Analysis of the electrical and rheological behavior of different processed CNF/PMMA nanocomposites

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ABSTRACT

Carbon nanofiber (CNF)/poly(methyl methacrylate) (PMMA) nanocomposites were prepared via melt-compounding, solvent casting and in situ polymerization. Mechanical properties, rheological behavior and electrical resistivity were investigated in specimens with varying CNF loadings. The three processing techniques were compared. Improved properties were obtained in the solvent processed and in situ poly-merized composites. The rheological and electrical percolation of these nanocomposites appeared in the same concentration set (between 1 and 5 wt%). No changes were found in melt-compounding, even by the addition of 10 wt% of CNFs. Electrical resistivity of the samples prepared by solvent casting was mea-sured before and after pressing in the hot plate press. It is remarkable that in the non-pressed samples the CNFs formed an efficient 3-D conductive network, yielding composites with percolation thresholds even six orders of magnitude lower than after pressing, where this 3-D network was destroyed.

1. Introduction

The possibility of combining polymers with other particles to obtain a unique material makes possible to tune their high resistivity, quite poor mechanical properties and low thermal stability, so proper conductive materials with enhanced mechanical and thermal properties can be achieved. In the recent years, nanoparticles have attracted many attention for enhancing polymer properties, and a variety of nanofiller morphologies have been proved: spherical such as silica [1,2], platelets such as clays [3,4] and, more recently, graphene [5,6], or nanofilaments such as carbon nanotubes (CNTs) or carbon nanofibers (CNFs) [7–10]. Among these, CNTs and CNFs, both with similar properties, have been widely investigated as a proper alternative to enhance the mechanical properties [11–13] and the electrical conductivity [14,15], as well as the thermal stability [16,17]. Some interesting results have been reported. Haggenmueller et al. [18] used solvent casting followed by melt mixing to fabricate SWCNT/poly(methyl methacrylate) (PMMA) nanocomposites fibers with 100% increase on modulus for 8 wt% loading. Du et al. [19] prepared SWCNT/PMMA composite fibers by coagulation method exhibiting increased modulus, conductivity and thermal stability. Mathur et al. [20] used solvent casting to prepare MWCNT/PMMA with improved modulus and strength, as well as enough conductivity for EMI shielding applications. Using in situ polymerization, Velasco-Santos et al.

[21] almost doubled the strength of neat PMMA by adding 1 wt% of SWCNTs. Improvement of the properties of nanocomposites containing CNFs are typically lower [22–25], probably due to their lower crystallinity. In addition, the processing method and the carbon nanofilament loading are critical factors influencing the composite properties. Pham et al. [26] detected, at the same concentration of MWCNTs (6 wt%) in PMMA, lower sheet resistance in the composites processed by solvent (9.7×10^2 Ω/sq.) than in the melt-compounded composites (5.7×10^6 Ω/sq.).

In this paper, we examine the effects of the processing method and the carbon nanofiber loading in the same matrix. Three usual techniques were employed: melt-compounding, solvent casting, and in situ polymerization. We studied and compared the mechanical and the rheological behavior, which are related to the structure of the materials, the state of the filler dispersion and the interactions between the CNFs and the polymer [19]. Electrical properties were also measured and compared to the rheological behavior for a better understanding of the influence of the carbon nanofibers in the polymer matrix.

2. Experimental

2.1. Materials

A commercial grade of poly(methyl methacrylate) Altuglas was used. Commercial carbon nanofibers GANF, quality debulked and stripped, by Grupo Antolin (Burgos, CNFs), were used. These CNF are helical ribbon type, and are produced in a continuous process

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by the floating catalyst method, using natural gas as a carbon feedstock, a Ni compound as catalyst and hydrogen and sulfur sources at temperatures above 1000 °C. It is highly graphitic with no presence of amorphous carbon coating. Characterization of this sample can be found elsewhere [27–29].

2.2. Composite preparation

Melt compounded PMMA composites containing 1, 5 and 10 wt% CNFs were prepared in a torque rheometer mixing chamber, Haake polylab QC, using can-type rotors, at 180 °C and 60 rpm for 30 min.

Solvent casting composites with 1, 5, 10, 15 and 20 wt% of CNFs were performed in acetone using the following procedure. CNFs were dispersed in acetone by high shear rotor–stator stirrer (Silverson LR4T, Silverson Machines, MA) at 8000 rpm for 10 min to form a CNF suspension of 1–2 wt%. An appropriate amount of PMMA for the corresponding loading of CNFs in the composite material was dissolved in the minimum amount of solvent in another container. The dispersed CNFs suspension and the dissolved PMMA were combined and mixed, first, via magnetic stirring for 30 min and then via high shear mixing for 10 extra min. The final mix was spread in a tray and dried at 50 °C for 24 h in the vacuum oven.

