AUTHOR(S): VISCO, A., YOUSEF, S., GALTIERI, G., NOCITA, D., PISTONE, A. and NJUGUNA, J.

TITLE: Thermal, mechanical and rheological behaviors of nanocomposites based on UHMWPE/paraffin oil/carbon nanofiller obtained by using different dispersion techniques.

YEAR: 2016

Publisher citation: VISCO, A., YOUSEF, S., GALTIERI, G., NOCITA, D., PISTONE, A. and NJUGUNA, J. 2016. Thermal, mechanical and rheological behaviors of nanocomposites based on UHMWPE/paraffin oil/carbon nanofiller obtained by using different dispersion techniques. JOM [online], 68(4), pages 1078-1089. Available from: https://doi.org/10.1007/s11837-016-1845-x

OpenAIR citation: VISCO, A., YOUSEF, S., GALTIERI, G., NOCITA, D., PISTONE, A. and NJUGUNA, J. 2016. Thermal, mechanical and rheological behaviors of nanocomposites based on UHMWPE/paraffin oil/carbon nanofiller obtained by using different dispersion techniques. JOM, 68(4), pages 1078-1089. Held on OpenAIR [online]. Available from: https://openair.rgu.ac.uk/

Thermal, Mechanical and Rheological behaviors of nanocomposites based on UHMWPE/Paraffin Oil/ Carbon Nano filler obtained by using different dispersion techniques

Annamaria Visco[a] , Samy Yousef [a,b] , Giovanna Galtieri[a] , Davide Nocita[a] ,
Alessandro Pistone[a], James Njuguna[c]

[a] *Department of Engineering, University of Messina, Contrada Di Dio, I-98166 Messina, Italy*
[b] *Dept. of Production Engineering and Printing Technology,*
Akhbar Elyom Academy 6th of October, Egypt
[c] *Centre for Advanced Engineering Materials, School of Engineering, Robert Gordon University,*
Riverside East, Garthdee Road, Aberdeen, AB10 7GJ United Kingdom

C**orresponding author**:
Annamaria Visco – *Associate Professor of Polymeric materials science*
Department of Engineering, University of Messina
Contrada di Dio, Vill. S.Agata, I-98166 Messina, Italy.
Tel.: ++39 090 3977249; Fax: ++39 090 3977464; e-mail: avisco@unime.it

Abstract

Ultra high molecular weight polyethylene (UHMWPE) is a very attractive polymer employed as 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 as assisted melt-mixing process.

In this work we have prepared nanocomposites based on UHMWPE, carbon nano filler (CNF) and paraffin oil mixed by different mixing methods: magnetic stirring (MS), ball milling (BM), ultrasonic (US) 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, the yielding strength improved to 18.6 MPa (+96%), the yield strain improved by 60% while stress at break improved by 13% for the BM method. In summary, the EX improved the stiffness while the BM produced better ductility, melting temperature and the crystalline degree of the nanocomposites.

Key words; UHMWPE, Carbon nano filler, Paraffin Oil, mixing techniques, rheological, mechanical test, thermal properties.

1. Introduction

Ultra high molecular weight polyethylene (UHMWPE) is a useful thermoplastic polymer that 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 improvement of the UHMWPE properties through the use of nanofiller materials such as carbon nanofiber (CNF), carbon nanotubes (CNT) and graphene [5]. Graphene and CNT are better nanofiller materials compared to CNF due to the higher aspect ratio, but due to a lower production cost, CNF is considered more economic [6]. This does not preclude that CNF is disadvantaged comparable to other carbon fillers on the electrical, mechanical and thermal properties [7]. So, CNF was used widely to reinforce a variety of thermoplastic polymers such as polypropylene, polycarbonate and nylon [8]. Also, CNF was used in biomaterial applications, particular 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 lead to very poor dispersion of the filler that negatively affects the final properties of the composite materials [10,11].

In the recent years, some researchers started to employ the paraffin oil (PO) to decrease the UHMWPE viscosity and favor of its work ability. Wood et al. (2011) used the PO as an assisted melt-mixing with UHMWPE and carbon nano fibers through several methods of dispersion (mortar and pestle, ultra-sonification, hot plate and magnetic stir, Haake torque rheometer), to decrease the viscosity and obtained UHMWPE/CNF nanocomposites with a good dispersion [12]. The result showed that the wear and mechanical properties were improved, but the preparation method of UHMWPE/CNF was more complicated and the paraffin oil must be extracted by soxhlet after mixing process. This last process is expensive and it takes more time improving the production period of the nanocomposite. Zhang et al. (2011) blended UHMWPE with PO by using a HAAKE HBI System without extracted PO to increase the crystallization behaviors [13]. Instead Shilei Lio et al. (2014) studied the effect of the PO mixed to the UHMWPE by magnetic stirring and they evidenced as the paraffin oil reduces the fusion defects of UHMWPE induced by the working techniques; this improved its mechanical and physical properties [14].

Generally, different dispersion methods of fillers were used in several literature papers in order to obtain a well distribution and mixing of the nanofiller (in particular carbon nano fibers and carbon nanotubes) in the UHMWPE. In particular, some researchers studied the effect of nanofiller on the thermal behavior (melting temperatures, onset temperature, crystallinity degree and apparent enthalpy) of UHMWPE by using differential scanning calorimeter (DSC) [15]. Additionally, other literature papers have studied the effect of filler materials on rheological behavior by using dynamic rheometry [16-20] because of the high complex viscosity of UHMWPE due to its high molecular weight. In particular, Chen Ma et al. (2014) 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 with antioxidant using a twin-screw blender. The results showed that the viscosity was decreased by the addition of the modified CNF [21]. Finally, few papers presented the mechanical properties of UHMWPE/CNT nanocomposites and their results were not good, due to a poor dispersion.

