

Mechanical and Rheological Studies on Polyethylene Terephthalate-Montmorillonite Nanocomposites

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In this work, a detailed investigation of the rheological and mechanical properties of nanocomposites based on polyethylene terephthalate (PET) and montmorillonite clays is presented. A series of additives [maleic anhydride (MAH), pentaerythritol (PENTA), and alkylammonium chlorides from amines of various chain lengths] were used as compatibilizers. The influence of the additives on the mechanical and rheological behavior of the PET matrix was evaluated separately, through their individual contributions. To shed more light on the reported decrease in melt viscosity of organoclay composites with respect to the matrix viscosity, observed in nylon and PET nanocomposites, the polymer molecular weight was related to the resulting rheological and mechanical properties of the systems. Results reveal that the PET nanocomposites behave quite differently in shear as opposed to elongation. The viscoelastic properties in shear present low values when the molecular weight decreases because of the processing operations. However, properties under tension increase over those of the matrix, manifesting the presence of a network formed between the clay and the polymer. *Polym. Eng. Sci.* 44:1094–1102, 2004. © 2004 Society of Plastics Engineers.

INTRODUCTION

Silicates like montmorillonite have been used as reinforcing materials for polymers owing to their high aspect ratio and unique intercalation/exfoliation characteristics. Nanocomposites of montmorillonite-polymer can be obtained by direct polymer melt intercalation where the polymer chains diffuse into the space between the clay galleries. This process can be carried out through a conventional melt-compounding process (1, 2).

The mechanical properties of the products are affected by the degree of exfoliation, which depends on both processing conditions and clay chemical treatment. Successful melt exfoliation requires the presence of strong interactions between clay and macromolecules, a stress field and an adequate residence time of the stress field. Once exfoliated, the clay platelets dispersed in the polymer matrix present high stiffness and strength.

Exfoliated and homogeneous dispersions of the silicate layers can be obtained straightforwardly when the polymer contains functional groups, for example, amide or imide groups (3, 4). This is because the silicate layers of the clay have polar hydroxyl groups, which are compatible with polymers containing polar functional groups.

Polyester-clay nanocomposites have been studied with regard to their crystallization properties (5). Non-isothermal crystallization dynamics show that the nanocomposites of PET have three times greater crystallization rates than that of pure PET. Modulus and HDT increase with clay concentration as much as threefold. The exfoliated clay particles play a nucleating role and have strong interactions with PET molecular chains. It is believed that the greater the interlamellar distance, the greater the interaction of PET with clay sheets. The increase of the apparent crystallinity with filler content also appears to result from the incidence of very rapid crystallization due to the nucleating effect of nanofillers. Normally, the apparent crystallinity increases with filler content and becomes asymptotic for more than 2% filler. Nanocomposites show many small and irregular spherulites.

Rheological studies of PET-nanocomposites are scarce, but show very interesting features. In the low-frequency range, the nanocomposites display a more

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elastic behavior than that of PET. It appears that there are some network structures formed because of filler interactions, collapsed by shear force, and after all the interactions have collapsed, the melt state becomes isotropic and homogeneous. Linear viscoelastic properties of polycaprolactone and nylon-6 (6) with montmorillonite display a pseudo solid-like behavior in the low-frequency part of the spectrum, consisting of power-law dependence of the moduli with frequency. If shear flow is applied before, the magnitude of the moduli decreases in the aligned sample, implying that the weak interactions are destroyed by the flow.

Solid-like response has also been observed in conventionally filled polymers in which there are strong interactions between the polymer and the filler attributed to the presence of yield phenomena in these systems. Large-amplitude oscillatory shear can significantly alter the linear viscoelastic response, inducing a mesoscopic arrangement of the silicate layers. Non-terminal low-frequency rheological behavior has also been observed in ordered block copolymers and smectic liquid crystalline small molecules (7, 8).

In highly interactive polymer-particle systems, solid-like yield phenomenon can be observed even at temperatures above the glass transition temperature of the polymer (9).

According to SANS and birefringence experiments by Schmidt *et al.* (10–12), the influence of shear on viscoelastic-polymer-clay solutions gives rise to an alignment of the platelets along the flow direction, and with increasing shear the polymer chains start to stretch. Polymer chains are in dynamic adsorption-desorption equilibrium with the clay particles to form a network. This network is highly elastic, since cessation of shear flow leads to fast recovery.

Another example of network formation is found in PEO-silica systems (13, 14). At relatively small particle concentrations, the elastic modulus increases at low frequencies, suggesting that stress relaxation of these hybrids is effectively arrested by the presence of silica nanoparticles.

