Improvement of Thermal and Mechanical Properties of Carbon Nanotube Composites through Chemical Functionalization

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Chemically functionalized multiwalled carbon nanotubes were incorporated into a polymer matrix by in situ polymerization, to improve the transfer of mechanical load through a chemical bond, which was demonstrated by Raman and infrared spectroscopies. The resulting composite shows higher storage modulus (E') and tensile strength than existing similar composites, with only 1 wt % of functionalized nanotubes. E' at 90 °C is increased by an outstanding 1135% and the glass transition temperature is exceptionally raised by ≅40 °C.

Introduction

Carbon nanotubes (CNs) represent attractive possibilities for developing new, strong composite materials[1−4] inasmuch as different studies have demonstrated that both single-walled nanotubes (SWNTs) and multiwalled nanotubes (MWNTs) have outstanding high Young's modulus, stiffness, and flexibility.[5−8] However, despite the many reports published in CN composites with a polymeric matrix,[3,9−14] only few papers have involved chemical groups to effectively improve the transfer of mechanical loads from the matrix to the nanotubes,[15,16] thus truly taking advantage of the properties of nanotubes. In fact, the functionalized carbon nanotubes with carboxyl groups that are produced via oxidation are used in different investigations, which involve addition of proteins,[17] coupling of other nanostructures to form building blocks in nanotechnology,[18] attaching functional groups via amide or ester linkages,[19,20] and addition of pyrenes in solution,[21] among others. These results show that the carboxyl groups found in the tip and surface of CN are useful for the interaction between CN and other compounds. Thus, the use of these moieties so as to improve the "link" in CN−polymer composites have been proposed,[22,23] inasmuch as inserting other chemical groups or using the carboxyl groups produced in the oxidation. In two recent reports about interaction of CN with polymer matrix, good results have been obtained.[15,16] In the study realized by Jia et al.[15] it is suggested that the initiator opens the π bonds found in CN and, in this way, CNs take part in the polymerization. Although opening π bonds in CN to join them with other chemical groups has been proposed,[24] oxidation provides more possibilities to bond the nanotubes to a matrix, due to reactive chemical groups such

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as COOH, COO^-, and C═O,[22,25−27] which are found on the tip and on the wall surface.

In another report Geng et al.[16] used fluorinated single-walled nanotubes (fl-SWNT) to improve the uniformity and nanotube dispersion using poly(ethylene oxide) (PEO) as matrix and dissolving the nanotubes in methanol. Definitively, the best moment to reach possible interactions between the functional groups (found in tips and walls in CN) and polymer chains is when the polymer is created by in situ processing, inasmuch as the free radical formed in monomer molecules by the initiator could either interact or react with the CN moieties easier than when the polymer is made and after dissolved or melted to produce the composites. Therefore, we present here the first report where initially functionalized carbon nanotubes are bonded to a thermoplastic polymer matrix (starting from monomer) to improve the mechanical properties such as storage modulus (E') and stress−strain behavior and the glass transition temperature (T_g). In the composite with functionalized multiwalled carbon nanotubes (f-MWNT), E' at 40 °C is increased by 66% and the T_g by about 40 °C as compared to 50% and 6 °C in the composite with unfunctionalized multiwalled carbon nanotubes (u-MWNT); both increases are measured with respect to the poly(methyl methacrylate) (PMMA) polymeric matrix used. In addition, E' for f-MWNT composites increases by a factor of 11-fold at high temperature and these composites show much higher plasticity than u-MWNT composites in stress−strain curves.

Experimental Section

Methyl methacrylate monomer (MMA) and 2-2 azoisobutyronitrile (AIBN) were supplied by Aldrich and GIRSA company, respectively; arc-discharge MWNTs were provided by the MER corporation (ground core material) and oxidized and functionalized by the method proposed by Hiura et al.[25] with slight variations in $KMnO_4$ quantity and reflux time. CN composites were produced in situ polymerization using AIBN as initiator. The AIBN quantity, reaction time, and temperature were controlled to have uniform molecular weights in all composites. The reaction to produce each composite was carried out in a flask with MMA monomer and AIBN, the CNs were added after 30 min of reaction and stirring constantly, the temperature was maintained at 70 °C for 2 h, and then the mix was cast into a glass mold with a latex frame to control the shrinkage.

