

The Transient Flow of the PET-PEN-Montmorillonite Clay Nanocomposite

F. Calderas,* A. Sanchez-Solis, A. Maciel, O. Manero

Summary: Polyethylene terephthalate (PET) and polyethylene 2, 6 naphthalene dicarboxylate (PEN) nanocomposites were prepared by an extrusion process with organic-modified montmorillonite clay. The steady-state viscosity of all blends diminished as compared to the system with no clay added. A rheological study was conducted to know more about the complex structure formed by the polymer matrix-clay interactions. Instantaneous stress relaxation curves are presented for the PEN, PEN-PET and PET-PEN-iphir clay systems. A Fourier Transform (FT) frequency response was obtained from the relaxation curves and compared to the linear oscillatory data, which lead to an extended frequency region. The results were modeled by a rheological equation of state which accounts for the formation-destruction dynamics of the microstructure during flow. Relaxation time spectra are presented and compared for both rheological tests, namely, instantaneous stress relaxation and linear oscillatory flow. Additional studies using scanning electron microscopy (SEM) are presented, which reveal the presence of a slip layer in capillary flow for the system with added clay.

Keywords: clay; Fourier transform; nanocomposites; rheology; stress relaxation

Introduction

Polymer nanocomposites are a relative new class of materials which contain a disperse phase with dimension of the order 1–100 nm. These materials have a great potential in several applications, such as gas barrier film, flame retardant products and in load-bearing structures.^[1] With small nanoparticle loads (1–5%) in different polymeric matrices these materials have shown improved properties over the unfilled polymeric matrix. These improved properties include barrier,^[2] mechanical,^[3] resistance to UV degradation,^[4] and so on.

The rheological behavior of these materials is still far from being fully understood but relations between their rheology and the degree of exfoliation of the nanopar-

ticles have been reported.^[5] An increase in the steady shear flow viscosity with the clay content has been reported for most systems^[6,7] while in some cases viscosity decreases with low clay loading.^[8,9] Other important characteristic of exfoliated nanocomposites is the loss of the complex viscosity Newtonian plateau in oscillatory shear flow.^[10–14] Transient rheology experiments have also been used to study the rheological response of polymer nanocomposites. The degree of exfoliation is associated with the amplitude of stress overshoots in start-up experiments.^[15] Two main modes of relaxation have been observed in the stress relaxation (step shear) test, namely, a fast mode associated to the polymer matrix and a slow mode associated to the polymer-clay network.^[16] The presence of a clay-polymer network has also been evidenced by Cole-Cole plots.^[17]

In the present study, nanocomposites of PET, PEN and organic-modified Montmorillonite clay (MMT) were prepared by melt

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extrusion processed at several temperatures and residence times. Instantaneous stress relaxation and stress relaxation after steady shear flow experiments have been conducted to characterize these systems.

Experimental Part

Materials

PET (Eastpack 9921 from Eastman Chemical) had a density of 1.40 g/cm^3 , melting temperature (262°C), glass transition temperature (61.2°C) and average molecular weight of $29,700 \text{ g/mol}$ with 4.9 polydispersity. PEN (Kalidar X-70 from Dupont) had a melting point at 258°C , T_g is 112°C and average molecular weight of $108,700 \text{ g/mol}$ with 3.6 polydispersity. Montmorillonite clay (Cloisite 15A) from Southern Co. is a natural clay modified with a quaternary ammonium salt, it had a density of 1.66 g/cm^3 and ion exchange capacity of 125 meq/100 g . Maleic anhydride (MAH) from Aldrich, was used as received.

Equipment

Preparation and characteristics of this system have already been reported elsewhere.^[18]

Exfoliation of the nanocomposites was probed by X-ray diffractometry. Details of the equipment and methods have also been reported elsewhere.^[18] No additives to prevent oxidation were used in compounding.

Blends were prepared in a 30 mm diameter co-rotating twin-screw extruder (Werner & Pfleiderer ZSK30) with a general-purpose screw configuration including two rows of kneading elements (15 elements by row and 5 mm width each) and $L/D = 30$. A scanning electron microscope (Leica-Cambridge-440) provided micrographs of samples. The steady shear viscosity was measured in a TA Instruments AR 1000-N controlled stress rheometer, with a parallel-plate geometry with 25 mm plate diameter and 0.75 mm gap. Stress relaxation experiments (step strain) were

carried out in a Rheometric Scientific ARES-LS (Advanced Rheometric Expansion System) controlled strain rheometer. In this device, a parallel-plate geometry with 25 mm plate diameter and 0.75 mm gap was also used. Temperature was set to 270°C for all experiments.