In the present study we have investigated the effect of the paraffin oil and of the carbon nano filler presence on the mechanical and thermal features of UHMWPE/PO/CNF composites blended with four different mixing methods. Among these, two methods have been particularly interesting for the improvements in mechanical performance that are much higher than those thus far experienced in similar nanocomposite systems. Moreover, not being necessary the PO removal, our processes are faster than similar methods which employ high amounts of PO, that then needs to be extracted. These two methods, in addition to being fast and effective to disperse the reinforcing filler inside the UHMWPE matrix, are also cheap. In fact, we employed carbon nano fillers obtained by milling carbon fibers because of their reasonable and inviting price with respect to other commons nano fillers as CNT or graphene, so that they can be well considered for prototyping device. Tensile, rheological, density and calorimetric analyses were performed in the samples in order to check the properties changes.

2. Materials and methods

2.1 Materials

The UHMWPE powder was medical grade GUR1020 (average molecular weight of 2-4×10^6 g/mol, density of 0.93 g/cm^3, without calcium stearate), supplied by Ticona (code "U").

The powder of Carbon Nano Filler (code "CNF") was obtained by milling carbon short fibers (supplied by Zoltek) in a ball milling at 50 rpm for a period of 10 minutes for 30 cycles. **Figure 1** shows the SEM images at low and high magnification of the carbon fiber after the ball milling treatment. The image indicates that the obtained carbon filler was composed by particles of irregular shape, ranging between ~100 nm and ~10 μm wideness.

Paraffin oil oil or Vaseline oil (code "PO") was a United states Pharmacopeia (U.S.P.) of pharmaceutical grade supplied by Sella pharmaceutical and chemical laboratory.

2.2 Nanocomposites preparation

The UHMWPE/CNF nanocomposites were obtained by mixing the white UHMWPE powder with the black milled CNF powder (1% wt.) as nanofiller and with 2 wt.% of paraffin oil as plasticizing filler to reduce the UHMWPE viscosity. 2 wt.% fraction was chosen because higher PO contents needs the residual oil extraction process while lower PO contents do not appreciably lower the UHMWPE viscosity. Galetz et al. and of Wood at al. [9,12] have used paraffin oil assisted compounding for bulk processing of UHMWPE composites. Paraffin oil was used since it is non toxic and is a saturated hydrocarbon of small molecules with the same composition of UHMWPE [9]. Toxic solvents, which are often used for processing of UHMWPE films and fibers, should be avoided when possible, especially if the composite is intended for biomedical applications. Using paraffin oil to assist in melt mixing eliminates any of these concerns [12].

Anyway, these Authors employed much high paraffin oil amounts then us (arriving also up to 50 vol.%); it was then removed in a long and complex extraction process in a Soxhlet extractor, using hexane solvent as final step. In this paper, our faster methods employ a small PO quantity. The low PO amount do not requires the long time necessary for all the extraction process, and it is also useful to our purpose.

In order to achieve a good dispersion of the CNF and oil into the polymeric matrix, four mixing processes were employed: hot plate and magnetic stir bar or simply, magnetic stirring (code “MS”), ultrasonic bath (code “US”), ball milling (code “BM”) and twin-screw extrusion (code “EX”).

The nanocomposites were codifies as “UPC” followed by the mixing technique code, as listed and detailed in Table I, where “U” stands for UHMWPE, “P” stands for paraffin oil and “C” stands for CNF. **Figure 2** resumes the steps necessary to prepare the UP sample (pure UHMWPE with paraffin oil) used as reference sample and the UPC nanocomposites, with the conditions of the four techniques, described in details 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 powder and blended together by using again MS for 4 min at 850 rpm at 120˚C in order to absorb the PO into UHMWPE and to produce a wet grey powder.

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

Ball Milling (BM), mod.Retsch-MM301: a grey powder with a high degree of fineness was produced with ball milling in air for 30 min at frequency 20 Hz. Then, the PO was added with the MS mixing method as described above.

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

Mini-Lab Extruder (EX)(Haake Thermo Scientific HAAKE MiniLab II): in this case the wet grey 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 that increased until 32 rpm at the exit, to produce UPC nanocomposite wires. The wires were then cut into small pieces of few millimeters length and then hot pressed. The EX technique was also used to prepare the UP sample powder. A picture of both the UP and the UPC cut wire pieces are presented in the same flow chart of **Figure 2**.

Sheets of U and UP samples with uniform thickness were prepared by compression moulding in a laboratory press: the polymer powder was kept at 200°C for 20 minutes 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/20min 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 copper die between two Teflon® sheets, 0.1 mm thick, in order to produce polymeric nanocomposites sheets with very fine surfaces. Therefore, the first step the material was compressed without any pressure (only contact between two dies) for 10 min to anneal the pellets and avoids any scratch or deformation in the Teflon sheet. The interval of 10 min was detected by experimental tests and this is considered the minimum time for anneal the pellets and disperse them uniformly inside the die. The second step was employed to generate a uniform heating from lower and upper plates of press then pellets start on uniform melting. The pressure was gradually increased in order to help the heating distribution inside the die. Then continue the next steps to produce the final sheets. The hot press conditions, both for powders and for cut wires, are given in details in the flow chart on **Figure 2**.

3. Characterization and Testing

The U, 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:

$$X_c\ (\%) = \frac{\Delta H_c}{(1-\emptyset)\ \Delta H_m^0}\ \mathrm{x}\ 100 \qquad (1)$$

where ΔH_c is the apparent enthalpy of crystallization of sample, ΔH°_m is the melting enthalpy of 100% crystalline UHMWPE and Ø is the weight fraction of CNF and paraffin oil in the UHMWPE composites.

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

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

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, σ_e = 9.3 x 10^{-2} J m^{-2} is the lamellar basal surface free energy, and Δh_f = 2.8 x 10^{8} J m^{-3} 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 that follows the Archimede’s principle. The density is valuated from dry and wet weight measurements of the sample before and after the immersion in ethanol, as indicated in the following equation:

$$\rho = \frac{P_{dry}}{P_{dry} - P_{wet}}\rho_{eth} \qquad (3)$$

where P_{dry} and P_{wet} are the weight of the sample measured before and after the immersion in ethanol, respectively, and ρ_{eth} is the ethanol density (0.790 g/cm^3).

