

Polymer Nanocomposites Containing Carbon Nanotubes and Miscible Polymer Blends Based on Poly[ethylene-*co*-(acrylic acid)]

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ABSTRACT: Four binary polymer blends containing poly[ethylene-*co*-(acrylic acid)] (PEAA) as one component, and poly(4-vinyl phenol-*co*-2-hydroxy ethyl methacrylate) (P4VPh-*co*-2HEMA) or poly(2-ethyl-2-oxazoline) (PEOx) or poly(vinyl acetate-*co*-vinyl alcohol) (PVAc-*co*-VA) or poly(vinylpyrrolidone-*co*-vinyl acetate) (PVP-*co*-VAc) as the other component were prepared and used as a matrix of a series of composite materials. These binary mixtures were either partially or completely miscible within the composition range studied and were characterized by differential scanning calorimetry (DSC) and Fourier transformed infrared spectroscopy (FTIR). Carbon nanotubes (CNTs) were prepared by a thermal treatment of polyester synthesized through the chemical reaction between ethylene glycol and citric acid over an alumina boat. High resolution transmission electron microscopy (HRTEM) was used to character-

ize the synthesized CNTs. Films of composite materials containing CNTs were obtained after evaporation of the solvent used to prepare solutions of the four types of binary polymer blends. Young's moduli of the composites were obtained by thermomechanical analysis at room temperature. Only one glass transition temperature was detected for several compositions on both binary blends and the composite material matrices. Evidence of hydrogen bond formation was recorded for both miscible blends and composite materials. The degree of crystallinity and Young's moduli of the CNT-polymer composites increased compared to the single polymer blends. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 1462–1472, 2008

Key words: blends; miscibility; nanocomposites; polyethylene

INTRODUCTION

The incorporation of nanoparticles into a polymer matrix has been of increased interest in materials engineering.¹ The resulting products are composite materials where nanoparticles are randomly dispersed. In this regard, polymers are a good choice as host materials, since they have a wide variety of bulk physical properties and possess flexible processability.² Several works have appeared in the literature in which the preparation of new nanoparticles/polymer composites was reported.³ Commonly, a problem persists for this type of materials;

particles of different types develop self-aggregation and as a result, uncontrollable wide size distribution occurs. Consequently, the development of easier synthesis techniques to produce new nanoparticles and nanodispersions with narrower size distribution in a polymer matrix is an actual challenge.

Carbon tubules (or carbon nanotubes; CNTs) are a new form of elemental carbon. Iijima isolated CNTs in 1991 from soot during the arc-synthesis of fullerenes.⁴ There are two kinds of CNTs, namely, single walled carbon nanotubes (SWNTs) formed by a single graphene sheet, and multiwalled nanotubes (MWNTs) formed with additional graphene sheets wrapped around the SWNT core. CNTs have exhibited remarkable chemical, electronic, and mechanical properties.^{5–9} These properties include, exceptionally high axial strength and Young's modulus of the order of TPa.^{10–12} CNTs have recently been considered as reinforcing elements in ceramic and polymer matrix composites as well.^{13,14} The addition of CNTs to a polymer matrix by covalent modification of CNTs was a pioneering strategy that made possible

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wrapping polymer molecules like poly(vinyl acetate-co-vinyl alcohol) (PVA-VA), poly(vinyl ketone)-polystyrene (PVK-PS), and polystyrene (PS), around individual CNTs.¹⁵⁻¹⁸ Despite the fact that chemical interaction between CNTs and a polymer matrix seems to be one of the main reasons to produce CNT-polymer composite materials, the difficulties to preserve the tubular structure of CNTs after any treatment inhibit the complete implementation of this synthesis path. Consequently, the most common route to successfully prepare novel CNT-polymer composite materials is by the simple addition of CNTs to some type of polymer.

Although there is controversy in the literature about the real dimensions of the submolecular scale of the mixing segment that indicates true miscibility in polymer blends, there is sufficient consensus to affirm that the existence of only one glass transition temperature (T_g) in a polymer binary blend indicates miscibility.¹⁹ Literature reports of new miscible blends have increased recently, which suggest that there is an interest in synthesizing new types of these materials.

Miscible polymer blends are attracting host materials to which CNTs can be inserted because this type of mixtures has a degree of mixing down to the molecular level. Many literature reports deal with the addition of CNTs as fillers into polymer matrices; however, just a few investigate the effect of adding CNTs to a polymer matrix specifically formed by a miscible polymer blend. In this work, we investigate the problem of whether the addition of CNTs to a miscible polymer can modify the spatial orientation of chemical groups that develop favorable heterocontacts (commonly responsible of inducing miscibility in several binary systems) as well as to elucidate if CNTs would induce segregation and immiscibility on the original blend. Furthermore, we assess the possibility that CNTs could act only as fillers of the polymer miscible blends without inducing any phase change behavior of the original blend.

The aim of this work is to report on the preparation and assessment of the thermal and mechanical properties of a new series of CNTs-polymer composites. To achieve this goal, a series of polymers known to be hydrogen bond formers was selected for the preparation of the CNTs-polymer composites. CNTs act as fillers while miscible polymers act as matrix of the composites. Differential scanning calorimetry (DSC) and Fourier transformed infrared spectroscopy (FTIR) techniques allowed us to detect changes in the thermal and structural properties of the composites prepared as a function of the CNT content, whereas changes in their mechanical properties were monitored by an evaluation of the Young's moduli.

EXPERIMENTAL

Figure 1 shows the chemical structure of the polymers employed in this work. Poly[ethylene-co-(acrylic acid)] (PEAA) was a common component of all polymer blends. PEAA (weight-average molecular weight, $M_w = 30,000$ g/mol) was purchased from Dow Chemical (Mexico City, Mexico) under the trade name of PRIMACOR-5980TM. This copolymer has an acrylic acid content of 20 wt %. Poly(4-vinyl phenol-co-2-hydroxy ethyl methacrylate) (P4VPh-co-2HEMA) (51 mol % of 4 vinyl phenol content, according to the manufacturer), poly(vinyl acetate) (PVAc) ($M_w = 12,800$ g/mol), and poly(vinylpyrrolidone-co-vinyl acetate) (PVP-co-VAc) ($M_w = 50,000$ g/mol) were purchased from Aldrich. Poly(2-ethyl-2-oxazoline) (PEOx) ($M_w = 50,000$ g/mol) was purchased from Polysciences (Warrington, PA). All polymers were used as received. Carbon graphite (CGr, 1 μ avg. dia.) was purchased from Aldrich (Toluca, Mexico). Ethylene glycol, methanol, and hydrochloric acid were reactive grade and purchased from Ferromont (Monterrey, Mexico). HPLC-grade tetrahydrofuran (THF) from Golden Bell (Zapopan, Mexico) was used to prepare the mixtures. Anhydrous citric acid was purchased from Spectrum (Gardena, CA), while the alumina boat was obtained from Alfa-Aesar (Ward Hill, MA).