Results and Discussion

Steady Shear Flow Experiments

The steady-state shear viscosity was measured for the pure polymer matrix and the polymer-clay nanocomposite, after processing the matrix at the same conditions used to process the nanocomposite. For this clay content, the viscosity for the nanocomposite is lower than that of the unfilled matrix. This behavior has been reported for similar systems.^[19]

Instantaneous Stress Relaxation

In this test, an initial small-amplitude strain is applied to the sample during a period t_1 (which depends on the equipment). This period in the present case is 0.06 s. Then, for all $t > t_1$, the stress is allowed to relax. The stress relaxation modulus $G(t)$, i.e., the shear stress divided by the applied strain, is plotted versus time. The stress was monitored as soon as a terminal slope was reached. The time necessary to reach the terminal slope was found to be about 60 s for all materials.

Figure 2 shows the instantaneous relaxation curves. All systems show two main modes of relaxation (λ), a slow mode associated to the initial slope (short times) and a fast one associated to the final slope (longer times).

As expected, pure PEN (highest steady shear viscosity) possesses the highest initial modulus ($\sim 600 \text{ Pa}$), but the transition between the two main modes of relaxation is smoother as compared to the other systems.

The sharpest shift between the two main modes is observed to occur in pure PET, while for the PET-PEN blend and for the nanocomposite, the shift is not as sharp as

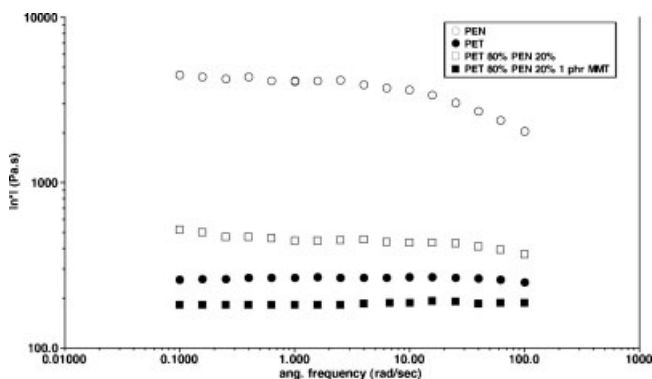


Figure 1.

Effect of the clay on the steady shear viscosity of the blend.

for pure PET, nor as smooth as for pure PEN.

Figure 3 shows the normalized relaxation curves for three systems in a log-log plot. PET shows a rapid and more pronounced initial relaxation, while in the other systems the presence of PEN and the clay somehow restricts the rapid relaxation and changes more rapidly towards the slow mode which is evidenced by an earlier change of slope. The response at long times for the instantaneous stress relaxation curve has been associated to the polymer-filler interactions.^[16] For these systems the terminal slope is similar for the pure PEN and for the nanocomposite system.

The normalized curves (Figure 3) show that at short times PEN relaxes slower than the other systems, while at long times, the blend and the nanocomposite the relaxations are somehow restrained. In the case of the polymer blend, the PET and PEN chains form a network promoted by the trans-esterification reaction that occurs at the processing conditions,^[18,20] which produces a copolymer and mutual cross-linking. For the nanocomposite, the relaxation is also restricted but the presence of the clay induces different dynamics. In this case, the relaxation is not as slow as for the polymer blend, (this is clearly observed in the larger slope at long times) possibly

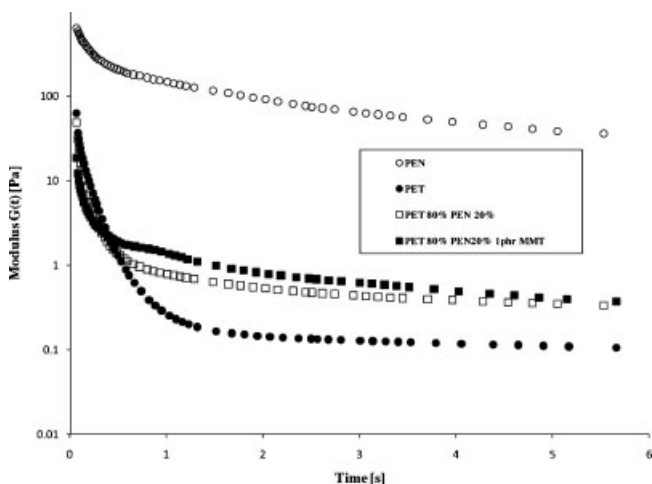


Figure 2.

