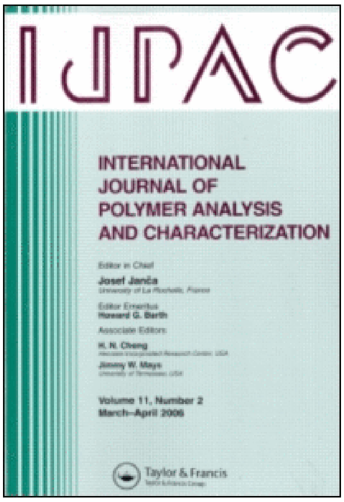

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Incorporation of Carbon Nanotubes into Ultra High Molecular Weight Polyethylene by High Energy Ball Milling

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INCORPORATION OF CARBON NANOTUBES INTO ULTRA HIGH MOLECULAR WEIGHT POLYETHYLENE BY HIGH ENERGY BALL MILLING

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Multiwalled carbon nanotubes, CNTs (0.3–1.0 wt.%), were incorporated in the ultra high molecular weight polyethylene (UHMWPE) matrix by solid state dry mixing in order to avoid the use of high temperature, solvents, and materials pretreatments. Physical, morphological, and mechanical tests were performed on both the pristine materials and the nanocomposites. Experimental results showed that the CNTs are homogeneously dispersed into the polymeric matrix but no close interaction occurs between the two components. In fact, no appreciable mechanical or thermal improvement was observed. Instead, a bi-dimensional CNT conductive network was formed within the polymeric matrix, which increased its crystalline order.

***Keywords*: Carbon nanotube; Chemical dissolution; Nanocomposite; Physical characterization; Polyethylene; Solid state mixing; Static mechanical tests

INTRODUCTION

Carbon nanotubes (CNTs) have received great attention since their discovery by Iijima in 1991.[1] They have been applied in several fields, from chemistry to materials science to electrical engineering, due to their intrinsic superconductivity,[2] ability to store hydrogen,[3] unusually high thermal conductivity,[4] potential use as sensors for gas detection,[5] and the potential for biomolecular recognition,[6] along with biocompatibility.

However, it is the combination of exceptional conductivity (electrical and thermal), low density, and mechanical properties of carbon nanotubes that have drawn attention to their use in filled composites.[5]

The use of CNTs as reinforcement to improve properties of various thermoplastic polymer matrix systems like polymethyl methacrylate,[7] polystyrene,[8,9]

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polyethylene terephthalate,[10] nylon,[11] polyvinyl chloride,[12] rubber,[13] polyethylene UHMWPE,[14,15] polycarbonate,[16] polypropylene,[17] and polyether ether ketone[18] has already been demonstrated. The results show enhancement in mechanical, thermal, and dielectric/electrical properties.[7–18]

The key technical challenges that remain for such nanotube-reinforced polymers are the achievement of homogeneous dispersion and good interfacial bonding. The smaller diameter and greater surface area of the nanotubes also imply stronger interactions among the nanotubes; hence, it is often difficult to disperse them into a polymer matrix. If the dispersion of the nanotubes is less than ideal, it impairs the resultant nanocomposite properties. Making composites with optimal properties requires adequate reinforce-matrix adhesion, which is governed by the chemical and physical interactions occurring at the interface. If the reinforcement-to-matrix adhesion is poor, a composite may fail at the interface, reducing in particular the tensile strength. As the filler in polymer matrix materials, multiwalled carbon nanotubes (MWCNTs) represent an extraordinary opportunity for the development of new products with many desirable physical properties. Significant property modifications can be obtained with a relatively low addition of MWCNT to the polymers, as compared to carbon black or carbon fiber materials. In fact, carbon nanotubes have excellent mechanical properties such as Young modulus (1000 GPa) that is much higher than the conventional carbon fibers (200–800 GPa).[19] As the matrix, ultra high molecular weight polyethylene (UHMWPE) has desirable properties such as chemical inertia, good mechanical and wear resistance, lightness, and biocompatibility.[14]

Commonly, three main methods have been applied for incorporating carbon nanotubes into thermoplastic polymers: physical mixing of the carbon nanotubes with the polymer in solution or in molten state and in situ polymerization. Generally, the presence of reactive groups in the carbon nanotubes, such as carboxylic, carbonyl, or hydroxyl, highly improves the mechanical strength of the nanocomposite.[20]

A few authors have already used a dry method with the aim to physically mix the polyethylene with the carbon nanotubes. This can be considered an interesting alternative technology for producing composite polymer/nanotubes since it avoids high temperatures, solvents, and the necessity of a chemical modification of the CNTs.