A noteworthy finding has been that all the materials show two distinct relaxation dynamics, a fast and a slow relaxation (15). The fast mode corresponds to relaxation of bulk polymer molecules, while the slow mode is related to relaxation of the filler structure with much longer time scales. As silica particles are physically connected with adsorbed polymer molecules, the formed polymer-particle network is a temporary network. Another very interesting phenomenon deals with the decrease in shear viscosity with filler addition. The shapes of the viscosity curves are similar to pure PET, but the viscosity values are slightly lower than those of PET over the frequency range (16). The low viscosity of the nanocomposite implies good melt processability over a wide range of processing conditions such as extrusion and injection molding. However, it is not clear what mechanism causes the reduction of melt viscosity of the nanocomposite. Two possible mechanisms have been invoked to explain this effect. One is the slip between

polymer matrix and filler, and another is the degradation of the polymer matrix resulting from high shear heating during melt compounding. Supported by evidence of low friction coefficient of smooth nonporous platelets of fumed silica, the fumed silica acts as a lubricant. The other possibility, i.e., the reduced molecular weight resulting from degradation in the presence of clay, needs a more systematic analysis, which is one of the subjects of the present work.

The present work investigates the exfoliation process of PET-montmorillonite nanocomposites in the presence of additives, such as MAH and PENTA. The crystallinity level of the resulting systems and their mechanical and rheological properties are measured to elucidate the effect of the additives and clay on PET properties separately through their individual contributions. A systematic study examines the use of amines of various chain lengths as compatibilizers of the clay and the polymer matrix. Particular attention is focused on the change of shear viscosity with the increase in filler content. For this purpose, PET was given the same method of preparation and thermomechanical treatment as that given to the nanocomposites. That is, primarily, the samples were extruded and then they were mold-injected. Viscosity measurements were taken in extruded and in mold-injected samples. The resulting rheological and mechanical properties were analyzed and compared, taking into account the loss in molecular weight due to the thermomechanical degradation at each stage in the processing operations.

EXPERIMENTAL

Materials

PET from Kosa-Mexico had a density of 1.425 g/cm³ according to ASTM D792, a melting point of 249°C and 37% crystallinity. A glass transition temperature of 74°C was determined by differential scanning calorimetry (DSC) with a heating speed of 10°C/min under nitrogen atmosphere. An intrinsic viscosity of 0.85 dl/g was measured with an Ubbelohde viscometer. Clay-montmorillonite-Na⁺ from Nanocor was utilized as received. This clay had a CEC of 135 meq/100 g, an aspect ratio of about 300–500, a specific gravity of 2.6 and an average dry particle size of 16–22 microns (17). Qualitative chemical analysis by X-ray revealed 94.8% montmorillonite and 5.2% quartz. The amines (n-Decylamine, n-Dodecylamine, n-Tetradecylamine and n-Octadecylamine) from Aldrich were used as received. Maleic anhydride and pentaerythritol from Aldrich were used without any previous treatment. No additives to prevent PET oxidation were used.

Equipment

A Haake Rheocord 90 TW-100 twin-screw conical counter-rotating extruder of 331 mm length was used for blending. Samples were dried in a Pagani dehumidifier. The specimens for traction tests were produced in a Mannesman Demag Ergotech 50 injection molding machine with L/D = 20 at 100 rpm screw speed. An Instron

machine model 1125 was employed for the traction tests following the ASTM D638 norm. Micrographs for the morphology studies were taken in a Leica Stereoscan 440 transmission electron microscope. A Störung Janke & Kunkel A10 S2 high-velocity grinder was used for crumbling the chemically modified clays. A model 910 differential scanning calorimeter and a model 951 thermogravimetric analyzer from DuPont Instruments were used for thermal characterization at a heating speed of 10°C/min. Infrared determinations were made in a FTIR Nicolet 510P. Interlayer distance among the clay platelets was determined in a Bruker-AXSD8-Advanced X-ray Diffractometer with a wavelength of $\text{CuK}\alpha = 1.5418 \text{ \AA}$ at 35 KV and 30 mA with a scanning speed of $1^\circ 2\theta/\text{min}$. Samples for SEM were gold-coated in a fine-coat ion sputter, Jeol JFC-110. Rheological measurements were carried out in a TA-Instruments AR-1000-N controlled stress rheometer equipped with parallel plates of 25-mm diameter. Finally, molecular weights were determined by liquid chromatography (GPC) in a high-temperature chromatographer, Waters 150C, at 110°C using m-cresol.

PROCEDURE

MAH Intercalation in Montmorillonite Clay

To calculate the quantities of ingredients necessary for intercalation, the chemical equivalents of MAH (98 g) and clay (135 meq/100 g clay) were considered. Thus, 37.5 g of MAH were dissolved in anhydrous acetone and 300 g of clay were added under stirring. The mixture was heated under nitrogen atmosphere to evaporate the acetone. Finally, the intercalated clay-MAH was dried under vacuum.

PENTA Intercalation in Montmorillonite Clay

Three hundred grams (300 g) of montmorillonite- Na^+ clay were dispersed in 4 L of distilled water at 80°C under high-shear-stirring. Fifty-one grams (51 g) of PENTA were added to 0.5 L water, and then this solution was poured into the 4 L of the clay dispersion. The mixture was stirred for 1 h, filtered and then placed in containers where the water was evaporated at 60°C. As soon as the clay was dried, it was cooled with liquid nitrogen and then powderized in a solids grinder.