The materials produced have a thickness of about 1.8 mm. The manufactured samples are identified as follows: sample A (only PMMA), sample B (1 wt % of u-MWNT), sample C (1 wt % of f-MWNT), and extra composite sample D (1.5 wt % of f-MWNT), which was produced to observe the behavior when the addition of f-MWNT was increased slightly.

For the dynamical mechanical analysis (DMA) the samples were cut at 5-mm width and 30-mm long and run in TA Instruments DMA 2980 using tension clamps, with 1 Hz frequency. For the scanning electron microscopy analysis (SEM) a LEO 1525 was used with silicon wafers as support. Infrared analysis (IR) was obtained using a Vector 33 Bruker spectrophotometer at 32 scans, and Raman spectra were obtained in a Micro-RAMAN Dilor with a 632-nm laser and spectral resolution of 3 cm^{-1}. The mechanical strength was realized in an Adamel Lhomarghy DY22 at 0.1 mm/min and Mini-instrom machine (MINIMAT) 2000 (miniature material tester) at 5 mm/min.

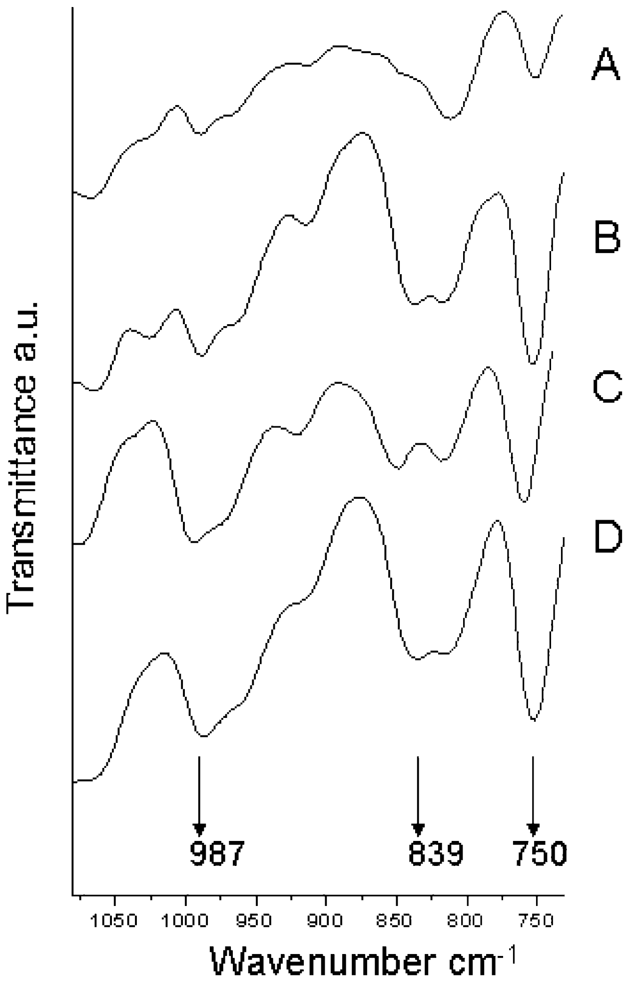

Figure 1. IR spectra: (A) PMMA, (B) 1 wt % u-MWNT composite, (C) 1 wt % f-MWNT composite, and (D) 1.5 wt % f-MWNT composite.

Results and Discussions

Infrared and Raman Spectroscopies. The characterization by Raman and IR spectroscopies of these functionalized carbon nanotubes to obtain chemical groups to connect other moieties has been published elsewhere.[22] The chemical groups present are COOH and COO−, which are found in tips and walls of MWNT; these groups take part in the polymeric reactions and permit linkage of the f-MWNT to the polymer. In addition, the oxidation yields CN with less impurities, which is an extra factor useful in the interaction between carbon nanotubes and polymer matrix. Figure 1 shows the IR spectra of the four samples from 700 to 1100 cm^{-1}. In curves C and D (which correspond to f-MWNT composites) a clear increase in the peaks at 987 and 750 cm^{-1} is observed with respect to sample A; the first band corresponds to νC−C of the main chain in PMMA[28,29] and the second corresponds to a combination νC−C and ρCH_2.[29,30] The increase in these bands is due to the addition of C atoms of f-MWNT in the PMMA chain; the u-MWNT composites (Figure 1B) show an increase in these bands too, so the suggestion by Jia et al.,[15] that π bonds in CN could be open and