For example, Mierczynska et al.[14] prepared a nanocomposite CNT/UHMWPE by using the filler pre-localization method. The composites were dry mixed with the CNTs in a mortar followed by sintering. The filler was not homogeneously dispersed, but a three-dimensional continuous network of filler-rich layer was formed within the polymer.[14] Gorrasi et al.[21] were the first researchers who incorporated a linear low-density polyethylene (LLDPE) with MWCNTs by a mechanical mill (high-energy ball milling, HEBM) at room temperature. They highlighted the efficiency of this dry technique and that the nanocomposite's thermal, mechanical, and electrical properties were relevantly improved with low nanotube content (2–3%).

Following this last study, in this work we similarly incorporated a UHMWPE with MWCNTs by a mechanical mill (HEBM) at room temperature and studied the morphological, physical, and mechanical features of the nanocomposites.

EXPERIMENTAL SECTION

Materials

UHMWPE resin GUR 1020 (average molecular weight of 3×10^6 g/mol, density of 0.93 g/cm^3, without calcium stearate) was supplied by Ticona. The average size of particle powder was 150 µm.

Multiwalled-type carbon nanotubes (CNTs) were obtained by the chemical vapor deposition (CVD) technique by using Fe/Al_2O_3 catalyst and isobuthane/hydrogen as reagent gas (molar ratio 1:1) at 750°C for 2 h. In order to eliminate traces of catalyst inclusions, the nanotubes were purified in a saturated solution of potassium hydroxide (KOH, Fluka) at the boiling temperature of 105°C for 12 h.

CNTs' typical outer diameter d_n is about 10 nm and their length l_n about 10 µm, which results in the aspect ratio l_n/d_n of about 1000.

Powders of CNTs and UHMWPE were milled in the solid state in a mechanical high energy ball mill (Fritsch MiniMill II) for 5 min at a speed of 250 rpm. This dispersion cycle was repeated 25 times for each sample.

Under these conditions, four UH/CNT nanocomposites with 0.3, 0.5, 0.7, and 1.0 weight percentage of carbon nanotubes were obtained.

The pure UHMWPE and the UH/CNT nanocomposite were molded in a hot press at 200°C for 20 min at 20 MPa pressure, obtaining sheets 60 mm × 60 mm across and 1 mm thick.[22]

Both pristine materials (UHMWPE, CNTs) and the nanocomposites were characterized by physical analyses (infrared spectroscopy, scanning and transmission electron microscopy, thermal analysis, conductivity measurements), besides a static mechanical tensile test, described in the following.

Characterization Methods

The IR spectroscopy of the CNT powders was studied with a Fourier transform-infrared (FT-IR) spectrometer (Thermo Nicolet, model Evolution 500). For this purpose, powders were pressed into KBr pellets.

Special attention was devoted to investigate in the wave number range 600–4000 cm^{-1}, containing information about the main chemical bond absorption peaks. The presence of four chemical bonds was investigated. They were: C–O stretching (at wave number $\sim$1100 cm^{-1}), COO$^-$ asymmetric stretching (at wave number $\sim$1640 cm^{-1}), the C–H asymmetric and symmetrical stretching (at wave numbers $\sim$2860 and $\sim$2944 cm^{-1}, respectively), and –COOH symmetric stretching (at wave number $\sim$3460 cm^{-1}).[23,24]

A JEOL JSM – 5066 LV scanning electron microscope (SEM) with an acceleration voltage of 20 kV was used to observe the morphology of the nanocomposite samples. Some samples were coated in vacuum with a very thin gold film to make them electrically conductive.

