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Ultra High Molecular Weight Polyethylene/Graphene Oxide Nanocomposites: Thermal, Mechanical and Wettability Characterisation

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Abstract

Ultra high molecular weight polyethylene (UHMWPE) is the material most commonly used among hard-on-soft bearings in artificial joints. However, the eventual failure of joint implants has been directly related to the wear and oxidation resistance of UHMWPE. The development of novel materials with improved wear and oxidative characteristics has generated great interest in the orthopaedic community and numerous carbon nanostructures have been investigated in the last years due to their excellent mechanical properties.

The effect of the addition of GO nanoparticles to UHMWPE and the optimal %wt GO addition were investigated. UHMWPE/GO nanocomposites with different GO wt% contents were prepared and their mechanical, thermal, structural and wettability properties were investigated and compared with virgin UHMWPE.

The results showed that the thermal stability, oxidative resistance, mechanical properties and wettability properties of UHMWPE were enhanced due to the addition of GO. UHMWPE/GO materials prepared with up to 0.5 wt% GO exhibited improved characteristics compared to virgin UHMWPE and nanocomposites prepared with higher GO contents. These findings suggest that GO nanoparticles might be an interesting reinforcing material for their use in orthopaedic applications, and more research concerning the biocompatibility and tribological performance of this material is currently under investigation.

1. INTRODUCTION

Over the last century, joint replacements have enabled thousands of people with joints damaged by disease or trauma to enjoy a more active lifestyle. Advances in manufacturing techniques, materials and implant designs, as well as operative techniques, have resulted in implants, able to last for more than 20 years [1]. Ultra high molecular weight polyethylene (UHMWPE) is the material most commonly used among hard-on-soft bearings in artificial joints. UHMWPE implants have exhibited excellent clinical performance during the last two

decades [2]. However, wear and oxidation of this material are two major problems directly related to the eventual failure of joint implants [3].

To date, crosslinking of the polyethylene molecular chains through gamma irradiation has been the method used to improve the wear performance of UHMWPE. Previous studies have demonstrated that, after exposure to 10 MRad irradiation, the wear resistance of UHMWPE is improved by up to 90% [4]. Although irradiation leads to enhanced wear characteristics, the mechanical properties of UHMWPE are compromised after crosslinking [5]. In addition, free radicals generated during the irradiation process lead to a higher susceptibility to oxidation. Different post-irradiation processing methods have been developed to minimise the negative impacts of irradiation on the final properties of polyethylene [6]. Nevertheless, a compromise between mechanical strength, oxidative resistance and wear resistance remains.

In order to address these issues, the development of novel materials with improved wear and oxidative resistance, able to extend the life of the implant, has generated great interest in the orthopaedic community. In particular, the addition of carbon nanostructures to improve the final performance of polyethylene has been a topic of interest over the last few years. For example, multi-walled carbon nanotubes have been investigated as a reinforcement material to improve the final mechanical properties of neat polyethylene [7]. These materials have demonstrated the ability to improve the wear characteristics and oxidative resistance of UHMWPE without compromising its biocompatibility [8-10] and research concerning material processing and manufacturing to achieve homogeneous nanocomposites are currently ongoing [11].

Graphene oxide has also been suggested as an interesting filler for polymers due to its superior mechanical properties, such as excellent in-plane strength and high surface area [12,13], but little attention has been paid to the possibilities of using graphene oxide as a reinforcement material for UHMWPE matrices [14,15].

The main objectives of this work were to investigate the effect of the addition of GO nanoparticles to UHMWPE and to determine the optimal %wt GO addition to achieve an enhanced nanocomposite performance. In this work, UHMWPE/GO nanocomposites with different GO wt% contents were prepared and their mechanical, thermal, structural and wettability properties were investigated and compared with virgin UHMWPE.

2. MATERIALS AND METHODS

2.1 Materials

UHMWPE/GO nanocomposites were manufactured with UHMWPE GUR 1020 powder supplied by Ticona (Germany) and GO monolayer powder obtained from Nanoinnova Technologies (Spain). UHMWPE GUR 1020 had an average molecular weight of $3.5x10^6$ g/mol, density of 0.93 g/cm^3 and the average size of particles was 140 μm. GO sheets had an average particle length of 3-5 μm and a thickness of 0.7-1.2 nm.

