TRIBOLOGICAL BEHAVIOR OF FUNCTIONALIZED 1-2 LAYERED GRAPHENE/UHMWPE COMPOSITES

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ABSTRACT

In this work we present the evaluation of pristine and functionalized graphene as reinforcements for UHMWPE-based composites. These composites were manufactured by physically blending graphene particles and medical grade UHMWPE powder followed by a thermo-compression process. Mechanical behaviour by means of uniaxial tension and biaxial load by small punch were carried out. Friction coefficient and wear rate were measured. In some cases composites enhanced stiffness and yield stress, although with loss of toughness. This mechanical behaviour was recuperated after a thermal treatment. Small positive changes were obtained with some graphene concentrations respect to the friction coefficient. However, 20 % of reduction in wear rate was obtained when the graphene was functionalized. In general these composites present a good trend to be a potential alternative to the current highly crosslinked polyethylenes.

KEY WORDS: friction, wear, UHMWPE, graphene.

1.- INTRODUCTION

In the field of total joint replacements, ultra high molecular weight polyethylene (UHMWPE) is considered one of the most relevant bearing materials because of its outstanding mechanical and tribological properties [1] besides its biocompatibility. Current UHMWPE components are limited in their thickness due to concerns about elevated stresses and the potential for fracture. The appearance in the last decade of 2D carbonaceous materials with very high aspect dimensional ratio, low density, high stiffness and strength has allowed to exploit their potential in novel UHMWPE composites [2]. Another expected advantage of the use of graphene as reinforcement is that 2D particles could provide a higher degree of lubrication according to previous [3,4] works. In this last study, graphene was shown to be very effective for friction and wear reduction, acting as a lubricant and as an additive to composites, oils and solvents. In this work, we assess the mechanical and tribological properties of functionalized and pristine 1-2 layered graphene as potential reinforcements of the medical grade UHMWPE.

2.- MATERIALS AND METHODS

2.1- Composites

UHMWPE powder was supplied by Celanese (Irving, USA) with an average particle size of 150 µm, a molecular weight of 3-6 10^6 g/mol and without additives. We use pristine 1-2-layered graphene provided by Avanzare (Spain) and in-house poly-

(ethylene oxide)-polyethylene (PEO-PE) functionalization, both in concentrations of 0.1, 0.3, 0.5 and 1 wt%.

These carbonaceous particles were blended in UHMWPE and the mixtures were homogenized in a ball mill for 8 hours at 400 rpm to obtain a homogeneous dispersion of the reinforcements in the polymer matrix. The compression process was carried out using a thermo-compression process cell (Perkin-Elmer) for 30 minutes at 175°C under 15 MPa pressure, followed by cooling in air down to 40°C under the same pressure. Samples were denoted as G-X/UHMWPE and GF-X/UHMWPE for the pristine and functionalized graphene, respectively, where X stands for the weight % of reinforcements in the polymer matrix. GT-X/UHMWPE is the notation for the composites underwent further thermal treatment.

2.2 - Mechanical properties

Uniaxial tensile tests were carried out according to ASTM D638M (UNE-EN ISO 527-2) in an Instron machine (model 5565). From the stress-strain curves different mechanical parameters were obtained: Young´s modulus, E, yield stress, σ_y, deformation of fracture, ε^*, and work of fracture, W.

Small punch test (SPT) were performed according to ASTM F2183 at a constant displacement of 1 mm/min. Several parameters were measured from this biaxial test: peak force, F_p, force and displacement of fracture, F_{uts}, and d_{uts} respectively, and biaxial work of fracture, W_{SPT}.

2.3.- Wear measurements

A commercial ball-on-disk tribometer (CSM instruments; Peseux, Switzerland) allowed assessing wear resistance and constantly monitoring the coefficient of friction for all materials. Wear tests were performed in at least three samples per material group working with a rotating vessel, which contained UHMWPE disks immersed in bovine serum (B-9433, Sigma Aldrich). The counterpart was a stationary ball, 6mm in diameter, made of alumina with an average roughness, Ra= 0.05 ± 0.02 μm, whereas the load applied to the ball was 5 N. The radius of the circular track was 4 mm and the sliding speed was 0.05 m/s. The environment temperature was set to 37 ◦C, the body temperature. Assuming hertzian contact, the previous loading conditions gave an approximate contact pressure of 37 MPa, which is in the range of peak contact stresses (≥30 MPa) found for some contemporary polyethylene tibial inserts. Wear rates were measured after 4400 m sliding distances. After each wear test, disks were removed from the tribometer and underwent a cleaning protocol following guidelines included in ASTM F2025.