Instantaneous stress relaxation curves, $G(t)$, versus time.

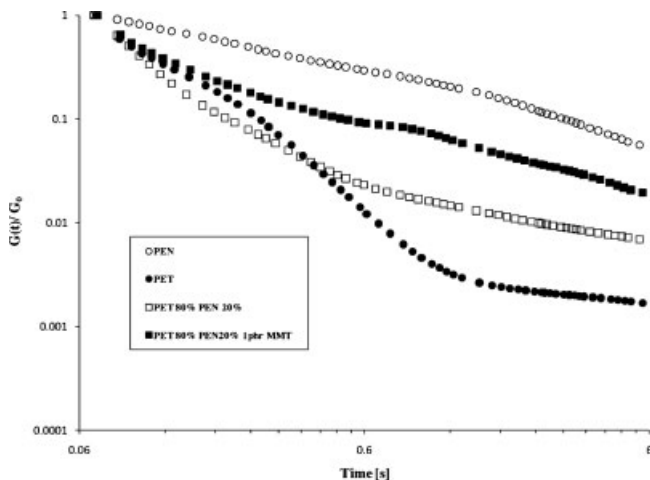


Figure 3.

Normalized modulus $G(t)/G_0(t)$ versus time for the systems studied. The imposed initial strain is 30%.

caused by particular polymer-clay interactions, since the high molecular weight chains are adsorbed preferentially in the clay galleries, thus allowing more mobility in the non-absorbed low-molecular weight chains. In addition, it has been reported that the presence of the clay in the polymer matrix somehow restricts the amount of cross-linking and thus the copolymer formation.^[18]

A Fourier Transform (FT) frequency response was obtained from the relaxation

curves and compared to the linear oscillatory data. Agreement is depicted in Figure 4.

The results were modeled by a rheological equation of state which accounts for the formation-destruction dynamics of the structure during flow.^[21] This constitutive equation can be generalized to a multi-modal model reported elsewhere.^[22] The model was used to find the characteristic times of the slow and fast modes for the systems. The model for pure PEN requires

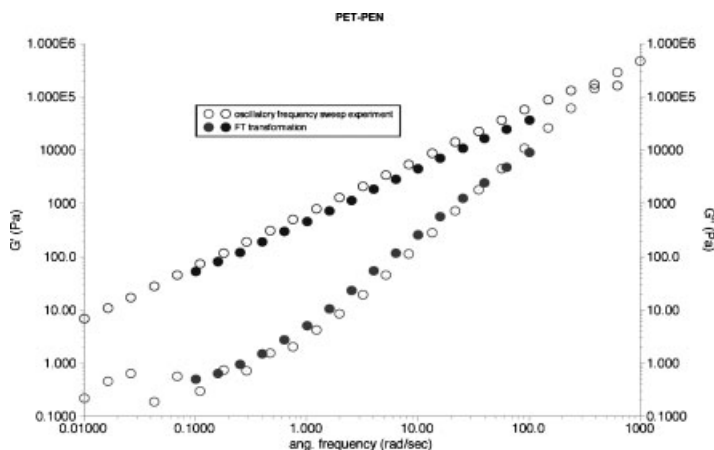


Figure 4.

Comparison between small-amplitude oscillatory data and FT of the instantaneous stress relaxation curve.

Table 1.

Main relaxation times λ [s] for the materials as obtained from instantaneous stress relaxation data.

Modes	PEN	PET	PET-PEN	PET-PEN/MMT
Slow	6.83	11.95	13.82	6.50
Fast	0.12	0.10	0.13	0.09

3 relaxation times or modes, pure PET and the PET-PEN blend require 4 relaxation times and the nanocomposite requires 5 modes, revealing the complexity added by the presence of the clay. The two main modes for the systems are disclosed in Table 1. Comparatively, the characteristic time of the slow mode in the PET-PEN system is the largest, reflected in the plateau of the relaxation curve and related to the effect induced by the transesterification reaction occurring in this system which produces an amount of cross-linking.^[23] The characteristic times of the fast modes have similar values.

