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Mechanical Behaviour of Polysulfide Phenylene Reinforced with Carbon Nanofibers Composites

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Abstract

Carbon nanofiber reinforced polysulfide phenylene (PPS) composites were prepared in different proportions through conventional kneading and compression molding techniques. In this paper, potential reinforcement offered by carbon nanofibers in a thermoplastic matrix of phenylene polysulfide was evaluated. In the assessment of mechanical properties, an increase in Young's modulus and tensile strength is observed as the content of carbon nanofibers increases the value per weight by 3% weight while ductility is reduced for fibers with a percentage per weight higher than 1%. Through differential scanning calorimetry (DSC), the typical thermal transitions of PPS were determined, these being the glass transition temperature, recrystallization point, and melting point. The micrographs in the AFM revealed the degree of dispersion of the carbon nanofibers in the matrix, confirming the results obtained in the tensile tests.

Keywords: Composite materials, carbon nanofibers, thermoplastic matrix, mechanical and thermal properties.

I. INTRODUCTION

The change in scale from micrometer length to nanometer diameter size is promising for preparation and characterization as well as for the making of new composite materials [1,2]. The development of compounds reinforced with carbon nanofibers (NFC) offer a new and interesting alternative to improve the physical and mechanical properties of a polymeric matrix such as poly (ether-ether-ketone), polycarbonate or polyethylene terephthalate [3.4].

Carbon nanofibers are produced from the thermal decomposition of hydrocarbons such as benzene and methane in the presence of metallic particles that act as catalysts around 1100ºC [5,6]. On the other hand, traditional carbon fibers are widely used as reinforcement for polymeric matrices and for high-tech purposes due to their excellent mechanical properties [7]. However, unlike carbon nanofibers, micrometric carbon fibers have a weak interaction with the matrix and they are manufactured from polyacronitrile (PAN) through several processes, which increases their cost, therefore limiting their use. CNFs (Carbon Nano Fibers) are made through a single procedure using the floating catalyst technique, which substantially reduces their cost [8].

K. Lozano, EV Barrera [9] carried out a study on the in traction mechanical properties' behavior of polypropylene with varying contents of carbon nanofibers, determining a 16% increase in the tensile strength value for percentages of 5% per weight of CNFs. However, the results of the dynamic-mechanical properties in relation to the elastic modulus confirmed an increase of 350% in nanofibers with values of 60% per weight.

Polyphenylene sulfide (PPS) is an engineering thermoplastic widely used for the manufacture of products that are prone to chemical agent attacks, it also has an excellent mechanical and thermal properties that offer good dimensional stability at high temperatures. [10].

The following paper aims to study the promise showed by carbon nanofibers when used as reinforcement in a thermoplastic matrix of phenylene polysulfide (PPS), analyzing its effect on mechanical and thermal behavior in varying contents of carbon nanofibers. The influence of nanofibers on the mechanical behavior of composites was carried out by means of tensile tests. Finally, in order to verify the degree of nanoparticles dispersion on the matrix, microscopic techniques were carried out in an atomic force analyzer (AFM).

II. MATERIALS AND METHODOS

II.I Materials

Carbon nanofibers were supplied by Grupo Español Antolín S.A. Its structure consists of an arrangement of tubular concentric rings forming an angle of 15º respecting the axial tube on their inside, while the outer side consists of graphite planes parallel to the axial tube. Its typical structure is known as bamboo [6]. Average CNF diameters range from 30-300nm, and the fiber length is over 30μm. Figure 1 shows a typical bamboo structure with a diameter of around 123nm. They have excellent mechanical properties with Young's modulus values 230 Gpa, and tensile strength of 2.7GPa.