Cation Exchange Alkylammonium in Montmorillonite Clay

n-Dodecylamine (12.5 g) was added to one liter of distilled water at 80°C under stirring, and thereafter a stoichiometric amount of hydrochloric acid was added to form the soluble alkylammonium chlorhydrate. In another beaker 50 g of clay were added to 6 liters of hot water, and subsequently the alkylammonium chlorhydrate was added to the clay-water suspension. The hydrophobic montmorillonite was then recovered from the suspension surface to be washed with plenty of hot water and dried at 40°C under vacuum. The resulting clay was ground, and this process was repeated for

each clay sample. According to their chemical equivalent, every 50 g of clay requires 10.5 g of n-Decylamine, 14.4 g of n-Tetradecylamine and 18.2 g of n-Octadecylamine.

RESULTS AND DISCUSSION

Procedure to Obtain the PET-Clay-Additives Nanocomposites

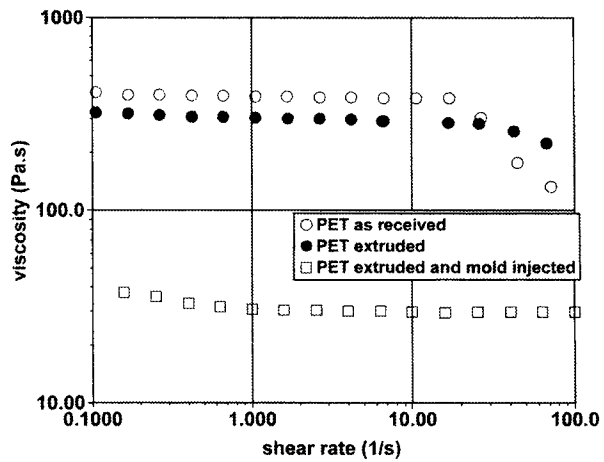
The previously dried ingredients (PET, clays and additives) were mixed in a twin-screw conical counter-rotating extruder under several rotational speeds, to obtain composites under variable shear stress levels. The processing conditions and structure of the additives strongly influence the dispersion of clays in the polymer matrix. Thereafter, the materials were ground and mold-injected to obtain samples for the rheological and tension tests. Some of the samples were powdered in a high-speed grinder. Characterization by X-rays determined the interlayer distance d_{001} between the clay galleries on the powder samples. Results of this characterization are shown in Table 1. The interlayer gap varies according to the type of amine chain lengths and additives used. The largest separation was obtained using n-Octadecylammonium. It is clear that the interlayer distance is not a linear function of the size of the aliphatic chain of the amine.

PET

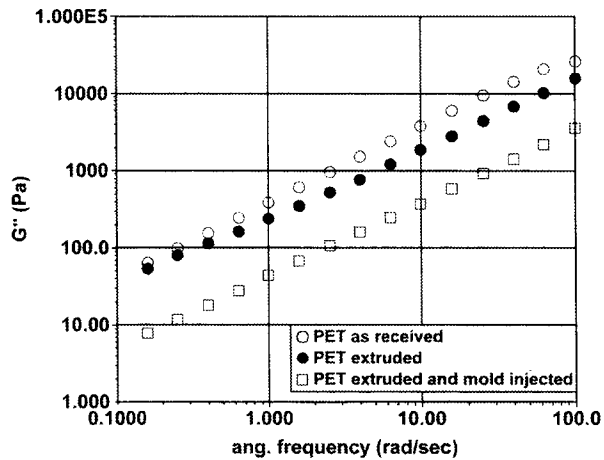
PET samples were subjected to the same thermomechanical history. Extrusion was carried out at 50 rpm. Subsequently the material was ground, and thereafter it was mold-injected at a mold temperature of 7°C. Results of the effect of PET processing stages on the rheological properties (linear viscoelastic modulus and shear viscosity) are shown in Figs. 1a, 1b and 1c. The shear viscosity of PET as received (pellets), PET extruded once, and PET extruded and mold-injected is shown, respectively, as a function of the shear rate in Fig. 1a. While the decrease in the viscosity due to extrusion is relatively small (from 400 to 300 Pa.s), the large drop observed in molded samples is quite drastic (from 300 to 30–40 Pa.s). This extremely large decrease in the shear viscosity in the molded samples is also accompanied with a strong decrease in the viscous modulus of almost a decade, as observed in Fig. 1b. The extruded samples show no substantial change in the elastic modulus, as seen in Fig. 1c. However, once

Table 1. Effect of the Intercalant on Clay Interlayer Distance.

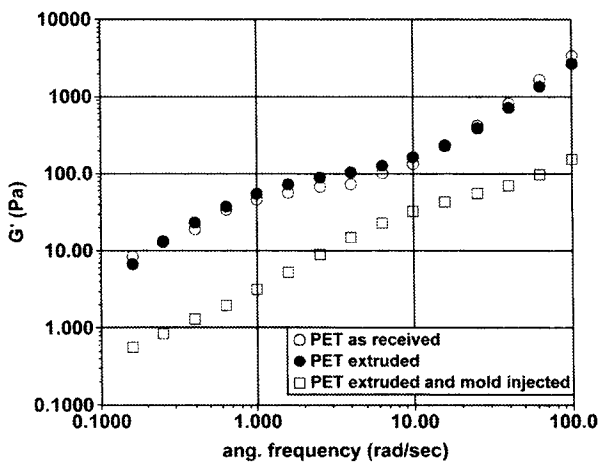
Clay-intercalants	d_{001} (Å)
Montmorillonite	12.4
Montmorillonite-PENTA	14.5
Montmorillonite-MAH	12.4
Montmorillonite-n-Decylammonium	17.1
Montmorillonite-n-Dodecylammonium	17.8
Montmorillonite-n-Tetradecylammonium	17.6
Montmorillonite-n-Octadecylammonium	23.0



