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Thermal, Mechanical and Rheological Behaviors of Nanocomposites Based on UHMWPE/Paraffin Oil/Carbon Nanofiller Obtained by Using Different Dispersion Techniques

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Ultra-high molecular weight polyethylene (UHMWPE) is a very attractive polymer employed as a high performance material. For its high viscosity, dispersion of fillers is considered a critical point in UHMWPE nanocomposites preparation process. Currently, paraffin oil (PO) is used extensively to overcome this issue in an assisted melt-mixing process. In this work, we have prepared nanocomposites based on UHMWPE, carbon nanofiller (CNF) and PO mixed by different mixing methods: magnetic stirring, ball milling (BM), ultrasonic and Mini-Lab extruder (EX). The aim of this work was to check the effect of the dispersion method on the mechanical and thermal features of UHMWPE/CNF nano composites in order to obtain a material with improved mechanical and physical properties. The samples were characterized by calorimetric, density, mechanical tensile and rheological analyses. Experimental results highlighted that the nanocomposites produced by EX and BM exhibits the best dispersion, good filler matrix interaction and had significantly improved mechanical properties compared to pure UHMWPE. For instance, for the BM method, the yield strength improved to 18.6 MPa (+96%), the yield strain improved by 60%, while stress at break improved by 13%. In summary, the EX improved the stiffness while the BM produced better ductility, melting temperature and the crystalline degree of the nanocomposites.

INTRODUCTION

Ultra-high molecular weight polyethylene (UHMWPE) is a useful thermoplastic polymer which has many excellent properties, such as high mechanical features, bio-compatibility, chemical stability, good wear resistance, low friction and electrical insulation.[1] For these reasons, UHMWPE is widely utilized in technological applications in the field of medicine, biomaterials, microelectronics, engineering, chemistry and the food industry, among many others.[2–4] Consequently, many researchers have dedicated their efforts to the improvement of the UHMWPE properties through the use of nanofiller materials such as carbon nanofibers (CNF), carbon nanotubes (CNT) and graphene.[5] Graphene and CNT are better nanofiller materials compared to CNF due to their higher aspect ratio, but, due to a lower production cost, CNF is considered more economic.[6] This does not preclude that CNF is disadvantaged compared to other carbon fillers in electrical, mechanical and thermal properties.[7] So, CNF has been used widely to reinforce a variety of thermoplastic polymers such as polypropylene, polycarbonate and nylon.[8] Also, CNF has been used in biomaterial applications, particularly with UHMWPE. Due to the extremely high viscosity of UHMWPE, CNF filler forms agglomerates during the mixing process with the polymeric matrix.[9] This often leads to very poor dispersion of the filler that negatively affects the final properties of the composite materials.[10,11]

In recent years, some researchers have started to employ paraffin oil (PO) to decrease the UHMWPE viscosity and improve its work ability. Wood et al.[12] used PO to assist melt-mixing with UHMWPE and carbon nanofibers through several methods of dispersion (mortar and pestle, ultra-sonification, hot plate and magnetic stirring, Haake torque rheometer) to decrease the viscosity and obtain UHMWPE/ CNF nanocomposites with a good dispersion. The results showed that the wear and mechanical properties were improved, but that the preparation method of UHMWPE/CNF was more complicated and the PO must be extracted by soxhlet after mixing process. This last process is expensive and takes more time improving the production period of the nanocomposite. Zhang et al.[13] blended UHMWPE with PO by using a HAAKE HBI System without extracted PO to increase the crystallization behaviors. Liu et al.[14] instead studied the effect of PO mixed with the UHMWPE by magnetic stirring and they found that the PO reduced the fusion defects of UHMWPE induced by the working techniques, which improved its mechanical and physical properties.

Generally, different dispersion methods of fillers have been used in the literature in order to obtain a good distribution and mixing of the nanofiller (in particular carbon nanofibers and carbon nanotubes) in the UHMWPE. In particular, some researchers have studied the effect of the nanofiller on the thermal behavior (melting temperatures, onset temperature, crystallinity degree and apparent enthalpy) of UHMWPE by using differential scanning calorimeters (DSC).[15] Additionally, in other literature, the effect of filler materials on rheological behavior has studied by using dynamic rheometry[16–20] because of the high complex viscosity of UHMWPE due to its high molecular weight. In particular, Ma et al.[21] studied all the above-mentioned thermal and rheological features of UHMWPE-based nanocomposites and CNF modified with ionic liquid by sonication, mixed by stirring and then added to an antioxidant using a twin-screw blender. The results showed that the viscosity was decreased by the addition of the modified CNF. Finally, a few papers have presented the mechanical properties of UHMWPE/CNT nanocomposites and their results were not good, due to poor dispersion.

In the present study, we have investigated the effect of PO and of the presence of carbon nanofiller on the mechanical and thermal features of UHMWPE/PO/CNF composites blended by four different mixing methods. Among these, two methods have been particularly interesting for the improvements in mechanical performance which were much higher than those thus far experienced in similar nanocomposite systems. Moreover, as the removal of PO is not necessary, our processes are faster than similar methods which employ large amounts of PO, which then needs to be extracted.

These two methods, in addition to being rapid and effective in dispersing the reinforcing filler inside the UHMWPE matrix, are also cheap. In fact, we employed carbon nanofillers obtained by milling carbon fibers because of their reasonable and inviting price with respect to other commons nanofillers such as CNT or graphene, so that they can be well considered for prototype devices. Tensile, rheological, density and calorimetric analyses were performed on the samples in order to check the changes in their properties.

MATERIALS AND METHODS

Materials

The UHMWPE powder was medical grade GUR1020 (average molecular weight $2–4 \times 10^6$ g/mol, density 0.93 g/cm^3, without calcium stearate), supplied by Ticona.