Confocal microscopy was performed using a SENSOFAR PLU 2300 optical imaging profiler and served to evaluate worn disk surfaces. Four line measurements diametrically opposed were carried out on the wear tracks of each sample. The average of the registered worn areas was used to calculate the wear factor, k, according to the following equation:

$$k = \frac{2\pi r A_m}{Ls} \tag{1}$$

where r is the wear track radius, L is the applied load, s is the sliding distance, and A_m is the average worn area a week after the sample was tested.

3.- UPSHOTS AND DISCUSSION

3.1.- Mechanical properties

The use of graphene as a filler should lead to strong increase in mechanical properties since the elastic modulus and strength are close to 1 TPa and 130 GPa, respectively. However, the results obtained from the uniaxial tension test indicated that this goal was not reached in our composites when we incorporated 1-2- layered graphene up to 1 wt%. In fact, the stiffness and yield stress practically remains constant with values of 288 MPa and 19 MPa, which are similar to those observed in the neat UHMWPE. On the other hand, the ultimate tensile strength and elongation at break, and consequently the work of fracture underwent a strong reduction when increasing graphene concentration. Small punch data provide some small changes as an increase of 15 % in the Young modulus at 0.5 wt%, maintaining the same fall in toughness. Similar mechanical behaviour was detected in other different UHMWPE composites reinforced with graphene fillers such as GO (graphene oxide), RGO (reduced graphene oxide), GNP (graphene nanoplatelets) and GNS (graphene nanosheets) [2]; the only difference between these three last graphene related materials is the number of graphene layers. The stiffness increases up to 20 % whereas toughness reduced up to 50 %. This loss of toughness is in general associated to the segregated structure formed during the consolidation process where the filler are set around the UHMWPE particles, together a lack of dispersion of these nanofillers in the matrix. The only positive outcome in both stiffness and ductility were obtained by Lahiri et al. [5] in composite films prepared by electrostatic spraying. This manufacture method seems to lead to a more uniform distribution of graphene particles than blending or mixing techniques as used in this work.

In order to enhance the adhesion between the filler and the matrix and therefore the transmission of load in the composite material, pristine 1-2- layered graphene was functionalized with PEO-PE. The result pointed out an increase of 15 % in elastic modulus and a leger rise in yield stress. However, toughness indicators went on undergoing strong reductions, since the dispersion method does not contribute to eliminate the aggregates and their associated concentrator effect.

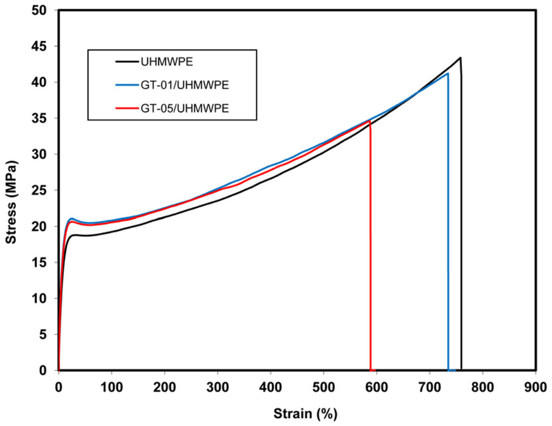

Figure 1. Stress-strain curve for composites after thermal method, GT-X/UHMWPE

Some attempts to enhance self-diffusion of the ultra-long polyethylene chains between the polymer granules during the consolidation process were carried out by means of thermal process [6]. We applied a heating process to our composites, at

240 ºC during 8 hours and the samples changed the color acquiring a darker color and mechanical properties (Figure 1) was enhanced compared to the untreated composites by increases of 16 %, 14 %, 25 % and 40% for E, σ_y, ε^* and W, respectively for 0.1 wt%. Similar rises were obtained for the composite with 0.5 %.