All polymer binary blends were prepared by dissolving both PEAA and P4VPh-co-2HEMA (or PEOx or PVAc-co-VA or PVP-co-VAc) in THF, followed by casting onto Petri dishes and dried at 50°C in an oven with airflow during 24 h. The films obtained were put in a vacuum oven at room temperature for 12 h to eliminate residual solvent. In this work, we use the notation PEAA/P4VPh-co-2HEMA, PEAA/PEOx, PEAA/PVAc-co-Va, PEAA/PVP-co-VAc to refer to each polymer system.

PVAc-co-VA was synthesized by hydrolysis-methanolysis of PVAc at 25°C in an acid medium. The degree of hydrolysis was determined by titration of the residual acetate groups. The reaction products with low degrees of hydrolysis were precipitated in water followed by dissolution in methanol and reprecipitation in water. Details of the experimental procedure are reported elsewhere.²⁰

CNTs were synthesized using polyester as a precursor obtained from the reaction between citric acid and ethylene glycol, according to the procedure described by Cho et al.²¹ Briefly, anhydrous citric acid was dissolved in ethylene glycol at a molar ratio of 1 : 4 and left to react with agitation at 50°C for 2 h until the mixture became transparent. The mixture was then heated at 150°C for 48 h with continuous agitation allowing the removal of excess solvent. As the reaction time increased, the solution became dark yellow, more viscous, and gelation occurred.

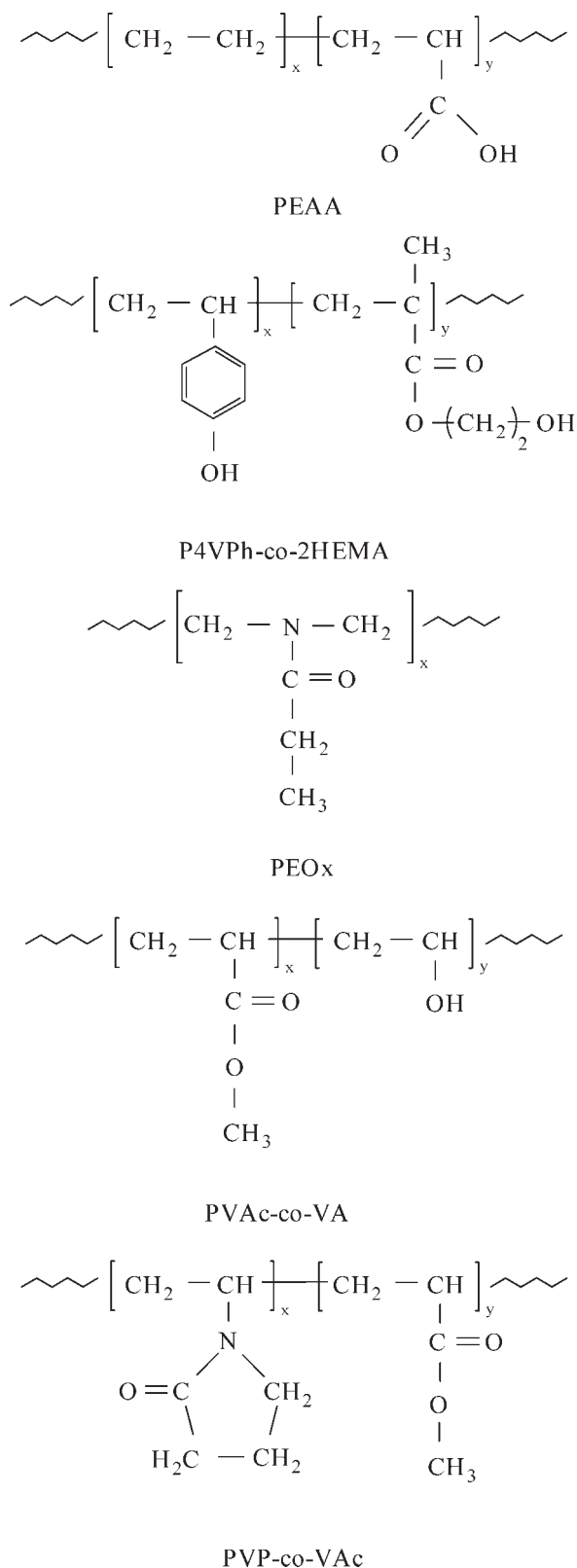


Figure 1 Chemical structures of polymers employed to prepare the mixtures studied in this work.

The resulting gel was a transparent brown resin. Charring the resin at 300°C for 2 h in an electric furnace resulted in a black solid mass, which was

ground into a powder with a Teflon rod. This powder is a precursor of CNTs. The precursor was deposited over an alumina boat and heated at 400°C for 8 h under an air atmosphere and cooled at room temperature. The CNTs thus obtained were used without any further treatment and were examined with a JEOL 2010 High Resolution Transmission Electron Microscope operated at 200 kV.

CNT-polymer composites were prepared by adding a fixed amount of CNTs (1 or 5 wt % with respect to the mass of polymer blend) to polymer solutions of PEAA/P4VPh-co-2HEMA or PEAA/PEOx or PEAA/PVAc-co-VA or PEAA/PVP-co-VAc with THF as solvent. The compositions of the polymer blends used to prepare the composites were 60 and 80 wt % PEAA. CNTs did not dissolve in THF; therefore, they were only dispersed in each solution. The suspension thus obtained was deposited onto Petri dishes and solvent was evaporated in an oven with an airflow obtaining thin films. On the other hand, amorphous carbon (graphite)-polymer composites were obtained by substituting CNTs by amorphous carbon following the synthesis procedure just described. Amorphous carbon contents on carbon-polymer composites were the same as the composites prepared with CNTs. This simple preparation method has been successfully used to obtain CNT-polymer composites polystyrene-based where CNTs were apparently homogeneously dispersed in a polystyrene matrix.²²

DSC thermograms were obtained with a TA Instruments Q100 model differential scanning calorimeter previously calibrated against indium under a nitrogen atmosphere. The calorimetric curves were recorded by heating from -50 to 150°C at 20°C/min and the second scan is reported. Sample weights of binary polymer blends ranged between 10 and 15 mg while composite sample weights were around 5 mg. The glass transition temperature was evaluated using the inflexion point criteria from the heat flow signal.