The powder of the CNF was obtained by milling carbon short fibers (supplied by Zoltek) in a ball mill at 50 rpm for a period of 10 min for 30 cycles. Figure 1 shows the SEM images of the carbon fibers at low and high magnification after the ball-milling treatment. The image shows that the obtained
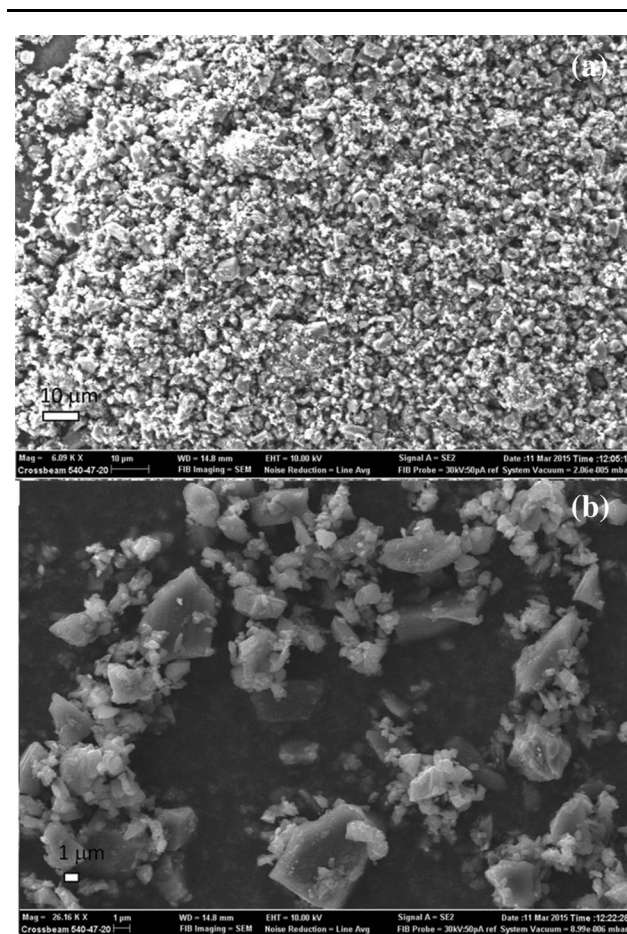

Fig. 1. SEM micrographs of the carbon nanofiller powder at two magnifications: 6 kx (a) and 43 kx (b).

carbon filler was composed of particles of irregular shape, ranging between ∼100 nm and ∼10 μm in width.

PO or vaseline oil was a United States Pharmacopeia (U.S.P.) of pharmaceutical grade supplied by the Sella pharmaceutical and chemical laboratory.

Nanocomposites Preparation

The UHMWPE/CNF nanocomposites were obtained by mixing the white UHMWPE powder with the ball-milled CNF powder (1 wt.%) as nanofiller and with 2 wt.% of PO as plasticizing filler to reduce the UHMWPE viscosity. A 2 wt.% fraction was chosen because higher PO contents require the residual oil extraction process while lower PO contents do not appreciably lower the UHMWPE viscosity. Galetz et al. and of Wood et al.[9,12] have used PO-assisted compounding for bulk processing of UHMWPE composites. PO was used since it is non-toxic and is a saturated hydrocarbon of small molecules with the same composition as UHMWPE.[9] Toxic solvents, which are often used for processing of UHMWPE films and fibers, should be avoided where possible, especially if the composite is intended for biomedical applications. Using PO to assist in melt mixing eliminates any of these concerns.[12] In any case, these authors employed much higher PO amounts then we did (also up to 50 vol.%), which was then removed in a long and complex extraction process in a Soxhlet extractor, using hexane solvent as the final step. In this paper, our more rapid methods employ a small quantity of PO, And this lower amount of PO does not require the long time necessary for the extraction process, and so is also useful for our purpose.

In order to achieve a good dispersion of the CNF and PO into the polymeric matrix, four mixing processes were employed: hot plate and magnetic stirring bar or simply, magnetic stirring (MS), ultrasonic bath (US), ball milling (BM) and twin-screw extrusion (EX). In Table I, the nanocomposites are named as UPC followed by these mixing technique codes. Figure 2 shows the steps necessary to prepare the UP sample (pure UHMWPE with PO)

used as a reference sample and the UPC nanocomposites, with the conditions of the four techniques, described in detail in the following.

Magnetic Stirring (MS)

UHMWPE and CNF were blended by using the hot plate and magnetic stir bar for 30 min at 1200 rpm without heating to produce a gray powder. Subsequently, the PO was added to the powder and blended together by using MS again for 4 min at 850 rpm at 120°C in order to absorb the PO into the UHMWPE to produce a wet gray powder.

Ultrasonic Bath (US)

Ethanol was used as a solvent to dispersed CNF in UHMWPE by using US for 3 h without heating; thereafter, the solution was dried in air for 48 h to extract all the solvent. Then, PO was added with the MS mixing method, as described above.

Ball Milling (BM), mod.Retsch-MM301

a gray powder with a high degree of fineness was produced by ball milling in air for 30 min at frequency of 20 Hz. Then, the PO was added with the MS mixing method as described above.

The same MS, US and BM techniques were also used to prepare the UP sample powder. A picture of both the UP and the UPC powders is presented in the Fig. 2.

Mini-Lab Extruder (EX) (Haake Thermo Scientific HAAKE MiniLab II)

in this case, the wet gray powder prepared by MS with the same conditions previously described was used as a raw material and hence fed through the extruder. The conditions used were: feeding time 2 min, melting temperature 195°C, mixing time 6 min, mixing speed 30 rpm which was increased at 32 rpm at the exit, to produce UPC nanocomposite wires. The wires were then cut into small pieces of a few millimeters length and then hot-pressed. The EX technique was also used to prepare the UP

Table I. Calorimetric parameters of UHMWPE and its nanocomposites

Sample name	Mixing method	Density (g/mL)	T_{Onset} (°C)	T_{Peak} (°C)	L_c (nm)	ΔH_c (J/g)	X_c (%)
U	–	0.866 ± 0.002	125.77	134.88	2.63	147.5	50.3
UP	Magnetic stirring	0.866 ± 0.001	125.47	134.90	2.63	139.4	48.5
UPC-MS	Magnetic stirring	0.868 ± 0.004	125.16	134.44	2.53	144.2	50.7
UPC-US	Ultrasound	0.868 ± 0.001	125.50	134.55	2.55	127.2	44.7
UPC-BM	Ball milling	0.862 ± 0.004	125.50	135.52	2.80	145.4	51.2
UPC-EX	Extrusion	0.865 ± 0.001	125.12	134.33	2.50	143.4	50.5

