Study on Phase Separation of PET/PEN Blends by Dynamic Rheology

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ABSTRACT: Blends of poly(ethylene terephthalate) (PET) and poly(ethylene naphthalate) (PEN) were processed into biaxially drawn films, and samples taken from the bi-oriented films were then investigated by dynamic rheology experiments in the melt state. Storage modulus G′ and loss modulus G″ were determined in the frequency range of 10^{-2}–10^{2} rad/s at temperatures between 260 and 300°C. Although the time–temperature superposition (TTS) principle was found to hold in the high frequency regime, a breakdown of TTS was observed at low frequencies, and the terminal behavior of the storage modulus G′ of the blends departs drastically from the terminal behavior observed for the blend components. This is caused by interfacial surface tension effects. The results indicate that despite the effect of transesterification reactions, the PET/PEN blend systems investigated consist of a microseparate phase of PEN platelets in a matrix of PET. This morphology is produced when the blends are processed into biaxially oriented PET/PEN films, and droplets of PEN are deformed into a lamellar structure consisting of parallel and extended, separate layers. The large interfacial surface area of the bi-oriented PET/PEN blends leads to remarkably strong interfacial tension effects in dynamic rheology measurements. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 177–182, 2008

Key words: PET/PEN blends; phase separation; dynamic rheology; bi-oriented films; time–temperature superposition; surface tension

INTRODUCTION

Poly(ethylene terephthalate) (PET) is known for its good mechanical properties, desirable injection molding performance, and chemical stability. Despite its desirable properties, PET is a polymer that lacks suitable barrier properties, rendering it unsuitable for many packaging applications. This is a shortcoming that can be overcome by blending PET with poly(ethylene 2,6-naphthalate) (PEN), which due to its rigid rod backbone structure features enhanced stiffness and improved gas barrier characteristics. As PEN is much more expensive than PET, properties of PET/PEN blends have been widely investigated recently, due to their enhanced mechanical, thermal, and barrier properties bestowed to these mixtures by the presence of a small amount of PEN.[1–9]

However, to achieve good barrier properties of PET/PEN blends, studies indicate that PEN needs to form the disperse phase in a continuous phase of PET, and also that a specific configuration and scale of the disperse PEN phase is necessary for optimal barrier properties. It is the disperse phase configuration of PEN that has a strong effect on the barrier properties of PET/PEN blends. Therefore, the barrier properties can be predicted by studying the phase separation of the blends. Commonly, PEN and PET are incompatible,[10–12] and the phase separation can be studied by the usual analytical methods like, for example, differential scanning calorimetry (DSC). However, when the mixture of PET and PEN is heated to a processing temperature above the melt temperatures and kept at this temperature for some time, transesterification reactions occur and block polymers are produced,[13,14] and the amount of phase separation can no longer be determined by DSC measurements.

Dynamic mechanical measurements represent a technique that can detect even very small traces of phase separation, as the linear viscoelastic properties of polymer melts are very sensitive to small changes of the phase structure. Phase separation of a blend results in a change of the linear-viscoelastic behavior of the polymer melt, and meaningful information about phase separation can be obtained from dynamic mechanical analysis. Masuda et al.[15] pointed out that time–temperature superposition (TTS) is observed

for many multiphase/multicomponent systems in the range of short relaxation times (i.e., at high frequencies), however, TTS breaks down in the range of long relaxation times (i.e., at low frequencies). This means that multiphase structure configurations result in a specific viscoelastic response in the long relaxation time regime. Dynamic rheology has successfully been used in studying a multiphase polymer system.[16] Recently, Zheng and Huang[17] gained useful information about structure and phase-behavior of a polymer blend by using dynamic mechanical measurements, which could not be obtained from other analytical methods.