2.2 Nanocomposite preparation

A ball milling technique was utilised under optimised conditions [15] to prepare UHMWPE/GO nanocomposite powders with different GO wt% content (0.1, 0.3, 0.5, 0.7, 1 and 2 wt%). Nanocomposite and UHMWPE GUR 1020 powders were molded into 65x25x2 mm^3 and 115x17x2 mm^{3}sheets using a hot press at 185 ^{o}C under 15 Mpa pressure.

2.3 Characterisation Techniques

Thermal characterisation

Differential scanning calorimetry (DSC, Mettler Toledo, Germany) measurements were performed to study the melting temperature, crystallization temperature and crystallinity of virgin UHMWPE GUR 1020 and the different UHMWPE/GO nanocomposites. Experiments were performed under nitrogen atmosphere at a rate of 80 ml/min and samples weighed between 6-7 mg. Samples were subjected to a heating-cooling-heating scan to eliminate thermal histories between 30 ^{o}C and 200 ^{o}C at 10 ^{o}C/min. The crystallinity of the samples was calculated according to Eq. (1).

$$X_c(\%) = \frac{\Delta H}{\Delta H_{100}} \cdot 100 \qquad (1)$$

Where ΔH is the total heat energy per unit mass and ΔH_{100} is the enthalpy of fusion of a 100% crystalline sample, fixed to be 289 J/g [16]. The range of integration used was 50-160 ^{o}C. The reported values were the average of three measurements.

Thermal stability of the samples was evaluated by thermogravimetry analysis (TGA). Tests were performed under air atmosphere on a TG Q500 (TA Instruments, New Jersey USA)

between room temperature and 700 ^{o}C at a heating rate of 10 ^{o}C/min and samples weighed between 6-7 mg, according to the method of Martinez-Morlanes et al. [17]. The reported values were the average of three measurements.

Mechanical Characterisation

Tensile tests were performed on a tensile machine (Instron 3366). Young's modulus, yield stress, fracture stress and fracture strain were determined from the stress-strain curves. Tests were performed at a crosshead speed of 10 mm/min with a gauge length of 60 mm. Fracture toughness tests were performed in selected samples (virgin UHMWPE GUR 1020, UHMWPE/GO 0.3 wt% and UHMWPE/GO 2 wt%). Tests were performed using a dynamic test machine (Instron Electropuls 10000) in nitrogen atmosphere at -100 ^{o}C. Single edged notched bend specimens were tested in three point bending and K_{ic} was calculated according to [18]. The reported values were the average of three measurements. Microhardness measurements were carried out with a load of 10 g in all the UHMWPE/GO nanocomposites and virgin UHMWPE GUR 1020. The reported values were the average of ten measurements.

Contact angle measurements

The wettability of the UHMWPE/GO nanocomposites and virgin UHMWPE GUR 1020 was determined by contact angle measurements. A 4 μl drop of distilled water was deposited on the sample surface and measurements were taken after one second. The sessile drop method was used to determine the water contact angles. The reported values were the average of ten measurements.

High Resolution Scanning Electron Microscopy (HR-SEM)

HR-SEM was employed to investigate the fracture surface of samples. Prior to observation, samples were frozen in liquid nitrogen and fractured.

Gamma irradiation and ageing effects

In order to determine the effect of gamma irradiation and aging on the UHMWPE/GO nanocomposites, selected samples (virgin UHMWPE GUR 1020, UHMWPE/GO 0.5 wt% and UHMWPE/GO 2 wt%) were prepared and subjected to gamma irradiation and posterior aging. Gamma irradiation of the samples was performed in air at room temperature with a dose of 75 KGy (Synergy Health, Netherlands). Ageing was performed in air at 80^{o}C for 3

weeks according to [19]. Tensile tests on irradiated samples and irradiated-aged samples were performed under same conditions described for non-irradiated samples. The reported values were the average of three measurements.