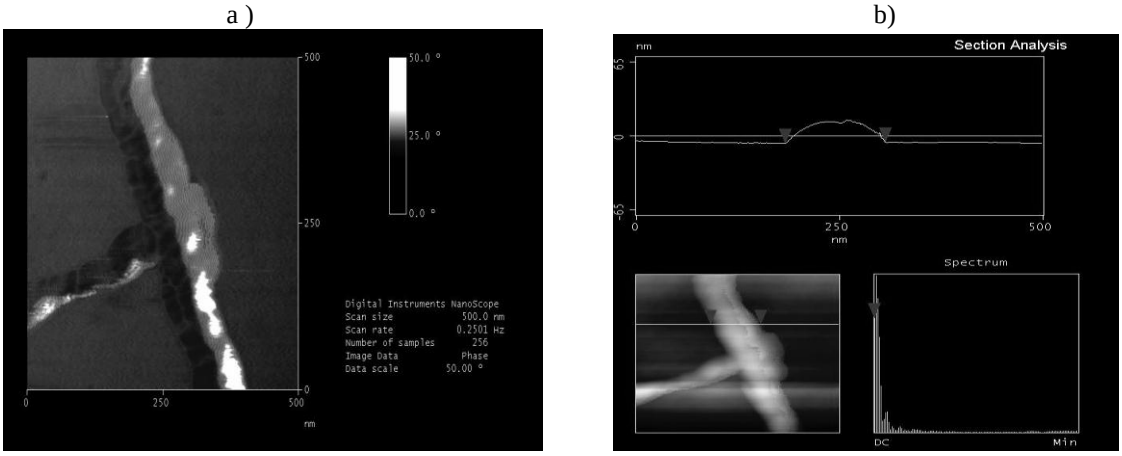


Figure 1. AFM images a) Typical bamboo structure of CNF b) The carbon nanofibers cross-section topography shows a diameter of around 123 nm.

The method used for the production of carbon nanofibers of vapor phase growth is carried out through the floating catalyst technique, which consists of introducing metallic particles such as Fe, Co, or Ni or alloys in them in a constant manner in a reaction chamber through its upper end. Catalysts descend through the furnace at a temperature of 1050ºC - 1100ºC and carbon sources such as benzene, methane or acetylene are decomposed on the surface of the catalysts, which causes of carbon nanofibers to grow and thicken [11].

On the other hand, we have the phenylene polysulfide thermoplastic matrix (PPS), supplied by Frontron Ticona Engineering Polymers, reference 0320, pellets. Its chemical structure, figure 2, is composed of a phenylene ring and a sulfur atom, its polymerization occurs from 1.4 dichlorobenzene with sodium sulfide, using N-methylpyridone as a solvent.

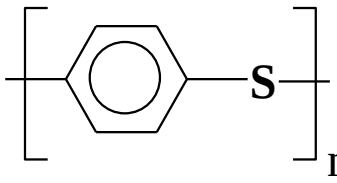


Figure 2. Chemical structure of polyphenylene sulfide PPS.

Higher PPS consumption occurs in the automotive, electronics and electrical industrial sectors, also in the aeronautical industry to a lesser extent. Another application for PPS is found as a component in the manufacture of polymeric matrix composites [12]

II.II Preparation of the composites

The PPS/CNF compounds were prepared in a Brabender Plasticorder PL 2000 internal mixer with a capacity of 50 g at 300 ºC and 20 minutes of mixing. The proportions of CNF used were 0.3, 0.6, 1, 3 and 5% per weight. The different compositions obtained in the mixer are compression molded in a Collin press at 300°C and rapidly cooled while in melt in water in order to prevent PPS crystallization. Finally, they are stamped in the shape of a long plate for different tests.

II.III Mechanical characterization

Tensile tests were carried out according to ISO 527 type 5A on a Zwick Z010 universal testing machine at room temperature and a strain rate of 5mm/min. For the study of thermal properties, a differential scanning calorimeter (DSC) 2920 from TA Instruments was used under an argon atmosphere at a heating rate of 20ºC/min. The assessment of CNF dispersion on the PPS matrix was performed using the atomic force microscopy (AFM) technique. AFM images were taken at room temperature using a Nanoscope IIIa Multimode atomic force microscope from Veeco Instruments in oscillatory or "Tapping" mode. The tips used for scanning the samples are made from silicon doped with phosphorus (model RTESPA, Veeco Instruments), they have an oscillation frequency of 300 kHz and their characteristic force constant is 40 N/m. Its small radius (R <10 nm) allows to obtain a high image resolution.

