

Rheology of a Textured Fluid Consisting of Poly(ethylene terephthalate) and Nylon 6,6

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SYNOPSIS

The rheology and development of the texture of immiscible polymer blends based on poly(ethylene terephthalate) (PET) and nylon 6,6 at composition ratios of 75/25, 50/50, and 25/75 w/w PET/nylon 6,6 were studied. The blends were prepared by mixing in an extruder and by dry blending and mixing between cone-and-plate fixtures in a nitrogen atmosphere. The rheology of these blends was found to be a function of both polymer degradation and the two-phase morphology. An accelerated degradation rate in air was observed for the 75/25 and 50/50 w/w PET/nylon 6,6 blends relative to the neat polymers while the blend at a weight ratio of 25/75 w/w PET/nylon 6,6 displayed a rate of degradation similar to that of the neat polymers. The values of the steady shear viscosity (η), $|\eta^*|$, storage modulus (G'), and steady-state first normal stress difference (N_1) for melt-blended 75/25 and 50/50 w/w PET/nylon 6,6 samples were lower than those of the neat polymers and were determined to be a consequence of the higher rate of degradation of these blends during extrusion relative to that of the neat polymers. The role played by the two-phase nature on the blends was observed for all samples prepared by dry blending and mixing in cone-and-plate fixtures under a nitrogen atmosphere and for the melt-blended 25/75 w/w PET/nylon 6,6 blend. The two-phase nature of the dry-blended samples and the extruded 25/75 w/w PET/nylon 6,6 sample resulted in values of $|\eta^*|$, η , G' , and N_1 which were higher than those of the neat polymers. Transient behavior observed for the blends using stepwise changes of shear rate was found to superimpose when plotted in reduced form, indicating that at rates lower than the longest relaxation time of the neat polymers there was no intrinsic time constant associated with the deformation of the interface in the blends. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Immiscible polymer blends represent complex systems in which the rheological properties are not only a function of the viscoelastic properties of the component polymers but also the morphology which is developed and any reactions which might occur at melt temperatures.¹ In the case of binary blends of immiscible polymers, the morphology can, in general, take the form of one component dispersed in a continuous phase of the second component or both components can be continuous, resulting in an interpenetrating network. The morphology of immis-

cible polymer blends during flow is constantly changing and, as a consequence, the blend may exhibit rheological properties which are functions of their texture and are not seen in the individual polymers.²⁻⁵

While the literature pertaining to immiscible polymer blends is extensive as demonstrated in an early review by Paul and Newman,¹ comprehensive rheological data including transient data and the corresponding development of texture is lacking. Rheological studies of polymer blends have generally focused on the correlation of specific rheological properties with the state of miscibility or lack thereof. Some of the rheological observations which were related to immiscibility in polymer blends include (1) lack of agreement between the blend viscosity and that based on the log additivity rule,⁶ (2)

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lack of agreement between the steady shear and corresponding small strain dynamic oscillatory responses,⁷ (3) bimodality in the Cole–Cole plot of the imaginary vs. real part of the dynamic viscosity,⁸ and (4) a broad relaxation spectrum relative to that of the neat polymers due to the contribution from the interface.⁴ While the above observations were reported for many immiscible polymer blends, they were not exclusive to immiscible systems and were also observed in miscible systems.^{9–11}