3. RESULTS

3.1 Thermal Characterisation

Differential scanning calorimetry (DSC) and thermogravimetric analysis were used to evaluate the effect of the addition of GO at different %wt on the thermal stability of UHMWPE. Melting temperature (T_m), crystallization temperature (T_c) and degree of crystallinity (X_c) of virgin UHMWPE GUR 1020 and the UHMWPE/GO nanocomposites are shown in Table 1. Melting and crystallization temperatures remained constant at all of the GO concentrations and similar values were observed to virgin UHMWPE. Little change in the degree of crystallinity was observed due to the addition of GO.

Table 1. Crystallisation parameters of UHMWPE/GO nanocomposites and UHMWPE

Material	T_m (°C)±SD	T_c (°C)±SD	X_c (%)±SD
Virgin UHMWPE	134.9±0.5	115.0±0.7	51.2±0.6
UHMWPE/GO 0.1 wt%	135.4±0.5	114.5±0.6	49.2±1.4
UHMWPE/GO 0.3 wt%	134.5±0.6	115.8±0.6	50.4±1.1
UHMWPE/GO 0.5 wt%	135.1±0.2	114.9±0.3	50.4±0.7
UHMWPE/GO 0.7 wt%	136.7±0.7	113.7±0.4	50.0±0.1
UHMWPE/GO 1.0 wt%	135.5±0.3	115.0±0.3	50.5±1.5
UHMWPE/GO 2.0 wt%	135.3±0.4	114.9±0.5	50.4±0.8
SD: Standard deviation			

An example of the TGA decomposition curves obtained for UHMWPE showing demarcated temperatures, T_o, T_1, T_2, and T_3, is shown in Fig. 1. Demarcated temperatures for virgin UHMWPE and UHMWPE/GO nanocomposites are reported in table 2.

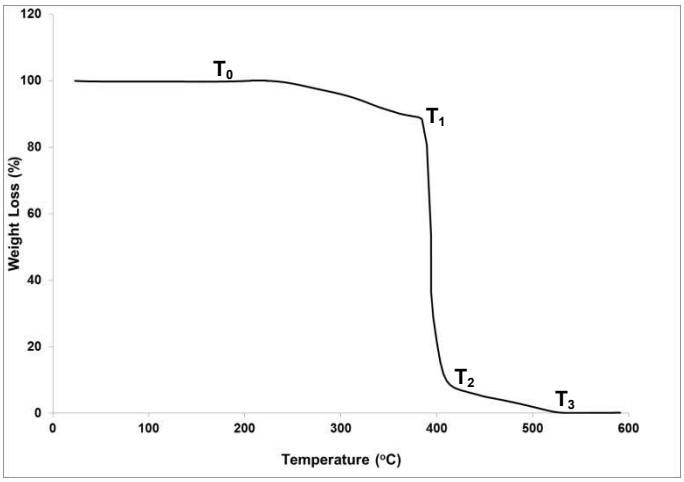

Figure 1. Thermogravimetry analysis. Typical decomposition curve for virgin UHMWPE

Table 2. Thermal stability parameters of UHMWPE/GO nanocomposites and UHMWPE

Material	T_0 (°C)±SD	T_1 (°C)±SD	T_2 (°C)±SD	T_3 (°C)±SD
Virgin UHMWPE	170.5±5.4	383.1±4.1	409.8±2.7	534.0±2.8
UHMWPE/GO 0.1 wt%	182.1±5.1	382.5±7.8	413.0±3.1	533.0±1.6
UHMWPE/GO 0.3 wt%	180.5±2.0	382.5±3.7	426.3±6.3	534.5±1.1
UHMWPE/GO 0.5 wt%	181.2±2.5	386.0±5.9	427.4±8.2	538.2±3.2
UHMWPE/GO 0.7 wt%	185.5±0.7	382.6±10.4	431.4±12.0	539.2±6.7
UHMWPE/GO 1.0 wt%	183.3±4.0	384.2±6.3	430.8±7.8	542.5±6.0
UHMWPE/GO 2.0 wt%	189.8±1.4	387.7±4.7	435.4±7.1	545.2±1.3

SD: Standard deviation

The addition of GO had a notable influence on the thermal behaviour of UHMWPE. The oxidation temperatures, T_o, measured for the UHMWPE/GO nanocomposites increased with increasing concentration of GO, being significantly higher than that of virgin UHMWPE at all the concentrations. The linear weight loss stage, T_1, experienced a slight increase due to the addition of GO. An increase at the end of the linear weight loss, T_2, compared with virgin UHMWPE was found for the UHMWPE/GO nanocomposites for all the concentrations, being more noticeable with increasing amounts of GO. A similar trend was found for the temperature of complete volatilisation, T_3, which experienced an increase compared to that of virgin UHMWPE due to the addition of GO.