Compression tests were performed on composite disk-shaped films at room temperature with a Perkin-Elmer TMA-7 thermomechanical analyzer. The Young's modulus (E) was obtained from the slope of the initial linear zone (strain less than 5%) of the stress-strain curve according to the equation²³:

$$\tau = -E(\lambda - 1) \quad (1)$$

where τ is the applied stress and λ is the deformation calculated from the ratio of the deformed thickness to the initial thickness of the composite disks.

Vibrational behavior of the four polymer binary blends was studied by FTIR spectroscopy with a Perkin-Elmer Spectrum One spectrophotometer. Samples of each type of blend were dissolved in

TABLE I
Time Evolution of M_n , M_w , and T_g for the Polyester
Product of the Reaction Between Anhydrous
Citric Acid and Ethylene Glycol

Time (h)	M_n (g/mol)	M_w (g/mol)	T_g (°C)
8	2110	3830	-26
20	2580	5920	-25
30	3280	6180	-20
40	4000	6600	-12

THF and a few drops of each solution (whose concentration was 0.02 g/mol) were deposited over NaCl pellets. After solvent evaporation, a thin film of each blend was obtained and analyzed. FTIR spectra of the CNTs-polymer blends composites were also recorded. In this case, the films were obtained when CNTs were added and dispersed into the polymer blend solutions allowing solvent evaporation. Additionally, due to the fact that the films of composites can be prepared only when the PEEA content is equal to or greater than 60 wt %, we carried out an FTIR analysis of the composites rich in PEEA. For all samples, the IR spectra were the average of 100 scans with a resolution of 4 cm^{-1} .

GPC was used to determine the M_w evolution as a function of time for the polyester precursor of CNTs. For this purpose, a dilute solution (10 mg/10 mL) of the polyester was prepared using THF as solvent and stirred for 1 h and filtered through a 0.45 μm filter (Fischer brand). GPC measurements were made in a Perkin-Elmer instrument at 25°C using polystyrene standards for the calibration.

RESULTS AND DISCUSSION

Table I shows the number-average molecular weight (M_n), weight-average molecular weight (M_w), and the glass transition temperatures of the polyester that resulted from the reaction between anhydrous citric acid and ethylene glycol, as a function of time. It is evident that as the time increases, both M_n and M_w increase. However, at 40 h of reaction, the molecular weights obtained are relatively low. Despite the fact that the synthesis of polyesters of high molecular weight requires the complete removal the excess of ethylene glycol,²⁴ the polyester synthesized in this work proved to be adequate in the preparation of CNTs, as evidenced by the high resolution transmission electron microscopy (HRTEM)-micrographs shown in Figure 2. On the other hand, as expected, the glass transition temperature of the polyester shows an increasing trend as the reaction time increases. This fact is a direct consequence of the increment of the molecular weight of the polyester.

Figure 2 depicts two HRTEM micrographs of CNTs obtained after charring the polyester oligomers over an alumina boat. Figure 2(A) shows the spider web-like structure characteristic of MWNTs. This type of structure is in agreement with reports from the literature for an experimental procedure carried out without metal catalyst, such as the procedure used in this work.²⁵ Figure 2(B) depicts a micrograph magnified at 20 nm where the CNTs structures are clearly observed. The inner tube dia-

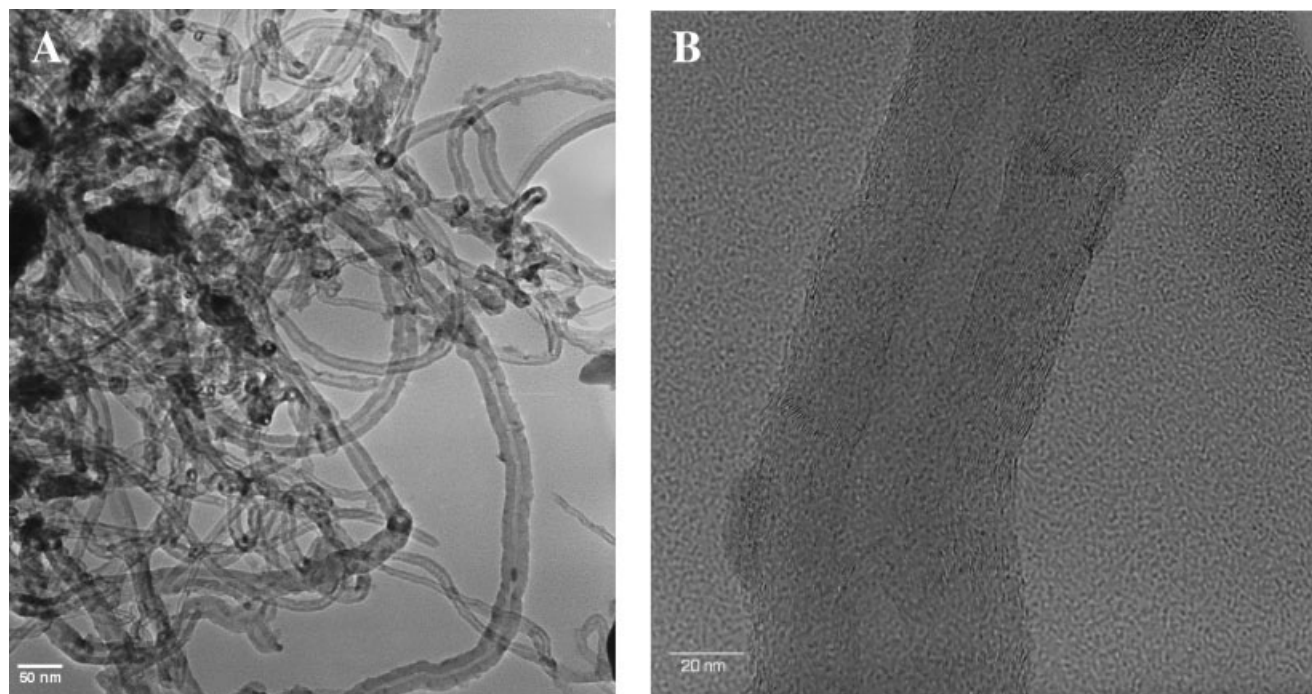


Figure 2 (A) Micrograph of carbon nanotubes. (B) Micrograph of CNTs obtained at higher magnification.