High-resolution transmission electron microscope (HRTEM) analyses were conducted on a 200 kV JEOL JEM 2010 analytical electron microscope (LaB6 electron gun) equipped with a Gatan 794 Multi-Scan CCD camera for digital imaging. Samples for TEM analyses were prepared by ultrasonic treatment in isopropyl alcohol for 2 min. Subsequently, a drop of the suspension was dried on the standard TEM sample grid covered with holey carbon film.

Changes in crystallinity content and melting temperature were assessed by heating samples (n = 3) in a differential scanning calorimeter (TA Instruments Q100). The sample and the reference were then heated from 25° to 180°C at a heating rate of 5°C/min in a nitrogen flux (50 mL/min). Lamellar thickness was calculated according to the Thomson-Gibbs equation.[22]

The tensile test was performed on the pristine polymer and on nanocomposite samples by using a Lloyd Universal Testing Machine, model LR10 K, with a cross-head 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.

The electrical resistivity measurements were performed by a four-probe method using a HP3457a multimeter and a voltage supply, at room temperature. The samples were cylindrically shaped, with a diameter of 12 mm and a height of 1 mm. A gold layer was coated on the surface of each sample to ensure good contact with the electrodes. The electrical conductivity, σ (S/cm), was determined as $1/\rho$ (electrical resistivity, Ω cm).

RESULTS AND DISCUSSION

In Figure 1, the FT-IR spectra of pure CNTs ("pristine" sample) and the HEBM mechanical stress ("mech" sample) are plotted.

Pristine CNT spectra show only a small peak, at about 1100 cm^{-1}, probably due to a little oxidation (C–O) induced by potassium hydroxide during sample preparation.

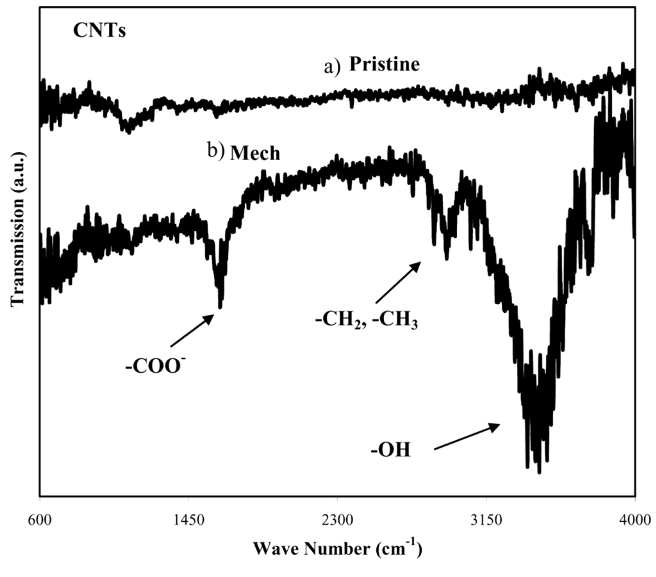

Figure 1. FT-IR spectra of pristine (a) and HEBM mechanically stressed (b) carbon nanotubes.

HEBM mechanical stress induced the presence of peaks at about 1640 cm^{-1} and 3460 cm^{-1} wave number, due to the presence of carboxylic ($-\mathrm{COO}^-$) and hydroxyl species ($-\mathrm{OH}$), respectively. Other peaks are also present, a larger one at about 2944 cm^{-1} and a smaller one at about 2860 cm^{-1} wave number, due to the presence of $-\mathrm{CH}_2$ and $-\mathrm{CH}_3$ species, respectively.

Generally, the powder particles crack during milling, clean surfaces are produced, and intimate mixing can be promoted. As a consequence of the prolonged milling action, when the energy transferred is enough to overcome the activation barrier, atom diffusion and chemical reactions may occur.[21]

So, FT-IR results suggested that the mechanical stress induced by means of the HEBM breaks the C–H bonds and oxidizes the CNTs. It also breaks the C–C bonds, forming new chain arrangements, like the $-\mathrm{CH}_2-$ and/or the $-\mathrm{CH}_3$ terminal species.