3.2 Mechanical Characterisation

The influence of GO on the Young's modulus, yield stress, fracture stress, fracture strain and fracture toughness of UHMWPE is shown in Table 3.

Table 3. Mechanical properties of UHMWPE/GO nanocomposites and UHMWPE

Material	Young's modulus (MPa)±SD	Yield stress (MPa)±SD	Fracture stress (MPa)±SD	Fracture strain (%)±SD	Fracture toughness K_{ic} (MPa $m^{1/2}$)±SD
Virgin UHMWPE	625.0±35.9	17.4±0.2	22.6±1.7	541.9±35.9	5.5±0.6
UHMWPE/GO 0.1 wt%	691.3±35.9	19.5±1.1	25.9±2.9	552.7±28	--
UHMWPE/GO 0.3 wt%	709.0±55.4	19.3±1.7	28.1±2.8	579.9±2.8	5.2±0.5
UHMWPE/GO 0.5 wt%	677.0±22.3	19.2±0.9	27.4±2.8	553.0±56.3	--
UHMWPE/GO 0.7 wt%	658.7±18.9	18.6±0.4	24.6±3.4	545.9±60.6	--
UHMWPE/GO 1.0 wt%	662.0±3.5	19.1±0.3	22.7±1.1	506.6±21.5	--
UHMWPE/GO 2.0 wt%	696.3±57.9	19.8±1.1	19.7±1.0	183.85±85.0	2.8±0.3

SD: Standard deviation

UHMWPE/GO nanocomposites showed enhanced mechanical properties compared to virgin UHMWPE. The Young's modulus and yield stress increased by approximately 15% due to the addition of GO. The fracture stress of the nanocomposites increased up to approximately 25% compared to virgin UHMWPE. Slight changes were measured in the fracture strain of the samples, except for the UHMWPE/GO 2 wt%, which exhibited a significant decrease compared to virgin UHMWPE. In general, the mechanical properties of the nanocomposites improved for samples prepared with a small wt % GO content, reaching an optimum up to 0.5 wt% and then started to decrease with the addition of higher concentrations of GO. This trend can be clearly seen in the reported fracture stress and fracture strain values, where optimum values were obtained for samples prepared with up to 0.5 wt% and significantly lower values compared to virgin UHWMPE were found for nanocomposites prepared with 2 wt % GO content. A similar trend was observed for the fracture toughness experiments performed on UHMWPE, UHMWPE/GO 0.3 wt % and UHMWPE 2 wt%. Virgin UHMWPE and UHMWPE/GO 0.3 wt% samples exhibited similar fracture toughness values, K_{ic}, while UHMWPE/GO 2 wt% exhibited a significantly lower K_{ic}. Microhardness measurements are detailed in Table 4. UHMWPE/GO nanocomposites showed higher hardness compared to virgin UHMWPE, exhibiting an increase with increasing amount of wt% GO content.

Table 4. Microhardness values for UHMWPE/GO nanocomposites and virgin UHMWPE

Material	Microhardness (HV)±SD
Virgin UHMWPE	4.8±0.4
UHMWPE/GO 0.1 wt%	5.0±0.4
UHMWPE/GO 0.3 wt%	4.9±0.3
UHMWPE/GO 0.5 wt%	5.0±0.0
UHMWPE/GO 0.7 wt%	5.0±0.0
UHMWPE/GO 1.0 wt%	5.1±0.3
UHMWPE/GO 2.0 wt%	5.4±0.6

SD: Standard deviation

3.3 Contact angle measurements

The contact angles measured for the UHMWPE/GO nanocomposites and virgin UHMWPE are reported in Table 5. Nanocomposites prepared with 0.1, 0.3 and 0.5 wt% exhibited significantly lower contact angles and, consequently, significantly enhanced wettability compared to virgin UHMWPE. Nanocomposites prepared with higher % wt GO content (0.7, 1 and 2 wt %) exhibited a similar contact angle and, consequently, similar wettability to that reported for virgin UHMWPE.