The viscosity of polymer blends relative to the log additivity of the viscosity of the neat polymer was used to classify polymer blends in investigations by Utracki and Kamal⁶ and LaMantia.¹² This method placed polymer blends in one of three categories based on a blend viscosity which relative to the log additivity of the viscosity of the blend components was lower (negative deviation), higher (positive deviation), or both lower and higher (positive–negative deviation) depending on concentration. Systems in which a positive deviation was observed included immiscible blends where strong interdomain interactions were present and miscible blends in which the intersegmental interactions may be nonrepulsive. Polymer blends which displayed partial miscibility or a limited miscibility at low concentrations fell into the category of negative deviation blends. Finally, polymer blends in which both positive and negative deviations were observed included those blends where, depending on concentration or shear rate, a phase inversion or a concentration-dependent transition of structure occurred. For example, in a study of high-density polyethylene (HDPE) and polystyrene (PS) blends by Han and Kim,¹³ the viscosity was seen to go through both a minimum and a maximum as the composition was varied for a given stress. The minimum in viscosity was observed at a composition of 50/50 HDPE/PS and the maximum at a composition of 75/25 HDPE/PS. The minimum in viscosity corresponded to a morphology of dispersed HDPE droplets and the maximum to a co-continuous morphology. With an increase in the stress, the minimum in viscosity was no longer observed and was correlated to a shift of the onset of the co-continuous morphology to a lower HDPE content.

The presence of yield stresses in immiscible polymer blends was described as evidence of interactions during the flow of the dispersed phase in an investigation by Utracki.² An apparent yield stress was reported in a study by Chuang and Han⁷ using an immiscible blend of poly(methyl methacrylate) (PMMA) with polystyrene (PS), a miscible blend of two low-density polyethylenes (LDPE) of different molecular weights, and a miscible blend of

PMMA with poly(vinylidene fluoride) (PVDF). In Chuang and Han's study, each material was examined over a range of compositions and temperatures. Their results showed an apparent yield stress by an upturn in the viscosity at low shear rates for the immiscible system consisting of PMMA with PS while a Newtonian plateau was observed for both miscible blends. On the other hand, an apparent yield stress was not always observed in immiscible systems as was demonstrated in a study by Utracki et al.^{6,14} In the study by Utracki et al., a Newtonian plateau was observed using an immiscible blend of poly(ethylene terephthalate) (PET) and nylon 6,6. Although a Newtonian plateau was observed, the shear rate at which the transition from Newtonian to shear thinning behavior occurred was lower in the blend than in either neat polymer.

Although transient data obtained from experiments such as the start up of steady shear flow could provide valuable insight into the development of texture in immiscible polymer blends, very little work of this nature has been reported. In an investigation by Nobile et al.,¹⁵ the transient behavior of a blend of polyetherimide (PEI) and a thermotropic liquid crystalline polymer (TLCP) based on hydroxybenzoic acid, terephthalic acid, hydroquinone, and 4-4'-dihydroxybiphenol (K161, from Bayer) at a weight ratio of 90/10 PEI/K161 was reported. The data showed an overshoot which appeared at shear rates lower than that required to produce an overshoot for the pure matrix. Additionally, it was observed that the steady state was not obtained even after 250 strain units while pure PEI reached the steady state in less than 50 strain units. Nobile et al.¹⁵ associated the continuous decrease in the stress with the continuous deformation and orientation of the TLCP phase during flow.

The rheological properties of immiscible polymer blends may, in addition to the morphology, be a function of chemical changes such as those associated with polymer degradation and reactions which may occur as the polymers are mixed. An example of a system in which reactions and degradation were observed in blends consisted of PET and nylon 6,6. The literature pertaining to polyester/polyamide blends is fairly extensive.^{2,6,14,16–19} At certain concentrations (e.g., nylon 6,6 concentrations of between 5 and 35 wt %), PET/nylon 6,6 blends were reported to fall into the category of negative deviation blends.^{6,14,20} The origin of a blend viscosity which is lower than that of the log additivity of the neat polymers was complicated by the fact that, in addition to a two-phase morphology, extensive degradation was also reported to occur in this system. While these observations were

each treated separately, it is likely that they were interrelated.

