxides and zirconia ceramics. They are used in femoral heads, bone plates, acetabular reconstruction and in ventilation tubes.

### Alumina toughened zirconia

Zirconia is frequently referred to as ceramic steel and has exceptional mechanical, chemical, and tissue compatibility qualities. Zirconia's use in load-bearing applications was made possible by the discovery of phase transformation toughening, or the transition from a stable monoclinic symmetry to a metastable tetragonal configuration.<sup>8</sup> Usually, divalent (MgO) or trivalent ( $Y_2O_3$ , Yttria) oxides are added (preferably, 3 wt% of  $Y_2O_3$ ) to stabilize it in tetragonal phase at ambient temperature and prevent it from reverting to its native monoclonal symmetry. Despite having remarkable load bearing and fracture resistant qualities, yttria stabilised zirconia is easily susceptible to the process known as "ageing," which occurs when it comes into contact with water in its tetragonal state.<sup>8</sup> Alumina hardened Zirconia is created by further combining it with Al<sub>2</sub>O<sub>3</sub> to slow down the pace of ageing (ATZ).

For mixing with ATZ resin powder, UHMWPE with an ideal mol. wt. of 3-6\*10<sup>6</sup> g/mol is preferred. Zirconia is vacuum dried and mixed with alumina (80 weight percent 3 mol yttria stabilized zirconia and 20 weight percent alumina). There are various mixing techniques available to aid the mixing process, such as wet mixing (the use of solvents such as ethanol) or dry mixing techniques (like ball milling and impact milling). The type of mixing method used in the preparation of UHMWPE/ ATZ composites has a significant impact on their mechanical properties because mixing techniques ensure the even distribution of filler composites.<sup>9</sup> Table 1 compares mechanical properties of various UHMWPE-ATZ composites at different concentrations. It was shown that zirconia distribution is relatively even if it is added in lesser concentrations like 2.5w.t% than compared to 5w.t%, 10w.t% and 20w.t% when mixed using dry mixing techniques, as mentioned already.<sup>10</sup>

### Mechanical properties

The effect of filler concentration on the composite material's Young's modulus is found to be linear. The Young's modulus increased slightly as the filler concentration increased (from 2.5 wt% to 20 wt% ATZ). Other properties, such as stress and strain at yield pattern, hardness, and plasticity index,

 
 Table 2: Comparison of tribological properties of various alumina zirconia combinations over UHMWPE composites

		1	
Composite & concentration material	Frictional coefficient	Wear rate (mm <sup>3</sup> /N m)	Ref.
Al <sub>2</sub> O <sub>3</sub>	0.39	105*10 <sup>-7</sup>	[11]
Al <sub>2</sub> O <sub>3</sub> -nZrO <sub>2</sub>	0.25	14.5*10 <sup>-7</sup>	[11]
Al <sub>2</sub> O <sub>3</sub> -nZrO <sub>2</sub> /Nb	0.22	6.7*10 <sup>-7</sup>	[11]

follow a different pattern, in which they initially increase (when the filler concentration is increased from 2.5 wt% to 10 wt% ATZ) and then decrease (when the filler concentration is increased further).<sup>10</sup> Aside from the amount of filler used, the mixing technique used has a significant impact on the overall mechanical properties because mixing ensures uniform distribution of the filler in the polymer, which aids in overall strengthening of the composite material. the composites were prepared using a blender (turbula mixer) yielding in poor tensile properties even at higher concentrations of fillers like 20 w.t%. Surprisingly, the fillers that are prepared using ball milling even at a filler concentration as low as 2.5 w.t % had almost similar Young's modulus and even better hardness and plasticity index than compared to composite prepared by using blender with filler concentration of 20 w.t%.<sup>9</sup>

### Tribological properties

Table 2 compares tribological properties of various alumina zirconia combinations over UHMWPE composites. The addition of a lubricating layer at the articulation junction, typically composed of ceramic on metal (COM), ceramic on polymer (COP), or ceramic on ceramic (COC), is one way to improve tribology using conventional UHMWPE. A lubricating layer applied to the polymer counter face reduces friction and wear volume. Niobium was chosen as a lubricant in the current study.<sup>11</sup> because it is bio-compatible and resistant to crack propagation. When discs made of alumina, ATZ, and niobium coated ATZ were allowed to slide against a load material (made of UHMWPE polymer) in a tribometer to evaluate tribology, they showed lower wear rate and frictional coefficient. This is due to the to the change in the grain boundary between ATZ and UHMWPE matrix, any stress that is generated due to the sliding motion are transferred to the lubricant that is in between the ceramic and polymer (as in case of COP)