III. RESULTS AND ANALYSIS

III.I Thermal properties

The PPS matrix's thermal behavior was analyzed using the differential scanning calorimetry (DSC) technique after being compression molded and cooled in water while in melt. Thermal transitions were obtained from thermograms of temperatures between 25ºC and 300ºC in order to evaluate possible changes in the matrix's crystal structure. From the information obtained from the thermograms, we can highlight the melting temperature (Tm) and fusion enthalpies (ΔHm) obtained from endothermic peaks. Similarly, the crystallization temperature (Tc) and crystallization enthalpy (ΔHc) measured from exothermic peaks. The degree of crystallinity was obtained from the fusion enthalpy for each of the formulations by means of the following equation.

$$X_c = \frac{\Delta H_f}{\Delta H_f^0} \times 100 \quad (1)$$

Xc is defined as the percentage of the crystalline fraction obtained from the fusion enthalpy ΔHf, on the theoretical value of the standard melting enthalpy ΔH_f^0 which is 76.5J/g for PPS.

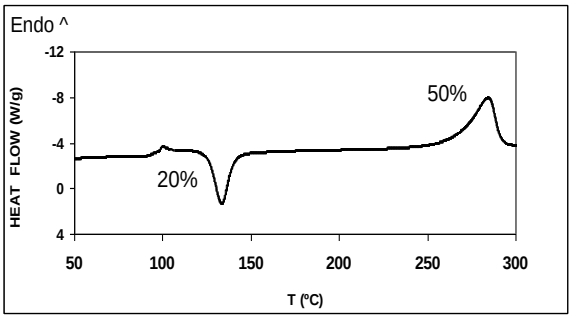


Figure 3. Thermogram of pure PPS at 10 ° C/min after cooling in water.

Through the analysis of the thermogram obtained through DSC in Figure 3, the thermodynamic critical points were determined. First, the glass transition temperature is observed around 95 ºC, followed by a first peak that corresponds to cold crystallization. A second peak is observed around 285ºC, equivalent to the fusion enthalpy. Cold crystallinity calculations for PPS reveal a 20% crystalline fraction that has not crystallized during cooling in water. The maximum value of the crystalline fraction obtained in the melting peak is 50%.

III.II Traction behavior

The efficiency of carbon nanofibers on the mechanical behavior of PPS depends on two fundamental factors, firstly, the degree of nanoparticles dispersion in the PPS matrix, this factor involves the method used to mix the CNFs with the PPS matrix and the manufacturing process used, either in melt or in solution. The second factor is related to the adhesion between the fiber and the matrix, taking into account that the mechanical behavior of the compounds depends on the interaction between the two constituents and therefore some surface modification with reactive groups that contain OH groups on the surface of nanofibers is a key aspect to improve the interaction forces during the interface of the two materials [13].

The number of samples tested for each composition is five. Figure 5 shows the stress-strain diagram curves of the PPS/CNF compounds.

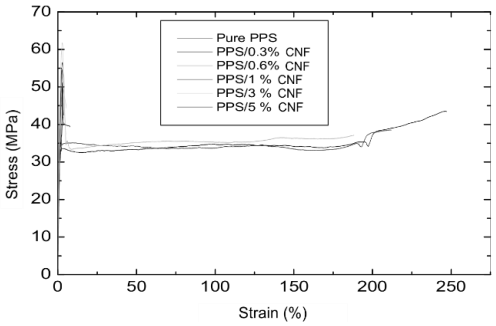


Figure 5. Representation of the stress-strain curve for PPS and its compounds PPS /%CNF.