The degradation behavior of PET/nylon 6,6 blends was investigated by Utracki et al.¹⁴ It was shown using measurements of viscosity vs. time that in blends consisting of nylon 6,6 levels ranging from 5 to 35 wt % the rate of decrease in the viscosity with time for the blends was greater than that of the neat polymers. In addition, the temperature dependence of the degradation process measured in terms of the apparent overall activation energy of degradation for the blends was higher than values calculated from a simple additivity rule using the activation energies of the component polymers. Utracki et al. attributed the degradation of PET to random chain scission and the degradation of nylon 6,6 to random cleavage of C—N bonds. The accelerated degradation of the blends was postulated to be a result of the initial catalytic effect of the amide groups on the degradation of PET which, in turn, accelerated the degradation of the nylon 6,6. On the other hand, although degradation may be purely thermal for these polymers, accelerated degradation in the presence of trace amounts of water for polymers containing hydrolyzable linkages such polyamides and polyesters may also play a role.

The formation of block copolymers by the ester interchange reaction in polyester/polyamide blends was documented in the patent literature.²¹⁻²³ The times required for the interchange reaction were reported to range from 5 to 30 h for reaction temperatures ranging from 220 to 290°C. The copolymers which were formed at the interface were found to compatibilize the system, reducing interfacial tension and the contribution of the interface to the rheological properties of the blend.³⁻⁵

In a study by Pillon and Utracki,¹⁶ the ester interchange reaction was used to form copolymers of PET and nylon 6,6 in order to compatibilize the blend. A catalyst consisting of *p*-toluenesulfonic acid (TsOH) was introduced to facilitate the ester–amide interchange reaction. It was shown that the extent of the interchange reaction reached 23.3% in the presence of the TsOH catalyst as measured by NMR methods. Blending was carried out in an extruder with a residence time of 2 min and a maximum barrel temperature of 370°C. No indication of the exchange reaction was detected when no catalyst was used by blending in an extruder with a maximum barrel temperature of 300°C and a residence time of 4 min. In a study by Kimura et al.,²⁰ the rate at which the exchange reaction occurred was demonstrated using a blend consisting of poly(butylene terephthalate) and polyarylate. Kimura et al. showed using intrinsic viscosity measurements and melting-point depres-

sion as a function of reaction time that appreciable transesterification occurred only after approximately 100 min. Although compatibilization of polyester/polyamide blends due to the ester interchange reaction was reported, the time scale for the reaction was on the order of hours and was much longer than the time scale of most blending processes.

It is clear that the rheology of blends of PET and nylon 6,6 can be complicated by several factors including degradation, transesterification, and interfacial tension. However, it is apparent that under most normal blending operations there is not sufficient time for transesterification to occur. Hence, the primary goal of this work is to separate the effect of degradation on the rheology of the blend from that of interfacial tension. To accomplish this, we compared the rheological properties of blends prepared under normal mixing conditions to those prepared under controlled conditions where degradation is minimized.

EXPERIMENTAL

The materials and methods used in this work are presented in this section. First, the polymers used and the blend preparation methods are presented. Next, the methods used to determine the state of the texture (microscopy) and the rheological properties are discussed.

Materials and Sample Preparation

The polymers used in this investigation were poly(ethylene terephthalate) (PET) and nylon 6,6. The PET supplied by DuPont was PTX-267 ($M_w = 25,000$) and has a melting temperature of 257°C determined using differential scanning calorimetry. The recommended drying conditions for PET are 120–125°C for 3–4 h in vacuum which yields a moisture content of 0.02%. The nylon 6,6 supplied by Monsanto was Vydne 66b ($M_w = 30,000$) and was determined to have a melting temperature of 263°C determined using differential scanning calorimetry. The recommended drying conditions for nylon 6,6 are 75–80°C for 3–4 h in vacuum.