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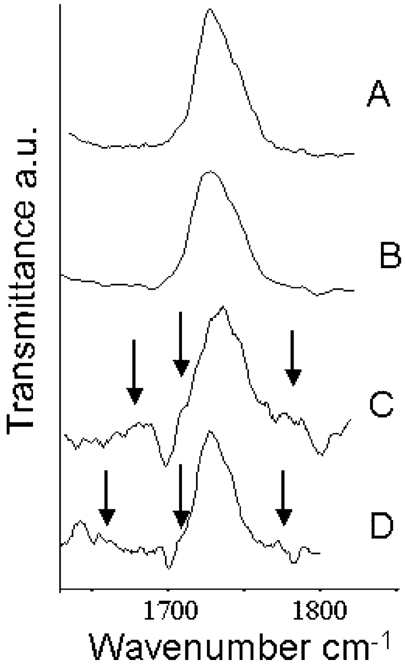

Figure 2. Raman spectra: (A) PMMA, (B) 1 wt % u-MWNT composite, (C) 1 wt % f-MWNT composite, and (D) 1.5 wt % f-MWNT composite.

interact with polymer, could be possible. However, the increase in the band at 987 cm^{-1} is smaller in sample B than that shown in samples C and D; this shows that chemical groups in f-MWNT have more interaction with the polymer. The band at 836 cm^{-1} shows an increase in B, C, and D spectra with respect to the slight shoulder shown in the A spectrum; this could be due to the A_2u IR phonon mode present in CN, found in this region,[31] but it also is attributed to a mixed motion ρCH_2 and COC deformation in PMMA.[32] Therefore, the increase presented leads to the conclusion that CO groups found in f-MWNT have a chemical connection with the polymer chain, which is corroborated with the Raman spectra. The CO vibration generates long peaks in the IR spectrum and it is difficult to detect shoulders near the intense signal at 1720 cm^{-1} $\nu C{=}O$; so in spite of the fact that little changes are present in IR spectra near this band, these shoulders are more visible in the Raman spectra for the CN composites, as is seen in Figure 2. The $\nu C{=}O$ vibration covers the range from 1680 to 1820 cm^{-1}.[29,33] In this region three new signs are presented in C and D Raman spectra corresponding to the f-MWNT composites; the first band appears from 1680 to 1693 cm^{-1} and belongs to $\nu C{=}O..\alpha C$[31] and is due to the interaction of C=O of f-MWNT and αC of PMMA. The second and third signals are found at 1706 cm^{-1} and from 1763 to 1773 cm^{-1}, respectively, as slight shoulders of the band at 1720 cm^{-1} (corresponding to the PMMA spectrum ($\nu C{=}O$)). The signal at 1706 cm^{-1} has been assigned as $\nu C{=}O\cdots OH$,[28] so OH present in COOH groups in f-MWNT has interaction with C=O of the PMMA chain; the other shoulder from 1763 to 1773 cm^{-1} corresponds to $\nu C{=}O..O$ bonded[30] and indicates that COO^- moieties in f-MWNT interact with C=O of PMMA. These bands are not present in A and B spectra and corroborate the interaction between f-MWNT and PMMA groups.

Dynamical Mechanical Analysis. Figure 3a shows the storage modulus (E') of samples A, B, C, and D. It is evident that sample C, which contains 1 wt % of the f-MWNT, shows better behavior, in terms of E', than sample B, which contains 1 wt % of u-MWNT. Figure 3b shows the behavior of tan δ of samples A, B, C, and D, where a significant increase in the glass transition temperature (T_g) (maximum of tan δ peak)[34,35] is observed in sample C. Sample D (containing 1.5 wt % of f-MWNT) repeats the behavior of sample C: increasing the T_g by 40 °C with respect to the PMMA (sample A), besides improving E' with respect to samples A, B, and C, showing that the addition of small quantities of f-MWNT increase the modulus significantly. Samples with f-MWNT (C and D) show an important increase in E' at 40 °C (E' 40 °C) by 66% and 88%, respectively, and both samples increase the T_g by ≅40 °C, unlike sample B with u-MWNT, which increases E'(40 °C) by 50% and the T_g by only 6 °C. Another important fact is that samples C and D increase E' at high temperature, more than 11-fold, inasmuch as samples C and D show an increase in E(90 °C) of 1135% and 1195%; with respect to the sample of PMMA, sample B (u-MWNT) increases E(90 °C) by only 250%.