#### Semi-inert ceramics

Also called as bio active ceramics, are the ceramic material that are capable of interacting with the living tissue and assist in

Material Properties of Orthoplastics for Implant Manufacturing

Table 3: Comparison of mechanical properties of various UHMWPE-hydroxyapatite composites						
Composite & concentration material	Preparation technique	Youngs modulus (E), Mpa	Yield strength (MPa)	Ref.		
UHMWPE / HA 10 w.t%	Swelling treatment followed by hot pressing	$568\pm46$	$17.46\pm0.4$	[14]		
UHMWPE / HA 10 w.t% / 0.1 w.t% GNP	Swelling treatment followed by hot pressing	$712 \pm 32$	$18.45\pm0.6$	[14]		
UHMWPE / HA 10 w.t% / 1.0 w.t% GNP	Swelling treatment followed by hot pressing	$861\pm93$	$18.93 \pm 0.9$	[14]		
UHMWPE / HA 30 w.t%	Without Ball milling and swelling treatment followed by hot pressing Ball milling and swelling treatment followed by hot pressing	$1364 \pm 78$	$8.6\pm0.4$	[15]		
UHMWPE / HA 30 w.t%	Swelling treatment followed by twin screw extrusion into pellets that are further compression molded	$1633 \pm 73$	$12.0 \pm .4$	[15]		
UHMWPE / HA 50 w.t%		$8000\pm800$	28.4 ± 1.6	[16]		

Table 3+	Comparison	of mechanical	properties of v	various I	IHMWPF_	hydroxyanatite	composite
rabic 5.	Comparison	of incentational	properties of v	various v		nyuroxyapanie	composite

Table 4: Comparison of tribological properties of various UHMWPE-hydroxyapatite composites

Composite & concentration material	Coefficient of friction	Wear rate (10 <sup>-6</sup> ) $m^3$	Wear volume (mm <sup>3</sup> )	Ref.
UHMWPE / HA 7 w.t%	$0.092\pm0.003$	0.056		[17]
UHMWPE / nano-HA 10 w.t%	0.070		0.40	[10]
UHMWPE / micro-HA 15 w.t%	0.080		0.40	[10]
UHMWPE / HA 10 w.t% / 0.1 w.t % GNP	0.082		0.38	[18]
UHMWPE / HA 10 w.t% / 1.0 w.t % GNP	0.077	0.310		[14]
		0.130		[14]
UHMWPE / HA 20 w.t%	0.055		0.0075	[19]
UHMWPE / HA 20 w.t% / BO 10 w.t%	0.035		0.0040	[19]

repairing them. Hydroxyapatite (HA) is a prominent member of this category owing to its ability in osteo-conduction.

# Hydroxyapatite

Because of its structural similarity to natural bone, hydroxyapatite is widely used in medical applications,<sup>12</sup> particularly as fillers in orthopaedic load bearing applications due to its superior biocompatibility. Despite its excellent biocompatibility, it has poor mechanical properties, so it is reinforced with a polymer with better mechanical properties, such as UHMWPE. There have previously been numerous attempts to develop HA composites so that the resulting composite material has superior mechanical properties without sacrificing biocompatibility and tribological properties. Because HA and UHMWPE interact poorly with each other, many strategies such as the addition of stabilizers and surface modification were used to improve the affinity. Many stabilizers, such as organophilic montmorillonite (Organophilic Bentonite, BO), have been used to make HA compatible with UHMWPE.<sup>13</sup> Because of its swelling and adsorption properties, bentonite is commonly used in drug delivery systems. When bentonite is combined with an organic molecule to increase its affinity for organic molecules, as in many biomedical applications, the result is known as Organophilic Bentonite. Furthermore, mixing techniques such as ball milling have been used to ensure uniform distribution and reduce particle size, thereby increasing total surface area and assisting in better load transfer. The composites can be prepared using both wet and dry mixing techniques. Other peer