U UHMWPE, *UP* UHMWPE + paraffin oil, *MS* magnetic stirring, *US* ultrasound, *BM* ball milling, *EX* extrusion.
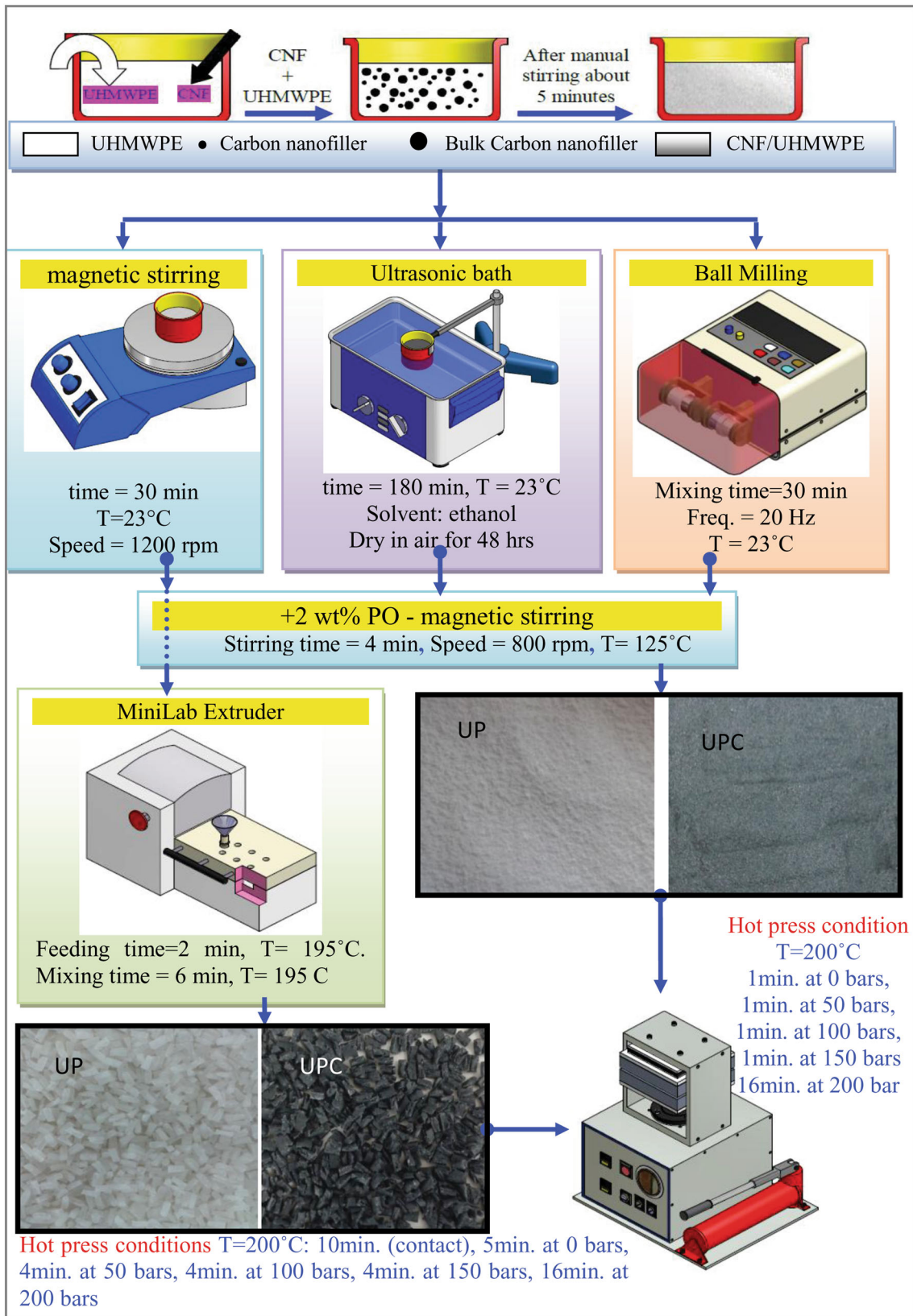
Fig. 2. Flow chart of UP and UPC nanocomposite preparations with images of powders and pellets produced; hot press conditions for powder and cut wires.

sample powder. A picture of both the UP and the UPC cut wire pieces are presented in the same flow chart of Fig. 2.

Sheets of UHMWPE and UP samples with uniform thickness were prepared by compression molding in a laboratory press; the polymer powder was kept at 200°C for 20 min at 20 MPa pressure, according to Suarez et al.[22] UPC sheets were obtained by hot-press compression molding of the powders at 200°C/20 min while the cut wires were compressed at 200°C/43 min, both at a pressure changing from 0 up to 200 bars. Generally, the materials were compressed in a copper die between two Teflon® sheets, 0.1 mm thick, in order to produce polymeric nanocomposites sheets with very fine surfaces. Therefore, in the first step, the material was compressed without any pressure (only contact between two dies) for 10 min to anneal the pellets and avoid any scratches or deformation in the Teflon® sheet. The interval of 10 min was detected by experimental tests and this is considered the minimum time to anneal the pellets and disperse them uniformly inside the die. The second step was employed to generate a uniform heating from the lower and upper plates of press when pellets start on uniform melting. The pressure was gradually increased in order to help the heating distribution inside the die. Then the next steps were continued to produce the final sheets. The hot press conditions, both for powders and for cut wires, are shown in detail in the flow chart in Fig. 2.

CHARACTERIZATION AND TESTING

The UHMWPE, UP and UPC samples were characterized by the following tests:

Changes in crystallinity content and melting temperature were assessed by heating samples ($n = 3$) in a Differential Scanning Calorimeter (DSC mod.Q-100 supplied by TA Instruments). Specimens were weighed with a microbalance and placed in aluminium pans. The sample and the reference were then heated from 30°C to 230°C with a heating rate of 10°C/min. Sample crystallinity was determined by integrating the enthalpy peak from 30°C to 230°C and normalizing it with the enthalpy of melting of 100% crystalline polyethylene, 291 J/g,[23] according to the following equation:

$$X_c(\%) = \frac{\Delta H_c}{(1 - \emptyset)\Delta H_m^o} \times 100, \tag{1}$$

where ΔH_c is the apparent enthalpy of crystallization of sample, ΔH_m^o is the melting enthalpy of 100% crystalline UHMWPE and $\emptyset$ is the weight fraction of CNF and PO in the UHMWPE composites.