Due to the extensive degradation and ester interchange reaction reported for blends of these two polymers, two different blend preparation methods were used. To provide blends with a minimum residence time and exposure to moisture during blending, PET and nylon 6,6 were mixed using the following procedure: First, the neat polymers in pellet form were granulated in a Thomas Scientific gran-

ulator which produced samples with particle sizes ranging from 0.05 to 0.5 mm in diameter. Quantities of the granulated polymers corresponding to the appropriate weights required to produce blends with weight ratios of 25/75, 50/50, and 75/25 w/w PET/nylon 6,6 were placed in separate containers and dried in a vacuum oven (PET at 125°C and nylon 6,6 at 75°C for 36 h). After drying, samples were dry-blended under vacuum by mixing in a plastic desiccator and then immediately placed back into a vacuum oven at 100°C. To provide further mixing, dry-blended samples were presheared for 1 min at 5 s^{-1} in a cone-and-plate fixture under a nitrogen atmosphere prior to performing all rheological experiments. The samples prepared in the above manner will be referred to as DB-75/25, DB-50/50, and DB-25/75 for the 75/25, 50/50, and 25/75 PET/nylon 6,6 w/w blends, respectively, and the neat polymers simply as PET and nylon 6,6 in the following discussion.

The second blend preparation method used consisted of melt blending in an extruder. The neat polymers in pellet form were dried in a vacuum oven prior to dry blending. PET was dried for 36 h at 125°C in a vacuum oven and nylon 6,6 was dried for 36 h in a vacuum oven at 75°C to ensure a minimum moisture content in the samples. Weighed amounts of the dried polymers were dry-blended and stored in a vacuum oven at 100°C. Dry-blended pellets in proportions of approximately 30 g at a time were removed from the oven and immediately loaded into the hopper of a 2.54 cm Killion extruder. New pellets from the oven were added to the hopper only after the last pellets from the previous charge had reached the feed section of the extruder. Extrusion was carried out at 20 rpm with an attached capillary die with a diameter of 0.3175 cm and a L/D of 10. The barrel temperatures from the feed zone to the die were 260, 275, 290, 290, and 270°C, respectively. The extrusion conditions described above correlate to a residence time at melt temperatures during the blending process of 4.5 min based on the flow rate and screw and barrel dimensions. The neat polymers were subjected to the same processing histories as were the blends. The samples prepared in the above manner will be referred to as MB-75/25, MB-50/50, and MB-25/75 for the 75/25, 50/50, and 25/75 w/w PET/nylon 6,6 blends, respectively, and MB-PET and MB-nylon 6,6 for neat PET and neat nylon 6,6, respectively, in the following discussion.

Rheological Measurements

Rheological experiments were carried out on the blends and neat polymers using a Rheometrics me-

chanical spectrometer (RMS-800) with a cone-and-plate fixture having a cone angle of 0.1 rad and a diameter of 12.5 mm. Steady shear viscosity (η) and first normal stress difference (N_1) data was obtained after the sample was sheared long enough to reach steady-state conditions. The magnitude of the complex viscosity ($|\eta^*|$) and storage modulus (G') were obtained as a function of angular frequency ($\omega = 2\pi f$) in the range 0.1–100 rad/s. Dynamic oscillatory experiments were run using strain amplitudes (γ_0) in the linear viscoelastic range (e.g., $\gamma_0 = 0.08$). All experiments were carried out at a temperature of 290°C under a nitrogen atmosphere unless otherwise stated. Dry-blended samples were presheared under a nitrogen atmosphere at 5 s^{-1} for 1 min to provide additional mixing. A recovery time of 30 s was allowed following the preshear prior to starting subsequent rheological measurements. Time sweep experiments were carried out on all samples at 280, 290, and 300°C under both nitrogen and air atmospheres in which $|\eta^*|$ at $\omega = 1 \text{ rad/s}$ and $\gamma_0 = 0.08$ was measured.

Microscopy

The state of mixing and morphology of the blends prepared by both dry and melt blending was examined by means of scanning electron microscopy. Scanning electron microscopy was carried out using a Cambridge Stereoscan S200 electron microscope. Melt-blended samples were prepared by means of cryogenic fracture of extruded strands after immersion in liquid nitrogen for 5 min. Dry blends were prepared by first preshearing each blend between parallel plates for 1 min at a shear rate of 5 s^{-1} . The blend was then removed from the test fixtures and was cryogenically fractured after immersion in liquid nitrogen for 5 min. The fractured samples were fixed to aluminum stubs and sputter-coated.