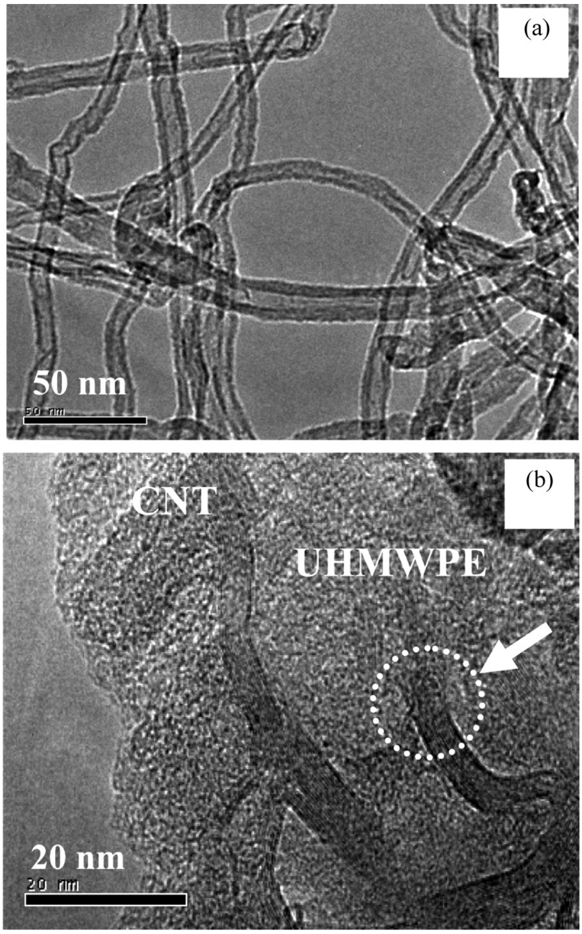

Figure 2. HRTEM analysis of CNTs: pristine (a) and with the polymeric matrix after the HEBM mechanical stress (b).

In addition, the CNT shape and regularity are modified by the mechanical stress, as shown by the images in Figure 2. In particular, Figure 2(a) shows the HRTEM image of pristine CNTs, which appears cylindrically shaped and regularly continuous with an average diameter of 10 nanometers. The mechanical stress of high-energy ball milling modifies the CNTs, changing their shape and breaking them (Figure 2(b)). This is due to a deforming and cutting action performed by the high mechanical stress of the HEBM machine.[25] The CNTs' average diameter (5–6 nm) is lower than that of the pristine sample. The CNTs are discontinuous (see the arrow in the picture) but outside are surrounded by the polymeric matrix.

The SEM micrographs at a magnification of 10000× of pure CNTs and of UH/CNT 0.5 are shown in Figure 3. The original bundle organization of the CNTs is shown in Figure 3(a). Figure 3(b) shows the surface of the UH/CNT0.5 nanocomposite, which represents the polymeric grains homogeneously covered by CNT threads. This reveals a good dispersion of the CNTs on the surface of the UHMWPE particles.