Material Properties of Orthoplastics for Implant Manufacturing

Table 5:         Comparison of mechanical properties of various UHMWPE-CNT composites						
Composite & concentration material	Composite preparation technique	Young's Modulus (MPa) ±SD (*SD = Standard Deviation)	Yield stress (MPa) ±SD	Ultimate tensile strength (MPa) ±SD	Ref.	
0.01 w.t% SWCNT- UHMWPE	Ultrasonication and hydraulic pressing	$1699.03 \pm 10.86$	$19.20\pm0.11$	$35.20 \pm 1.60$	[26]	
0.1w.t% SWCNT- UHMWPE	Ultrasonication and hydraulic pressing	$1739.83 \pm 5.86$	$28.00 \pm 0.11$	$51.20\pm0.78$	[26]	
1w.t% MWCNT-UHMWPE	Solution casting	$1352.3 \pm 40.70$	$12.38\pm0.84$		[28]	

fillers, such as GNP, are sometimes used in conjunction with HA to reinforce UHMWPE. Furthermore, swelling treatment has been found to be effective in facilitating uniform dispersion of the filler in the polymer as it reduces swelling. Sometimes, other peer fillers like GNP are also used in together with HA to reinforce UHMWPE. In addition, swelling treatment is found to be effective in easing uniform dispersion of the filler in the polymer as it reduces the viscosity and improves the chain mobility of the polymer.

# Mechanical properties

Table 3 compares mechanical properties of several UHMWPEhydroxyapatite composites. The effect of HA on the mechanical strength of the composite is dependent not only on the amount of filler used and the type of treatment used in the preparation of the composite, but also on the mixing technique used (such as ball milling). Mixing techniques not only aid in better dispersion but also significantly reduce the size of the filler particles (HA), allowing for more surface area and thus better load transfer. Fillers that have been ball milled have a 19% higher Young's modulus and a 39% higher yield strength than those that have not been mixed (that have undergone the same conc. processing conditions with the same concentrations.<sup>15</sup> When it comes to the amount of filler added to the composite, it has a positive effect (linear dependency between the amount of filler added to the polymer and the mechanical strength of the composite) on its strength.<sup>16</sup> When the filler concentration was increased from 10% to 50% HA, the Young's modulus increased from 568 to 8000 MPa. Within the same concentration range, the yield strength nearly doubled. When HA is added in higher concentrations (such as 50 wt%), the Young's modulus of the composite increases dramatically.<sup>16</sup> These values are nearly identical to cortical bone values, but the coefficient of friction and tribological properties are inferior. As a result, other fillers with excellent tribological properties, such as GNP (graphene nano platelets), are added in low concentrations to the polymer alongside HA. However, the optimum HA concentration range for reinforcement purposes has been determined to be 10-20 wt%.

# Tribological properties

Table 4 compares tribological properties of UHMWPEhydroxyapatite composites at different concentrations. The tribological properties of a composite material are influenced not only by the amount of filler added to the polymer, but also by the particle size of the filler.<sup>18</sup> The optimal amount of filler for micro-sized HA required for reinforcing was determined

to be 15% by weight. However, it was only 10% for nano-sized HA. In terms of the effect of filler concentration on properties such as coefficient of friction, wear rate and wear volume decrease significantly as filler concentration increases. From 7 wt% HA to 20 wt% HA, the coefficient of friction decreased from 0.092 to 0.055.<sup>17,19</sup> Although the coefficient of friction is better at lower HA concentrations (such as 10 wt%) when compared to virgin UHMWPE, other tribological properties such as wear rate and wear volume are not satisfactory. To address this issue, other fillers (such as GNP) are added to the polymer alongside HA (at concentrations less than or equal to 10 wt% HA).<sup>14</sup> When compared to HA alone and HA combined with GNP, adding BO to HA resulted in a lower coefficient of friction because BO acted as a thin line of interface for better load transfer.19

# (iii). Non inert ceramics

They are also known as resorbable ceramics because the implants made of them degrade and are replaced by endogenous tissue over time. Tricalcium phosphate is a well-known resorbable ceramic.

# **Polymer based fillers**

Polymeric (synthetic) biomaterials have an advantage over ceramic biomaterials in terms of shape-ability (film, sheet, fibre). Carbon-based nanoparticles, in particular, have excellent physical, chemical, and mechanical properties, making them an appealing choice of implant material in orthopaedics. Recent advances in various fabrication and modification techniques such as chemical vapour deposition, arc-discharge deposition, laser vaporization deposition, and ion beam assisted deposition have resulted in an exponential increase in evaluating the biomedical applications of carbon nanotubes (SWCNT, MWCNT) and carbon nano-structured diamond.<sup>20</sup>