RESULTS

The rheological results of this work are organized as follows: The stability of the samples with respect to degradation is discussed in terms of the decrement of $|\eta^*|$ with time. The information obtained on the degradation behavior of the blends and neat polymers is then used to isolate the effect of degradation which occurred during melt blending from that due to the two-phase morphology on the rheological properties of the blends. Specifically, the role played by the two-phase nature of the blends and degradation on the dynamic oscillatory, steady shear, and transient behavior of the blends is discussed.

Viscosity

The change in the magnitude of the complex viscosity, $|\eta^*|$, of the blends and neat polymers as a function of time and temperature was examined because of the extensive degradation reported to occur in PET and nylon 6,6 as well as their blends.¹⁴ Once the decrease in $|\eta^*|$ due to degradation for the samples was determined, the role played by the two-phase nature of the blends on $|\eta^*|$ and the steady shear viscosity, η , as a function of angular frequency and shear rate, respectively, was examined.

The decrease in $|\eta^*|$ with time for the blends and neat polymers in air at temperatures of 290 and 300°C is shown in Figure 1. A logarithmic decay of $|\eta^*|$ with time is observed for all samples. Similar results were reported for PET, nylon 6,6, and their blends by Utracki et al.¹⁴ and were explained in terms of the mechanism of random chain scission which was described by first-order degradation kinetics.²⁴ The magnitude of the complex viscosity of PET is seen to decrease by 30 and 45% in 5 min at 290 and 300°C, respectively. The magnitude of the complex viscosity of nylon 6,6 is seen to decrease by 10 and 28% in 5 min at 290 and 300°C, respectively. At 290°C, the DB-25/75 and DB-50/50 blends degrade at a rate intermediate to that observed for the two neat polymers while the blend rich in PET (e.g., DB-75/25) degrades at a rate faster than that observed for both neat polymers. Both the DB-50/50 and DB-75/25 blends show a rate of decrease in complex viscosity with time as the temperature is increased to 300°C which is faster than that of the neat polymers at the same temperature.

To quantify the decrease in the magnitude of the complex viscosity with time, the isothermal logarithmic decrement of viscosity (D) for all samples was computed by fitting time sweep data taken at $\omega = 1$ rad/s, $\gamma_0 = 0.08$, and temperatures of 280, 290, and 300°C using the relationship

$$D = \left(\frac{d \ln |\eta^*|}{dt} \right) \cdot (-10^3) \quad (1)$$

The parameter D was estimated for the samples subjected to extrusion. Assuming that the degradation occurring during extrusion resulted in a logarithmic decrease in viscosity with time as described by eq. (1) and based on a residence of 4.5 min, a value for parameter D was calculated for each sample using the magnitude of the complex viscosity of the samples measured before extrusion (e.g., $|\eta^*|$ at time = 0) and after extrusion (e.g., $|\eta^*|$ at time = 4.5 min). The estimated value of parameter D for