(a)



(b)



(c)

Fig. 1. Shear viscosity as a function of the shear rate (a), loss modulus as a function of frequency (b), and storage modulus as a function of frequency (c), for three samples: PET as received (pellets), extruded PET and extruded and molded PET.

again, a drastic change in the elastic modulus throughout the frequency range is observed in the molded samples. The strong decrease in the viscoelastic properties (linear and nonlinear) due to extrusion and molding is accompanied by a large drop in the molecular weight, as shown in Table 2. In fact, in the molded samples (sample 1c) the decrease in molecular weight (\bar{M}_w) is almost half the value of the original PET (without processing, sample 1a). As observed, the decrease in molecular weight or degradation due to the processing stages scale with the diminution in the magnitude of the viscoelastic properties.

PET-Clay System

Nanocomposites of PET have three times greater crystallization rates than those of pure PET. The increase of crystallinity with particle content results from rapid crystallization due to the nucleating effect of the fillers (18). The increase in crystalline content produces larger moduli but lower mechanical properties for larger clay contents. In Table 3, the modulus is shown to increase 45% with clay content of 3%, but simultaneously, the strain at break diminishes drastically, and there is an optimum concentration of clay where a maximum in the tension strength occurs (1%) followed by a decrease for larger clay concentrations. X-ray analysis shows no apparent signal in the low angle region $2\theta < 8^\circ$, corresponding to the interlayer distance d_{001} , which indicates that exfoliation occurs.

It is interesting to observe the effect of particles on the crystallinity of compounds. With only 1% clay, crystallinity of the PET matrix increases more than twofold, which is reflected in the change of the strain at break. At 2% clay concentration, a maximum in the percentage of crystallinity is attained and the minimum in the strain at break is observed. This clay concentration is close to the percolation threshold where a mesoscopic structure is formed, inducing high crystallinity (19). For larger clay contents, the threshold is surpassed and the crystallinity decreases, but the reinforcing effect of the crystals leads to larger moduli.

Table 2. Weight-Average Molecular Weight Determinations by GPC.

Sample		\bar{M}_w
1a	PET as received	233,900
1b	PET extruded	216,000
1c	PET extruded and mold-injected	166,300
2	PET + 1% clay	182,000
3	PET + 2% clay	193,400
4	PET + 3% clay	169,100
5	PET + 1% clay-PENTA	103,600
6	PET + 1% clay-MAH	164,000
7	PET + 2% clay-MAH	162,500
8	PET + 1% (2/3 clay-MAH + 1/3 clay-PENTA)	162,600
9	PET + 2% (2/3 clay-MAH + 1/3 clay-PENTA)	122,800
10	PET + 1% clay-n-Dodecylammonium	164,100
11	PET + 2% clay-n-Dodecylammonium	113,000

Table 3. Tensile Mechanical Properties of PET-Clay Nanocomposites.

Samples	Tension Strength MPa	Strain at Break %	Young's Modulus MPa	Crystallinity %	d_{001} Å
PET extruded	47	150	1091	37	
PET + 1% clay	62	36	1379	86	Exfoliated
PET + 2% clay	41	3	1443	93	Exfoliated
PET + 3% clay	32	5	1614	78	Exfoliated
PET + 1% clay-MAH	43	4	1287	—	Exfoliated
PET + 2% clay-MAH	37	3	1441	—	Exfoliated
PET + 3% clay-MAH	25	2	1540	—	Exfoliated
PET + 1% clay-PENTA	59	119	1246	—	Exfoliated
PET + 2% clay-PENTA	32	3	1373	—	Exfoliated
PET + 3% clay-PENTA	24	2	1586	—	Exfoliated
PET + 1% (clay-MAH, PENTA)	61	259	1335	—	Exfoliated
PET + 2% (clay-MAH, PENTA)	62	365	1299	—	Exfoliated

A very interesting result is shown in Fig. 2a, where the shear viscosity of PET and PET-clay systems is displayed. The shape of the curves is similar to that of PET, but the viscosity decreases with respect to the extruded PET with increasing clay content. The Newtonian plateau extends to higher shear rates as the clay concentration increases, i.e., the onset for shear thinning is shifted to higher shear rates as the clay content augments. The decrease in the shear viscosity due to mold injection is not as drastic as in the pure PET sample, from 400 Pa.s for PET down to 65 Pa.s for PET + 3% clay (sample 4). This decrease is larger than those observed in the nylon 6-clay systems studied by Cho *et al.* (20) and the PET-fumed silica treated by Chung *et al.* (16), although it is not clear if these authors compare the systems' viscosities with that of PET having the same thermomechanical history. Slip between the polymer and filler due to low friction coefficient of the smooth platelets has been invoked to explain this phenomenon, as well as polymer degradation due to high shear heating during the melt-compounding process.