3.2.- Tribological behavior

Friction coefficient of pristine graphene/UHMWPE composites presented high dispersion for each of the filler concentrations studied from 0,1 to 1 wt% (n =3). There was not a clear trend respect if graphene layers contribute to reduce the friction against Al_2O_3 counterpart.

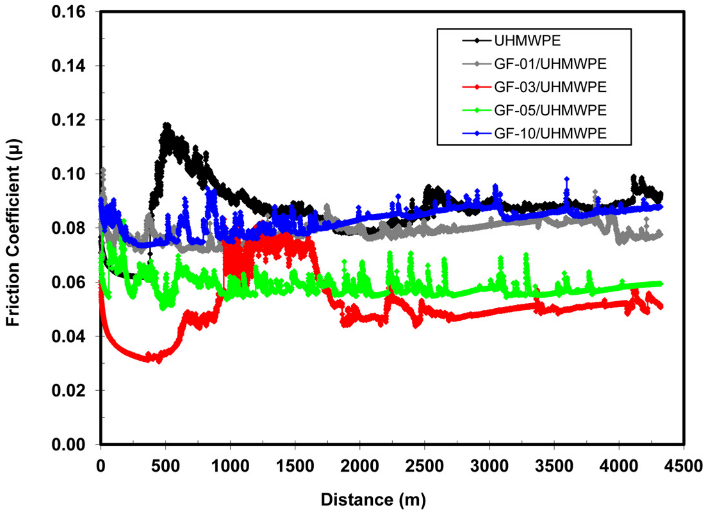

Figure 2. Evolution of the friction coefficient for GF-X/UHMWPE composites

In Figure 2 we show the results of the functionalized graphene as reinforcements for UHMWPE-based composites. After running-in period, friction coefficient for the intermediate concentrations, 0.3 and 0.5 wt%, were lower than the neat UHMWPE however for the extreme concentrations, 0.1 and 1 wt%, the coefficient was similar to the resin. This behavior is in the line of the controversy appeared in literature where some researcher obtained an increase of the friction for GO/UHMWPE composites [7], whereas other authors [8] indicated that UHMWPE reinforced with graphene platelets reduce the friction.

The knowledge of wear resistance is relevant in any bearing material. Table 1 reflect the wear rate for each of the studied composites.

Table 1. Wear factor of the pristine and functionalized graphene/UHMWPE composites

Materials	**Wear rate** $\boldsymbol{k \cdot 10^{-6}}$ **(mm^3/N·m)**
UHMWPE	2.64 ± 0.21
G-01/UHMWPE	2.74 ± 0.18

G-03/UHMWPE	2.74 ± 0.44
G-05/UHMWPE	2.64 ± 0.19
GF-01/UHMWPE	2.04 ± 0.13
GF-03/UHMWPE	1.74 ± 0.10
GF-05/UHMWPE	1.95 ± 0.10
GF-10/UHMWPE	2.43 ± 0.11

We realize that the lubricant effect of the pristine graphene layer practically do not contribute to enhance the wear behaviour of the neat UHMWPE. A better result was obtained for the PEO-PE functionalized graphene with a reduction around 20 % at the lowest concentrations. So far, very few works [7,8] have dealt with the wear concern using graphene or related materials as fillers of UHMWPE. In the first case, authors reached a reduction close to 50% for a very high concentration, 3 wt% and more than four times for the second one. However in both cases they used zircona instead of alumina and dry conditions instead of biological conditions. New research should be carried out with thermal treated composites due to the better dispersion of the nanofillers.

CONCLUSIONS

Although graphene/UHMWPE composites present mechanical properties far of the theoretically expected ones, wear resistance present improved behaviour in some cases. These results could be enhanced after gamma or electron beam irradiation due to the positive effect introduced by means of polymeric chains crosslinking and therefore to be an alternative to the current highly crosslinked polyethylenes.

ACKNOWLEDGEMENTS

We thank the Ministry of Science and Education of Spain by means of the projects MAT2010-16175) and CONSOLIDER CSD2008-00023 (FUNCOAT) for financial support

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