For the in situ polymerization samples, the PMMA was produced by free radical emulsion polymerization in a jacketed stirred reactor. A CNF/water suspension, previously, prepared in a high shear mixer, was introduced in the reactor and heated to 70 °C, together with dodecyl sulfate as the surfactant and ammonia persulfate as the initiator. After this, the monomer methyl methacrylate (MMA) was semicontinuosly poured by a peristaltic pump for an hour. The reaction continued for 3 more hours. Finally, the mix was spread in a tray and dried at 65 °C in a vacuum oven for 24 h. Composites at 1, 5 and 10 wt% of CNFs were prepared.

Three samples of neat PMMA were prepared using each one of the three different processing methods and used as blank. Once dried, all the composites were pressed in a hot plate press to get the appropriate specimens using an aluminum mold, under vacuum at 150 °C for 10 min at 2 ton. The rough surfaces of the specimens were smoothed by polishing.

2.3. Dispersion

Transmission electron microscopy ultramicrotomy was used to examine dispersion on the nanoscale. The composite samples were cut with a diamond blade yielding thin slices between 80 and 120 nm thick. A total area of 750 μm^2 was examined. The electron transparent slices were imagined in a JEOL 2010 transmission electron microscope (TEM).

2.4. Mechanical properties

The tensile and flexural properties of the composites were determined using the standard set forth in UNE-EN-ISO 527-1 [30] and ASTM D 790 [31], respectively. The cross-head rates were 0.5 mm/min for tensile tests and 1.37 mm/min for flexural tests. The tests were performed on an INSTRON dynamometer, model 3344, with interchangeable clamps.

2.5. Rheological behavior

Rheological behavior was measured on a parallel plate rheometer (ARES N2, Rheometric, Scientific) equipped with parallel plate geometry using 25 mm diameter with gap of 1.5–2 mm at 200 °C, using dynamic oscillation frequency sweeps from 0.1 to 100 rad/s and 0.5% strain under a nitrogen atmosphere.

2.6. Electrical properties

For the electrical surface resistivity measurements, two parallel electrode strips were painted with conductive silver paint in hot plate pressed composite films. Surface resistivity was measured using a digital multimeter (up to $5 \times 10^8 \ \Omega$) and a wide range resistance measurement instrument Prostat PSI-870 (up to $10^{12} \ \Omega$) with an accuracy of ½ decade.

3. Results

3.1. Dispersion

Fig. 1 shows TEM micrographs of the nanocomposites containing 1 wt% of CNFs processed by melt-compounding (Fig. 1A), solvent casting (Fig. 1B) and in situ polymerization (Fig. 1C). The dispersion is better in the nanocomposites processed by solvent casting and in situ polymerization than by melt-compounding. In this further case more and bigger agglomerations tend to appear, especially at higher loading concentrations (Fig. 2). The aspect of the agglomerations is also different. In melt compounding they look cramped, as if the original CNF bundles were not unwounded, or even tighter by the shear forces during the processing. On the other hand, in solvent casting, they look more porous, as if the polymer had penetrated. Finally, the aspect of the agglomerates of the in situ polymerized samples is more similar to the solvent casting case.

3.2. Mechanical properties

The variation of the tensile and flexural properties with the CNF concentration is shown in Fig. 3 for the nanocomposites processed by melt-compounding, solvent casting and in situ polymerization at 1, 5, 10 wt% of CNFs. The increase in the mechanical properties with the CNF content is more pronounced in the nanocomposites processed by-solvent and in situ polymerization, in which the dispersion of even high CNF concentrations is easier than using melt-compounding, due to the much more reduced viscosity. At 10 wt% the tensile modulus increases 6% for melt-compounding and over 15% for solvent casting and in situ polymerization. At the same loading level, and compared to the neat PMMA, the flexural modulus in melt compounding, solvent casting and in situ polymerization is 10%, 20% and 35% higher, respectively. The tensile strength is similar at 1 and 5 wt% and decreases at 10 wt%, while the flexural strength abruptly decreases already at 5 wt%. For example, at 5 wt%, tensile strength increases a 7%, 20% and 34% respect to the neat PMMA for, respectively, melt-compounding, solvent casting and in situ polymerization. These results suggest that there is an optimum content of CNF for the improvement of the mechanical properties. Higher concentrations do not produce an enhancement, but even a damage [32–35]. This optimal concentration can be set between 1 and 5 wt% for solvent processing and in situ polymerization and at 1 wt% for melt-compounding. These results are lower than the results reported for SWCNTs and MWCNTs [20,36,37], but still satisfying considering other contributions of CNFs that even show damage on the mechanical properties.

SEM imaging of the fracture surface, revealed an increase of the roughness in the nanocomposites, which is attributed to an improvement of the toughness by the addition of the CNFs [35]. Fig. 4 shows the fracture surface of the PMMA and 1 wt% CNF/PMMA nanocomposite, both processed by solvent. The increase on the roughness of the fracture surface can be noticed in the further material.