Table 2 displays the loss in molecular weight for samples 2, 3 and 4, with varying clay content. The sample with 3% clay content exhibits approximately the same M_w as molded PET, and this is reflected in the same value in the loss modulus throughout the frequency range, as shown in Fig. 2b. However, this contrasts with the trend in G' shown in Fig. 2c, where the 3% clay-PET system has much higher values in the low-frequency range than those of molded PET, comparable to those of extruded PET. These data reveal that the structure induced by the presence of the clay platelets is independent of the molecular weight and promotes the formation of a network with the polymer chains.

PET With Intercalated Clay and Additives

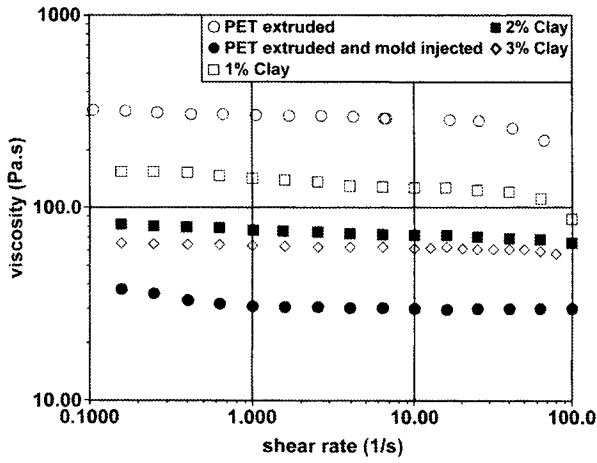
Clays were treated with MAH and PENTA (following the procedures in the **Experimental** section) to obtain intercalated samples (clay-MAH and clay-PENTA) where the additive molecules are placed in the clay galleries. These treated clays were then mixed with PET in the extruder. Table 3 shows the mechanical properties

of the resulting nanocomposites for various clay contents. The modulus increases with clay content, but the tension strength diminishes with increasing clay concentration. The strain at break diminishes drastically with respect to that of PET, except in sample 5, which presents an unusually high value. These results reflect the behavior of fragile materials with generally small strain at break values, when the clay content is more than 1%. A comparison of the results reveals that the additives have a detrimental effect on the mechanical properties of the nanocomposites.

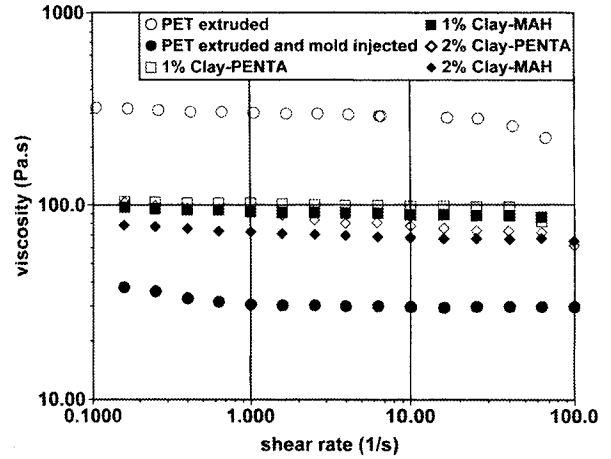
Figure 3a shows the shear viscosity of various PET nanocomposites with additives MAH and PENTA. Two clay contents with either MAH or PENTA are considered. The flow behavior of these nanocomposites is similar to that observed in the unmodified clay with PET shown in the previous figures, which means that the dominant effect on the viscosity of the nanocomposite is that of the clay. An interesting observation is the behavior observed in the 2% clay sample, where the viscosity is constant and the Newtonian region extends to 100 s^{-1} . The storage modulus (Fig. 3b) shows increases over the molded PET sample in the low-frequency region and also in the high-frequency region, especially in the 1% clay samples. In Fig. 3c the loss tangent is plotted versus angular frequency. The relative low magnitudes in the low-frequency region of the nanocomposites manifest the presence of a weak elastic network. The molecular weights of samples 5–7 shown in Table 2 reveal values similar to that of the molded PET sample, which implies that the increase in the viscoelastic properties above those of the molded PET values is due entirely to the effect of clay and additives together on the PET matrix, independently of the molecular weight.

PET-Treated Clay Systems

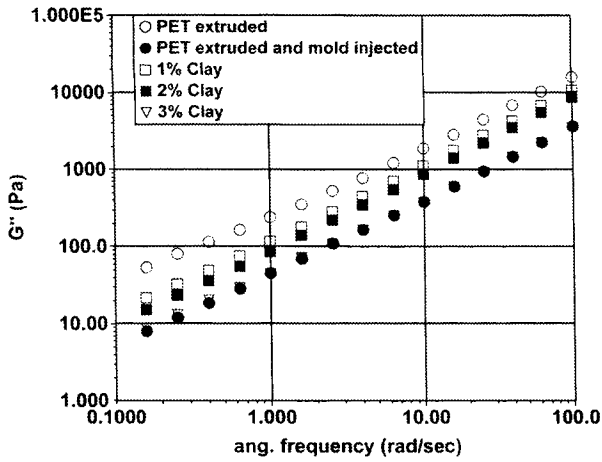
In this study, nanocomposites of PET with a combination of clays treated with either MAH and PENTA are analyzed. First, clay-MAH and clay-PENTA were mixed in a 3/1 proportion. Thereafter, this mixture was fed with PET in the extruder and afterwards they were mold-injected. The results of the mechanical properties