Stress–Strain Analysis. Figure 4 shows the stress–strain curves, where it is clear that the tensile strength and modulus are increased in the sample with 1 wt % of u-MWNT (B) with respect to the reference sample (sample A). The behavior of sample B corresponds to a strong material but not as tough and is unlike that of sample C (with 1 wt % of f-MWNT), which improves the tensile strength and modulus. It additionally shows more elastic behavior than sample B; this elastic behavior is also observed in sample D, which contains 1.5 wt % of f-MWNT. This effect is more noticeable, by obtaining the area under the stress–strain curves, which is proportional to the toughness of the material.[36] The complete results of the samples are summarized in Table 1. The samples were run in MINIMAT at a different rate with the same stress–strain curves behavior.

Table 2 compares the increase in dynamical mechanical results of this paper with those published by Geng et al.[16] and Table 3 shows a comparison of a tensile test with those reported by Jia et al.,[15] Geng et al.,[16] and Qian et al.[10]

Scanning Electron Microscopy. Figure 5 shows the SEM images of u-MWNT and f-MWNT composites in the fractured area after the tensile strength tests. It

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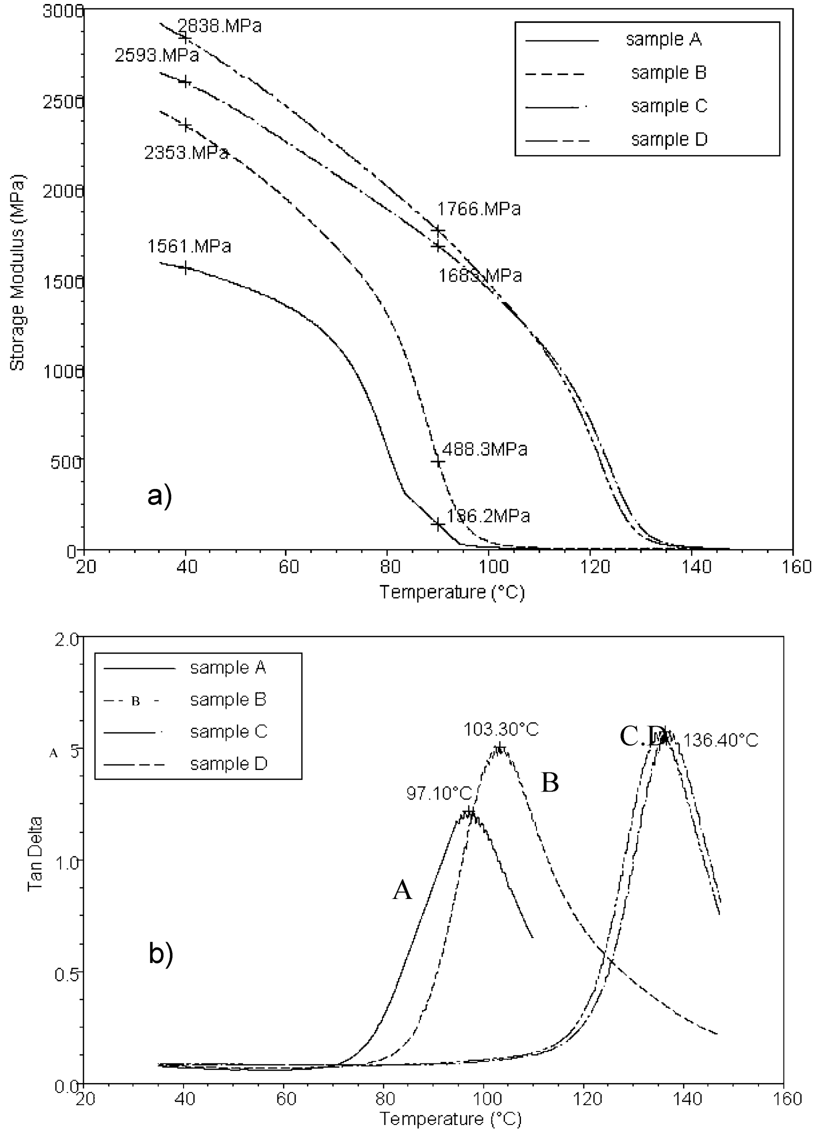