Lamellar thickness (lc) was calculated according to the Thomson–Gibbs equation:

$$d_c = \frac{2\sigma_e}{\Delta h_f}\left(1 - \frac{T_m}{T_m^o}\right)^{-1} \tag{2}$$

where, $T_m^o = 418.95°K$ is the extrapolated equilibrium melting temperature of a PE crystal of infinite thickness, $T_m(°K)$ is the melting peak absolute temperature of CNF/UHMWPE, $\sigma_e = 9.3 \times 10^{-2}$ J/m² is the lamellar basal surface free energy, and $\Delta h_f = 2.8 \times 10^8$ J/m³ is the heat fusion per unit volume.[24]

Density (ρ) tests were performed by means of an Oahu's Balance (mod. Explorer pro EP 214C, precision of 0.1/1 mg) equipped like a hydrostatic balance which follows Archimedes' principle. The density is valuated from dry and wet weight measurements of the sample before and after immersion in ethanol, as indicated in the following equation:

$$\rho = \frac{P_{dry}}{P_{dry} - P_{wet}}\rho_{eth} \tag{3}$$

where P_{dry} and P_{wet} are the weight of the sample measured before and after immersion in ethanol, respectively, and ρ_{eth} is the ethanol density (0.790 g/cm³).

A Scanning Electron Microscope Zeiss Crossbeam 540 FEG-SEM was used to carry out morphological investigations of the carbon filler and of the UPC cut surface. For the SEM investigations, the UPC samples were coated in vacuum with a very thin gold film to make them electrically conductive. The samples were cut and mounted on an aluminum stab with a conductive adhesive film. The electron acceleration voltage was of 10 kV.

The rheological properties of UPC/MS, UPC/US, UPC/BM and UPC/EX were carried out by means of a rotational rheometer (Mod. SR5, Rheometric Scientific) equipped with an environmental controller. The experiments were performed with parallel plate geometry, diameter 25 mm, 1 mm gap and a stress-controlled rheometer in constant strain mode. UHMWPE and UP were also studied for comparison purposes. The tested samples were cut into circular shapes having 25 mm diameter and 1 mm thickness. The experiment was performed in the linear viscoelastic region (LVR) at temperature sweeps of 200°C, frequency range from 0.01 Hz to 100 Hz while the applied strain was 1%. Test measurements give the complex viscosity, η^*, the shear storage modulus, G', and the shear loss modulus (G'').

The tensile test was performed on the pristine polymer and on nanocomposite samples by using a Lloyd Universal Testing Machine, model LR10K, with a crosshead speed of 1 mm/min. The specimen geometry used for the tensile stresses was made according to the ASTM 638 M-3 international protocols (60 mm total length, 10 mm useful length, 2.5 mm minimal width, 1 mm thickness) by using a manual DGT System sample cutting press. For each analytical condition adopted, five samples were tested and the average measurements were compared.

SHORE D hardness mechanical tests were performed on joints by means of a PCE-HT 210, according to the ASTM D 2240 international protocol. The resolution was of 0.1 degrees of hardness and precision of ±1 degrees, in the scale range from 0 to 100.

RESULTS AND DISCUSSION

Morphological Investigation by SEM Analysis

The SEM investigation was performed with the aim of checking the dispersion of the carbon nanofiller particles inside the polymeric matrix in the nanocomposite samples prepared with the different techniques. Figure 3 shows the SEM micrographs of the UP, UPC-US, UPC-BM and UPC-EX samples. In particular, Fig. 3a and b shows two magnifications (low, about 20 Kx and high, at about 100 Kx) of the cut surface of the UP sample. The surface appears smoothed with several nano-cracks that propagate parallel to each other, generally along a preferential direction, for tens of microns.

The other SEM micrographs show the nanocomposite surfaces, both at low and high magnifications. The UPC-US sample exhibits a highly rough surface with evident micro-cracks (Fig. 3c) in which several particles are present (some of them evidenced by dashed circles), tens of micrometers wide, dispersed under the polymer surface (Fig. 3d).

The morphology of the UPC-BM (Fig. 3e) and UPC-EX (Fig. 3g) samples is again smoothed similar to the UP sample. A very few filler particles (some of them evidenced by dashed circles) can be highlighted, though with difficulty because of their extremely small size under the polymeric surface of the UPC-BM in the high magnification micrograph at about 100 Kx (Fig. 3f). Their amount is lower than that evidenced in the UPC-US surface probably due to the more intimate dispersion into the inner polymeric bulk.

No filler particles can be evidenced in the high magnification UPC-EX micrographs probably due to their very small size and because of the intimate distribution into the matrix (Fig. 3h).

These morphological observations suggest that the US technique favors the aggregation of filler in the visible micro-cluster; instead, the BM and EX technique allows a better dispersion of the filler of the order of nanometers, and is much more intimately dispersed into the polymeric matrix, hence progressively less visible at the same magnification.

The morphological analysis observation highlights the different effect of the mixing technique upon the nanocomposite composition. The optimal dispersion is obtained in the UPC-EX sample where the mechanical action and the thermal effect of the melting provides the best effect in filler particle homogenization and distribution inside the matrix.

Physical Properties

CNF did not significantly affect the thermal parameters as observed in Fig. 4 and Table I. This is associated with the low volume ratio of nanofiller in the developed nanocomposite. Table I lists the measured density and calorimetric parameters values, while the DSC curves of all the samples studied in this paper, UPC/MS, UPC/US, UPC/BM and UPC/EX, are shown in Fig. 4.

The melting temperature noted was around 134°C for all the samples since it is not affected by the addition of 1 wt.% CNF except for the UPC/BM sample which gradually increased to 135.52°C probably due to the better dispersion and interaction of the filler within the polymeric matrix observed on SEM analysis. The UPC-EX sample showed the lowest melting temperature which was associated with the sum of two opposite effects: an improvement of CNF dispersion (which improves the T_m) and a modification in the macromolecular UHMWPE structure during the extrusion, which lowers the T_m. The PO in the UHMWPE had an effect only upon the melting enthalpy and on the crystalline degree, which both decreased in the UP sample (139.4 J/g and 48.5%, respectively) with respect to the neat UHMWPE (147.5 J/g and 50.3%, respectively). This is due to the higher plasticizing effect induced by the PO presence in the polymer which enhances the macromolecular chains mobility reducing the overall structural order.

The addition of CNF to the UP sample generally re-improves both the melting enthalpy and the crystalline degree which reach maximum values of 145.4 J/g and of 51.2% in the UPC/BM sample. This last sample also has a higher lamellar thickness values of 2.80 nm with respect to the UP sample (2.63 nm), thus suggesting that CNF acts as effective heterogeneous nucleating agent to facilitate the re-crystallization of UHMWPE.[16] Instead, the UPC-US nanocomposite exhibits the lowest crystalline degree probably due to the CNF agglomeration into the polymeric matrix observed on SEM analysis rather than their dispersion so that they destroy the UHMWPE structural order.