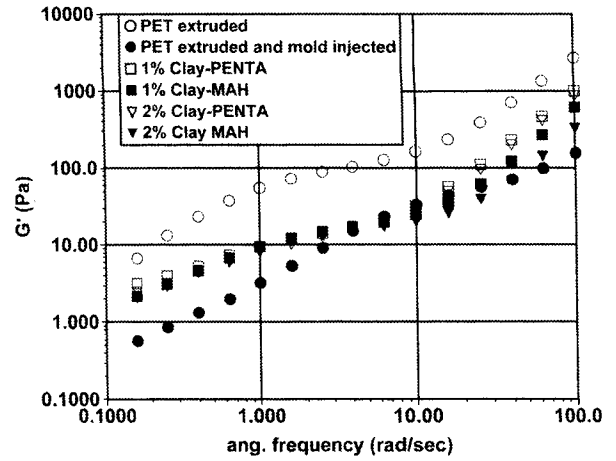
(a)



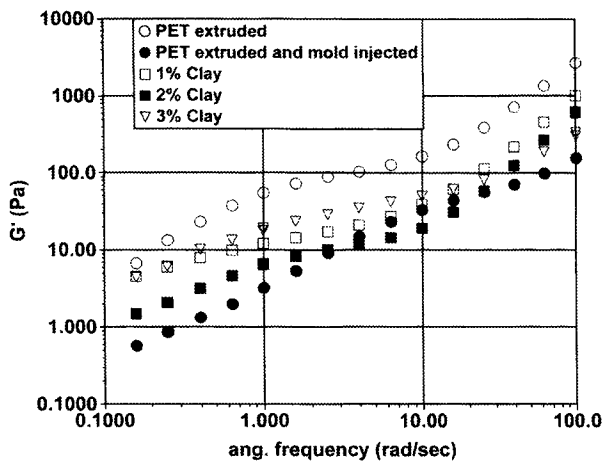
(a)



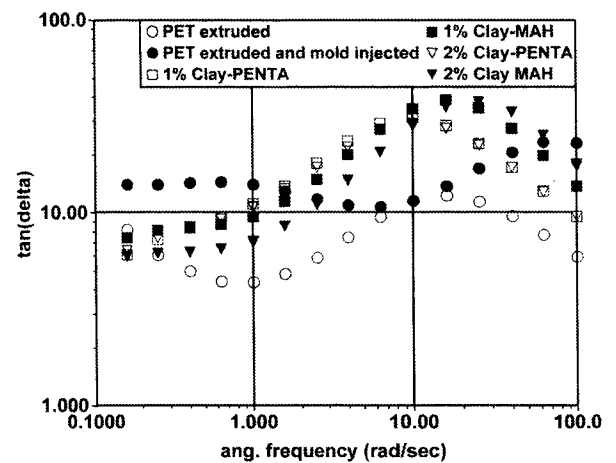
(b)



(b)



(c)



(c)

Fig. 2. Shear viscosity as a function of shear rate (a), loss modulus as a function of frequency (b), and storage modulus as a function of frequency (c). PET-clay systems for various clay concentrations. Data of PET extruded and PET extruded and molded are shown for comparison.

Fig. 3. Shear viscosity as a function of shear rate (a), storage modulus as a function of frequency (b), and loss tangent as a function of frequency (c). PET-clay systems (two clay concentrations). The clays were treated with MAH and PENTA previously to mixing with PET.

are also shown in *Table 3*. Tension strength increases with clay content and the Young's modulus has a maximum at 1% clay content. Improvements of 18% and 30% with clay addition are achieved, respectively. The most impressive result is the increase of 140% observed in the strain at break. The combination of clays treated with different additives produces a synergistic effect on the ductile behavior, since the systems PET-clay (MAH) and PET-clay (PENTA) separately with 2% clay content have low values of strain at break. The viscoelastic properties reveal that for these systems the flow behavior is very similar to that of the molded PET sample 1c, and for this reason they are not shown. Also, the molecular weights displayed in *Table 2* for samples 8 and 9 are similar to or lower than those of sample 1c, corresponding to the molded PET sample. These results highlight the fact that the behavior in shear is very different from that under tension and unambiguously show that the increases in the mechanical properties are due to the presence of an elastic network independent of the molecular weight.

Amines and Intercalated Alkylammoniums in PET-Clay Nanocomposites

In this study we have considered alkylammonium cations from amines of different aliphatic chain lengths, which can interact strongly with the oxygen groups of the clay. The intercalated clays can make numerous contacts with the polymer matrix if the aliphatic part of the alkylammonium and the polymer are compatible. Also, the acid hydrogen of the end-hydroxyl groups of the PET molecule are likely to strongly interact with clay surface, promoting the diffusion of the polymer into the clay galleries, and finally leading to exfoliation of the clay. PET nanocomposites with intercalated alkylammonium cations present the mechanical properties shown in *Table 4*. One exfoliated sample, that with 1% clay and n-Dodecylammonium (sample 10), presents the largest tension strength and strain at break values.