Start-up of Shear Flow

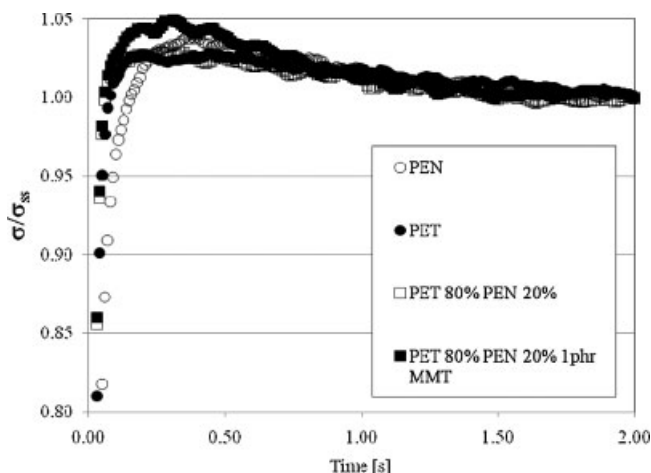
Stress growth was recorded as a function of time, and results are disclosed in Figure 5. Results show that the material with added clay reaches the maximum stress. This maximum value reflects the initial elasticity of the system, evidencing the formation of

an elastic network induced by strong polymer-matrix interactions in the nanocomposite. Curves for PET and PET-PEN blend overlap, showing no significant change. The amplitude of the overshoots has been proposed to be related to the degree of exfoliation of the nanoclays. Furthermore, overshoots in polymer-clay systems have been attributed to the breakdown of a clay platelet network.^[15]

Relaxation after Cessation of Steady Flow

In this experiment, the sample is sheared at constant and steady shear rate (10 s^{-1}). At time $t = 0$, the flow is suddenly stopped and the relaxation of the stress is followed as a function of time. Figure 6 shows the relaxation curves for the samples shown in Figure 5. PET shows a fast relaxation, while PET-PEN and PET-PEN/MMT display a similar initial slope at short times and also a similar slope at long times. The behavior at long times reflects chain cross-linking in the case of the PET-PEN blend and a polymer-clay interactions in the case of the nanocomposite.

Table 2 shows the two main relaxation times for the samples. With exception of PEN, all curves display similar initial fast relaxation time. At long times, PET shows a

**Figure 5.**

Normalized start-up flow curves for the different materials. A constant shear rate of 5 s^{-1} was applied to all samples.

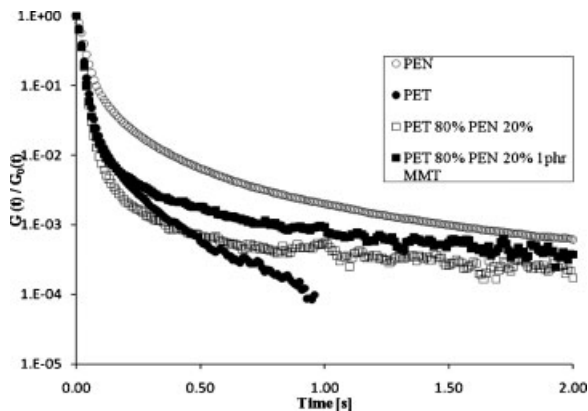


Figure 6.

Stress relaxation curves after cessation of steady shear flow (Shear rate: 10 s^{-1}).

Table 2.

Main relaxation times λ [s] obtained from stress relaxation after cessation of steady shear.

Modes	PEN	PET	PET-PEN	PET-PEN/MMT
Slow	1.24	0.312	1.74	1.50
Fast	0.10	0.017	0.016	0.016

fast decay to very low values of stress, i.e., below the equipment resolution. The relaxation curve for the PET-PEN system seems to stabilize at long times (Figure 6) and presents the largest characteristic time of the slow mode (see Table 2). This may be attributed again to the cross-linking induced from the reaction among the polymers, while the PET-PEN-clay blend shows a small relaxation time of the slow mode. This system is thought to have experienced a structure break up due to the constant shear flow imposed before

the relaxation dynamics and thus the system becomes less structured (possibly flow alignment of clay nanoparticles) affecting the relaxation dynamics after flow cessation.

Morphology

SEM was used to explore the surface of a filament obtained by using a capillary rheometer with a die of $L/D=20$ (at 270°C , 10 s^{-1}). A flexible peel thought to be formed by low molecular weight polymer was observed in the section of the filament exposed to the wall die. This may be the cause of the decrease in the shear viscosity as clay is added. This peel was not observed in the systems with no added clay (see Figure 7). An internal slip layer was also observed. Similar observations are reported in pure polymer blends.^[24]

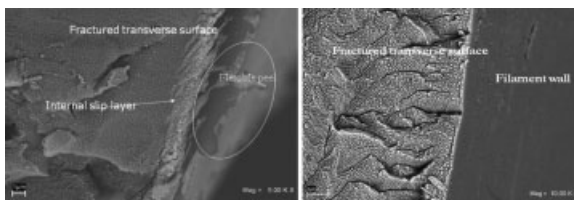


Figure 7.