Mechanical Tensile and Hardness Properties

The tensile parameters of UHMWPE, UP and UPC nanocomposites are listed in Table II and the average stress–strain curves are shown in Fig. 5.

In particular, in order to check the effect of the PO presence on the neat UHMWPE, in Fig. 4a we compare the tensile behavior of the pure UHMWPE and the UP sample. The curves and the data highlight that the PO has a plasticizing action upon the pure polymer since all the mechanical parameters greatly decrease while the deformation at break improves; in any case, the work at fracture does not appreciably change, suggesting that the material toughness is not compromised.
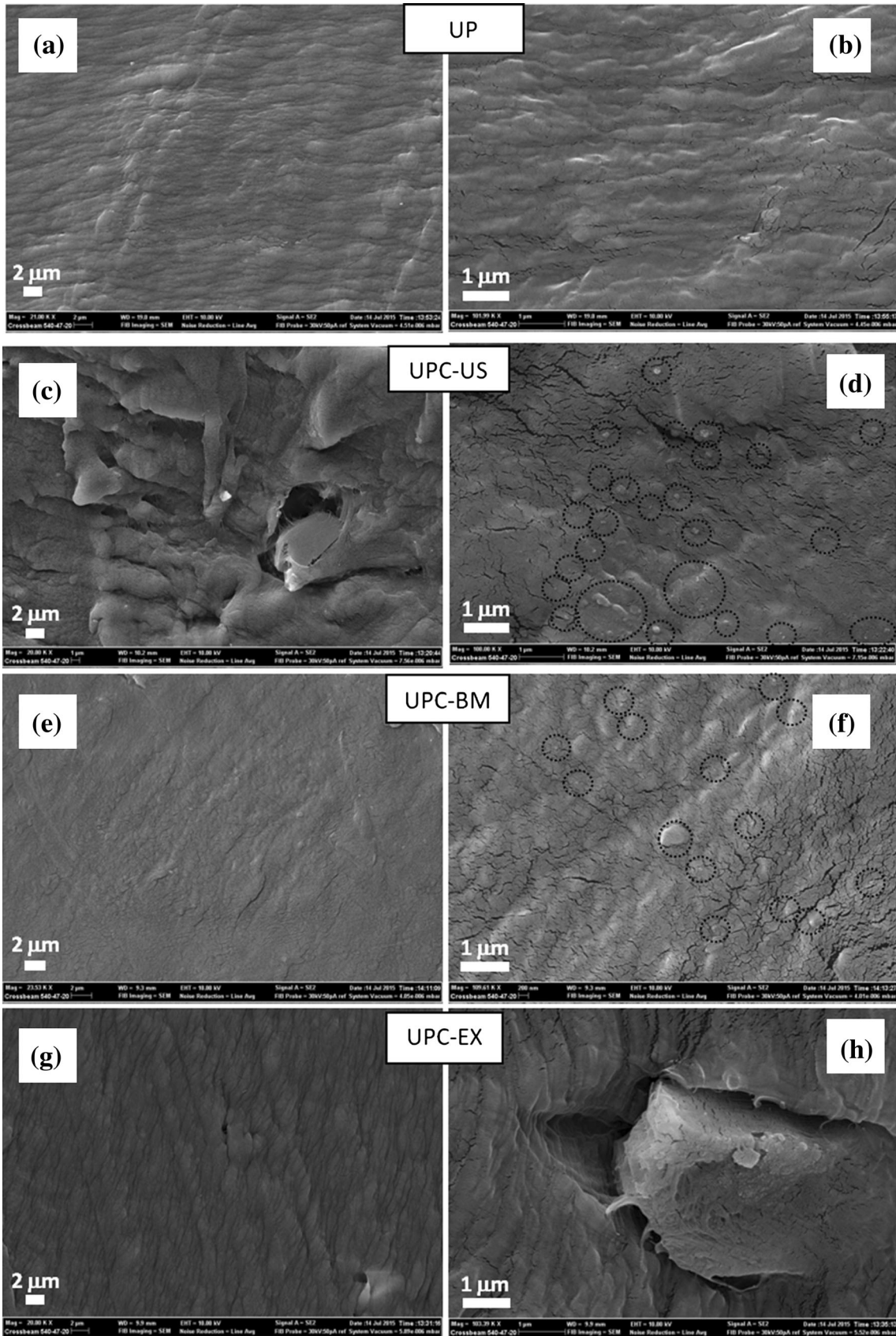
Fig. 3. SEM micrographs of UP (a, b); UPC-US (c, d); UPC-BM (e, f); UPC-EX (g, h); the dashed circles in d and f indicate the filler particles.
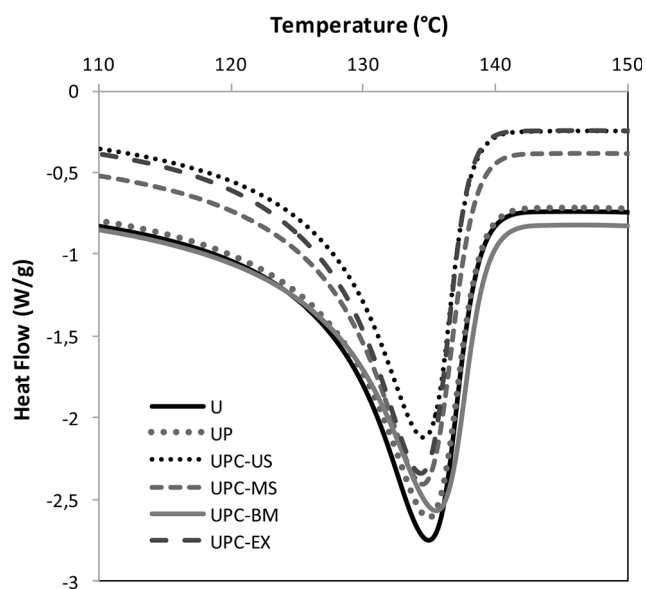
Fig. 4. DSC curves of UHMWPE, UP and UPC samples.

In Fig. 5b, the UP sample is compared to the UPC-US and UPC-MS nanocomposites in order to observe the effect of the CNF presence mixed by the US and MS techniques upon the tensile mechanical properties of the nanocomposites. The data indicate a decreasing of the tensile properties after the US mixing technique that lowered the material toughness. In fact, the strength, deformability and work at fracture of the UPC-US sample (which are 47.6 MPa, 608% and 6.8 J, respectively) decrease with respect to the UP sample (53 MPa, 722% and 7.5 J, respectively). The MS technique only improves the material stiffness and its deformability a little, and the changes are within the 10% experimental error.