In micrographs 4a, 4b and 4c, the deformed regions of samples tested under tension are illustrated. In 4a, PET morphology presents the typical ductile fracture with voids that reflect large energy absorption. In 4b, corresponding to the sample 10 in *Table 2* (exfoliated),

we observe ductile fracture with multilayer formation, where matrix yielding is present. When the clay content is increased to 2% as shown in 4c (sample 11, with no exfoliation) morphology is not regular and fracture occurs in various and different planes. In this case the fracture is fragile and sample deformation is very small (6.7%).

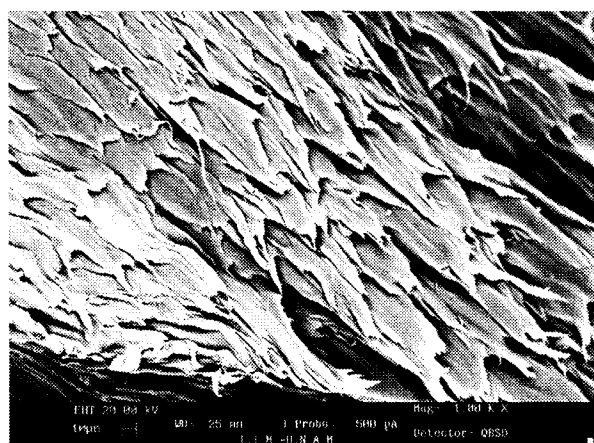
The rheological properties of the 1% and 2%-clay (n-Dodecylammonium) systems are presented in *Figs. 5a* and *5b*. Here, a good correlation is observed between the magnitude of the viscoelastic functions and the molecular weight. In fact, the molecular weight of sample 10 (see *Table 2*) is similar to that of sample 1c corresponding to molded PET. As a result, the shear viscosity in *Fig. 5a* of both systems is very similar, and displays a near-Newtonian behavior up to shear rates around 100 s^{-1} . This behavior contrasts with that of the 2% clay sample, where shear thinning is present in the range of shear rates of the experiments, in accordance with the low value of the molecular weight reported in *Table 2*. The same trend is displayed in G'' and G' , and *Fig. 5b* shows the behavior of the elastic modulus. Although sample 11 has one of the lowest molecular weights (lower than molded PET), G' in this sample is larger than that of molded PET. These results show the different behaviors of exfoliated clays as compared to the non-exfoliated samples. In this study, it is shown that mechanical properties are improved only in exfoliated systems.

CONCLUDING REMARKS

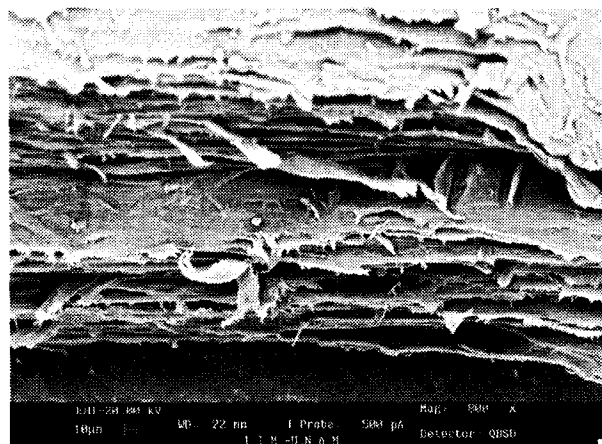
A detailed experimental investigation of the rheological and mechanical properties of PET-montmorillonite nanocomposites has been given attention in this work. Thermomechanical degradation was monitored in most of the samples by molecular weight measurements, and comparisons among the various systems were carried out, taking into account those with the same thermomechanical history. Results reveal that mechanical properties (tension strength, Young's modulus and strain at break) are improved when a combination of clays treated with MAH with those treated with PENTA are considered. A decrease in the viscoelastic properties (shear viscosity, storage and loss modulus) is observed if we relate the magnitudes of the viscoelastic functions

Table 4. Effect of Intercalated Alkylammonium Clays on Tensile Properties of PET and Clay Interlayer Distance in the Nanocomposite.

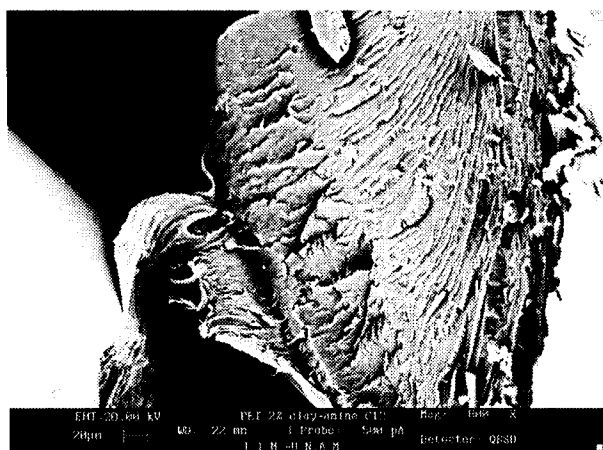
Samples	Tension Strength MPa	Strain at Break %	Young's Modulus MPa	d_{001} Å
PET extruded	47	150	1091	
PET + 1% clay-n-Decacylammonium	64	99	1336	Exfoliated
PET + 1% clay-n-Dodecylammonium	64	292	1319	Exfoliated
PET + 1% clay-n-Tetradecylammonium	46	6	1392	34.0
PET + 1% clay-n-Octadecylammonium	59	57	1376	33.8
PET + 2% clay-n-Decacylammonium	36	3	1466	23.1
PET + 2% clay-n-Dodecylammonium	7	7	1375	22.2
PET + 2% clay-n-Tetradecylammonium	57	10	1344	31.5
PET + 2% clay-n-Octadecylammonium	54	24	1423	32.5