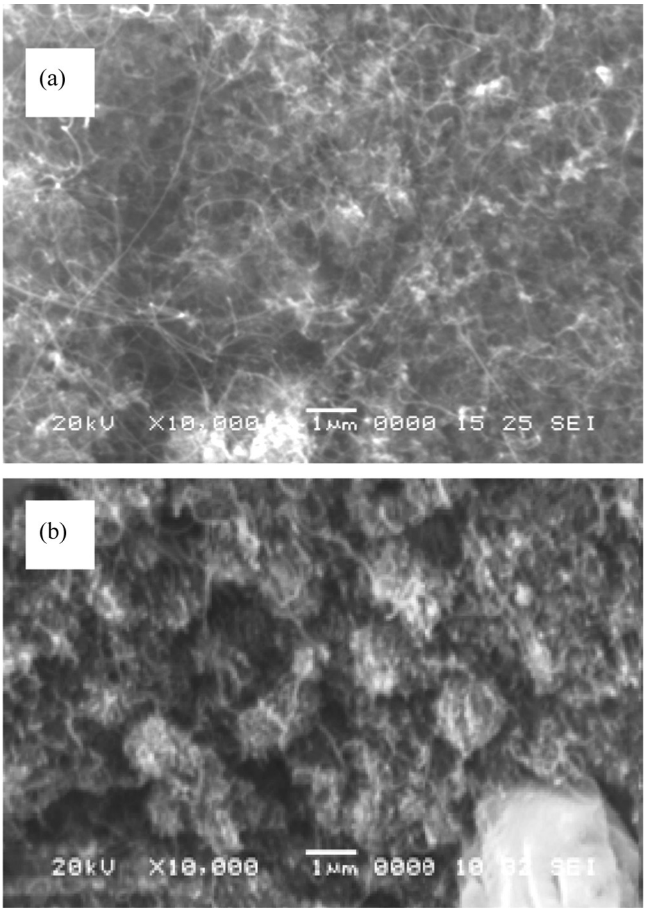

Figure 3. SEM micrographs of pristine CNTs (a) and UH/CNT0.5 nanocomposite (b) at magnification of 10.000×.

In order to check the effect of CNT distribution and the presence of an interaction with the polyethylene matrix, mechanical tensile investigation, calorimetric analysis, and conductivity measurements were performed and discussed as follows.

In Figure 4, the mechanical tensile parameters (Young's modulus, E_T, yielding strength, σ_y, strength at break, σ_R, deformation at break, ε_R) as a function of the CNT weight percentage are shown. Young's modulus of pristine UHMWPE is 355 MPa and after the addition of CNTs, it progressively increases up to the highest value of 456 MPa (Figure 4(a)). Similarly, the yielding strength values increase with increasing the CNTs, from 21.5 MPa, up to the highest value of 23.8 MPa.

The tensile strength and elongation at break instead decrease with increasing CNT content from initial values of 55 MPa and 918% up to the lowest values of 48 MPa and 726%, respectively (Figures 4(c) and (d)). These results show that CNT presence increases the nanocomposite yielding strength and stiffness, although it decreases deformability and the tensile strength.

Calorimetric analysis results of the pristine UHMWPE and of the UH/CNT nanocomposites with different CNT weight percentages are given in detail in Table I. They do not show any appreciable any structural changes in the polymer since the melting temperatures (T_m) and the lamellar thickness (l_c) of the nanocomposites are close and similar to those of pristine UHMWPE, ~133°C and ~22 nm, respectively. The only appreciable change is the crystallinity degree, which increases because of the CNTs' presence since they can act as nucleating sites.[26]

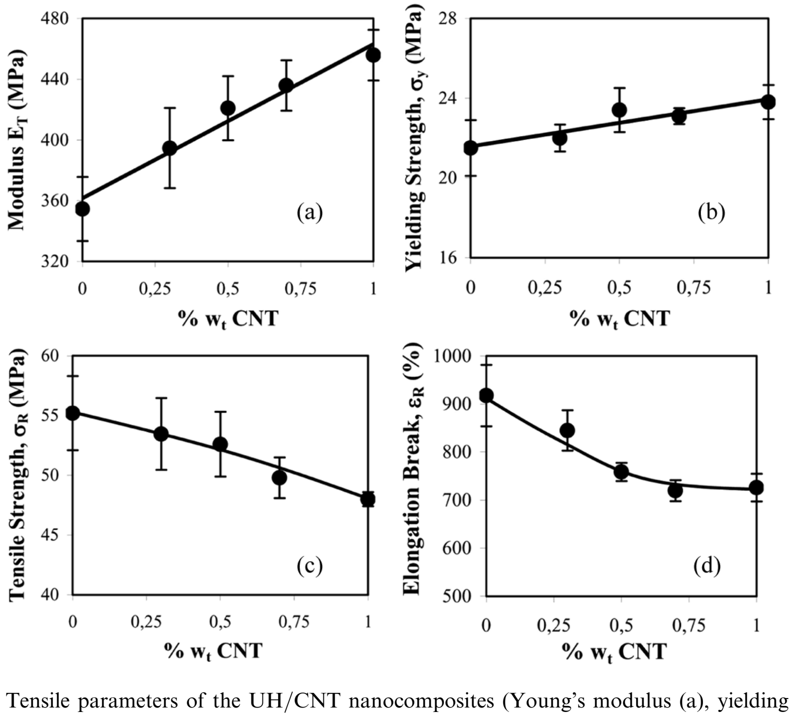

Figure 4. Tensile parameters of the UH/CNT nanocomposites (Young's modulus (a), yielding strength (b), strength at break (c), deformation at break (d)), as a function of weight percentage of CNT.