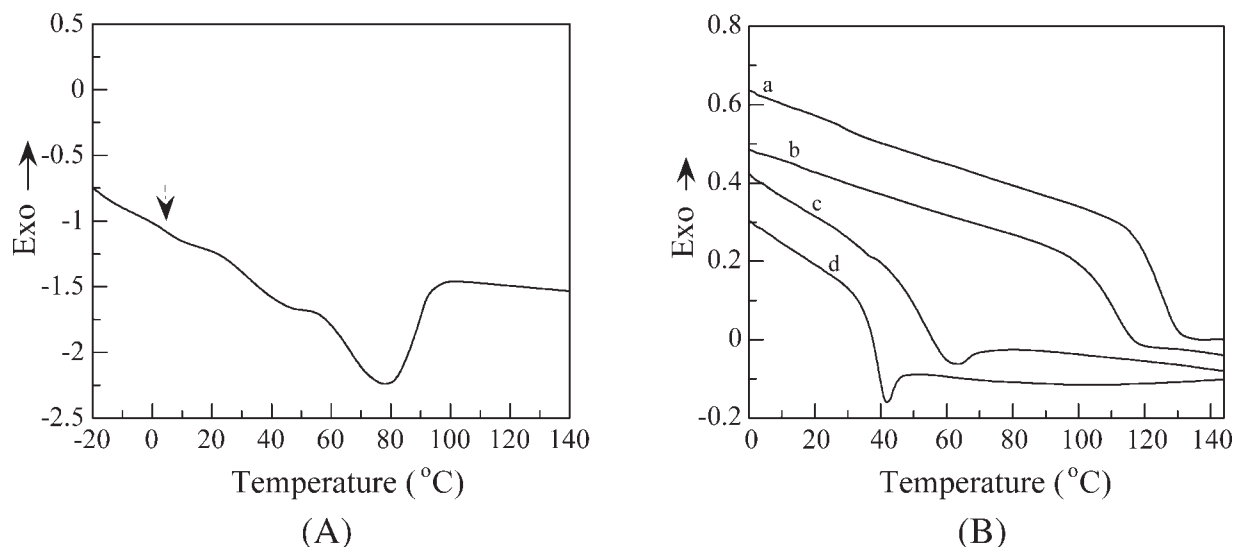


Figure 3 (A) DSC results for PEAA pure. (B) Thermograms of (a) P4VPh-*co*-2HEMA, (b) PVP-*co*-VAc, (c) PEOx, and (d) pure PVAc-*co*-VA.

meter of our samples ranged from 10 to 25 nm whereas the length was less than 1.5 μ . The spacing between graphene sheets in the tube walls was about 0.33 nm (all values observed from the micrographs). On the average, the highest inner diameter of the tubes was 25 nm with up to 30 graphitic layers comprising the tube, whereas in the case of tubes with the smallest inner diameter (10 nm), around 15 graphitic layers were observed. These results are consistent with other work presented elsewhere.²¹

Figure 3 (A) shows a thermogram of pure PEAA. This copolymer is a semicrystalline polymer. The T_g of PEAA that appears as a subtle transition is 4°C (indicated by the arrow). Two peaks form the wide endotherm produced by melting of crystalline regions of PEAA, typical of a polyethylene. The first centered around 40°C, and the second is clearly defined at 79°C. These two peaks are related to the melting of nonsegregated (high melting temperature) and segregated (low melting temperature) crystalline regions of PEAA.²⁶

Figure 3(B) depicts the calorimetric curves of pure polymers P4VPh-*co*-2HEMA, PVP-*co*-VAc, PEOx, and PVAc-*co*-VA. All these polymers are amorphous. The corresponding glass transition temperatures (T_g) are: 127°C for P4VPh-*co*-2HEMA, 111°C for PVP-*co*-VAc, 52°C for PEOx, and 39°C for PVAc-*co*-VA. In the cases of PEOx and PVAc-*co*-VA, an enthalpy recovery peak was detected on the temperature ranges where the glass transition temperature was detected. Since the difference between the T_g s of PEAA and anyone of the other polymers used to prepare the binary polymer blends studied in this work is larger than 30°C, it is possible to use the DSC technique to

evaluate the behavior of amorphous phases of the four binary systems, as discussed below.

Figure 4 shows calorimetric curves obtained by DSC of the PEAA/PVAc-*co*-VA mixtures. PVAc-*co*-VA was obtained by the smooth hydrolysis of pure PVAc. The hydrolysis degree was about 4%. This low hydrolysis degree has little effect on the glass relaxation behavior of this copolymer. In fact, the T_g of PVAc-*co*-VA is practically equals to the T_g of pure PVAc. For each PEAA/PVAc-*co*-VA mixture, only one glass transition was detected. This fact strongly suggests that PEAA/PVAc-*co*-VA polymer blends are miscible in all composition range. For the remaining three binary systems studied in this work, we found similar calorimetric results (DSC curves

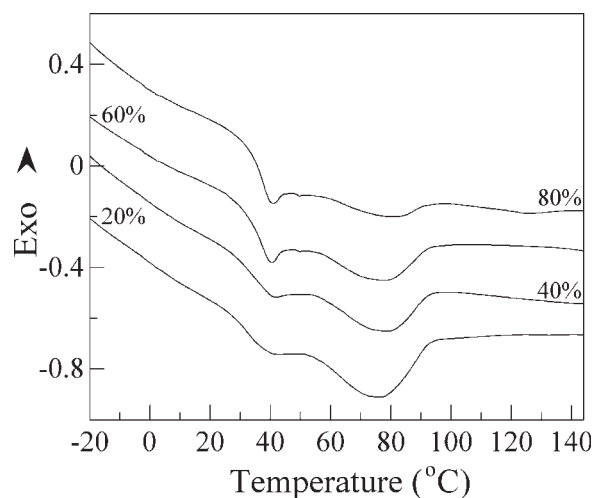


Figure 4 Thermograms of PEAA mixtures with PVAc-*co*-VA. The composition is given in wt % PVAc-*co*-VA.

