Properties of poly(ethylene terephthalate)–poly(ethylene naphthalene 2,6-dicarboxylate) blends with montmorillonite clay

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Abstract: The production and properties of blends of poly(ethylene terephthalate) (PET) and poly(ethylene naphthalene 2,6-dicarboxylate) (PEN) with three modified clays are reported. Octadecylammonium chloride and maleic anhydride (MAH) are used to modify the surface of the montmorillonite–Na⁺ clay particles (clay–Na⁺) to produce clay–C18 and clay–MAH, respectively, before they are mixed with the PET/PEN system. The transesterification degree, hydrophobicity and the effect of the clays on the mechanical, rheological and thermal properties are analysed. The PET–PEN/clay–C18 system does not show any improvements in the mechanical properties, which is attributed to poor exfoliation. On the other hand, in the PET–PEN/clay–MAH blends, the modified clay restricts crystallization of the matrix, as evidenced in the low value of the crystallization enthalpy. The process-induced PET–PEN transesterification reaction is affected by the clay particles. Clay–C18 induces the largest proportion of naphthalate–ethylene–terephthalate (NET) blocks, as opposed to clay–Na⁺ which renders the lowest proportion. The clay readily incorporates in the bulk polymer, but receding contact-angle measurements reveal a small influence of the particles on the surface properties of the sample. The clay–Na⁺ blend shows a predominant solid-like behaviour, as evidenced by the magnitude of the storage modulus in the low-frequency range, which reflects a high entanglement density and a substantial degree of polymer–particle interactions.
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INTRODUCTION

The blending of clays of nanometer-size and polymers leads to materials with modified rheology and improved mechanical, gas barrier and fire-resistant properties.[1–4] Materials with adequate performance require that the polymer be intercalated in the clay galleries to promote exfoliation and high dispersion of the particles in the polymer. To this aim, a degree of compatibility between the polymer matrix and the clay is necessary. Particle–polymer compatibility is usually induced by chemical modification of the particle surface.

When these modified particles are mixed with crystallizable polymers such as polyesters, some processing problems arise because the polymer crystallization process is modified by nucleation effects induced by the nanoparticles. Moreover, the particles also influence the kinetics of the transesterification reaction between PET and PEN, besides other factors

such as the reaction time and extruder processing temperature; the latter has been reported elsewhere for a single proportion of PEN–clay.[5–10] In the present work, a quaternary alkylammonium compound and maleic anhydride were used to modify the surface properties of sodium montmorillonite clay particles. After this process, the particles were mixed with poly(ethylene terephthalate) (PET) and poly(ethylene naphthalene 2,6-dicarboxylate) (PEN) to produce blends whose properties were examined in detail.

EXPERIMENTAL
Materials
PET (Eastpack 9921, from Eastman Chemical, USA) had a density of $1.40 \, \text{g cm}^{-3}$, a melting point of $262 \, °\text{C}$, a glass transition temperature (T_g) of $61.2 \, °\text{C}$ and a weight-average molecular weight of $29\,700 \, \text{g mol}^{-1}$, with a polydispersity of 4.9. PEN (Kalidar X-70, from

DuPont, Ontario, Canada) had a melting point of 258 °C, a T_g of 112 °C and a weight-average molecular weight of 108 700 g mol^{-1}, with a polydispersity of 3.6. Sodium montmorillonite clay nanoparticles (PGN, from Nanocor, Inc., Arlington Heights, IL, USA), with a cation-exchange capacity of 135 meq (100 g)$^{-1}$, were employed. Maleic anhydride (MAH) and *n*-octadecylamine (from Aldrich, Milwaukee, WI, USA) were used as received. No additives to prevent oxidation were used on compounding.