In Fig. 5c, the UP sample is compared with the UPC-BM and UPC-EX nanocomposites in order to observe the effect of the CNF presence in the polymeric matrix mixed by the BM and EX techniques upon the tensile mechanical properties of the nanocomposites. This time, the experimental data indicate that a significant improvement in tensile properties with respect to the UP sample and also to the pure UHMWPE one.

In particular, the BM mixing generally improved all the parameters with respect to the UP sample: yield strength grows from 9.5 MPa up to 18.6 MPa (+96%), the yield strain from 16.8% to 41.5% (+60%) and stress at break from 52 MPa to 58.7 MPa (+13%). In addition, the strain at break grows from 723% to 793% (+9.6%), the tensile modulus from 272 MPa to 286 MPa (+6%) and the work at fracture (from 7.5 J to 8.0 J, an improvement of +6.6%); in any case, these parameters change within the 10% experimental error.

Furthermore, the EX method produced improvements in the nanocomposite although not in all the parameters. In particular, noticeable improvements

in the yield strength (from 9.5 MPa up to 19 MPa (+100%) and in the tensile modulus (from 271 MPa to 377 MPa (+40%) were observed. However, a decrease in the other parameters was also noted suggesting stiffness enhancement in the polymer with a decrease in deformability. In fact, the elongation at break decreased from 723% to 489% (−32%). The enhancement in stiffness and in yield strength could be due to the good dispersion of the filler within the matrix and to its interaction among the two components. Instead, the decrease of ductility could be due to the thermal and mechanical stress that the polymer suffers during the extrusion process.

It is also important to highlight that both the EX and BM dispersion mixing methods improve the features, not only with respect to the UP sample but also with respect to those of the neat UHMWPE sample. In particular, the UPC-BM improves the yield strength and strain, the deformability, the work at fracture and, so, the ductile character of the pure UHMWPE while the UPC-EX only improves its stiffness and its yield strength and strain.

The Shore D hardness value measurements are in agreement with the stiffness changes of the nanocomposites with respect to the UHMWPE and UP sample discussed above. In particular, the hardness of the UHMWPE sample (63.2 shore D) decreases after the addition of PO (62.4 Shore D) for the plasticizing action already discussed. The hardness in the UPC-US, UPC-MS and UPC-BM are similar or lower than the UP (62.5, 61.8 and 61.5 Shore D, respectively) while it greatly increases in the UPC-EX sample (65.3 Shore D). These results suggest a ductile character of the UPC-US, UPC-MS and UPC-BM samples which results to them being less hard, and a higher stiffness of the UPC-EX sample which results in it being the hardest among all the samples, all in agreement with the mechanical tensile previously discussed.

The mechanical and the calorimetric test results discussed above are in agreement with the SEM observations, showing a correlation between the different effects of the mixing techniques upon the nanocomposite microscopic composition resulting in a different macroscopic behavior.

The above-discussed mechanical tests highlighted a very high improvement in mechanical features of UPC-BM and of UPC-EX nanocomposites. In already published papers, the addition of CNFs in UHMWPE by means of melt mixing assisted by PO resulted in moderately improved mechanical properties: for example, Wood et al.[12] obtained an improvement of about 7% in stiffness (from 40 N/mm of pure UH, to 43.6 N/mm of 1 wt.% CNF/UH nanocomposite) and of about 5% in toughness, or area under the stress–strain curve (from 259 N·mm of pure UH to 271 N·mm of 1 wt.% CNF/UH nanocomposite) and, similarly, a very low improvement in mechanical properties also was obtained by Galetz et al.[9]

Table II. Mechanical and hardness data of UHMWPE and its nanocomposites

Sample name	Tensile modulus (MPa)	Yield strength (MPa)	Yield strain (%)	Stress at break (MPa)	Elongation at break (%)	Work at fracture (J)	Hardness (Shore D)
U	356.9 ± 12.3	18.1 ± 0.2	21.2 ± 0.7	55.8 ± 1.2	630.5 ± 13.7	7.6 ± 0.6	63.2 ± 0.2
UP	271.7 ± 12.4	9.5 ± 0.6	16.8 ± 1.4	52.9 ± 1.3	722.8 ± 18.6	7.5 ± 0.6	62.4 ± 0.1
UPC-US	328.6 ± 23.2	14.5 ± 1.2	20.8 ± 2.5	47.6 ± 0.8	608 ± 16.57	6.8 ± 0.7	62.5 ± 0.1
UPC-MS	261.0 ± 14.7	9.4 ± 0.5	18.1 ± 0.4	55.6 ± 1.4	766.1 ± 22.2	7.8 ± 0.4	61.8 ± 0.3
UPC-BM	286.7 ± 10.8	18.6 ± 0.4	41.5 ± 2.5	58.7 ± 1.1	793.8 ± 10.7	8.0 ± 0.4	61.5 ± 0.1
UPC-EX	377.6 ± 5.7	19.0 ± 0.4	36.0 ± 1.1	36.7 ± 0.9	489.1 ± 11.4	4.3 ± 0.3	65.3 ± 0.3