Theory of dynamic rheology

According to the linear-viscoelastic theory,[18] the storage and loss modulus in the terminal frequency zone (ω→0) are given by

$$G'(\omega)|_{\omega \to 0} = J_e^0 \eta_0^2 \omega^2 \qquad (1)$$

$$G''(\omega)|_{\omega \to 0} = \eta_o \omega \qquad (2)$$

J_e^0 is the steady-state compliance, and η_0 is the zero-shear rate viscosity. With these equations, we can obtain two important scaling relationships for the dynamic viscoelastic functions in the terminal frequency zone (i.e., for frequency ω→0)

$$\lg G' = 2 \lg \omega + A \qquad (3)$$

$$\lg G'' = \lg \omega + B \qquad (4)$$

Based on TTS theory, the dynamic viscoelastic functions at different temperatures T and T_0 are related as follows:

$$G'(\omega \alpha_T, T_0) = b_T G'(\omega, T) \qquad (5)$$

$$G''(\omega \alpha_T, T_0) = b_T G''(\omega, T) \qquad (6)$$

α_T and b_T are called the horizontal and vertical shift factors, respectively.

In earlier work,[19] we have investigated the morphology of biaxially oriented PET/PEN blends by Scanning Electron Micrography (SEM), and the barrier properties by air permeation experiments. In the present work, we intend to concentrate on the linear-viscoelastic properties of PET/PEN blends, and to evaluate the phase separation of biaxially oriented PET/PEN blends as recognized by dynamic mechanical measurements. The TTS method is used to study the phase-separation of the blends.

EXPERIMENTAL

Materials

The polymers used were a PET with intrinsic viscosity of 0.81 dL/g (produced in Korea), and a PEN with intrinsic viscosity of 0.61 dL/g (Du Pont, Wilmington, DE).

Preparation of PET/PEN blends

PET and PEN were dried at 120°C for 8 h, then PET, PEN, and an antioxidant agent were proportioned and dry mixed. The mixture was molten and blended in a TE-34 Double Screw Extruder at a melt temperature of 220–280°C. The extruded blends were granulated and dried for further analysis and processing into flat sheets of width 140 mm and thickness of 0.8 mm. From the sheets, plates of dimensions 100 × 100 mm were cut. Plates were inserted in a Biaxial Film Drawing Machine (Toyoseiki, Japan) to prepare bi-oriented films. The biaxial draw ratio was 1 : 3.7 at a draw rate of 2500–3000 mm/min. Drawing was performed at temperatures of 103–105°C (PET/PEN = 90/10); 106–107°C (PET/PEN = 80/20); and 108–109°C (PET/PEN = 70/30).

Dynamic rheology measurements

Dynamic rheological measurements were conducted with a Rheo Stress RS 150(RS 150) rheometer (HAAKE, Germany), using a parallel plate system with plate of diameter 20 mm. Samples taken from the bi-oriented films were dried for 4 h in a vacuum dryer at 120°C, and the rheometer was purged with dry nitrogen throughout the test. Frequency sweeps were performed over the range of 10^{-2}–10^2 Hz at temperatures between 260 and 300°C. The shear strain range used was 3–10%. Storage (G') and loss modulus (G'') were monitored in the linear-viscoelastic region. Master curves were obtained by superposition of the moduli measured in the high frequency range according to the TTS method. 260°C was taken as the reference temperature.