Equipment

Blends were prepared in a Leistritz LSM34 corotating twin-screw extruder (Leistritz, Nuremberg, Germany). The latter was equipped with a volumetric feeder working under a nitrogen atmosphere to prevent moisture absorption and consequent hydrolysis or chemical degradation of the polyesters. Moisture determinations were carried out on an Omnimark Mark 2 moisture analyser (Omnimark, AZ, USA). Rheological properties were measured on a TA Instruments AR 1000-N controlled stress rheometer with parallel plates of 25 mm diameter (TA, New Castle, DE, USA). ^{1}H NMR spectroscopic determinations were performed on a Bruker Avance 400 spectrometer (Bruker AG, Czech Republic), using a solution of deuterated chloroform and trifluoroacetic acid (60:40 v/v) as the solvent system for the PET–PEN blends. Determination of the mechanical properties was made on an Instron 1125 machine (Instron, Norwood, MA, USA), at a strain rate of 50 mm min^{-1}. Dynamic contact angle measurements were carried out by the Wilhelmy method, using a Sigma 70 balance (KSV Instruments Ltd., Finland). A Bruker AXS X-ray diffractometer (Advance 8 model from Siemens, Karlrue, Germany) was used to determine intergap and clay exfoliation. Thermal properties were determined on a DuPont 910 differential scanning calorimeter (DuPont, Wilmington, DE, USA), at a heating rate of 10 °C min^{-1}.

Procedures

Three clay types were used in the blends, namely sodium montmorillonite clay (clay–Na$^+$), maleic anhydride-modified clay (clay–MAH) and alkylammonium-modified clay with *n*-octadecylamine as precursor (clay–C18).

Clay–MAH

MAH (37.2 g) was dissolved in 300 mL of anhydrous acetone, after which sodium montmorillonite (300 g) was added to the boiling solution and the mixture then left for 10 min under stirring. Thereafter, the clay in suspension was decanted and dried.

Clay–C18

Sodium montmorillonite (100 g) was mixed with 6 L of water at 80 °C. In another container, 36.3 g of *n*-octadecylamine and 135 meq of concentrated hydrochloric acid were mixed with 2 L of water at 80 °C to produce the alkylammonium chlorhydrate. The latter solution was then poured into the clay solution and the system then stirred vigorously for 30 min. The resulting montmorillonite compound was washed with hot distilled water and the absence of any chlorides verified by the use of a 1 % solution of silver nitrate. The modified clay was finally dried and ground to obtain 37 µm-size particles.

Preparation of the polymer nanocomposites with 90, 9 and 1 wt% PET, PEN and clay contents, respectively, was carried out in an intermeshing corotating twin-screw extruder at 50 rpm (2 min residence time) under nitrogen to avoid degradation by oxidation and hydrolysis. The processing temperature was kept at 280 °C. The extruded material was received in a water bath at 15 °C and then pelletized.

The mechanical properties of cylindrical specimens (2 mm diameter and 30 mm length), produced in a Maxwell micro-extruder with further cooling at ambient temperature, were measured on an Instron machine at a rate of 50 mm min^{-1}.

RESULTS AND DISCUSSION

Mechanical tensile properties

In the blends prepared with clays, a reduction in the tension strength and elastic modulus with respect to the values of PET and PEN was observed, whereas the strain at break increases (with respect to the value of PEN). The lowest tensile strength and strain at break values were observed in the blend with clay–C18 (Table 1). The PET–PEN/clay–C18 system is not exfoliated and the blend is more fragile, hence confirming the lower compatibility of the ingredients of this blend when compared to those of the exfoliated clays.

Thermal properties

Samples for these tests were produced in the twin-screw extruder. Similar values for the glass transition temperature (T_g), crystallization temperature (T_c) and melting temperature (T_m) were measured for the three blends (Table 2). The crystallization and melting enthalpies are similar for PET–PEN/clay–Na$^+$ and PET–PEN/clay–C18, although differences are observed in the clay–MAH blend. This blend has

Table 1. Mechanical tensile properties of PET–PEN/clay blends and neat polymers

Sample	Tensile strength (MPa)	Elastic modulus (MPa)	Strain at break (%)	X-ray data
PET	51	1447	917	—
PEN	70	1752	356	—
PET–PEN	50	1296	525	—
PET–PEN/clay–Na$^+$	42	1369	663	Exfoliated
PET–PEN/clay–MAH	46	1383	756	Exfoliated
PET–PEN/clay–C18	38	1571	19	33.24 (Å)

substantially lower enthalpies of crystallization and melting than those of the other systems. The melting enthalpy for this blend is even lower than those of PET and PEN. These results indicate that crystallization is largely restricted and proceeds in a very slow manner, which leads to a large proportion of the amorphous phase with high transparency.