Table 5. Contact angle measurements of UHMWPE/GO nanocomposites and UHMWPE

Material	Contact angle (°)±SD
Virgin UHMWPE	86.7±2.9
UHMWPE/GO 0.1 wt%	78.3±1.4
UHMWPE/GO 0.3 wt%	80.6±3.8
UHMWPE/GO 0.5 wt%	78.8±2.8
UHMWPE/GO 0.7 wt%	87.0±2.2
UHMWPE/GO 1.0 wt%	90.4±2.9
UHMWPE/GO 2.0 wt%	83.2±3.7

SD: Standard deviation

3.4 Gamma irradiation and ageing effects

The influence of gamma irradiation and ageing on the mechanical properties of virgin UHMWPE and UHMWPE/GO 0.5 wt% and 2 wt% is reported in Table 6. The Young's modulus increased for all the samples exposed to the gamma irradiation treatment and further increased due the ageing treatment, however the Young's Modulus of UHMWPE/GO samples (0.5 and 2 wt%) were affected to a lesser extent by the ageing treatment than virgin UHMWPE (~28% increase versus ~5% and 7% increase, respectively). The yield stress of virgin UHMWPE and UHMWPE/GO samples increased after gamma irradiation and ageing, again UHMWPE/GO nanocomposites were affected to a lesser extent than the virgin UHMWPE. The fracture stress for virgin UHMWPE followed a different trend compared to the GO nanocomposites. While the fracture stress of virgin UHMWPE increased after gamma irradiation, the fracture stress of the UHMWPE/GO nanocomposites decreased after treatment. After ageing, the fracture stress of virgin UHMWPE significantly decreased (~32%) however, the UHMWPE/GO nanocomposites were much less affected (~18% decrease for 0.5 wt% and ~3% decrease for 2 wt%).

Table 6. Mechanical properties of irradiated and irradiated plus aged UHMWPE/GO nanocomposites and UHMWPE

Material	Young's modulus (MPa)±SD	Yield stress (MPa)±SD	Fracture stress (MPa)±SD
Virgin UHMWPE	625.0±35.9	17.4±0.2	22.6±1.7
Virgin UHMWPE-I	662.7±29.3	19.6±0.6	26.1±1.2
Virgin UHMWPE-I-Aged	845.5±36.0	21.6±0.6	17.6±0.6
UHMWPE/GO 0.5 wt%	677.0±22.3	19.2±0.9	27.4±2.8
UHMWPE/GO 0.5 wt%-I	716.3±20.8	20.1±0.5	22.8±0.5
UHMWPE/GO 0.5 wt%-I-Aged	754±25.2	21.0±0.3	18.6±0.5
UHMWPE/GO 2.0 wt%	696.3±57.9	19.8±1.1	19.7±1.0
UHMWPE/GO 2.0 wt%-I	709.7±13.6	20.0±0.3	18.4±0.1
UHMWPE/GO 2.0 wt%-I-Aged	758.3±19.2	21.3±0.3	17.9±0.8

SD: Standard deviation, I: Gamma irradiated at 75 kGy, I-Aged: Gamma irradiated at 75 kGy and aged at 80°C for 3 weeks

3.5 Fracture surfaces

The fracture surfaces of virgin UHMWPE and the UHMWPE/GO nanocomposites are shown in Fig. 2. Samples prepared with 0.1, 0.3 and 0.5 wt% GO content exhibited an even fracture surface, similar to that of virgin UHMWPE. No aggregates of GO were observed for any of the UHMWPE/GO samples. However, samples prepared with higher concentration of GO exhibited a different fracture surface compared to that of virgin UHMWPE, showing a more uneven surface for the sample with the highest wt% GO amount (UHMWPE/GO 2 wt%).