According to the results obtained in the mechanical behavior for the different formulations of PPS/%CNF, an increase in Young's modulus is observed, as well as in the tensile strength, however, ductility is affected, it decreased as the content of nanofibers increased due to the presence of small agglomerates formed during the manufacturing process that can subsequently behave as stress concentrators, which can cause the appearance of cracks that will evolve to fractures on the material.

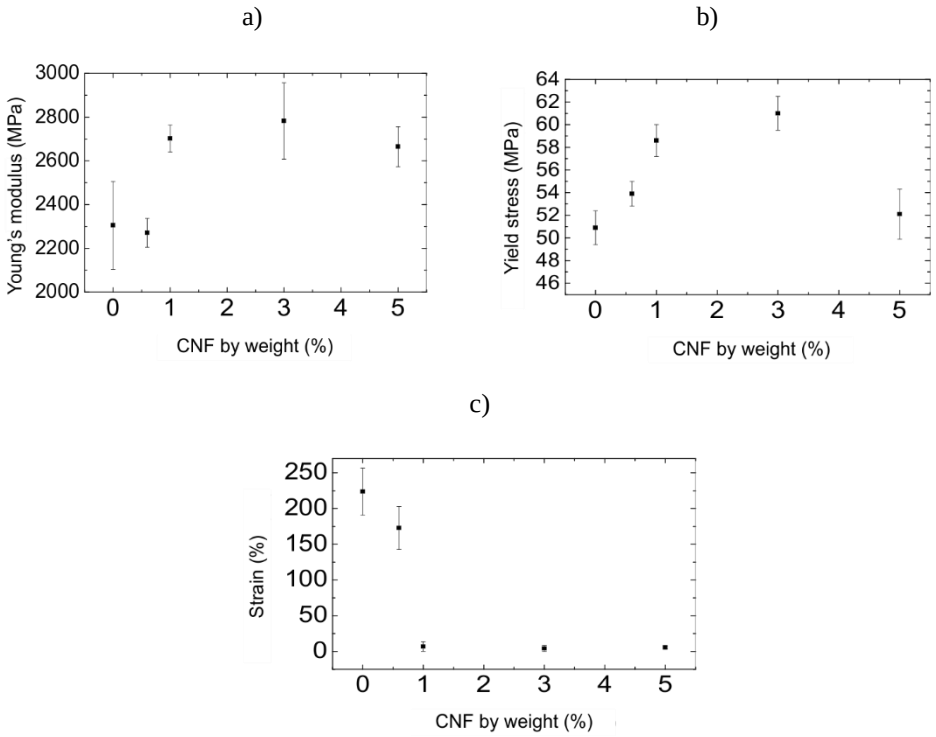


Figure 6. Tendencies of the mechanical properties of the compounds PPS/%CNF a) Young's modulus b) Yield stress c) Deformation at break.