# Carbon nanotube (CNT)

Carbon nanotubes are made up of sheet-like six-membered carbon rings that are rolled up (either arm chaired or zig-zag) to form cylinders that can be single or multi-walled depending on the number of concentric layers surrounding them. They are commonly manufactured using Laser Ablation (graphite), Chemical Vapor Deposition (hydrocarbons), or Arc Vaporization (carbon rods). As a result of their high hydrophobicity, low biocompatibility, and high toxicity, prepared CNTs are unsuitable for medical applications. Depending on the interacting biomolecules, they are functionalized by oxidizing them with strong acids and conjugating them with amino acids,

Material Proper	rties of Or	thoplastics for	·Implant	Manufactur	ing
-----------------	-------------	-----------------	----------	------------	-----

Table 6: Comparison of tribological properties of various UHMWPE
CNT composites

crist composited						
Composite & concentration material	Wear rate (10 <sup>-6</sup> ) mm <sup>3</sup> /nm	Coefficient of friction	Ref.			
0.5 w.t% MWCNT- UHMWPE	0.35	0.12	[27]			
1w.t% MWCNT- UHMWPE	0.30	0.096	[27]			

or by coating them with amphiphilic molecules (like PEG, Poly Ethylene Glycol).<sup>21</sup> Today, their applications are being vigorously researched in a variety of biomedical engineering disciplines (imaging diagnostics, tissue engineering, drug delivery, and biosensors).<sup>22</sup> CNTs were introduced into the field of biomaterials due to their excellent mechanical, thermal, and electrical properties, as well as their durability. Despite numerous reports supporting CNT cytotoxicity and carcinogenicity on cells, their biocompatibility is being called into question. It has been demonstrated that different cell types respond dynamically to CNTs based on cell type, diameter (number of walls), chirality, and length. CNTs, on the other hand, promote osteocyte proliferation and calcification in bone cells. They are currently being studied as scaffolds for tissue regeneration due to their morphological (structural) similarity to commercially available scaffolds such as Tricalcium phosphate (TCP) and Hydroxyapatite (HA), as well as as a composite material with Poly Methyl Metha Acrylate (bone cement) due to their affinity for bone tissues.<sup>23</sup> UHMWPE is first dissolved in ethanol (which is later removed using vacuum filtration), and then SWCNTs produced through ultrasonication and hydraulic pressing (with an ideal diameter of 1-2 nm and a length of 5-30 m) are ultrasonicated into it for better dispersion before compression moulding.<sup>24</sup> A similar protocol is used to prepare MWCNT.<sup>25</sup>

Mechanical properties

Table 5 compares mechanical properties of various UHMWPE-CNT composites at distinct concentrations. CNTs have a high elastic modulus of 1 TPa and tensile strengths ranging from 30 to 100 GPa, making them an excellent candidate for reinforcement. Stress-strain curves and tensile testing are used to evaluate the mechanical behaviour of UHMWPE-CNTs composites. SWCNTs are known for their unusual behaviour because they are made up of a single layer, as opposed to MWCNTs, which have many layers wrapped around them. In comparison to 0.01% and 0.1% CNT, 0.1% CNT has higher young's modulus, ultimate tensile strength, and yield stress.

#### Tribological properties

Table 6 compares the tribological properties of various UHMWPE-CNT composites. The wear rate of CNT-UHMWPE composite reduced when added in 1w.t%, contrary to the mechanical properties where 1w.t% yielded lower properties in tribological aspect it has better wear rate and coefficient of friction than compared to 0.5w.t%. This is due to structural changes but not shear strength.<sup>27</sup>

### Graphene

Graphene is made up of a single layer of carbon atoms that are arranged in a two-dimensional pattern, as opposed to graphite, which has multiple layers of carbon atoms. Because of their larger surface area, they have better load transfer than CNTs. Due to its excellent mechanical, chemical, and electronic properties, graphene has a wide range of applications in biomedical,<sup>29</sup> electronics, membrane technologies, and composite coatings. It has an elastic modulus of 1TPa (Tera Pascal) and an intrinsic strength of approximately 130 GPa (Gigapascal), for example, which is why it is used as a composite material in UHMWPE to improve wear resistance and other mechanical properties.<sup>30,31</sup> Graphene-based UHMWPE composites can be prepared in a variety of ways, depending on the type of graphene used. Ball milling, for