Differential scanning calorimetry

DSC (Perkin–Elmer Pyris 1) was used to measure the melting and crystallization temperatures of samples of bi-oriented film under nitrogen atmosphere. Sample weight was 5 mg. All samples were heated from room temperature to 280°C and kept at 280°C for 1 min to eliminate the thermal prehistory, cooled down to 50°C to record the crystallization curve, and then reheated to 280°C to determine the melting curve. Heating and cooling rates were 20 K/min. First cooling and second heating curve were recorded.
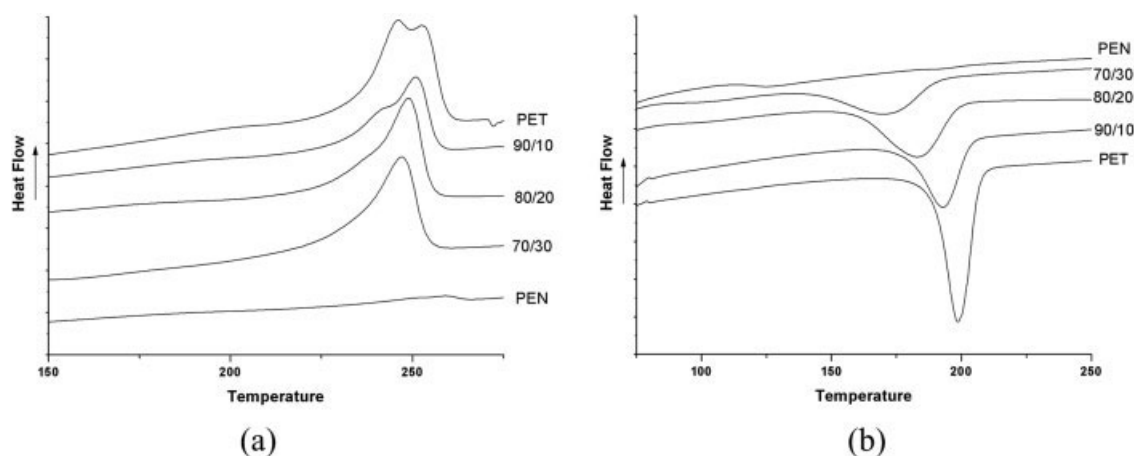
Figure 1   DSC curves of PET, PEN, and PET/PEN blends, (a) Melting curves, (b) Crystallization curves.

RESULTS AND DISCUSSION

Crystallization and melting behavior

The DSC curves of several samples are shown in Figure 1. Figure 1(a) presents the melting curves, and Figure 1(b) the crystallization behavior. Because of the high cooling and heating rates, crystallization of PEN was small and could not be resolved. Detailed information is summarized in Table I.

As observed in Figure 1, there are only one melting apex and one crystallization apex for PET/PEN blends. From this result, it may be speculated that PET/PEN blends are materials that have a homogeneous structure. However, previous SEM studies in our group have demonstrated[19] that the PET/PEN blends show phase separation, with PEN being the dispersed phase and PET being the continuous phase, and the PET/PEN blends investigated here are typical heterogeneous materials.

The glass transition temperatures of PET and PEN are 81°C[20] and 125°C,[21] and the melting temperatures are 250°C[22] and 260°C[23] respectively. Polydispersity of molecular weight and imperfection of crystallite structure result in a broadening of the melting peaks. Therefore, the melting peaks of PET and PEN overlap to some extent, and the two phases cannot be differentiated by DSC measurements. Also, transesterification reactions occur between PET and PEN, and the interface will be thickened by transesterification products as shown by SEM analysis,[19] which makes the difference between the PET and PEN melting peaks even more difficult to detect. A further indication of transesterification is the difference of the melting and crystallization enthalpies as observed for the blends PET/PEN-80/20% and 70/30% (Table I), indicating that any additional thermal exposure of the blends will lead to increased transesterification. For these reasons, PET/PEN phase-separation cannot be investigated within the sensibility range of DSC test.

Dynamic rheology of PET and PEN

The master curves of PET and PEN as obtained by TTS are presented in Figures 2 and 3 at a reference temperature of 260°C. Both polymers obey TTS for the total frequency range investigated. As seen from Figure 2, the dynamic rheology of PET is characteristic for a polymer melt in the terminal frequency zone, that is, the storage G′ exhibits a slope of 2 [eq. (3)], and the loss modulus G″ a slope of 1 [eq. (4)] in a double-logarithmic plot. From eqs. (1) and (2), values of $\eta_0 = 1.83 \times 10^2$ Pa s are obtained for the zero-shear rate viscosity and $J_e^0 = 6.88 \times 10^{-6}$ Pa^{-1} for the steady-state compliance. For PEN, a crossover of G′ and G″ is observed at high frequencies (Fig. 3),