TABLE II
Compositions and Glass Transition Temperatures of the Binary Polymer Blends
PEAA/PVP-*co*-VAc, PEAA/P4VPh-*co*-2HEMA, PEAA/PVAc-*co*VA, and PEAA/PEOx

Composition wt.% PEAA	T_g (°C)			
	PEAA/PVP- <i>co</i> -VAc	PEAA/ P4VPh- <i>co</i> - 2HEMA	PEAA/PVAc- <i>co</i> -VA	PEAA/PEOx
0	111	127	39	52
20	35 103	30 120	38	35
40	27 117	42	37	28
60	29	32	34	27
80	28	30	31	26
100	4	4	4	4

not shown here). A previous study carried out by our group on the dynamic mechanical thermal analysis (DMTA) of the PEAA/PEOx blends demonstrated that this system is miscible.²⁶ Here, the results obtained by DSC for this blends support the fact that the mixtures of PEAA with PEOx are miscible, since only one glass transition temperature was detected for each composition. On the other hand, in the case of mixtures of PEAA with P4VPh-*co*-2HEMA, two glass transition temperatures were detected for the mixture with 20 wt % PEAA. This result indicates immiscibility. In a similar way, the PVP-*co*-VAc /PEAA blends have a window of immiscibility. For this system, the blends with 20 and 40 wt % PEAA have two T_g s, whose values were in the range of the T_g of the parent pure polymers. All calorimetric results for the four binary blends are listed in the Table II. It is evident from this table that the four types of polymer blends are miscible are richer in PEAA (when the PEAA content is at least ≥ 60 wt %).

The most common driving force known to induce favorable hetero-contacts at the molecular scale between complementary chemical groups of parent polymers of miscible polymer blends is the hydrogen bond. PEAA is a copolymer that develops strong self-associations between its carboxyl groups. Reports about polymer blends prepared with PEAA indicate that the natural tendency of this copolymer to self-association changes when it is mixed with an acceptor proton polymer.^{26,27} We carried out an analysis by FTIR spectroscopy of the four polymer blends and the composites materials prepared in this work. For all spectra presented, the maximum intensity of each region analyzed was normalized to unity to facilitate comparisons.

For the composite materials prepared from polymer matrix, PEAA/PEOx blend the spectral behavior was analyzed in detail [Figs. 5 (A,B)]. Figure 5(A) depicts spectra of the composites prepared with 1 wt % CNTs in the region of 1750–1680 cm^{-1} where the stretching vibration due to self-association by hydro-

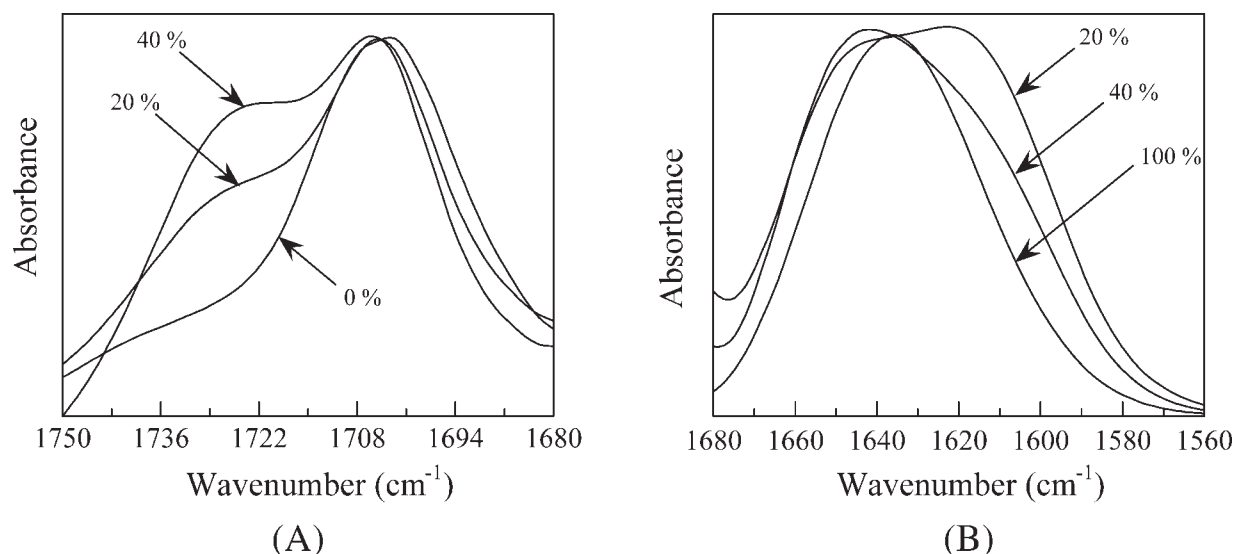


Figure 5 (A) FTIR partial spectra of composites prepared with 1 wt % CNTs and PEAA/PEOx blends in the region of 1750–1680 cm^{-1} . The composition is given in wt % PEOx. (B) FTIR partial spectra of composites prepared with 5 wt % CNTs and PEAA/PEOx blends in the region of 1680–1560 cm^{-1} . The composition is presented in wt % PEOx.

gen bonds in the form of dimmers created between carboxyl groups of PEAA, causes a broad band at 1704 cm^{-1} . Despite the fact that PEOx does not absorb IR radiation within this range, another band at higher wavenumbers (1725 cm^{-1}) was detected. The intensity of this band increases as the amount of PEOx in the blends increase (0–40 wt %), as in the case of the simple PEAA/PEOx blends,²⁶ this band is related to hydrogen bonding interassociations between the PEAA carboxyl groups and the amide groups of the PEOx. A higher content of CNTs in the composites does not change the tendency to form hydrogen bonds between PEAA and PEOx. Figure 5(B) shows the spectra of composites containing 5 wt % CNTs in the region of $1680\text{--}1560\text{ cm}^{-1}$. In this region, PEAA does not absorb IR radiation and the stretching band of the amide I of the PEOx appears at 1635 cm^{-1} . In the case of the composites, a new spectral contribution develops at lower wavenumbers (ca. 1617 cm^{-1}) whose intensity increases as PEAA content increases. This band corresponds to the amide groups of the PEOx, which are hydrogen bonded to the carboxyl groups of the PEAA. These results are a clear signal that the addition of CNTs to PEAA/PEOx blend does not modify the formation of positive hetero-contacts (of the hydrogen bond type) and which has a crucial role in miscibility phenomenon detected in the polymer matrix comprising the PEAA/PEOx polymer blend.