Composite & concentration material	Composite preparation technique	Young's Modulus (MPa) ±SD (*SD = Standard Deviation)	Yield stress (MPa) ±SD	Ultimate tensile strength (MPa) ±SD	Ref.
0.1 w.t% GO UHMWPE	Ball milling	$634.75\pm30.59$	23.86±0.92	33.51±4.05	[32]
0.1w.t% GNP-UHMWPE	Liquid phase (acetone) ultrasonication	$690 \pm 20$	$35 \pm 1.4$	77 ± 3.1	[33]
	Ball milling				
0.5 w.t% GO-UHMWPE	Liquid phase	$664.38 \pm 28.32$	$24.57\pm1.19$	$36.91\pm3.98$	[32]
0.5 w.t% GNP-UHMWPE	(ethanol) ultrasonication	$770.4\pm9.0$	$14.30\pm0.40$	$20.60 \pm 1.10$	[34]
1 w.t% GO-UHMWPE	Ball milling	644.26±29.40	23.97±1.13	33.12±4.09	[32]
1 w.t% GNP-UHMWPE	Liquid phase (acetone) ultrasonication	1190 ± 80	42 ± 2.1	$68 \pm 3.4$	[33]

 Table 7: Comparison of tensile properties of various UHMWPE-graphene composites

Table 8: Comparison of	of tribological propert	ies of various U	JHMWPE-
	graphene composite	s	

Composite & concentration material	Coefficient of friction	Wear rate (10 <sup>-6</sup> ) mm <sup>3</sup> /Nm	Ref.
0.1 w.t% RGO-UHMWPE	0.068	550	[35]
1.0 w.t% RGO-UHMWPE	0.062	800	[35]
3.0 w.t% RGO-UHMWPE	0.036	200	[35]

example, is used to prepare graphene oxide (GO)-UHMWPE composites. When GO is reduced to form reduced graphene oxide (RGO), it is mixed with UHMWPE. While Graphene nano platelets (GNP)-UHMWPE composites are prepared by mechanical exfoliation of graphite, the suspension is then coated over UHMWPE using electrostatic spraying (ESP). GO and RGO are typically preferred over others due to their superior hydrophilicity and low-cost synthesis methods.

# Mechanical properties

Table 7 compares tensile properties of various UHMWPEgraphene composites at varying concentrations. Because of its high intrinsic strength and elastic modulus, graphene as a filler improves wear resistance in composites. Tensile properties such as Young's modulus, yield stress, and ultimate tensile strength are the three major mechanical properties that are evaluated using tensile testing, which is done using a tensile machine that produces stress strain curves. All mechanical property parameters are derived from stress strain curves. The mechanical properties of various graphene materials at various concentrations that are combined with UHMWPE using various mixing techniques are listed in the table below. The amount of graphene fillers added matters because mechanical properties tend to decrease with increasing filler content after a certain amount. Even the processes that the material went through are directly reflected in its mechanical properties. When it comes to GO, its peak Young's modulus, yield stress, and ultimate tensile strength are achieved at 0.5 wt%, after which they decrease. GNP 1 wt% has better overall tensile properties than other concentrations. Tensile properties tend to decrease beyond 0.5 wt% GO and 1 wt% GNP. As a result, these concentrations are thought to be optimal for reinforcing UHMWPE.

### Tribological properties

Table 8 compares tribological properties of various UHMWPEgraphene composites. Reduced Graphene Oxide (RGO) is obtained by reducing graphene in order to prevent graphene oxide aggregation during hot pressing. It is added in various concentrations ranging from 0.1 to 3.0 wt% to determine the smallest concentration with the best properties. Tribological properties are evaluated using de-ionized water. RGO filler performed better at higher loading concentrations. For example, 3 wt% RGO-UHMWPE has the lowest coefficient of friction, making it tribologically superior to 0.1% and 1% RGO concentrations in UHMWPE.

### **Summary and Future Prospects**

CNTs stand out in mechanical properties due to their exceptional tensile properties, which they induce into the composite material even at very low concentrations such as 0.01 wt% and 0.1 wt%. Because of issues with biocompatibility, CNT reinforced UHMWPE is still in the testing stage and is not yet on the market. However, their tribological properties are adequate but not exceptional when compared to their competitors. Hydroxyapatite reinforced UHMWPE has the best tensile properties (but only at high concentrations such as 30wt%), followed by CNT. Because of their structural similarity to natural bone, they do not have biocompatibility issues like CNT. They also have superior tribological properties to CNT and ATZ composites. As a result, they are best suited for reinforcing purposes (with UHMWPE).