TABLE I
Thermal Data of PET and PET/PEN Blends from DSC Measurements

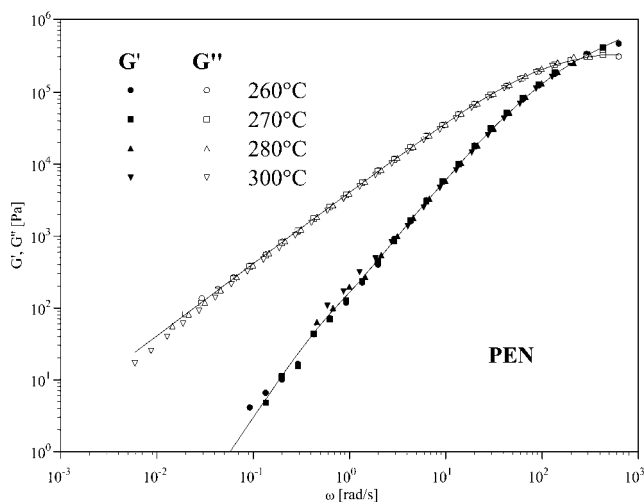|	Melting parameters				Crystallization parameters			
	Melting begin (°C)	Temp. apex (°C)	Melting end (°C)	ΔH (J/g)	Crystal begin (°C)	Temp. apex (°C)	Melting end (°C)	ΔH (J/g)
PET	234.5	246.2	259.3	34.99	206.7	198.6	189.5	−36.24
90/10	237.8	250.9	256.8	34.23	203.4	193.0	179.0	−34.40
80/20	235.7	249.0	255.1	28.45	198.5	183.4	160.2	−24.70
70/30	231.6	247.1	254.0	29.76	190.2	171.2	143.5	−17.45
PEN	–	–	–	–	–	–	–	–
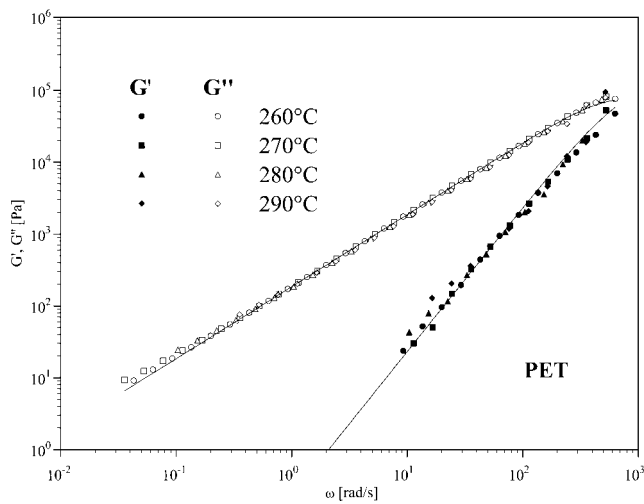
Figure 2 Storage modulus G′ and loss modulus G″ of PET (reference temperature 260°C). Solid lines indicate fit by relaxation spectrum (Table II).

and the terminal behavior is approached at low frequencies, characterized by $\eta_0 = 4.05 \times 10^3$ Pa s and $J_e^0 = 1.84 \times 10^{-5}$ Pa^{-1}.

Discrete linear-viscoelastic spectra were calculated using the IRIS software of Winter and Mours,[24] and are summarized in Table II. Although the terminal behavior of PET can be represented by a single relaxation mode (solid lines in Fig. 2), a spectrum of relaxation modes is needed to fit G′ and G″ of PEN in the frequency range investigated.

Dynamic rheology of PET/PEN blends

Measurements of storage (G′) and loss modulus (G″) of the PET/PEN blends containing 10, 20, and 30% of PEN are presented in Figures 4–6. The measured