Table I. Calorimetric analysis results of pristine UHMWPE and UH/CNT nanocomposites with different CNT weight percentages

Sample code	CNT content (wt.%)	Melting temperature T_m (°C)	χ_C (%)	Lamellar thickness lc (nm)	Conductivity σ (μmS/cm)
UHMWPE	0	133.2 ± 0.6	49.7 ± 1.0	21–23	10^{-12}
UH/CNT0.3	0.3	132.7 ± 0.1	56.6 ± 1.7	21–22	5×10^{-9}
UH/CNT0.5	0.5	133.6 ± 0.2	53.4 ± 4.3	23	2.8
UH/CNT1.0	1.0	133.4 ± 0.3	54.1 ± 2.3	22–23	55.0

In any case, both the mechanical and the calorimetric results suggest that the mixing technique is not enough to induce strong chemical bonds between the polymeric matrix and the CNTs. The mechanical stress mainly forms unstable species (generally, free radicals) in the CNTs that can react with oxygen, generating the oxidized species, or it can break the carbon nanotube chains, rearranging themselves in new C-H species. This is possible by considering the fragility of high modulus CNTs, which can be broken by the stress imposed during the mechanical mixing so that free radicals can be produced as a consequence of C-C bond breaks. Instead, no break occurs in the polyethylene since its plasticity allows the recovery of its shape after the stress. Besides, the high viscosity of the UHMWPE and the generally high aspect ratio of the nanotubes inhibit an easy matrix/reinforcement interaction. In fact, the high viscosity hinders the polymer penetration into the CNT bundles while the high value of aspect ratio of the CNTs favors the segregation of nanotubes inside the polymeric matrix and greatly inhibits their chemical or physical interaction.

Figure 5 shows the conductivity as a function of the CNT content for the UH/CNT nanocomposites. The concentration at which the largest rise of electrical conductivity occurs determines the crucial parameter, the percolation threshold. It is at around 0.3 wt.%, according to literature results for UHMWPE/MWCNT

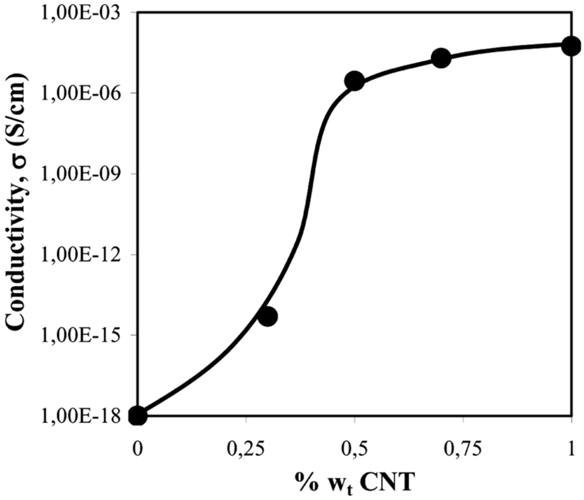

Figure 5. Conductivity values of UH/CNT nanocomposites as a function of weight percentage of CNT.

composites.[14] All the conductivity results of the UH/CNT nanocomposites are given in detail in Table I. The ultralow percolation threshold indicates a 2-D distribution of CNTs, suggesting the presence of a bi-dimensional conductive network in the composite where the charge can flow along the surface and the interface with the matrix.[27]

In fact, the SEM images of Figure 6 explain the presence of the conductive network within the nanocomposites. It shows the fracture surfaces of the UH/CNT nanocomposites containing 0.3, 0.5, 0.7, and 1.0 wt.% of CNTs. So, the images at low magnification (50×) display the macroscopical distribution of the CNTs in the UH/CNT nanocomposites. CNTs are located on the surface and at the interfacial regions of the composites. The images clearly shown as white areas of polymeric matrix are progressively reduced, while the black CNT network expands better into the nanocomposite with increasing CNT content.