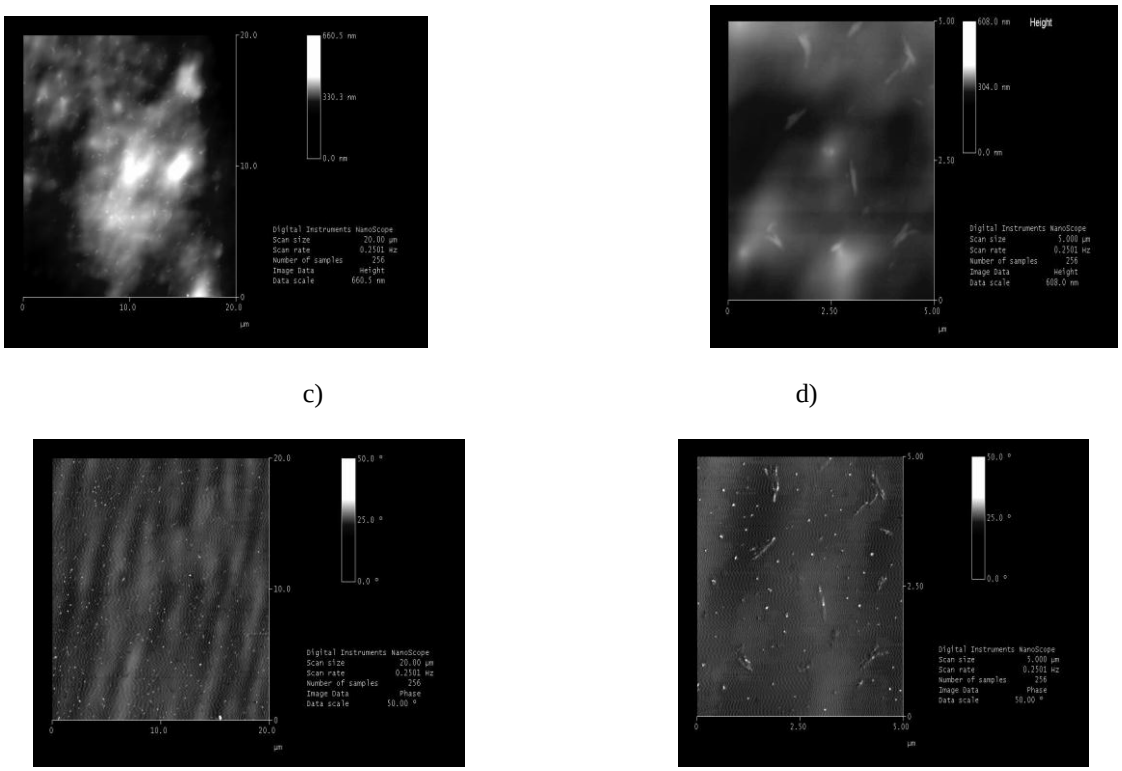
The values obtained in the tensile mechanical properties are shown in Figure 6. respecting Young's modulus, an increase proportional to the content of carbon nanofibers is observed, going from a modulus value for pure PPS of 2221 MPa to a 2783 MPa value corresponding to 3% per weight of CNF, with a percentage increase of 25.3%. The yield stress behavior reflects a behavior similar to Young's modulus with percentage increases of 21.5% in the same range of CNF compositions. The behavior in ductility presents a drastic drop for CNF contents above 1%, which can be attributed to the presence of CNF agglomerates in the PPS matrix. These results can be confirmed later with atomic force microscopy techniques AFM to study the NCFs degree of dispersion.

III.III Atomic Force Microscopy

The samples for the AFM analysis were from films obtained from a mixed process, the composition taken as a reference was that of1% of CNFs.

The AFM micrographs in figure 7 represent the morphology of PPS/1% CNF composites at 20 μm and 5 μm both in phase and in height, analyzing the NFCs degree of dispersion in the PPS matrix where two phases are evidenced. According to reports in the literature, the phase with the lighter hue corresponds to relatively harder material, which in this case belongs to the carbon nanofibers, while the darker phase indicates softer material corresponding to the PPS matrix. [14]. In-phase images at 20 μm and 5 μm indicate a good degree of dispersion of the carbon nanofibers in the PPS matrix.

a) b)



c) d)

Figure 7. AFM images for PPS/1%CNF compounds in height mode a) 20 μm b) 5 μm and in phase mode c) 20 μm d) 5 μm.

VI. CONCLUSIONS

The development of new materials reinforced with carbon nanofibers represents a new alternative for the manufacture of organic matrix composites that can be competitive in the market with systems reinforced with traditional fibers. For the following study, a matrix of Phenylene Polysulfide was used with different amounts of carbon nanofibers (0.3 and 5% per weight).

The results respecting the mechanical behavior show an increase in both Young's modulus and the yield strength for contents up to 3% per CNF weight, however, a decrease in ductility is observed that can be attributed to the presence of small agglomerations.

The AFM images show a good dispersion of NFCs on the PPS matrix, small agglomerates that can influence the mechanical behavior are also seen in them.

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