TABLE II
Discrete Relaxation Spectra (Moduli g_i and Relaxation Times λ_i) of PET and PEN at Reference Temperature of 260°C
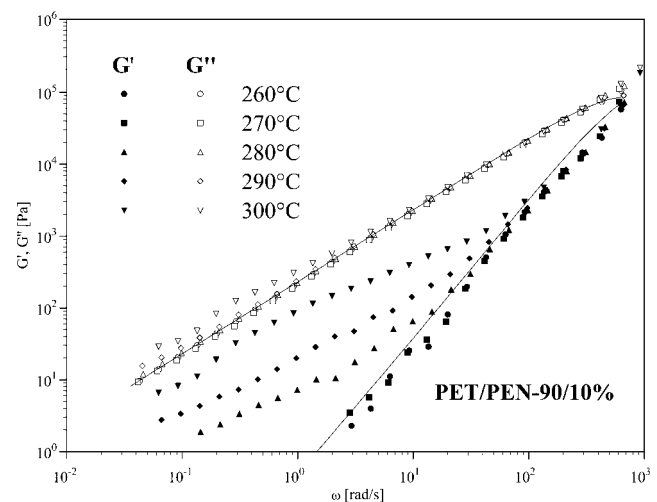
	Number of mode	g_i (Pa)	λ_i (s)
PET	1	1.453×10^5	1.256×10^{-3}
PEN	1	5.474×10^5	1.555×10^{-3}
	2	2.266×10^5	7.469×10^{-3}
	3	3.377×10^4	3.094×10^{-2}
	4	1.961×10^3	1.677×10^{-1}
	5	9.006×10^1	1.492

data were time–temperature shifted in such a way that superposition at the high frequency regime was obtained. For the two blends PET/PEN-90/10% (Fig. 4) and PET/PEN-80/20% (Fig. 5) and temperatures of 260 and 270°C, the terminal scaling behavior as obtained for pure PET is still observed, that is, G′ exhibits a slope of 2, and G″ a slope of 1. Indeed, values of G′ and G″ for these two temperatures are only slightly higher than the master curves obtained for pure PET, that is, the influence of the PEN component is limited. A simple additivity rule of the moduli in the form of

$$G'_{\text{Blend}} = w\ G'_{\text{PET}} + (1 - w)\ G'_{\text{PEN}}$$
$$G''_{\text{Blend}} = w\ G''_{\text{PET}} + (1 - w)\ G''_{\text{PEN}} \qquad (7)$$

where w is the weight fraction of PET in the blend, gives a nearly quantitative description of the moduli of the blends (solid lines in Figs. 4 and 5).

In the case of the blend PET/PEN-70/30% (Fig. 6), a slight bending of the curves at high frequencies towards a crossover of G′ and G″ is seen as observed for pure PEN, and for this blend, the linear mixing

Figure 3 Storage modulus G′ and loss modulus G″ of PEN (reference temperature 260°C). Solid lines indicate fit by relaxation spectrum (Table II).
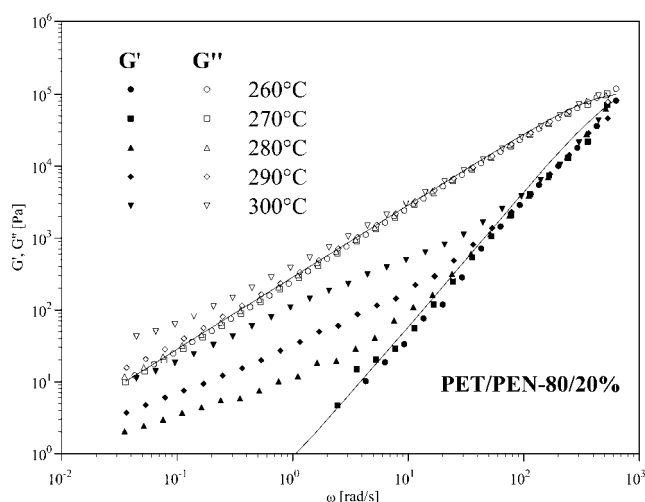

Figure 4 Storage modulus G′ and loss modulus G″ of blend PET/PEN-90/10% (reference temperature 260°C). Solid lines indicate additivity rule of eq. (7).

rule of eq. (7) underpredicts the measured moduli (solid lines in Fig. 6).