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 at stress controlled rheometer in constant strain mode. U and UP were also studied for comparison purposes. The tested samples were cut into circular shapes having diameter 25mm and thickness 1mm. The experimental was performed in the linear viscoelastic region (LVR) at temperature sweeps 200°C, frequency range from 0.01 to 100 Hz and the applied strain was of 1%. Test measurements give the complex viscosity, η^*, the shear storage modulus, G', 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 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.

Hardness 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 scale range from 0 to 100.

4. Results and discussion

4.1 Morphological investigation by SEM analysis

The SEM investigation was performed with the aim to check the dispersion of the carbon nano filler particles inside the polymeric matrix in the nanocomposite samples prepared with the different techniques. In **Figure 3** are shown the SEM micrographs of the UP, UPC-US, UPC-BM and UPC-EX samples. In particular, **Fig.3a,b** show two magnifications (low, about 20Kx and high, at about 100 Kx, respectively) of the cut surface of the UP sample. The surface appears smoothed with several nano cracks that propagate parallel among 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 are present several particles (some of them evidenced by dashed circles), of 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. Very little filler particles (some of them evidenced by dashed circles) can be highlighted with difficulty for its 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.

Instead no evident filler particles can be evidenced in the high magnification UPC-EX micrographs probably due to the very low size and for the intimate distribution into the matrix (**Fig.3h**).

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

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.

4.2 Physical properties

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

The melting temperature noted was around 134°C for all the sample since it is not affected by the addition of 1 wt.% CNF except for the UPC/BM sample which was gradual increase 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 shows the lowest melting temperature which was associated to the sum of two opposite effects: an improvement of CNF dispersion (that improves the T_m) and a modification in the macromolecular UHMWPE structure during the extrusion, which lowers the T_m. The paraffin oil in the UHMWPE had an effect only upon the melting enthalpy and on the crystalline degree, which both lowers in the UP sample (139.4 J/g and 48.5% respectively) with respect to the neat U (147.5J/g and 50.3% respectively). This is due to the higher plasticizing effect induced by the oil presence in the polymer which enhance 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 that reach maximum values of 145.4 J/g and of 51.2% in the UPC/BM sample. This last sample has also a higher lamellar thickness values of 2.80 nm with respect to the UP sample (2.63nm) thus suggesting that CNF acts as effective heterogeneous nucleating agents 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.

4.3 Mechanical tensile and hardness properties

The tensile parameters of U, UP and UPC nanocomposites are listed in **Table II** and the average stress –strain curves are shown on **Figure 5**.

In particular, in order to check the effect of the paraffin oil presence on the neat UHMWPE, in **Figure 4a** we compared the tensile behavior of the pure U and the UP sample. The curves and the data highlight as the paraffin oil has a plasticizing action upon the pure polymer since all the mechanical parameters highly decrease while the deformation at break improves; anyway the work at fracture does not appreciably changes suggesting that the material toughness is not compromised.

In **Figure 5b** 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 ultra sound and magnetically stirring techniques upon the tensile mechanical properties of the nanocomposites. The data indicates a decreasing of the tensile properties after the US mixing technique that worse the material toughness. In fact the strength, deformability and work at fracture of the UPC-US sample (that are of 47.6 MPa, 608 % and 6.8 J, respectively) decrease with respect to the UP one (53 MPa, 722 % and 7.5 J). The MS technique little improves the material stiffness and its deformability; anyway the changes are within the 10% (experimental error).

On **Figure 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 ball milling and extrusion technique, upon the tensile mechanical properties of the nanocomposites. This time the experimental data indicates that a significant improvement in tensile properties with respect to the UP sample and also to the pure U one.

In particular the BM mixing generally improved all the parameters with respect to the UP sample: yielding strength grows from 9.5 MPa up to 18.6 MPa (+ 96%), the yield strain from 16.8% to 41.5% (improving of +60%) and stress at break from 52MPa to 58.7 MPa (improving of +13%). Besides, the strain at break grows from 723% to 793% (improving of +9.6%), the tensile modulus from 272 MPa to 286 MPa (improving of +6%) and the work at fracture (from 7.5 J to 8.0 J an improvement of +6.6 %); anyway 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, a noticeable improvement 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% improvement) was 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 yielding 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 improves the features not only with respect to the UP sample but also with respect to those of the neat U sample. In particular the UPC-BM improves the yielding 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 U and UP sample before discussed. In particular, the hardness of the U sample (63.2 shore D) decreases after the addition of PO (62.4 Shore D) for the plasticizing action already discussed of oil. The hardness in the UPC-US, UPC-MS and UPC-BM are similar or lower than the UP one (62.5, 61.8 and 61.5 Shore D, respectively) while it highly 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 be less hard and the higher stiffness of the UPC-EX sample which results to be the hardest among all the samples, all in agreement with the mechanical tensile previously discussed .

The mechanical and the calorimetric test results before discussed, in agreement with the SEM observations, evidenced a correlation among the different effect of the mixing technique upon the nanocomposite microscopic composition resulting in a different macroscopic behavior.

The above discussed mechanical test 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 paraffin oil, 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 1wt.% 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 1wt.% CNF/UH nanocomposite) and similarly, a very low improvement in mechanical properties was obtained also by Galetz et al.[9].

A low improvement was also checked by Chen et al. [26] 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 yielding strength and of 1.4% in elongation at break.

This suggest that our 2 wt.% PO assisted BM and EX processes let 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 here discussed can be appealing for both research and industry.

4.4 Rheological properties

Rheological tests were performed in order to check the behavior of the melted U, 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.