Figure 3. Dynamical mechanical analysis of carbon nanotubes composites: (a) storage modulus (E') results; (b) tan δ results.

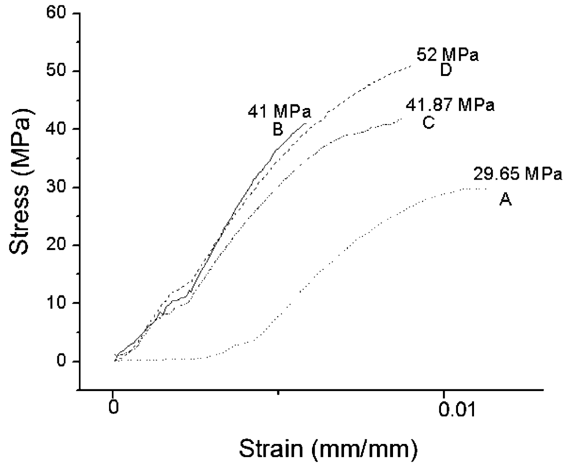

Figure 4. Stress–strain curves of carbon nanotubes composites.

Table 1. Stress–Strain Parameters in CN Composites

sample	stress (MPa) σ_{Max}	strain mm/mm ϵ	(toughness) area under curve
(A) PMMA	29.65	0.0113	0.15
(B) 1 wt % u-MWNT	41	0.0058	0.1157
(C) 1 wt % f-MWNT	41.87	0.0087	0.209
(D) 1.5 wt % f-MWNT	52	0.009	0.262

is clear that f-MWNT composites are covered by the polymer matrix, causing a good interaction. the u-MWNT composites in the part free of impurities seems to have the same behavior; however, two important differences in the interface boundaries in the CN and polymer matrix in f-MWNT composites with respect to u-MWNT composites must be noticed: less impurities and the links caused by the chemical groups that result in a much better interface.

Conclusions

IR results show that u-MWNT could have chemical interaction with a polymer through opening π bonds in CN as suggested by Jia et al.[15] However, more research in this field is needed. Nevertheless, f-MWNT has reactive groups in the tip and surface, which are more useful for bonding them with polymer chains while the polymerization is carried out. The IR and Raman spectra show the interaction produced in the composites with f-MWNT, which improves effectively the mechan-

Table 2. Dynamical Mechanical Results of Carbon Nanotubes Composites

parameter	this paper	reference 16[a]
E' blank (MPa)	(at 40 °C) 1561	(at 20 °C) 400
E' 1 wt % f-MWNT	(at 40 °C) 2593	(at 20 °C) 600
increment in E' (1 wt % f-MWNT)	66%	50%
E' (other concentration of f-MWNT)	(at 40 °C and 1.5 wt %) 2838	(at 20 °C and 4 wt %) ≅1300
increment in E' (other concentration of f-MWNT)	81%	225%
tan δ max. (T_g °C) blank	97.1	*b*
tan δ max (T_g °C) 1 wt % f-MWNT	136.4	*b*
increment in T_g °C	39.3 °C	*b*

[a] Functionalization in ref 16 consists of fluorinated single-walled nanotubes (fl-SWNT). [b] tan δ max is not presented; however, DSC results are present where the Tm diminishes with the addition of fl-SWNT at 1, 4, and 10 wt %. with respect to the matrix used.

Table 3. Mechanical Results in Carbon Nanotubes Composites

reference	σ (MPa) blank	σ (MPa) 1 wt % CN	% increment (1%)	σ (MPa)	% increment[c] (other concentration)
here (f-MWNT)	29.65	41.87	41	(1.5%) 52	75
11 (MWNT)	12.8	16	25		
16 (t-MWNT)[a,b]	54.9	58.7	6.9	(7%)	30.5
17 (fl-SWNT)	≅3	≅9	≅200		

[a] t-MWNTs are CN treated that were ground in a ball mill and boiled with HNO_3. [b] In this reference PMMA was used as a blank, which is the same matrix used in this paper. [c] The increases are reported with respect to the matrix used (blank).