Transesterification reaction

The transesterification (NET) reaction between PET and PEN is mostly affected by temperature and residence time in the extruder. In this experiment, these two variables were maintained constant in order to elucidate, straightforwardly, the effect of the various ingredients on the blend properties. In Table 3, the proportion of the terephthalate (TET), naphthalate (NEN) and terephthalate–naphthalate (NET) groups, measured by ^{1}H NMR spectroscopy on the copolymer samples (product of the reaction), are shown for each blend. It is known[11–13] that increasing the transesterification degree leads to a larger proportion of random sequences, thereby reducing blend performance. The PET–PEN/clay–C18 blend has the larger proportion of NET groups and a more random microstructure which leads to poor mechanical properties (Table 1).

Contact angles

Films (1 cm wide and 2 cm long) were prepared by using a high-temperature press with previously

extruded samples. All samples had a similar surface roughness. The advancing contact angles, shown in Table 4, indicate a similar hydrophobic character of the samples to that found in PET and PEN, and therefore the particles do not influence the 'global' surface properties of the blends. However, the receding contact angle and hysteresis properties present useful information. In the clay–Na$^+$ and clay–MAH blends, a hysteresis of 13.7 and 14.3°, respectively, was observed. This indicates that the test liquid (triply distilled and deionized water at 24 °C) is adsorbed on the clay–Na$^+$ and clay–MAH samples in a minor proportion when compared to that on the neat polymers,[14,15] thus implying that the surfaces of these samples are highly hydrophobic. This is an expected result for the clay–MAH blend, but not for the clay–Na$^+$ blend, which is supposed to be hydrophilic, and its departure from the behaviour of the neat polymers, due to the presence of particles in the blend, are expected in both of the advancing and receding angles. However, the blend behaves as a hydrophobic system, like the precursor polymers, as measurements of the large receding angle indicate. This is an interesting result which itself deserves further investigation. In this regard, it is possible that at the surface of the sample the particle concentration decreases with respect to that in the bulk, and hence the surface properties of the sample are dominated by the polymer surface properties

Rheological properties

As reported elsewhere,[1,2] a decrease in the shear viscosity upon clay addition is expected in the polymer–clay blends, due to the adsorption of high-molecular-weight fractions on the clay surface and the lubrication–flow effects brought about along the particle–polymers interface. The clay–Na$^+$ blend presents a slightly larger zero-shear viscosity than the other blends, but the onset for shear-thinning is similar to that of the precursor polymers (Fig. 1). The linear viscoelastic properties are shown in Fig. 2, i.e. the variation of the storage modulus with frequency. It is very interesting that the clay–Na$^+$ blend exhibits larger comparative values of the modulus in the low-frequency region of the spectrum. This indicates a more accentuated solid-like behaviour than those shown by the other systems. Such behaviour can be ascribed to larger particle–polymer interactions, which lead to a larger number of molecular entanglements in the blend.
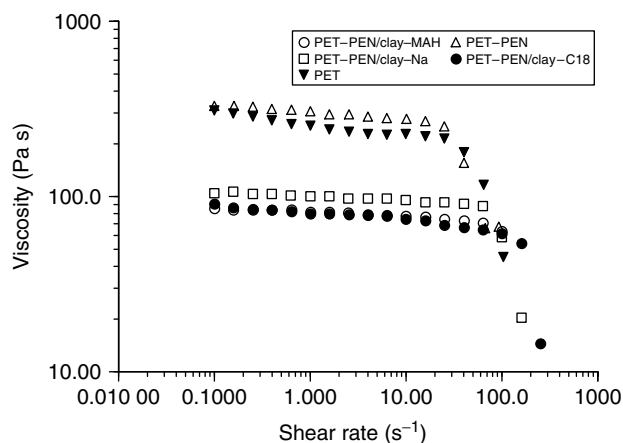
Table 2. Thermal properties of PET–PEN/clay blends and neat polymers