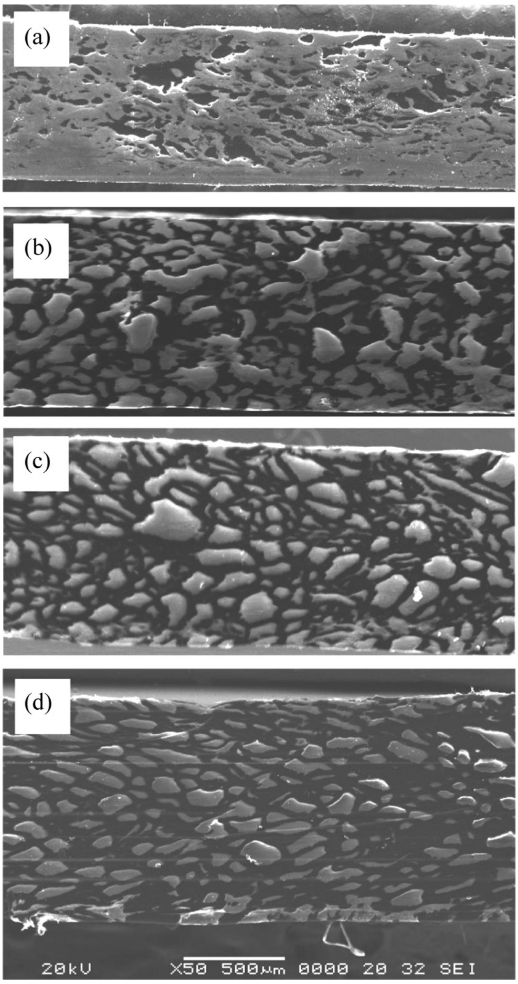

Figure 6. SEM analysis of fracture surfaces of UH/CNT0.3 (a), UH/CNT0.5 (b), UH/CNT0.7 (c), and UH/CNT1.0 (d) nanocomposites.

CONCLUSIONS

In this work we studied two nanocomposites containing UHMWPE and CNTs, prepared by using a dry solid mechanical mixing technique with high-energy ball milling. The CNT content was within the 0.3–1.0 wt.% range.

The mixing method changed the shape of CNTs, mainly inducing breaks. CNTs loose their regularity and oxidized species are formed. Mechanically mixed samples showed also the presence of new chemical rearrangements, probably originated by the presence of free radicals. UHMWPE was instead not appreciably modified by the mechanical stress of the ball milling.

In this case, the alternative technique of HEBM proved to be not very efficient in producing composites based on UHMWPE, without using high temperatures or solvents or any other physical or chemical treatment of the components, contrary to other composites based on LLDPE, already studied by other authors.[21] In the LLDPE/MWCNT composites, a general improvement of physical and mechanical properties was found compared to those of the pristine LLDPE. In this work, we found that the MWCNT are homogeneously dispersed within the polymeric matrix but no appreciable interaction can be noticed. In fact, the CNT presence stiffened the material, increasing its yielding strength but reducing its deformability and tensile strength. In addition, the thermal resistance of the polymer was not changed. In any case, the CNTs' presence increased the crystallinity degree of UHMWPE and the nanocomposites show the origin of electrical conductivity.

The difference of behavior observed in the two composite systems (LLDPE/MWCNT and UHMWPE/MWCNT) obtained with the same dry mixing method can be due to the much higher molecular weight of UHMWPE and so to its much higher viscosity than LLDPE. As a matter of fact, the high-energy mechanical milling action resulted in inducing the UHMPE powder particles to crack during the milling so as to promote an intimate mixing between the polymer and the nanotubes.

For the above discussed reasons, studies are in progress to improve the solid state mixing or to try alternative ways to induce chemical or physical interactions between CNTs and UHMWPE favoring the formation of intramolecular bonds between each other.

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