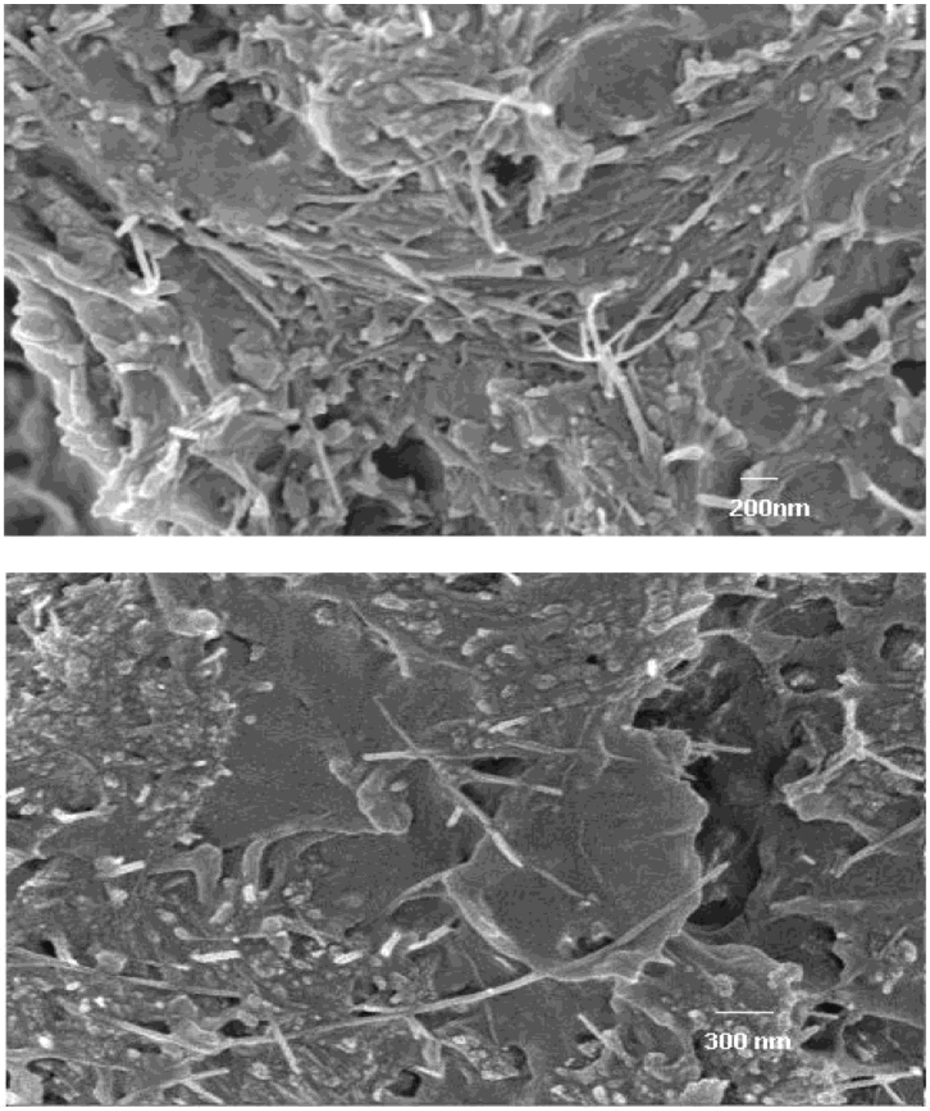

Figure 5. SEM images of carbon nanotube composites after tensile test: (a) f-MWNT composite; (b) u-MWNT composite.

ical transfer, taking advantage of the outstanding mechanical properties of carbon nanotubes, as is reflected in the mechanical and thermal results of f-MWNT composites with respect to the u-MWNT composites and matrix used. These results shows that the functionalization, in combination with in situ polymerization, is an excellent method for producing truly synergetic composite materials with carbon nanotubes.

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