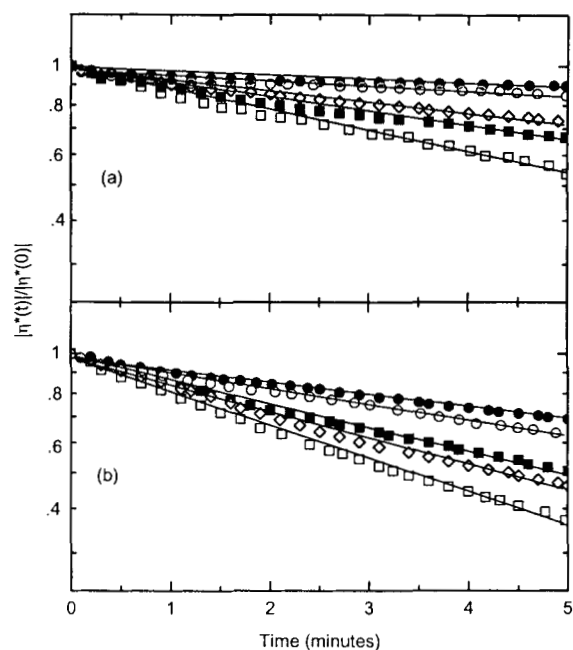


Figure 1 Normalized magnitude of the complex viscosity as a function of time at a fixed frequency of 1 rad/s and a strain of 5% in air at (a) 290°C and (b) 300°C for melt-blended PET/nylon 6,6 samples: (■) 100/0; (□) 75/25; (◇) 50/50; (○) 25/75; (●) 0/100. The lines represent best fits using eq. (1).

the blends was calculated using the value of $|\eta^*|$ at 1 rad/s for the presheared dry blends and the value of $|\eta^*|$ at 1 rad/s for the extruded blends. The estimated value of parameter D for the extrusion process for the neat polymers was calculated using $|\eta^*|$ at 1 rad/s for the neat polymers measured before and after subjecting them to extrusion. The values of D calculated by fitting eq. (1) to the time sweep data and estimated for the extrusion process for the blends and neat polymers are shown in Figure 2 and listed in Table I. The results show that the rate of decrease of $|\eta^*|$ with time due to degradation for the blend at a weight ratio of 25/75 w/w PET/nylon 6,6 corresponds to that predicted using the weighted average of the values of D for the neat polymers. On the other hand, blends of 75/25 and 50/50 w/w PET/nylon 6,6 have values of D higher than the weighted average of D for the neat polymers. Based on these results, the magnitude of the viscosity of melt-blended 25/75 PET/nylon 6,6 blend relative to the extruded neat polymers is independent of the degradation occurring during extrusion. However, the viscosity of the melt-blended 75/25 and 50/50 PET/nylon 6,6 system is reduced relative to that of the neat polymers.

The temperature dependence of the degradation process was calculated in terms of the apparent

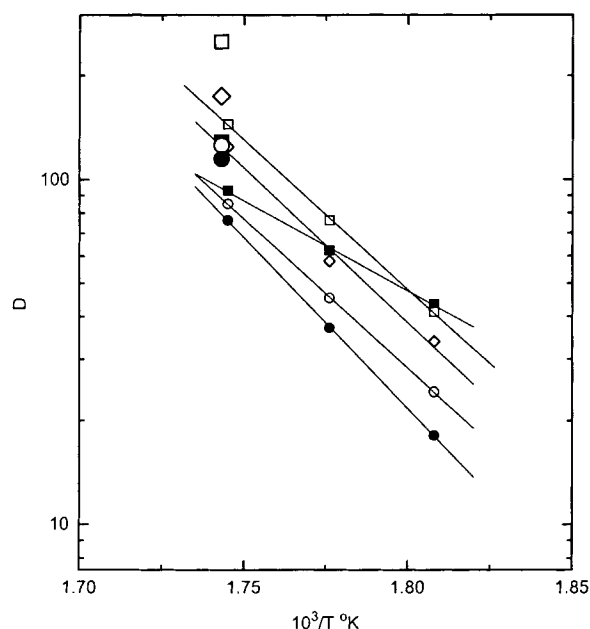


Figure 2 Logarithmic decrement of viscosity as a function of reciprocal temperature based on time sweep measurements for PET/nylon 6,6 samples: (■) 100/0; (□) 75/25; (◇) 50/50; (○) 25/75; (●) 0/100; and estimated for PET/nylon 6,6 samples subject to extrusion: (■) 100/0; (□) 75/25; (◇) 50/50; (○) 25/75; (●) 0/100, estimated for the extrusion process. The lines represent best fits using eq. (2).