Figure 6 shows partial FTIR spectra of mixtures and composites prepared with PEAA and PVP-*co*-VAc. The PEAA/PVP-*co*-VAc mixtures are partially miscible. Figure 6(A) depicts the spectra of PEAA, PVP-*co*-VAc, and their blends in the region of $1800\text{--}1600\text{ cm}^{-1}$. The spectrum of the PEAA depicts the

well-known intense band at 1704 cm^{-1} . The spectrum of the PVP-*co*-VAc exhibits two bands: (i) a broad band at 1665 cm^{-1} due to the stretching vibration of the carbonyl group which appears at low frequency as consequence of resonance effects of carboxyl groups and nitrogen atoms both included in the amide group of the vinyl pyrrolidone (VP) and, (ii) at high frequencies, another band appears at 1732 cm^{-1} due to the stretching vibration of the carbonyl group comprising the vinyl acetate (VAc) groups. The IR vibration behavior of the blends in this region becomes more complex. For all blends, the band associated to the stretching vibration of the carbonyl groups (of VP) appears shifted to lower frequencies, while the band due to carbonyl groups (from acetate groups) appears at higher frequencies. This trend is more evident in the case of mixtures rich in PEAA. In fact, for blends with 20 and 40% PVP-*co*-VAc, these two bands appear at ca. 1640 and 1740 cm^{-1} , respectively. The band at 1740 cm^{-1} can be attributed to the stretching of the free carboxyl groups of the PEAA and therefore capable to form hydrogen bonds with carbonyl groups of both VP and VAc. The band at 1640 cm^{-1} corresponds to the spectral contribution of the carbonyl groups of VP associated by hydrogen bonds with carboxyl groups of PEAA.²⁸ The behavior described above suggests that carboxyl groups of PEAA and carbonyl groups of both VP and VAc, form more intense hydrogen bonding as the PEAA content in the mixture increases. The same behavior can be observed from the IR spectra of the composites with 5 wt % CNTs [see Fig. 6(B)]. In fact, for this last case, the band at 1640 cm^{-1} is clearly detected. In this sense, it seems that the inclusion of 5 wt % CNTs to the mixture

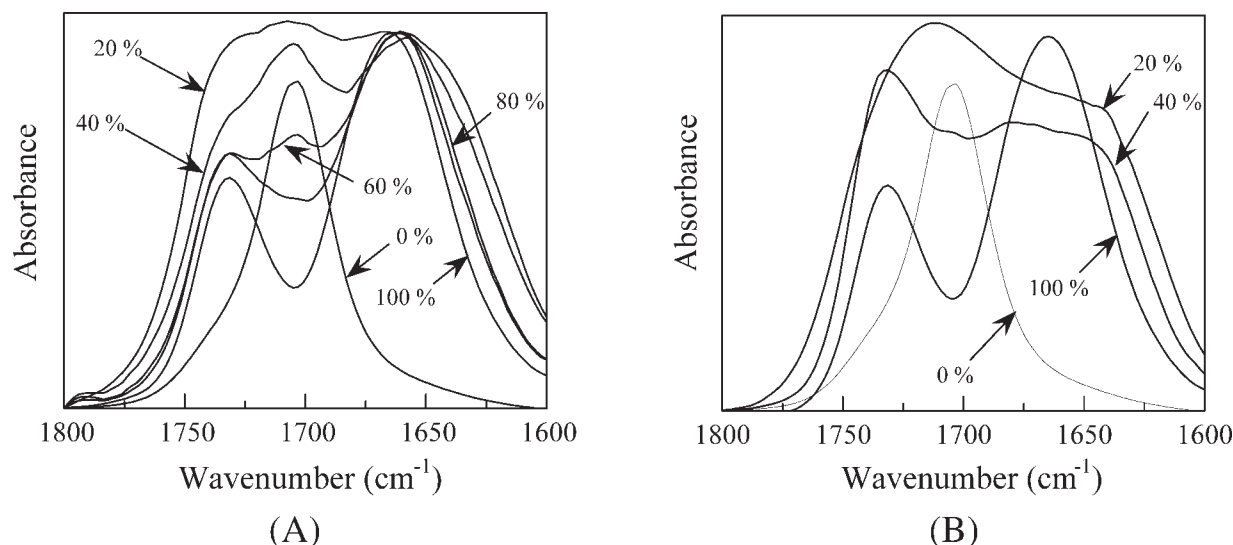


Figure 6 (A) FTIR spectra of PEAA, PVP-*co*-VAc and their mixtures in the region between 1800 and 1600 cm^{-1} . The composition is given in wt % PVP-*co*-VAc. (B) FTIR spectra of the composites containing 5 wt % CNTs and a matrix of PEAA/PVP-*co*-VAc blends in the region between 1800 and 1600 cm^{-1} . The composition is presented in wt % PVP-*co*-VAc.

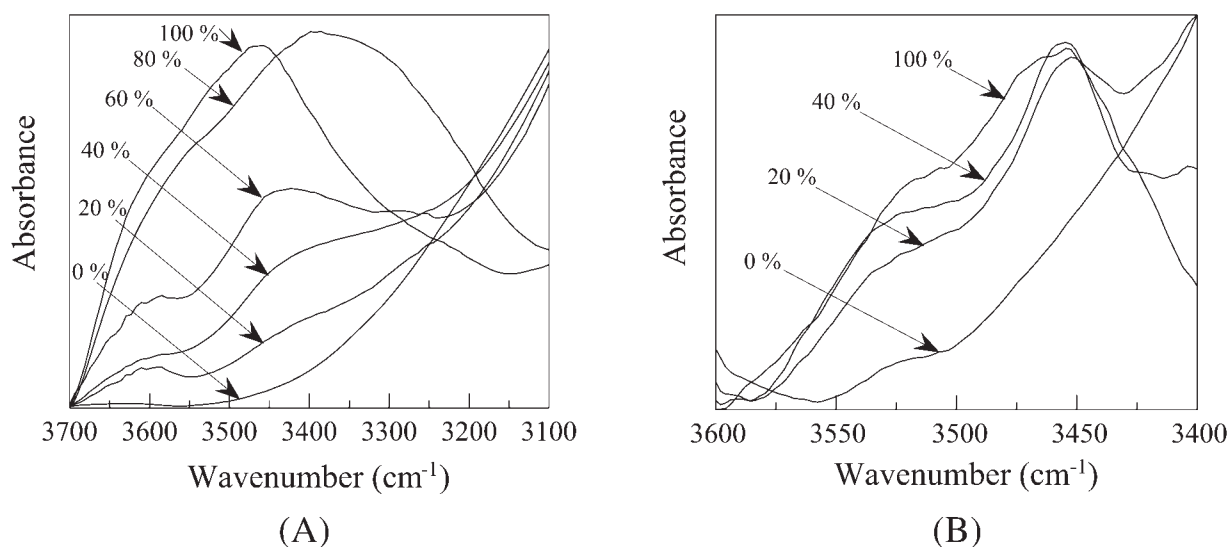


Figure 7 (A) FTIR spectra of PEEA, PVAc-co-VA and their blends in the region of 3700–3100 cm^{-1} . The composition is given in wt % PVAc-co-VA. (B) FTIR spectra of composites prepared with 5 wt % CNTs and a matrix of the mixture of PEEA/PVAc-co-VA in the region from 3600 to 3400 cm^{-1} . The composition is given in wt % PVAc-co-VA.

does not modify the tendency to create hydrogen bonds between carboxyl and carbonyl groups of PEEA and PVP-co-VAc, respectively.