SEM micrographs of the edge of the capillary filament. Left: blend with clay. Right: blend with no added clay.

Conclusions

The nanocomposite PET-PEN/MMT clay was studied under steady shear, instantaneous stress relaxation and relaxation after cessation of steady flow. Relaxation times of the slow mode in instantaneous stress relaxation were longer for the systems that have presumably permanent cross-linking networks (PET-PEN) or dynamic networks (PET-PEN/MMT). These results are consistent with those found in relaxation after cessation of flow. Nano-clay addition somehow restricts the slow relaxation (due to polymer-particle interactions). The nanocomposite exhibits lower steady-state viscosity as compared to the polymer matrix system. This is thought to be caused by polymer-polymer slipping, as revealed by the SEM observations.

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- [1] M. Okamoto, *Mat. Sci. Tech.* **2006**, 22, 756.
- [2] O. Gain, E. Espuche, E. Pollet, M. Alexandre, P. Dubois, *J. Polym. Sci. part B. Polym. Phys.* **2005** 43, 205.
- [3] J. Njuguna, K. Pielichowsky, *Adv. Eng. Mat.* **2004**, 6, 193.
- [4] A. Tidjani, *Polym. Deg. Stab.* **2005**, 87, 43.
- [5] R. Wagener, T. Reisinger, *Polymer* **2003**, 44, 7513.
- [6] R. Krishnamoorti, R. A. Vaia, E. P. Giannelis, *Chem Mat.* **1996**, 8, 1728.
- [7] L. A. Utracki, J. Lyngaae-Jorgensen, *Rheol. Acta* **2002**, 41, 394.
- [8] T. D. Fornes, P. J. Yoon, H. Keskkula, D. R. Paul, *Polymer* **2001**, 42, 9929.
- [9] J. Cho, D. Paul, *Polymer* **2001**, 42, 1083.
- [10] Y. Hyun, S. Lim, H. Choi, M. Jhon, *Macromol.* **2001**, 34, 8084.
- [11] M. McAlpine, N. Hudson, J. Liggat, J. Pethrick, D. Pugh, I. Rhoney, *J. Appl. Polym. Sci.* **2006**, 99, 2614.
- [12] Z. Wang, G. Xie, X. Wang, Z. Zhang, *J. Appl. Polym. Sci.* **2006**, 1000, 4434.
- [13] W. Lertwimolnun, B. Vergnes, *Polymer* **2005**, 46, 3462.
- [14] W. Lertwimolnun, B. Vergnes, *Polym. Eng. Sci.* **2006**, 46, 314.
- [15] W. Lertwimolnun, B. Vergnes, G. Ausias, P. J. Carreau, *J. Non-Newtonian Fluid Mech.* **2007**, 141, 167.
- [16] Q. Zhang, L. A. Archer, *Langmuir* **2002**, 18, 10435.
- [17] A. Abrányi, L. Százdli, B. Pukánszky, Jr., G. J. Vancsó, B. Pukánszky, *Macromol. Rapid Comm.* **2006**, 27, 132.
- [18] A. Sanchez-Solis, A. Garcia-Rejon, M. Estrada, A. Martinez-Richa, G. Sanchez, O. Manero, *Polym. Int.* **2005**, 54, 1669.
- [19] A. Sanchez-Solis, A. Garcia-Rejon, O. Manero, *Macromol. Symp.* **2003**, 192, 281.
- [20] R. Medina, D. Likhatchev, L. Alexandrova, A. Sanchez-Solis, O. Manero, *Polymer* **2004**, 45, 8517.
- [21] F. Bautista, J. M. de Santos, J. E. Puig, O. Manero, *J. Non-Newt. Fluid Mech.* **1999**, 80, 93.
- [22] Y. Caram, F. Bautista, J. E. Puig, O. Manero, *Rheol. Acta* **2006**, 46, 45.
- [23] A. Sanchez-Solis, A. Garcia-Rejon, A. Martinez-Richa, F. Calderas, O. Manero, *J. Polym. Eng.* **2005**, 25, 553.
- [24] A. Maciel, V. Salas, J. F. A. Soltero, J. Guzman, O. Manero, *J. Polym. Sci. part B. Polym. Phys.* **2002**, 40, 303.