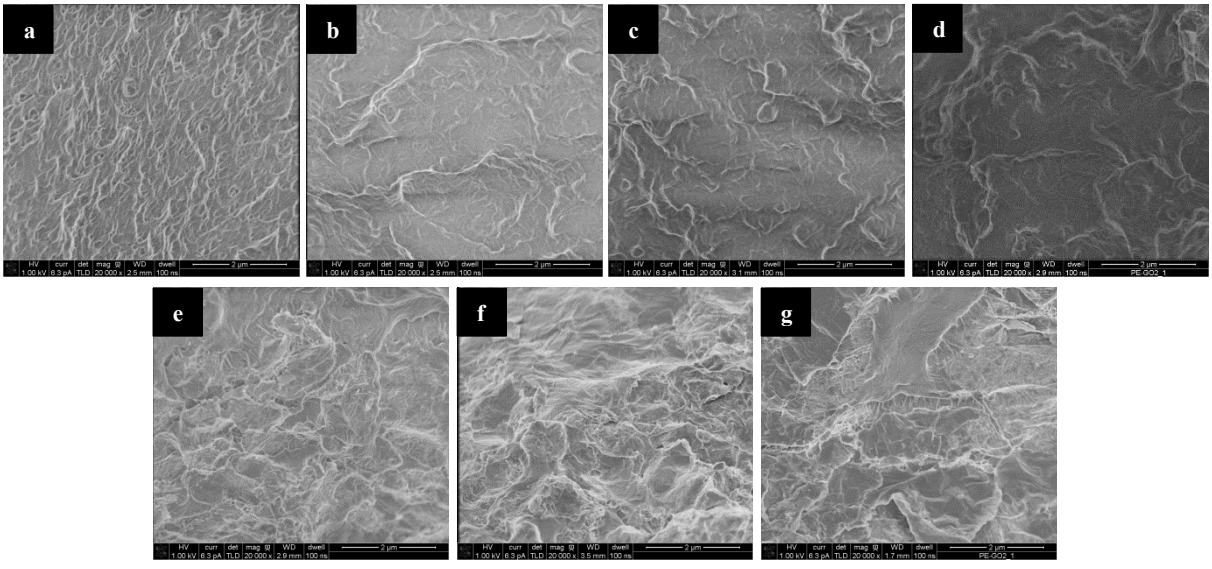

Fig 2. SEM images of fracture surfaces of virgin UHMWPE (a) and UHMWPE/GO nanocomposites with 0.1 (b), 0.3 (c), 0.5 (d), 0.7 (e), 1 (f) and 2 wt% (g)

4. DISCUSSION

Through the present study, the effect of the addition of GO as a UHMWPE reinforcement has been investigated, and differences between nanocomposites prepared with different GO wt% content have been analysed. Although the thermal behaviour of UHMWPE was enhanced with increasing concentrations of GO, the mechanical and wettability properties, as well as the SEM investigation, showed a different trend for nanocomposites prepared with up to 0.5 wt% GO content compared to nanocomposites prepared with higher GO concentrations (0.7 to 2 wt%). For example, nanocomposites prepared with 2 wt% GO content exhibited a ~30% reduction in fracture stress compared to nanocomposites prepared with 0.3 wt% GO content. In general, UHMWPE/GO materials prepared with concentrations of GO up to 0.5 wt% exhibited optimal mechanical and wettability properties compared to virgin UHMWPE and nanocomposites with higher GO content. These differences might be attributed to the formation of GO clusters when high concentration is added to the polymer, leading to inhomogeneous samples and, consequently, failure to achieve optimal properties. It could also be hypothesised that the polyethylene matrix might be saturated when high concentrations of GO are added, leading to a decrease in the mechanical performance of the material. This hypothesis is supported by results from a study by Tai et al. [14] who found that the wear resistance of UHMWPE/GO composites decreased as the GO content increased, up to values of 0.7 wt %, but after that the wear rate showed little change.

In order to maximise the potential of GO as a reinforcement material for polyethylene matrices, it is not only the wt% of GO that is important, but also the method of preparation of the materials. In a study performed by Chen et al. [20] UHMWPE/GO nanocomposites were prepared by ultrasonication. However, the reported tensile test values showed little or no enhancement compared to virgin UHMWPE. In our investigation, UHMWPE/GO nanocomposites were prepared using an optimised ball mill technique [15], and significant improvements in the mechanical properties of the materials where found, indicating the potential of ball milling as a processing method for synthesising nanocomposites.