Figures 6 shows the effect of CNF and 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 at highest at (100 rad/s) frequency. In particular **Figure 6a** compares the rheological behavior of pure U with UP sample. The presence of paraffin oil in the UHMWPE decreases its upper Newtonian viscosity at low frequency from $2.65 \cdot 10^6$ Paxs to $2.1 \cdot 10^6$ Paxs at 0.1 rad/s (-20.75%). Instead at higher frequency of 100 rad/s (in the shear sensitivity zone), the viscosity of the pure U ($0.050 \cdot 10^6$ Paxs) decreased quicker than that of the UP sample ($0,066 \cdot 10^6$ Paxs). The decrease of the starting viscosity confirms that the 2 wt.% of oil has a plasticizing effect upon the UHMWPE, according to the tensile test results reported. Furthermore the oil presence further stabilizes the materials since the viscosity drop at high frequency is less than that of the pure U sample. This result is in agreement with the results of Liu et al. (2014) which emphasis on the fact that the paraffin oil presence is important since it reduces the fusion defects of UHMWPE induced by the working techniques [14].

In **Figure 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 ultra sound and magnetically stirring techniques upon the rheological properties of the nanocomposites. The data indicates that the CNF presence in the magnetically stirred sample little changes the rheological properties of the P sample from $2.65 \cdot 10^6$ Paxs to $2,31 \cdot 10^6$ Paxs at 0.1 rad/s (-12%). This result suggests a poor mixing effect obtained by the MS technique such that the presence of the filler effect could not be appreciated in the nanocomposite formed. This result is in agreement with the mechanical tensile ones that did not result into any better performance. Instead, a more evident improvement in viscosity is noted in the UPC-US sample, from $2.65 \cdot 10^6$ Paxs to $3.8 \cdot 10^6$ Paxs at 0.1 rad/s (+43%). According to the mechanical tensile behavior of this nanocomposite that was worsened with respect to the UP sample, the improving in viscosity could be reasonably due to an agglomerations effect of CNF within the polymeric matrix, due to a poor dispersion. The viscosity remains still higher than that of the U and UP samples also at high frequency with a value of $0.082 \cdot 10^6$ Paxs.

In **Figure 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 ball milling and extrusion techniques upon the rheological properties of the nanocomposites. The data indicates 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 $2.65 \cdot 10^6$ Paxs to $1.34 \cdot 10^6$ Paxs in the UPC-BM sample (-50%) and to $0.82 \cdot 10^6$ Paxs in the UPC-EX sample (-69%).

These results highlighted that ball milling and the extrusion process have a strong effect upon the nanocomposite composition and produces a good dispersion of the CNF inside the polymeric matrix. In particular, the extrusion 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 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 ball milling mixing method had no effect on the solid powder of polymeric macromolecular structure since the UHMWPE is a ductile plastic [25]. The process acted upon the CNF filler that is broken in smaller size powder during the milling process and so better dispersion in the polymeric matrix. The intercalation of the so milled CNF filler in the polymer is wider and it can separate the chains favoring their mobility. This effect decreases the stiffness but highly enhance the yielding mobility and hence the overall ductile character of the polymer.

The extrusion process that melts and mix the components acted on the macromolecular chains of the polymer without influencing the CNF length. The mixing intimately connected the CNF with the 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 thermo mechanical degradation effect due to the extrusion, changed the molecular chains structure resulting into 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 ductile bearing component in medical prostheses. Here a high ductility can be very attractive, especially a high yielding strength, which defines the elastic limit of the material. Instead the high stiffness of a UHMWPE could be employed in other typology of engineer field, 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 the rain, to the photo degradation of the UV ray 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 ray exposure resistance should be improved considering the presence to the UV ray 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 hypotize.

Conclusions

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

- the paraffin oil plasticize the UHMWPE decreasing its structure order (the crystalline degree is lower) while do not appreciably change the melting temperature;
- generally, the mixing in the extruder and in the ball milling 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 to the UMMWPE deformability with no change in the thermal properties; the ball milling improves both the ductility of

polyethylene (despite to its stiffness) and the thermal features in terms of melting temperature, crystalline degree and lamellae thickness;

- on the contrary, the other two mixing techniques poorly dispersed nanofiller the filler in this study thereby decreasing the overall mechanical feature 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/Paraffin Oil/Carbon Nano filler based (UPC) nanocomposites and tailored possible application of these materials due to the different features of the nanocomposites. Works are 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 compounded by extrusion UPC ones.

Acknowledgment

The authors gratefully acknowledge the support from Erasmus Mundus through Emmag Program.

References

1. B. Aldousiri, A. Shalwan, and C. W. Chin, *Adv. Mater. Sci. Eng.* 8, 2013, (2013), doi:10.1155/2013/645923
2. A.M Visco, L.Torrisi, N. Campo, U. Emanuele, A.Trifirò, and M. Trimarchi, *J. Biomed. Mater. Res., Part B* 89B (1), 55 (2009), doi: 10.1002/jbm.b.31187
3. D.I. Chukov, A.A. Stepashkin, M.V. Gorshenkov, V.V. Tcherdyntsev, and S.D. Kaloshkin, J. of Alloys and Compounds 586, S459 (2014).
4. S.K. Raghuvanshi, Bashir Ahmad, Siddhartha, A.K. Srivastava, J.B.M. Krishna, and M.A. Wahab. *Nucl. Instrum. Methods Phys. Res., Sect. B* 271, 44, (2012).
5. J.A.Puertolas, and S.M.Kurtz," *J. of the Mech. Behavior of Biomed. Mat.* 39, 129 (2014).
6. M.C. Evora, J.R. Araujo, E.H.M. Ferreira, B.R. Strohmeier, L.G.A. Silva,and C.A. Achete, *Appl. Surf. Sci.* 335, 78 (2015).
7. A. Eitan, K. Jiang, D. Dukes, R. Andrews, and L.S. Schadler, *Chem. Mater*. 15, 3198 (2003) Doi: 10.1021/cm020975d.
8. J. Zhang, in *Functional nanofibers and their applications*, ed. Qufu Wei (Woodhead Publishing Limited, 2012), doi: 10.1533/9780857095640
9. M. C. Galetz, T. Bla, H. Ruckdäschel, J. K. W. Sandler, V. Altstädt and U. Glatzel, *J. Appl. Polym. Sci.* 104(6), 4173 (2007)
10. S.Ge , S. Wang, and X. Huang , *Wear* 267, 770 (2009).
11. B.C. Anderson, P.D. Bloom, K.G. Baikerikar, V.V. Sheares, and S.K. Mallapragada, *Biomaterials* 23, 1761(2002).
12. W. J. Wood, R. G. Maguire and W. H. Zhong, *Composites, Part B* 42, 584 (2011)