At lower frequencies and higher temperatures, TTS clearly breaks down for all three blends. The effect is most dramatic for the storage modulus G′, while for the loss modulus G″ only small deviations from TTS are found at low frequencies. The storage moduli G′ measured increase with increasing measurement temperature, and the difference between G′ measured at a temperature of 260°C and of 300°C can be as high as two orders of magnitude. In the frequency regime where TTS breaks down, it is also seen that G′ approaches approximately a slope of 1, that is, shows a slope similar to G″. The breakdown of TTS is already strong for the blend PET/PEN-90/10% and it is maximal for blend PET/PEN-80/20%, while it is somewhat smaller for the blend PET/PEN-70/30%. This may be a consequence of the transesterification reactions between PET and PEN, which lead to improved compatibilitiy.

The breakdown of TTS is a clear indication of phase separation of PET and PEN. Because of the biaxial drawing of the blends prior to dynamic rheology testing, a microstructure consisting of parallel extended and separated layers of PEN exists in the matrix of PET.[19] Dynamic shear oscillations deform these platelets, thereby increasing their surface area. Because of the difference in surface tension of PET and PEN, an increase of the interface surface requires additional energy. This effect is predominantly elastic, and therefore shows up in the G′-signal. At higher frequencies, the surface tension effect is masked by the entropic elasticity of the polymer chains, and therefore TTS is observed at higher frequencies. At higher temperature, relaxation of both PET and PEN is faster, while the effect of surface
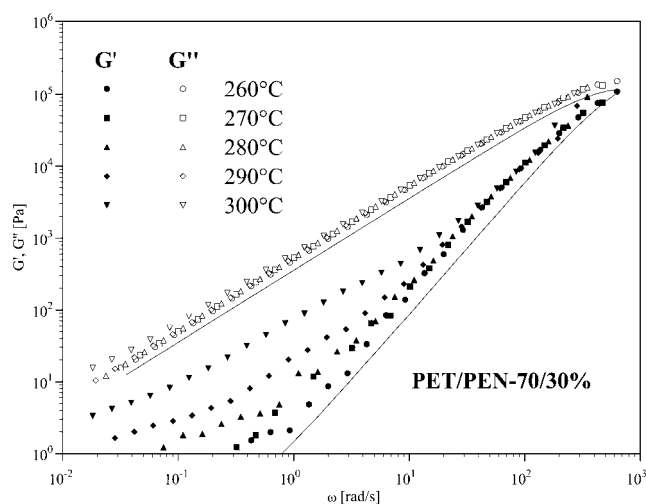
Figure 6 Storage modulus G′ and loss modulus G″ of blend PET/PEN-70/30% (reference temperature 260°C). Solid lines indicate additivity rule of eq. (7).

tension shows only minor temperature dependence. Therefore, the additional elastic effect of the PET/PEN interface is more pronounced at higher measurement temperatures.

It should be noted that the surface tension effects observed here are much larger than commonly expected from emulsion models assuming spherical inclusions of one phase in the matrix of a second phase (see e.g., Ref. 25). In the case of bi-oriented PET/PEN blends investigated here, the processing of the blends by biaxial drawing leads to a platelet morphology of the PEN phase.[19] For this specific morphology, the interfacial surface area is much larger than for a morphology of spherical inclusions, leading to strongly enhanced interfacial tension effects in dynamic rheology measurements.

CONCLUSIONS

The phase separation of PET/PEN blends cannot always be determined by DSC analysis. By using dynamic rheology experiments in the melt state, phase-separation of the blends can be confirmed by a breakdown of TTS, and by deviations of the storage modulus G′ of the blends from the terminal behavior observed for the blend components. This is caused by strong interfacial tension effects. The results confirm that despite the effect of transesterification reactions, the PET/PEN blend systems investigated consist of a microseparate phase of PEN platelets in a matrix of PET. This morphology is produced when the blends are processed into biaxially oriented PET/PEN films. Thereby droplets of PEN are deformed into a lamellar structure consisting of parallel and extended, separate layers. The multilayer microstructure results in improved barrier

Figure 5 Storage modulus G′ and loss modulus G″ of blend PET/PEN-80/20% (reference temperature 260°C). Solid lines indicate additivity rule of eq. (7).

properties, since air permeation is delayed as the air has to detour around the PEN layers, and therefore this morphology guaranties that maximum use is made of the excellent barrier properties of PEN in PET/PEN blends.

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