UHMWPE/GO nanocomposites (up to 0.5 wt%) showed little change in the degree of crystallinity due to the addition of GO. A more notable effect on the degree of crystallinity of nanocomposites has been previously reported. A study performed by Todd et al. [21], reported up to a 9 % decrease in crystallinity for a thermally reduced graphite oxide reinforced polyethylene composite compared to virgin polyethylene. Martinez-Morlanes et al. [22] also reported a lower crystallinity for multi-walled carbon nanotube reinforced UHMWPE. On the other hand, a higher degree of crystallinity due to the addition of graphene has been reported [20]. These differences may be attributed to the quality of the nanoparticles and their ability to create bonding with the polyethylene matrix.

Thermogravimetric analysis demonstrated enhanced thermal stability of UHMWPE due to the addition of GO. This effect was also reflected in the mechanical behaviour of irradiated samples subjected to accelerated aging. Aged UHMWPE samples exhibited a reduction of more than 30% in fracture stress, which was associated to the oxidative degradation of the polyethylene. However, when GO was added, the reduction was only ~18% and 3% for

UHMWPE/GO 0.5 wt% and 2 wt%, respectively. Similar effects have been reported previously when adding carbon nanoreinforcements to UHMWPE. Sreekanth et al. [10] reported limited degradation of the mechanical properties of UHMWPE when multi-walled carbon nanotubes were added and Martinez-Morlanes et al. [9] demonstrated the positive contribution of MWCNTs in increasing the oxidative stability of virgin UHMWPE. Prior to implantation, UHMWPE implants are subjected to irradiation, post-irradiation processing and storage, undergoing natural aging and resulting in oxidative degradation of the material [23]. It has been postulated that graphene oxide has the ability to quench the effect of free radicals generated during the thermal decomposition of UHMWPE [13]. Chemical reactions between the oxygen molecules present in the polyethylene and free radicals generated due to irradiation causes scission in the polymer chains, leading to a reduction in the properties of UHMWPE[24], and causing a reduction in wear resistance [25]. The addition of graphene oxide to UHMWPE matrix might be an interesting alternative to moderate the negative effects of irradiation and oxidation on the long term performance of UHMWPE implants.

In addition, GO was shown to have beneficial effects on the wettability of UHMWPE. The hydrophobic nature of virgin UHMWPE has generated some concerns in joint bearing applications. Since increased friction between the bearings can lead to modifications in the lubrication of the joint [26], previous investigations have focused on modifying the surface of UHMWPE or adding particles to improve its hydrophilicity [27,28]. By adding GO, enhanced wettability was achieved, which may lead to enhanced lubrication and improved friction in the bearing [29], improving the tribological performance of the artificial joints.

The results of this study have shown the ability of GO to improve the performance of conventional UHMWPE and further research concerning the tribological performance and biocompatibility of UHMWPE/GO nanocomposites is currently under investigation.

5. CONCLUSIONS

This work has focused on the influence of graphene oxide nanoparticles on the performance of UHMWPE. UHMWPE/GO nanocomposites with different concentrations of GO wt% were successfully prepared by means of an optimised ball milling technique and their thermal, mechanical and wettability properties were evaluated. The following conclusions can be drawn:

1. Graphene oxide nanoparticles have the ability to improve the thermal, mechanical and wettability properties of virgin UHMWPE.
2. The final properties of UHMWPE/GO nanocomposites can vary depending on the wt% concentration of GO nanoparticles added. The selection of the optimal %wt GO concentration is fundamental to maximise the benefits of the GO nanoparticles on the final performance of UHMWPE.

3. UHMWPE/GO materials prepared with up to 0.5 wt% GO exhibited improved characteristics compared to virgin UHMWPE and nanocomposites prepared with higher GO contents.
4. The incorporation of GO has been shown to have the potential to counteract the negative effects of gamma irradiation and the subsequent oxidation process of UHMWPE.
5. Further studies concerning the tribological performance and biocompatibility of UHMWPE/GO nanocomposites are required in order to fully assess the suitability of these materials for use in total joint replacements.

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