As more patients require joint replacement surgery, the orthopaedic community is looking for new biomaterials that will help artificial joints last longer. Polymer nanocomposites have demonstrated the ability to improve the wear behaviour of virgin UHMWPE in orthopaedic implants through the use of selected fillers.

# DECLARATION OF COMPETING INTEREST

The authors declare that no work in this paper is influenced by any financial interests or personal relationships.

### ACKNOWLEDGEMENTS

We would like to acknowledge the support of Center of excellence in Additive Manufacturing which is an integral part of Andhra Pradesh Med Tech Zone (AMTZ) ecosystem and would like to extend our special thanks to Medi Valley Incubation Center (MVIC) for their constant moral support.

### REFERENCES

- Steven M. Kurtz, Chapter 4 The Origins of UHMWPE in Total Hip Arthroplasty, Editor(s): Steven M. Kurtz, UHMWPE Biomaterials Handbook (Second Edition), Academic Press, 2009, Pages 31-41, ISBN 9780123747211, https://doi.org/10.1016/B978-0-12-374721-1.00004-3.
- Melissa Machado Rodrigues, Cristian Padilha Fontoura, Charlene Silvestrin Celi Garcia, Sandro Tomaz Martins, João Antonio Pêgas Henriques, Carlos Alejandro Figueroa, Mariana Roesch-Ely, Cesar Aguzzoli, Investigation of plasma treatment on UHMWPE surfaces: Impact on physicochemical properties, sterilization and fibroblastic adhesion, Materials Science and Engineering: C, Volume 102, 2019, Pages 264-275, ISSN 0928-4931, https://doi.org/10.1016/j.msec.2019.04.048.
- Deng, M., & Shalaby, S. W. (2001). Long-term gamma irradiation effects on ultrahigh molecular weight polyethylene. Journal of biomedical materials research, 54(3), 428–435. https://doi.org/10.1002/1097-4636(20010305)54:3<428::aidjbm170>3.0.co;2-4
- 4. Dai D, Shi M. Effects of electron beam irradiation on structure and properties of ultra-high molecular weight polyethylene fiber. Journal of Industrial Textiles. 2018;47(6):1357-1377. doi:10.1177/1528083717690612
- Stephen Spiegelberg, Adam Kozak, Gavin Braithwaite, 29
   Characterization of Physical, Chemical, and Mechanical

Properties of UHMWPE, Editor(s): Steven M. Kurtz, UHMWPE Biomaterials Handbook (Third Edition), William Andrew Publishing, 2016, Pages 531-552, ISBN 9780323354011, https:// doi.org/10.1016/B978-0-323-35401-1.00029-6.