13. C.F. Zhang, Y.X.Bai, J. Gu, and Y.P. Sun, *J. Appl. Polym. Sci.* 122(4) , 2442 (2011) DOI 10.1002/app.34429
14. S. Liu, F. Wang, J. Chen, and Ya Cao, *Int. J. Polym. Anal. Charact.* 20, 138 (2015)
15. J. Zuo, Y.M. Zhu, S.M. Liu, Z.J. Jiang, and J.Q. Zhao, *Polym. Bull.* 58, 711 (2007).
16. H.T. Chiu, and J.H. Wang, *J. Appl. Polym. Sci.* 70, 1009 (1998).
17. E. M. Lee, Y. S. Oh, H. S. Ha and B. K. Kim, *Polym. Adv. Technol*. 20, 1121 (2009).
18. Y. Chen, H. Zou, M. Liang, P. Liu, *J. Appl. Polym. Sci*. 129(3), 945 *(*2013), doi: 10.1002/APP.38374
19. Y. Chen, H. Zou, Y. Cao, and M. Liang, *Polym. Sci., Ser. A* 56(5), 630 (2014).
20. H. S. Jaggi, B. K. Satapathy, and A. R. Ray, *J. Polym. Res*. 21, 482 (2014).
21. H. Ma, X. Chen, B. S. Hsiao,and B. Chu, *Polymer* 55,160 (2014).
22. J.C.M. Suarez,and R.S. De Biasi, *Polym. Degrad. Stab.* 82, 221 (2003)
23. E. Oral, A,S. Malhi,and O.K. Muratoglu, *Biomaterials* 27, 917 (2006)
24. U. Goschel, and C. Ulrich, *J. Appl. Polym. Sci.* 113, 49 (2009)
25. N. Campo, and A.M.Visco, *Int. J. Polym. Anal. Charact.* 5, 438 (2010)
26. Y. Chen, Y. Qi, Z. Tai, X. Yan, F. Zhu, and Q. Xue, *Eur. Polym. J.* 48, 1026 (2012)

Captions to tables and figures

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

Figure 2- Flow chart of UP and UPC nanocomposite preparation with images of powders and pellets produced; hot press conditions for powder and cut wires.

Fig.3 – SEM micrographs of UP (a,b); UPC-US (c,d); UPC-BM (e,f); UPC-EX (g,h); the dashed circles in fig.3 d,f indicate the filler particles

Figure 4- DSC curves of U, UP and UPC samples

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

Fig.6 - Rheological curves of: U,UP (a); UP, UPC-US, UPC-MS (b); and UP, UPC-BM, UPC-EX (c) samples.

Table I- Calorimetric parameters of and UHMWPE and its nanocomposites

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

Table III- rheological parameters of UHMWPE and its nanocomposites

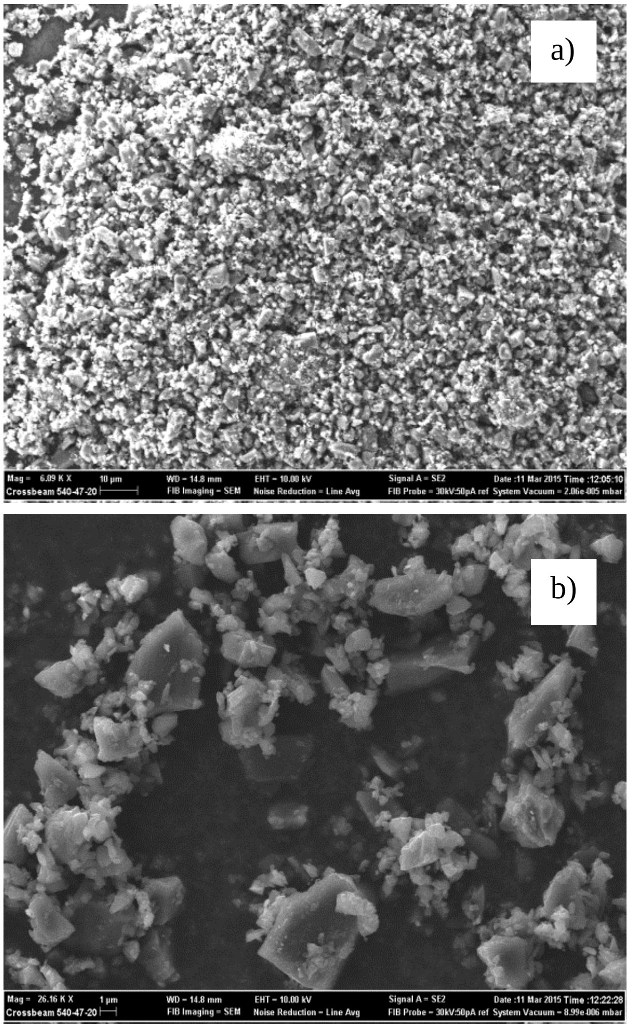

Figure 1- SEM micrographs of the carbon nanofiller powder at two magnifications: 6 kx(a) and 43 kx (b)