Figure 7 shows IR partial spectra of blends and composites prepared with PEEA and PVAc-co-VA. Figure 7(A) depicts IR spectra of PEEA, PVAc-co-VA, and its mixtures in the region where hydroxyl-stretching band appears. The vibration of the hydroxyl groups that form part of PVAc-co-VA produce the wide band whose maximum intensity is resolved around 3460 cm^{-1} . To produce this band, several contributions corresponding to the summation of different vibrations were included: (i) contributions due to different types of hydroxyl-hydroxyl self-association movements occurring at low wavenumbers, and (ii) contributions due to the vibration of the free hydroxyl groups at high wavenumbers (detected as a shoulder centered at 3615 cm^{-1} of the main band). On the other hand, for the case of blends, a clear change in the IR behavior took place. In fact, two changes were detected: (i) as the blends become richer in PEEA, the intensity of the hydroxyl band decreased due to a lower amount of hydroxyl groups and, (ii) the hydroxyl band shifts to lower frequencies. The second effect is clearly evident for the blend with 80 wt % PVAc-co-VA. We attributed the last effect to a decrease of the force constant of the covalent bond that has the H donor and which in turn strongly suggests the formation of new hydrogen bonds. From the chemical structure point of view of PEEA, it is evident that carboxyl groups of this substance can develop hydrogen bonds with the hydroxyl groups of PVAc-co-VA. A similar behavior was previously reported for other polymer blends prepared with polyols and poly-

acids.²⁹ Figure 7(B) depicts IR spectra for composites when 5 wt % of CNTs were included in a polymer matrix of PVAc-co-VA/PEEA blends. It can be observed from these spectra that, as the composites become richer in PEEA, the two effects described for the case of PEEA/PVAc-co-VA simple mixtures are also present. However, for this last case, the displacement of the hydroxyl band to lower frequencies is less evident, whereas decrease of the free hydroxyl band is well resolved. These results suggest that for composites, the formation of hydrogen bonding between PEEA and PVAc-co-VA is also possible. The spectra of the PEEA/P4VPh-co-2HEMA blends and its composites (not shown here) are very similar to the observed for the PEEA/PVAc-co-VA system. The results obtained support the fact that in either of these materials (polymer blends or composites) hydrogen bonds exist and were formed between hydroxyl groups of P4VPh-co-2HEMA and carboxyl groups of PEEA.

It is known that for polymer miscible blends, in which there is hydrogen-bonding formation, the free volume changes due to orientation affects.²⁰ Based upon this evidence, it is reasonable suppose to CNTs do not modify the orientation between chemical groups responsible of hydrogen bonding and which in turn have a positive influence on the miscibility detected in both the four polymer blends and in the matrix of the series of composites prepared from them.

Table III shows the glass transition temperatures, melting enthalpy (ΔH_m), melting temperatures (T_m), and degree of crystallinity (X_c) of PEEA rich composites (whose PEEA content is 60 and 80 wt %). The value of X_c for the series of composites prepared was evaluated using the following equation³⁰:

TABLE III
Compositions, Glass Transition Temperatures, Melting Temperatures, Melting Enthalpies, and Degrees of Crystallinity of the Composites Containing CNTs and a Polymer Matrix Prepared with Blends of PEAA and PVP-co-VAc or P4VPh-co-2HEMA or PVAc-co-VA or PEOx

Matrix type	PEAA content (wt %)	CNTs content (wt %)	T_g (°C)	T_m (°C)	ΔH_m (J/g)	X_c (%)
PEAA/PVP-co-VAc	80	0	28	76	17.4	20.0
	80	1	28	79	24.4	28.1
	80	5	31	77	23.3	26.8
	60	0	29	71	10.6	15.4
	60	1	29	79	10.8	15.7
PEAA/P4VPh-co-2HEMA	60	5	31	77	18.0	26.2
	80	0	31	78	15.0	17.4
	80	1	32	81	22.1	25.6
	80	5	32	79	22.2	25.8
	60	0	32	82	10.7	15.9
PEAA/PVAc-co-VA	60	1	35	81	12.3	18.2
	60	5	36	81	14.2	21.1
	80	0	31	78	16.0	17.8
	80	1	32	80	18.0	20.0
	80	5	37	80	16.1	17.9
PEAA/PEOx	60	0	34	78	11.5	15.6
	60	1	39	80	14.2	19.3
	60	5	38	80	15.7	21.4
	80	0	26	76	18.4	21.5
	80	1	27	81	23.3	27.3
	80	5	28	78	20.3	23.8
	60	0	27	75	12.2	18.4
	60	1	32	76	15.1	22.8
	60	5	32	81	13.2	19.9

$$X_c = \frac{\Delta H_m \phi_{PEAA}}{\Delta H_{m,0}} \quad (2)$$

where ΔH_m is the DSC measured fusion enthalpy of blend (J/g), ϕ_{PEAA} is the PEAA volume fraction in the blend determined using the density values of the polymers included in the different polymer blends and provided by the manufacturer ($\rho_{PEAA} = 0.96$ g/cm³, $\rho_{PEOx} = 1.14$ g/cm³, $\rho_{P4VPh-co-2HEMA} = 1.20$ g/cm³, $\rho_{PVP-co-VAc} = 1.27$ g/cm³, and $\rho_{PVAc-co-VA} = 1.01$ g/cm³), and $\Delta H_{m,0}$ is the heat of fusion for completely crystallized PEAA, and taken as $\Delta H_{m,0} = 103.2$ J/g for pure PEAA.³¹ Despite the fact that the polymers comprising the matrix are different, it can be observed from this table for all composites that: (i) only one glass transition temperature was detected for each composite and it appears at higher temperatures compared to the corresponding for simple blends. This result suggests that the polymer matrix preserves the miscibility previously detected in the simple mixtures prepared under similar compositions (see Table II), and (ii) the melting temperatures, melting enthalpies, and degree of crystallinity, all increase as the CNTs content increase, compared to the ones observed for simple mixtures. These observations indicate that the amorphous phase became more rigid or constrained and that the tend-

ency to crystallize of the PEAA macromolecules (basically composed of polyethylene) in the composites, increased. On the other hand, more energy is needed to reach the melting state since the T_m value of all composites is higher than the T_m of simple polymer mixtures. Therefore, the differences observed in the T_m values are a direct consequence of the CNTs inclusion on the polymer matrix. Previous reports indicate that CNTs act as nucleation sites in a polymer matrix thus improving the amount of the crystalline phase.³²