Sample	T_g (°C)	T_c (°C)	ΔH_c (J g^{-1})	T_m (°C)	ΔH_m (J g^{-1})
PET	71	—	—	242	40
PEN	116	—	—	258	36
PET–PEN	75	161	18	244	18
PET–PEN/clay–Na$^+$	75	138	198	248	228
PET–PEN/clay–MAH	71	139	21	248	27
PET–PEN/clay–C18	75	143	185	247	216

Table 3. Transesterification extent (%) in PET–PEN/clay blends

Sample	TET	NET	NEN
PET–PEN	93.3	2.4	4.3
PET–PEN/clay–Na$^+$	93.3	0.1	6.6
PET–PEN/clay–MAH	93.5	0.7	5.8
PET–PEN/clay–C18	92.5	2.2	5.3

Table 4. Contact angles of PET–PEN/clay blends and neat polymers

Sample	Advancing contact angle (degrees)	Receding contact angle (degrees)	Film Thickness (mm)	Hysteresis (degrees)
PET	93.2	68.8	0.11	24.4
PEN	91.7	69.0	0.26	22.7
PET–PEN/clay–Na$^+$	93.8	80.1	0.07	13.7
PET–PEN/clay–MAH	91.4	77.1	0.08	14.3
PET–PEN/clay–C18	91.9	68.7	0.08	23.2

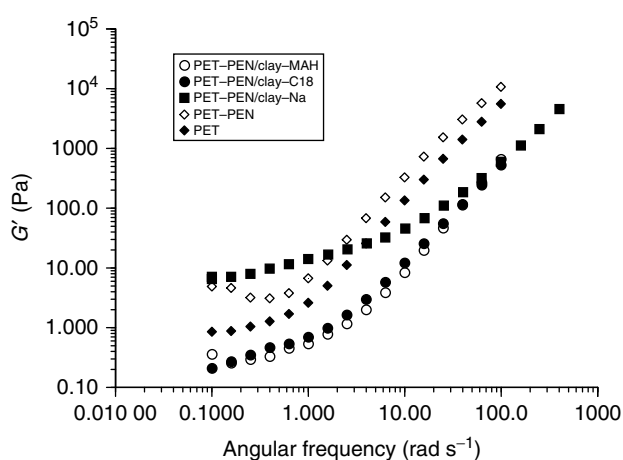**Figure 1.** Shear viscosity as a function of shear rate for the indicated systems.

Figure 2. Variation of the storage modulus with frequency for the indicated systems.

CONCLUSIONS

The PET–PEN/clay–C18 blend exhibits poor mechanical properties, attributed to a limited degree of exfoliation, and hence the particle–polymer compatibility level in this system is lower than that observed in the other blends. The PET–PEN/clay–MAH blend possesses a higher proportion of amorphous phase, due to the restriction to the normal crystallization process due to the particles, as evidenced in the low value of the crystallization enthalpy. The transesterification reaction of PET and PEN, which produces a copolymer, is affected by the clay particles, in which clay–C18 induces the largest proportion of NET groups as opposed to clay–Na$^+$, which produces 22 times less NET groups. In spite of the fact that clay–Na$^+$ is hydrophilic, the surfaces of all samples possess a hydrophobic character. This clay is highly incorporated in the polymer and presumably has a low concentration at the surface, as evidenced in the receding contact-angle results which show a predominantly hydrophobic character of the surface. This blend also presents a large solid-like behaviour, as disclosed by the values of the storage modulus in the low-frequency range of the spectrum, which provides evidence for the presence of a high entanglement density and large polymer–particle interactions.

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