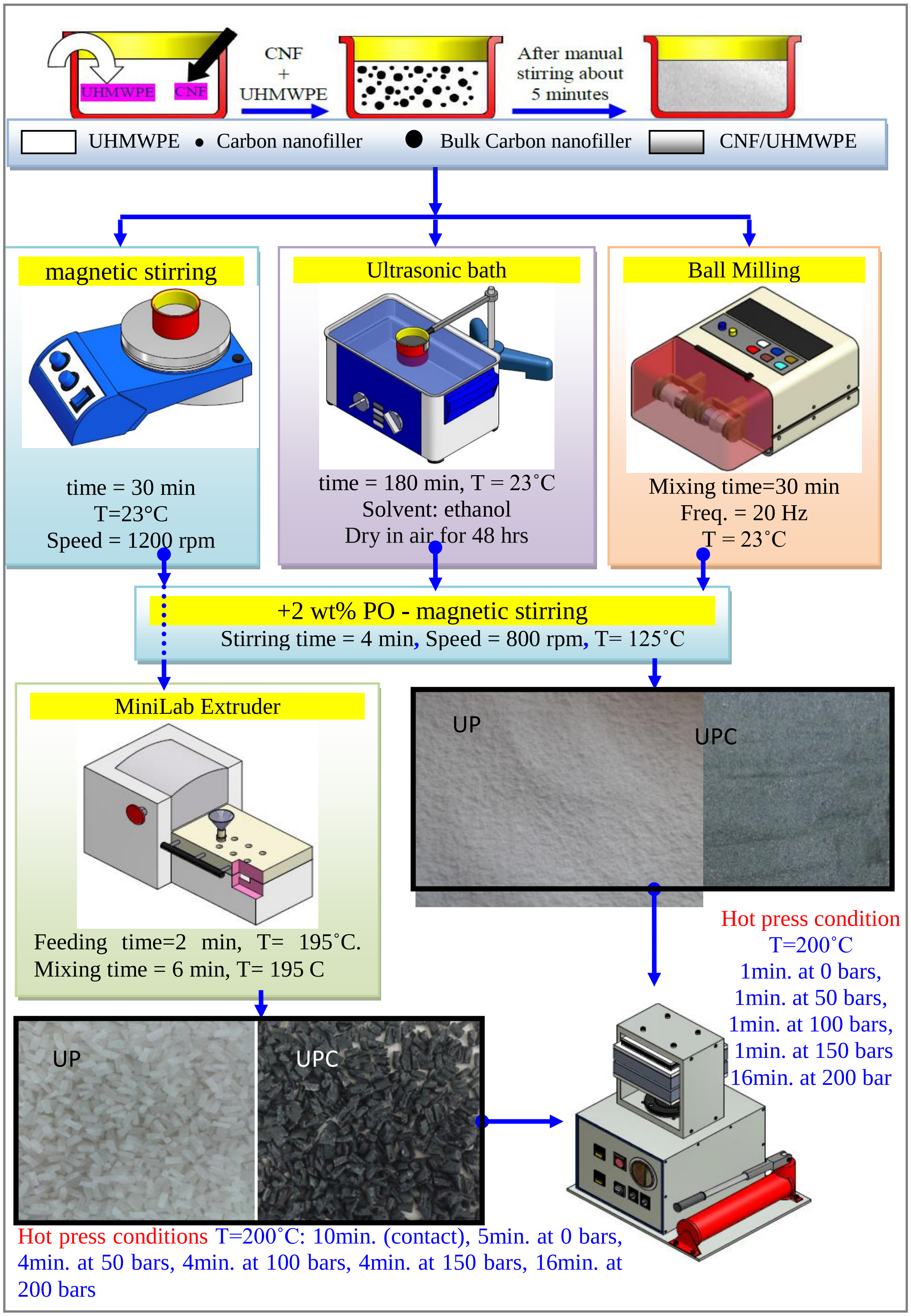

Figure 2- Flow chart of UP and UPC nanocomposite preparation with images of powders and pellets produced; hot press conditions for powder and cut wires.