(a)

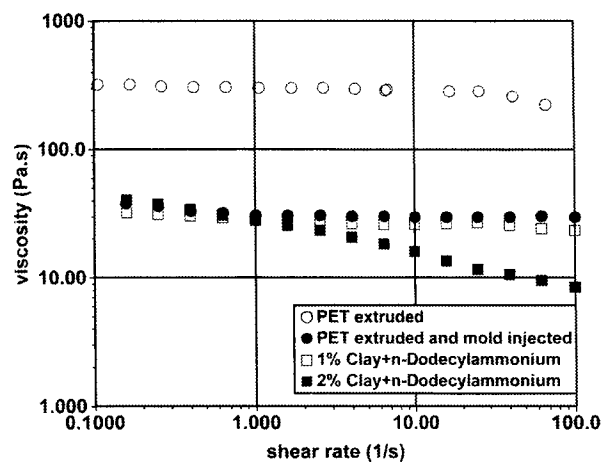


(b)

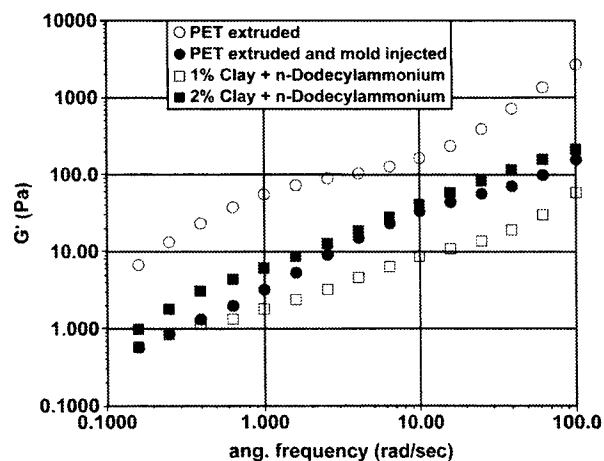


(c)

Fig. 4. Micrographs showing the center strained region of the sample in tensile specimens. (a) PET, (b) PET + 1% clay treated with n-Dodecylammonium, sample 10, (c) PET + 2% clay treated with n-Dodecylammonium, sample 11.



(a)



(b)

Fig. 5. Shear viscosity as a function of shear rate (a) and storage modulus as a function of frequency (b). Samples treated with n-Dodecylammonium for varying clay concentration. Data of PET extruded and PET extruded and molded are shown for comparison.

to the values of the PET extruded sample. On the contrary, if the magnitude of the viscoelastic functions is related to those values of the PET extruded and mold-injected samples (i.e., possessing the same thermorheological history), an increase is observed. A very interesting aspect of these results is, on one hand, that the increases in the viscoelastic properties above the values of the PET molded sample are entirely due to the presence of the clays and additives, although they share the same molecular weight (see, for example, in Table 2, \bar{M}_w values of samples 1c, 4, 6, 7 and 8). The remarkable increases in the elastic modulus at low frequency with such low values of the molecular weight reflects the fact that an elastic network is formed because of the presence of the clays, as independence from molecular weight indicates. On the other hand, another

remarkable result is that the largest increases in the mechanical properties are observed in some samples (8 and 9, Table 2) where the viscoelastic properties are the smaller in magnitude and have some of the lowest molecular weights. It seems that the nanocomposites behave drastically different under tension as opposed to shear. This is advantageous with regard to molding operations, where the viscosity is low and the mold fills conveniently. For example, the observed decrease in the shear viscosity with the addition of MAH and PENTA leads to lower pressure in the filling of the mold in the mold-injection operation. In fact, the injection pressure diminishes from 5900 psi for PET to 3600 psi in the system PET-clay-MAH (1 wt%) and to 2000 psi in the system PET-clay-PENTA under the same processing conditions. This corresponds to a threefold decrease in the viscosity, as verified in data shown in Fig. 3a. However, it is necessary to point out that the viscosity curves reported consider simple shear rheometric flows. In the actual process operation, the fluid that fills the mold is subjected to a non-homogeneous stress field, which is likely to develop slip at the walls and another complicated flow behavior (21). In these circumstances, the *in-situ* viscosity is probably lower than that measured in the rotational rheometer. Measurements of pressure drop versus flow rate made on the fluid that enters the mold would surely provide a more reliable value of the "process viscosity," and hence a better evaluation of the effect of the nanoparticles on the flow behavior of PET. This aspect is currently under investigation in this laboratory.

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