U UHMWPE, *UP* UHMWPE + paraffin oil, *MS* magnetic stirring, *US* ultrasound, *BM* ball milling, *EX* extrusion.
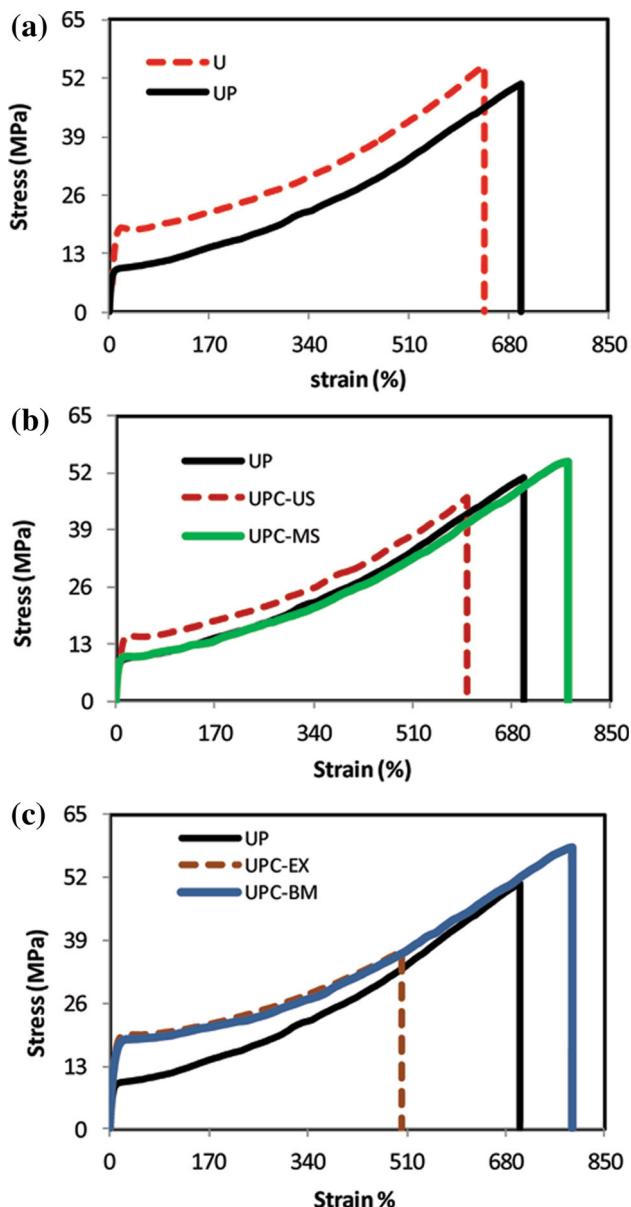

Fig. 5. Average stress–strain curves of: UHMWPE, UP (a); UP, UPC-US, UPC-MS (b); and UP, UPC-BM, UPC-EX (c) samples.

A low improvement was also demonstrated by Chen et al.[25] in graphene oxide (GO)/UHMWPE composites prepared by liquid-phase ultra-sonication (in alcohol) dispersion followed by hot-pressing: the 0.5 wt.% GO reinforced sample exhibited an improvement of 3% in yield strength and of 1.4% in elongation at break.

This suggests that our 2 wt.% PO-assisted BM and EX processes led to a good filler dispersion in the nanocomposites, macroscopically confirmed by their mechanical features.

There is currently a high demand for the ability to process UHMWPE composites effectively and efficiently. An efficient processing of UHMWPE will not only be beneficial for biomedical use but also for many other uses of UHMWPE, such as aerospace, body shielding, and other tribological applications. This suggests that our cheap, effective and fast processes discussed here can appeal to both research and industry.

Rheological Properties

Rheological tests were performed in order to check the behavior of the melted UHMWPE, UP and UPC samples and to verify the changes induced in the polymeric structure by the mixing methods suggested by the mechanical tensile and hardness test results.

Figure 6 shows the effect of CNF and the dispersion method on the complex viscosity of all the samples within a frequency range from 0.1 rad/s to 100 rad/s. The rheological parameters details are provided in Table III with the lowest (0.1 rad/s) and highest (100 rad/s) frequencies. In particular Fig. 6a compares the rheological behavior of pure UHMWPE with the UP sample. The presence of PO in the UHMWPE decreases its upper Newtonian viscosity at low frequencies from 2.65×10^6 Paxs to 2.1×10^6 Paxs at 0.1 rad/s (−20.75%). Instead, at a higher frequency of 100 rad/s (in the shear sensitivity zone), the viscosity of the pure UHMWPE (0.050×10^6 Paxs) decreased more quickly than that of the UP sample (0.066×10^6 Paxs). The decrease of the starting viscosity confirms that the 2 wt.% of PO
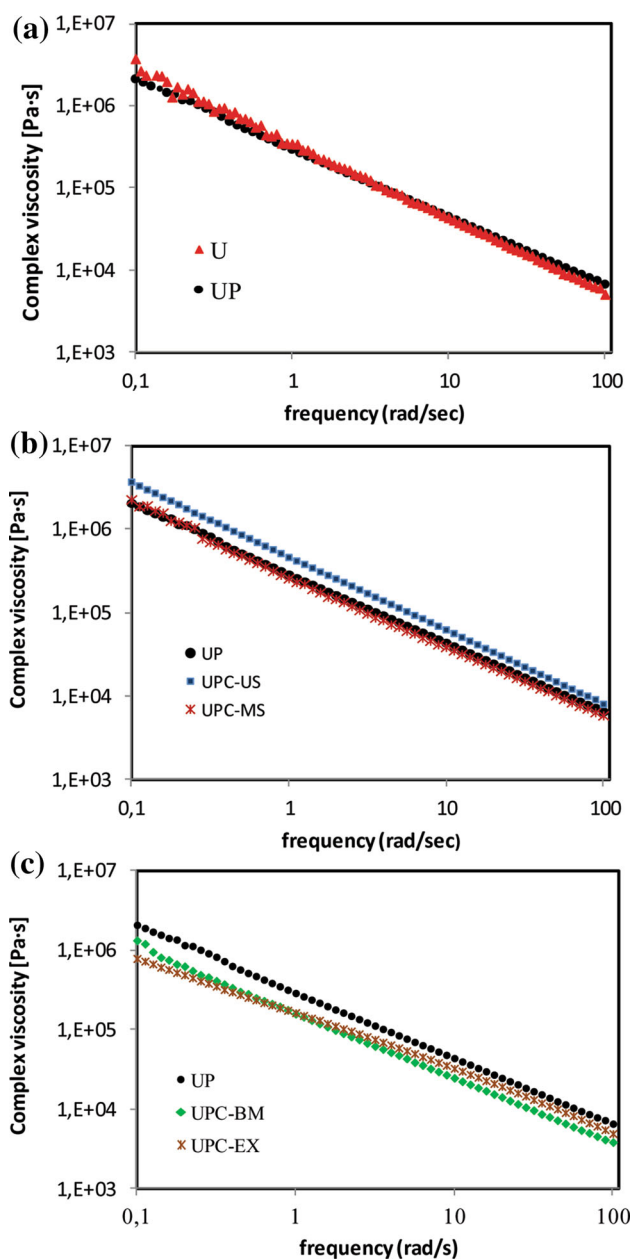
Fig. 6. Rheological curves of: UHMWPE, UP (a); UP, UPC-US, UPC-MS (b); and UP, UPC-BM, UPC-EX (c) samples.

has a plasticizing effect upon the UHMWPE, according to the reported tensile test results. Furthermore, the presence of PO further stabilizes the materials since the viscosity drop at high frequency is less than that of the pure UHMWPE sample. This result is in agreement with the results of Liu et al.[14] which emphasises that the PO presence is important since it reduces the fusion defects of UHMWPE induced by the working techniques.