- dos Santos V., Brandalise R.N., Savaris M. (2017) Ceramic Biomaterials. In: Engineering of Biomaterials. Topics in Mining, Metallurgy and Materials Engineering. Springer, Cham. https:// doi.org/10.1007/978-3-319-58607-6
- Prakash L. Ceramics in Arthroplasty, Arthritis and Orthopaedics. Res Arthritis Bone Study. 1(1). RABS.000504.2018. 4/4,
- Chevalier, Jérôme and Laurent Grémillard. "1.6 Zirconia as a Biomaterial." Comprehensive Biomaterials 1 (2017): 122-144. https://doi.org/10.1016/B978-0-12-803581-8.10245-0
- D. Duraccio, V. Strongone, M.G. Faga, F. Auriemma, F.D. Mussano, T. Genova, G. Malucelli, The role of different dry-mixing techniques on the mechanical and biological behavior of UHMWPE/alumina-zirconia composites for biomedical applications, European Polymer Journal, Volume 120, 2019, 109274, ISSN 0014-3057, https://doi.org/10.1016/j. eurpolymj.2019.109274.
- Kevin Plumlee, Christian J. Schwartz, Improved wear resistance of orthopaedic UHMWPE by reinforcement with zirconium particles, Wear, Volume 267, Issues 5–8, 2009, Pages 710-717, ISSN 0043-1648, https://doi.org/10.1016/j.wear.2008.11.028.
- Gutiérrez-González, C. & Bartolomé, Jose. (2013). Tribological behavior of a novel alumina/nano-zirconia/niobium biocomposite against ultra-high molecular weight polyethylene. Wear. 303. 211–215. https://10.1016/j.wear.2013.03.015.
- Rajan M., Sumathra M. (2019) Biomedical Applications of Hydroxyapatite Nanocomposites. In: Sadasivuni K., Ponnamma D., Rajan M., Ahmed B., Al-Maadeed M. (eds) Polymer Nanocomposites in Biomedical Engineering. Lecture Notes in Bioengineering. Springer, Cham. https://doi.org/10.1007/978-3-030-04741-2 6
- 13. Domingos Lusitâneo Pier Macuvele, Guilherme Colla, Karina Cesca, Luiz F.B. Ribeiro, César E. da Costa, Janaína Nones, Everton R. Breitenbach, Luismar M. Porto, Cíntia Soares, Márcio Antônio Fiori, Humberto Gracher Riella, UHMWPE/HA biocomposite compatibilized by organophilic montmorillonite: An evaluation of the mechanical-tribological properties and its hemocompatibility and performance in simulated blood fluid, Materials Science and Engineering: C, Volume 100, 2019, Pages 411-423, ISSN 0928-4931, https://doi.org/10.1016/j.msec.2019.02.102.
- 14. Sara Mohseni Taromsari, Meysam Salari, Reza Bagheri, Mohammad Ali Faghihi Sani, optimizing tribological, tensile & in-vitro biofunctional properties of UHMWPE based nanocomposites with simultaneous incorporation of graphene nanoplatelets (GNP) & hydroxyapatite (HAp) via a facile approach for biomedical applications, Composites Part B: Engineering, Volume 175, 2019, 107181, ISSN 1359-8368, https:// doi.org/10.1016/j.compositesb.2019.107181.
- Liming Fang, Yang Leng, Ping Gao, Processing of hydroxyapatite reinforced ultrahigh molecular weight polyethylene for biomedical applications, Biomaterials, Volume 26, Issue 17, 2005, Pages 3471-3478, ISSN 0142-9612, https://doi.org/10.1016/j. biomaterials.2004.09.022.
- Liming Fang, Yang Leng, Ping Gao, Processing and mechanical properties of HA/UHMWPE nanocomposites, Biomaterials, Volume 27, Issue 20, 2006, Pages 3701-3707, ISSN 0142-9612,

https://doi.org/10.1016/j.biomaterials.2006.02.023.

- Xiong, L., Xiong, D., Yang, Y., & Jin, J. (2011). Friction, wear, and tensile properties of vacuum hot pressing crosslinked UHMWPE/nano-HAP composites. Journal of biomedical materials research. Part B, Applied biomaterials, 98(1), 127–138. https://doi.org/10.1002/jbm.b.31842
- Kang, Xueqin & Zhang, Wei & Yang, Chunmin. (2015). Mechanical properties study of micro- and nano-hydroxyapatite reinforced ultrahigh molecular weight polyethylene composites. Journal of Applied Polymer Science. 133. n/a-n/a. 10.1002/ app.42869. https://doi.org/10.1002/app.42869
- 19. Nayak, C., Ariharan, S., Kushram, P., & Balani, K. (2019). Fretting of Aluminum Oxide, Hydroxyapatite and Carbon Nanotubes Reinforced Ultra High Molecular Weight Polyethylene.
- 20. Domingos Lusitâneo Pier Macuvele, Guilherme Colla, Karina Cesca, Luiz F.B. Ribeiro, César E. da Costa, Janaína Nones, Everton R. Breitenbach, Luismar M. Porto, Cíntia Soares, Márcio Antônio Fiori, Humberto Gracher Riella. UHMWPE/HA biocomposite compatibilized by organophilic montmorillonite: An evaluation of the mechanical-tribological properties and its hemocompatibility and performance in simulated blood fluid, Materials Science and Engineering: C, Volume 100, 2019, Pages 411-423, ISSN 0928-4931, https://doi.org/10.1016/j.msec.2019.02.102.
- P.E. Mikael, J.A. Wallace, S.P. Nukavarapu, 16 Nanotubes for tissue engineering, Editor(s): Thomas J. Webster, In Woodhead Publishing Series in Biomaterials, Nanomedicine, Woodhead Publishing, 2012, Pages 460-489, ISBN 9780857092335, https:// doi.org/10.1533/9780857096449.3.460.
- Yang, L., Zhang, L., & Webster, T. J. (2011). Carbon nanostructures for orthopedic medical applications. Nanomedicine (London, England), 6(7), 1231–1244. https://doi.org/10.2217/nnm.11.107
- He, H., Pham-Huy, L. A., Dramou, P., Xiao, D., Zuo, P., & Pham-Huy, C. (2013). Carbon nanotubes: applications in pharmacy and medicine. BioMed research international, 2013, 578290. https:// doi.org/10.1155/2013/578290
- Simon, J., Flahaut, E., & Golzio, M. (2019). Overview of Carbon Nanotubes for Biomedical Applications. Materials (Basel, Switzerland), 12(4), 624. https://doi.org/10.3390/ma12040624
- Kaoru Aoki, K. Aoki, Nobuhide Ogihara, N. Ogihara, Manabu Tanaka, M. Tanaka, Hisao Haniu, H. Haniu, & Naoto Saito, N. Saito. (2020). Carbon nanotube-based biomaterials for orthopaedic applications. Journal of materials chemistry B, 8, 9227-9238. doi: 10.1039/d0tb01440k
- 26. José M. Diabb Zavala, Héctor Manuel Leija Gutiérrez, Emmanuel Segura-Cárdenas, Narsimha Mamidi, Rodolfo Morales-Avalos, Javier Villela-Castrejón, Alex Elías-Zúñiga, Manufacture and mechanical properties of knee implants using SWCNTs/ UHMWPE composites, Journal of the Mechanical Behavior of Biomedical Materials, Volume 120, 2021, 104554, ISSN 1751-6161, https://doi.org/10.1016/j.jmbbm.2021.104554.
- Silvia Suñer, Catherine L Bladen, Nicholas Gowland, Joanne L Tipper, Nazanin Emami, Investigation of wear and wear particles from a UHMWPE/multi-walled carbon nanotube nanocomposite for total joint replacements, Wear, Volume 317, Issues 1–2, 2014, Pages 163-169, ISSN 0043-1648, https://doi.org/10.1016/j. wear.2014.05.014.
- 28. S.L. Ruan, P. Gao, X.G. Yang, T.X. Yu, toughening high performance ultrahigh molecular weight polyethylene using multiwalled carbon nanotubes, Polymer, Volume 44, Issue 19,