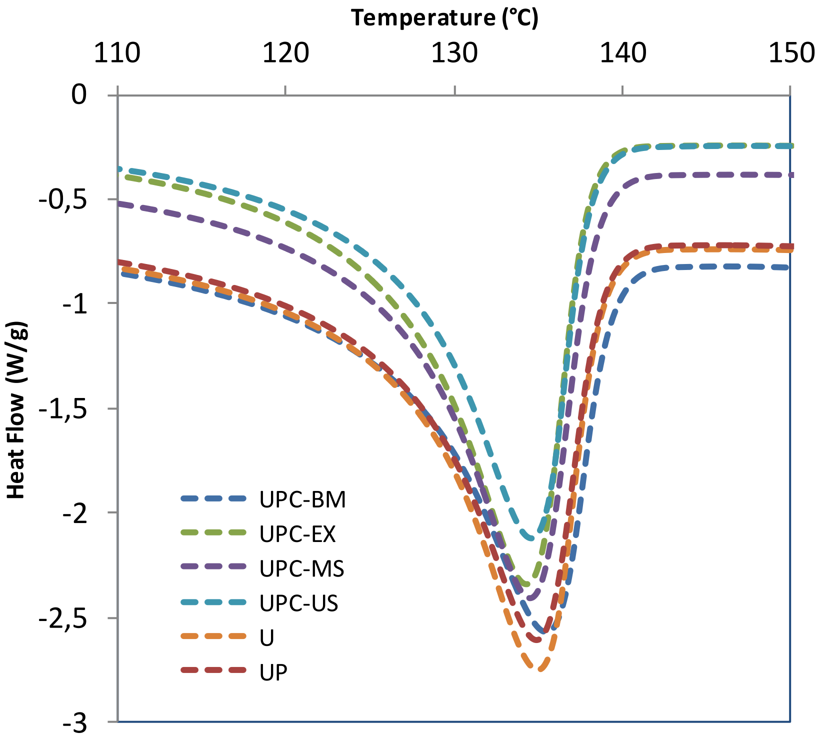

Figure 3- DSC curves of U, UP and UPC samples

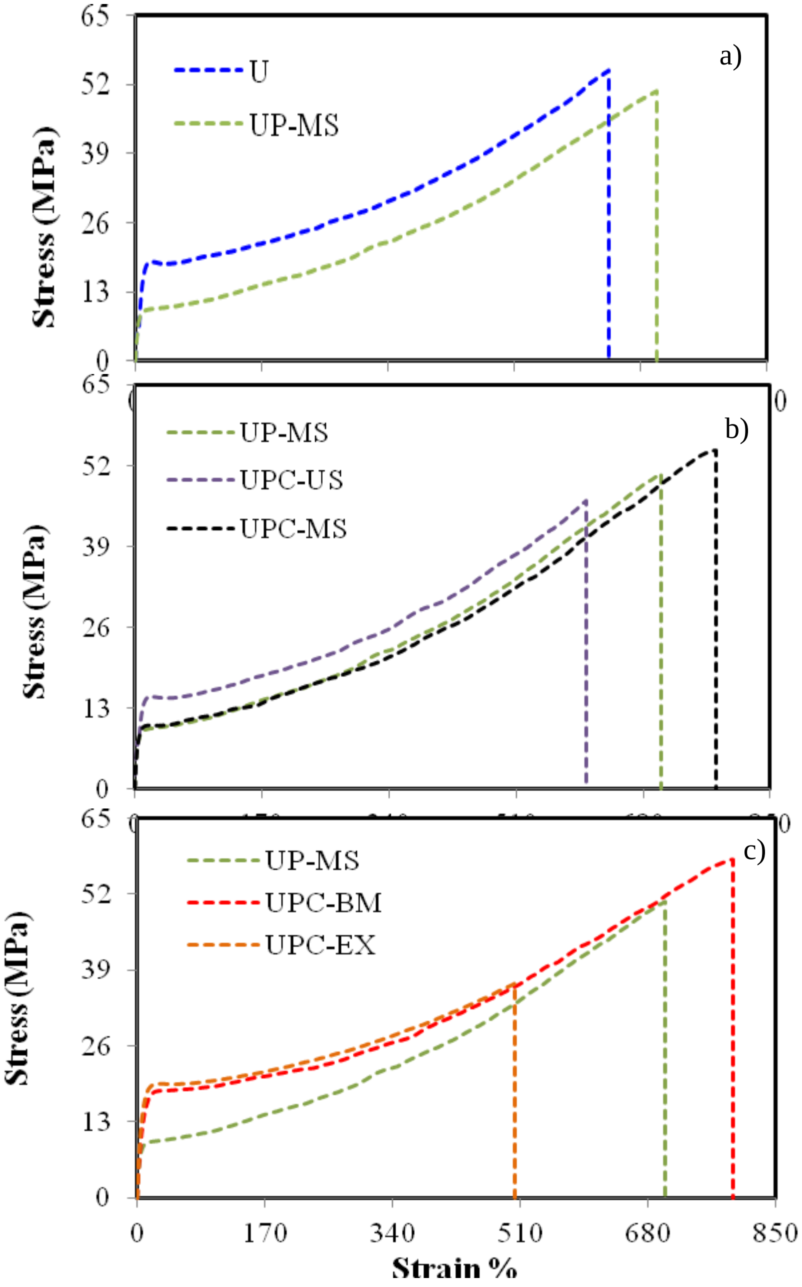

Fig.4 - Average tress strain curves of pure U, UP, and the UPC samples

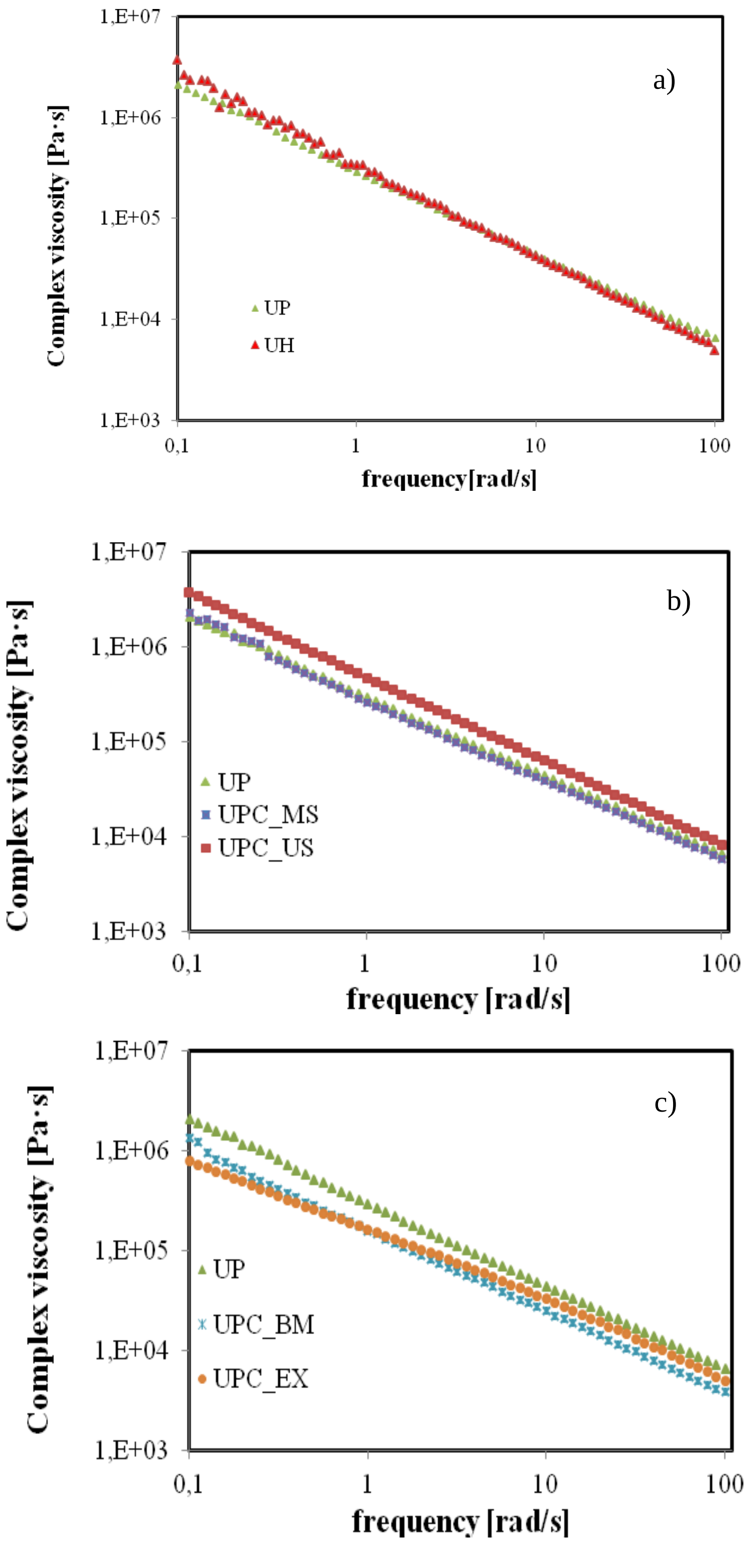

Fig.5 - Rheological curves of pure U, UP, and the nanocomposites

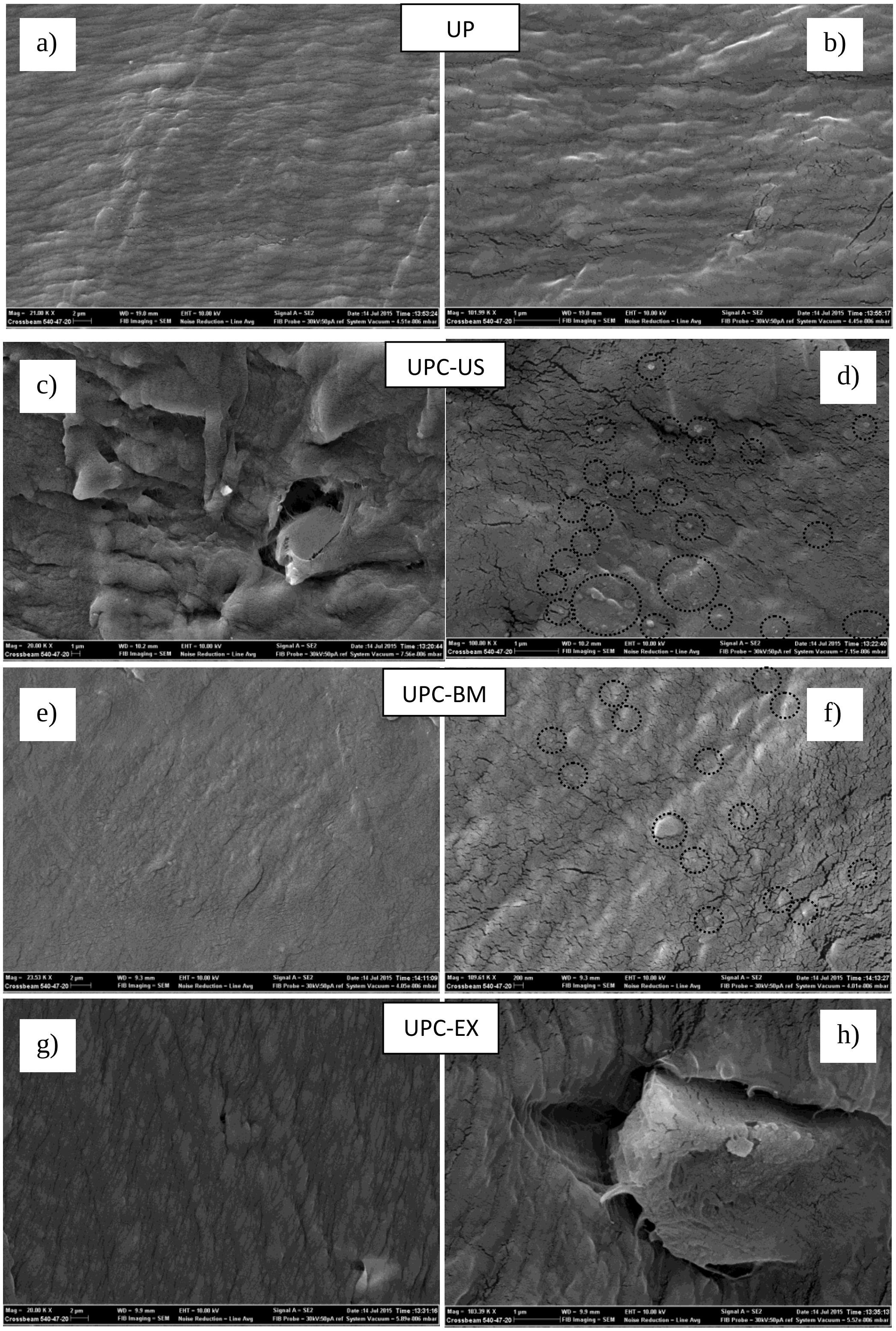

Fig.6 – SEM micrographs of UP (a,b); UPC-US (c,d); UPC-BM (e,f); UPC-EX (g,h).

Table I- Calorimetric parameters of and UHMWPE and its nanocomposites

Sample code	**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	Ultra sound	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

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 [Joule]**	**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

Table III- rheological parameters of UHMWPE and its nanocomposites

Sample name	*low frequency 0.1 [rad/s]*			*high frequency 100 [rad/s]*		
	η* [x 10^6 Pa.s]	**G' [x10^5MPa]**	**G'' [x10^5MPa]**	**η* [x 10^6 Pa.s]**	**G' [x10^5MPa]**	**G'' [x10^5MPa]**
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