In Fig. 6b the UP sample is compared with the UPC-US and UPC-MS nanocomposites in order to observe the effect of the CNF presence mixed with the US and MS techniques upon the rheological

properties of the nanocomposites. The data indicate that the CNF presence in the MS sample changes the rheological properties of the UP sample only a little, from 2.65×10^6 Paxs to 2.31×10^6 Paxs at 0.1 rad/s (-12%). This result suggests a poor mixing effect obtained by the MS technique such that the effect of the presence of the filler could not be appreciated in the nanocomposite formed. This result is in agreement with the mechanical tensile ones that did not lead to any better performance. Instead, a more evident improvement in viscosity is noted in the UPC-US sample, from 2.65×10^6 Paxs to 3.8×10^6 Paxs at 0.1 rad/s ($+43\%$). According to the mechanical tensile behavior of this nanocomposite which was worsened with respect to the UP sample, the improvement in viscosity could be reasonably due to an agglomeration effect of CNF within the polymeric matrix, due to poor dispersion. The viscosity also remains still higher than that of the UHMWPE and UP samples at high frequency with a value of 0.082×10^6 Paxs.

In Fig. 6c, the UP sample is compared with the UPC-BM and UPC-EX nanocomposites in order to observe the effect of the CNF presence mixed with the BM and EX techniques upon the rheological properties of the nanocomposites. The data indicate that the CNF presence in both the nanocomposites changes the rheological properties, decreasing their starting Newtonian viscosity. In particular, the viscosity at low frequency (0.1 rad/s) decreases from 2.65×10^6 Paxs to 1.34×10^6 Paxs in the UPC-BM sample (-50%) and to 0.82×10^6 Paxs in the UPC-EX sample (-69%).

These results highlight that BM and the EX processes have a strong effect upon the nanocomposite composition and produce a good dispersion of the CNF inside the polymeric matrix. In particular, the EX process has an effect upon the macromolecular chains and, hence, upon the polymeric structure of the melted nanocomposites: the lowering in viscosity could be related to a decrease in the macromolecular chain complexity due to the melt mixing of the polymer with the filler and the better intercalation of the CNF among the polymeric chains.

The BM mixing method had no effect on the solid powder of polymeric macromolecular structure since the UHMWPE is a ductile plastic.[26] The process acted upon the CNF filler which is broken into smaller size powder during the milling process and so has better dispersion in the polymeric matrix. The intercalation of the milled CNF filler in the polymer is wider and it can separate the chains, favoring their mobility. This effect decreases the stiffness but highly enhances the yield mobility and hence the overall ductile character of the polymer.

The EX process which melts and mixes the components acted on the macromolecular chains of the polymer without influencing the CNF length. The mixing intimately connected the CNF with the

Table III. Rheological parameters of UHMWPE and its nanocomposites

Sample name	Low frequency 0.1 (rad/s)			High frequency 100 (rad/s)		
	η^* ($\times 10^6$ Pa s)	G' ($\times 10^5$ MPa)	G'' ($\times 10^5$ MPa)	η^* ($\times 10^6$ Pa s)	G' ($\times 10^5$ MPa)	G'' ($\times 10^5$ MPa)
U	2.65	0.25	0.19	0.050	4.95	0.74
UP	2.10	0.16	0.17	0.066	6.54	0.98
UPC-US	3.78	1.24	0.43	0.082	8.11	0.85
UPC-MS	2.31	1.24	0.39	0.059	5.84	1.07
UPC-BM	1.34	0.65	0.26	0.038	3.81	0.73
UPC-EX	0.82	0.31	0.25	0.049	4.85	1.09

U UHMWPE, *UP* UHMWPE + paraffin oil, *MS* magnetic stirring, *US* ultrasound, *BM* ball milling, *EX* extrusion.

polymer such that the stiffness of the material improved significantly. The CNF are well dispersed into the matrix and so this improvement is relevant, as expected. On the other hand, it was noted that the thermomechanical degradation effect due to the EX process changed the molecular chains structure resulting in a general reduction in nanocomposite ductility. This decreased the material viscosity and its deformability.

The study shows that these dispersion techniques could be selectively chosen in order to project a material with different features and, hence, different mechanical applications. For example, UHMWPE GUR1020 has a great application in the biomedical field as a ductile bearing component in medical prostheses. Here, a high ductility can be very attractive, especially a high yield strength, which defines the elastic limit of the material. Instead, the high stiffness of a UHMWPE could be employed in other typologies in engineering fields, such as that of the Aeolian turbine in which the material must be highly resistant to the erosion of the wind, to the hydrolytic degradation of wet present in the air and of rain, to the photo-degradation of UV exposure. For this last purpose, the high chemical and hydrolytic resistance of polyethylene together with the improved stiffness and its good dimensional stability could be attractive in this application. In such a case, the UV exposure resistance should be improved considering the presence to the UV absorber fillers in its formulation. Studies are in progress in order to verify the possible applications of the UPC-BM and UPC-EX as above suggested.

CONCLUSION

In this paper, four techniques of dispersion (magnetically stirring, ball milling, ultrasound and extrusion) were used to blend 1 wt.% of carbon nano filler with medical grade UHMWPE. Also, a 2 wt.% of PO was added to the mixing to overcome the higher viscosity of UHMWPE, and thus produce uniform dispersion. The experimental results highlighted:

- the PO plasticizes the UHMWPE decreasing its structure order (the crystalline degree is lower) while not appreciably changing the melting temperature;
- generally, the mixing in the extruder and in the ball mill induces a good mixing of the filler inside the polymeric matrix, changing its mechanical properties and thermal features;
- in particular, the extrusion improves the stiffness despite the UMMWPE deformability with no change in the thermal properties; the ball milling improves both the ductility of polyethylene (despite its stiffness) and the thermal features in terms of melting temperature, crystalline degree and lamellae thickness;
- in contrast, the other two mixing techniques poorly dispersed the nanofiller in this study thereby decreasing the overall mechanical features of the UHMWPE.

These results proposes the use of the ball milling and the extrusion processes as the best techniques for the preparation of UHMWPE/PO/carbon nanofiller-based nanocomposites and tailored possible applications of these materials due to the different features of the nanocomposites. Work is in progress to investigate the biomedical application of the ball milling-prepared UPC nanocomposites and to check the high stiffness resistance application fields of the extrusion-prepared composites.

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