2003, Pages 5643-5654, ISSN 0032-3861, https://doi.org/10.1016/ S0032-3861(03)00628-1.

- Puértolas, J. A., & Kurtz, S. M. (2014). Evaluation of carbon nanotubes and graphene as reinforcements for UHMWPE-based composites in arthroplastic applications: A review. Journal of the mechanical behavior of biomedical materials, 39, 129–145. https://doi.org/10.1016/j.jmbbm.2014.06.013
- A. Chih, A. Ansón-Casaos, J.A. Puértolas, Frictional and mechanical behaviour of graphene/UHMWPE composite coatings, Tribology International, Volume 116, 2017, Pages 295-302, ISSN 0301-679X, https://doi.org/10.1016/j. triboint.2017.07.027.
- M.J. Martínez-Morlanes, F.J. Pascual, G. Guerin, J.A. Puértolas, Influence of processing conditions on microstructural, mechanical and tribological properties of graphene nanoplatelet reinforced UHMWPE, Journal of the Mechanical Behavior of Biomedical Materials, Volume 115, 2021, 104248, ISSN 1751-6161, https://doi.org/10.1016/j.jmbbm.2020.104248.
- 32. Pang, Wenchao & Ni, Zifeng & Chen, Guomei & Huang,

Guodong & Huang, Huadong & Zhao, Yongwu. (2015). Mechanical and thermal properties of graphene oxide/ultrahigh molecular weight polyethylene nanocomposites. RSC Adv 5. https://doi.org/10.1039/C5RA11826C.

- Lahiri, D., Dua, R., Zhang, C., de Socarraz-Novoa, I., Bhat, A., Ramaswamy, S., & Agarwal, A. (2012). Graphene nanoplateletinduced strengthening of ultrahigh molecular weight polyethylene and biocompatibility in vitro. ACS applied materials & interfaces, 4(4), 2234–2241. https://doi.org/10.1021/am300244s
- Alam, Fahad & Choosri, M. & Gupta, Dr. Tejendra & Varadarajan, Kartik & Choi, Daniel & Kumar, S. (2019). Electrical, mechanical and thermal properties of graphene nanoplatelets reinforced UHMWPE nanocomposites. Materials Science and Engineering: B. 241. 82-91. https://doi.org/10.1016/j.mseb.2019.02.011.
- 35. Mindivan, Ferda & Göktaş, Meryem & Çolak, Alime. (2019). DRY WEAR STUDIES ON REDUCED GRAPHENE OXIDE FILLED UHMWPE COMPOSITES. Proceedings on Engineering Sciences. 1. 10.24874/PES01.01.089.