Tables IV and V show Young's moduli of the composites prepared with a matrix of each type of polymer binary blends studied here. CNTs and CGr were used in this work as fillers for comparison purposes. It is observed from Table IV that Young's moduli of the composites containing 60% PEAA are very sensitive to the type of carbon filler used. Even though the polymer matrix used to prepare the composites is different, when the filler content is 1 wt % CNTs, we detected higher Young's moduli compared to the case when CGr is used as filler. In fact, the highest Young's moduli shown in Table IV correspond to composites with 1 wt % CNTs. These results indicate that the average size of filler particles plays a crucial role in improving the Young's module of the composite prepared. In general, an incre-

TABLE IV
Young's Moduli of Composites Prepared with a Polymer Blend of PEEA and PVP-co-VAc or P4VPh-co-2HEMA or PVAc-co-VA or PEOx. For All Binary Blends the PEEA Content is 60 wt %

Content of the filler in the composites (wt %)	Young's modulus (Pa)			
	PEAA/PVP-co-VAc	PEAA/P4VPh-co-2HEMA	PEAA/PVAc-co-VA	PEAA/PEOx
0	20544 ± 1951	17470 ± 1659	13785 ± 275	15964 ± 1516
1% CGr	23775 ± 1188	18115 ± 1720	15096 ± 1097	17506 ± 752
1% CNTs	29264 ± 2393	21444 ± 1170	22138 ± 1817	24386 ± 1782
5% CGr	23980 ± 2160	19069 ± 1735	15708 ± 314	18175 ± 370
5% CNTs	26329 ± 2501	18387 ± 367	16937 ± 924	19799 ± 395
10% CGr	21340 ± 2027	20475 ± 409	17182 ± 1685	17730 ± 567

ment of filler content does not produce higher Young's modulus. As it can be seen from Table IV, the Young's moduli decrease when CNTs content is 5 wt % and practically do not change for composites with 5 wt % CGr. On the other hand, when CGr content is 10 wt %, the Young's moduli increase for composites with P4VPh-co-2HEMA or PVAc-co-VA and decrease when the composites contain PVP-co-VAc or PEOx. These results have been attributed to the fact that at lower CNTs content the dispersion is favored while at higher CNTs content, the dispersion is inhibited, as reported elsewhere.³³ The poor CNTs dispersion is a direct consequence of the preparation method (without ultrasonication) of the CNTs-polymer nanocomposites employed in this work, since the initial dispersion has an impact on the CNTs dispersion in the polymer matrix. Based on these results, it seems reasonable to suppose the cluster formation of CNTs and CGr when their concentration increases, causing a more heterogeneous distribution in the polymer matrix and affecting in a negative way the mechanical response of the composites.³⁴ Although possible agglomeration of CNTs could take place, the fact that the polymer blend used as matrix of these nanocomposites be miscible, is an important result. Furthermore, in the case of all composites containing 80 wt % PEEA (Table V), the Young's moduli are lower than the ones corresponding to composites with 60 wt % PEEA (Tables IV

and V). These results were observed on composites either with or without any filler type and are a direct consequence of the increment of the rubber-like characteristic followed by the increase of PEEA in the composites. This change in the viscoelastic nature of the polymer matrix modifies the effect of filler addition. In general, the highest Young's moduli are detected when the CNTs content is 5 wt % while composites with 10 wt % CGr show higher Young's moduli compared to composites with 1 wt %. For this last series of composites, two factors contribute to their viscoelastic properties, in particular to their Young's moduli: (i) the positive influence of the filler which increases the stiffness of CNTs-polymer composites, and (ii) the rubber-like nature of PEEA. Pure PEEA is a semicrystalline polymer with a relatively low Young's modulus (2.4 ± 1.3 MPa) and its deformation strain at break point is $373.8 \pm 4.6\%$.²⁶ For a simple mixture of pure PEEA with anyone of the four amorphous polymers used in this work, the Young's modulus of the mixture is greater than pure PEEA (ca. 13 MPa; see Table V). This can be attributed to the mechanical contribution of anyone of the amorphous polymer included in the mixtures. In the case of the composite series, the mechanical resistance of filler apparently surpasses the rubber-like nature of PEEA since higher Young's moduli were detected for these materials with respect to the simple blend, even though the filler content increased.

TABLE V
Young's Moduli of Composites Prepared with Four Polymer Blends Containing 80 wt % PEEA

Content of the filler in the composites (wt %)	Young's modulus (Pa)			
	PEAA/PVP-co-VAc	PEAA/P4VPh-co-2HEMA	PEAA/PVAc-co-VA	PEAA/PEOx
0	13854 ± 845	12254 ± 925	12147 ± 768	14645 ± 726
1% CGr	16420 ± 1236	13051 ± 382	13331 ± 719	15532 ± 1028
1% CNTs	17343 ± 1208	15936 ± 339	16966 ± 1564	14136 ± 537
5% CGr	18057 ± 1184	14480 ± 422	15707 ± 314	14736 ± 445
5% CNTs	18747 ± 1199	14196 ± 634	17289 ± 779	16339 ± 326
10% CGr	17998 ± 970	15082 ± 301	14880 ± 669	15599 ± 910

CONCLUSIONS

CNTs were prepared via a chemical route of polyester oligomers synthesized by a chemical reaction between ethylene glycol and citric acid. The incorporation of CNTs to a polymer matrix formed by miscible blends does not modify the existence of positive hetero-contacts mainly responsible of miscibility of the polymer blends. In the case of the four binary mixtures containing PEAA studied here, we found experimental evidence of the existence of hydrogen bonding. This specific interaction was preserved in the composites polymer matrices containing up to 5 wt % CNTs. CNTs induce an increase of X_c of composites with respect to single polymer mixtures. Similarly, CNTs act as effective stiffener fillers because the Young's moduli of the composites are higher than Young's moduli of the composites containing graphite. It was demonstrated that the mechanical and thermal properties were enhanced while maintaining the original polymer blend miscibility.

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