overall activation energy of degradation (E_D). The overall activation energy of the degradation process was calculated by fitting the logarithmic decrement of viscosity data shown in Figure 2 obtained using time sweep experiments at $\omega = 1$ rad/s, $\gamma_0 = 0.08$, and temperatures of 280, 290, and 300°C in air using the following relationship:

$$E_D = R \left(\frac{d \ln D}{d(1/T)} \right) \quad (2)$$

where R is the gas constant. The values for E_D determined using eq. (2) are listed in Table I. The values for E_D reported here are within the range reported in the literature for PET^{14,24-26} and nylon 6,6.^{14,27-29} In addition, the value of E_D for the 75/25 w/w PET/nylon 6,6 blend is in agreement with E_D reported for this blend at the same weight ratio by Utracki et al.¹⁴ The estimated values of D for the samples subjected to the extrusion process are also shown in Figure 2 plotted at the maximum barrel temperature used during extrusion (e.g., 290°C). It can be seen that for the extruded neat polymers and blends the values of D estimated for the samples subjected to the extrusion process at 290°C far exceed those calculated from time sweep measurements at 290°C and do not fall on the curves predicted using eq. (2). This discrepancy may be related to the conditions during extrusion (e.g., viscous heating and exposure to moisture) which are not experienced during time sweep experiments.

To determine the stability of the blends and neat polymers during rheological experiments, time sweeps were also performed on the samples at 290°C under a nitrogen atmosphere. The change in $|\eta^*|$ with time for the melt- and dry-blended samples and the neat polymers before and after extrusion in a nitrogen atmosphere are shown in Figure 3. A logarithmic decrease in the viscosity with time is also observed for samples tested in nitrogen. The values of parameter D for the samples tested in nitrogen calculated using eq. (1) are listed in Table II. It can be seen by comparison of the values of D listed in Tables I and II that the rate of degradation in nitrogen is lower than in air. The degradation behavior of the neat polymers both before and after extrusion is seen to be the same. In the case of PET, a decrease in $|\eta^*|$ of approximately 9% in 5 min is observed, while $|\eta^*|$ for nylon 6,6 is seen to remain essentially constant within a time frame of 5 min. The rate of

Table I Logarithmic Decrement of Viscosity (D) and the Apparent Overall Activation Energy of Degradation (E_D) in Air for PET/Nylon 6,6 Blends

PET/Nylon 6,6 (w/w)	D (± 2) [ln(Pa-s)/s]				E_D (± 4) (kcal/mol)
	280°C	290°C	300°C	Extrusion ^a	
100/0	43.53	62.52	93.03	129.32	26
75/25	41.28	76.35	145.01	251.81	38
50/50	33.89	58.22	124.85	175.26	41
25/75	24.25	45.42	85.32	125.97	49
0/100	18.12	37.19	76.42	114.87	45

^a Calculated from the magnitude of the complex viscosity of samples before and after extrusion.

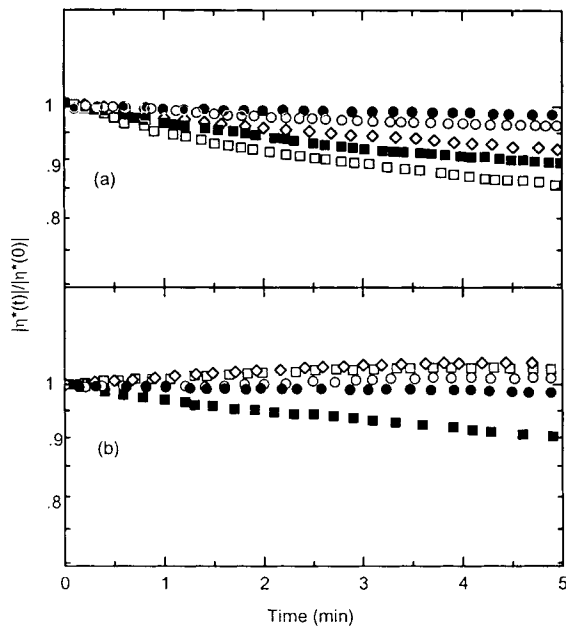


Figure 3 Normalized magnitude of the complex viscosity as a function of time at a fixed frequency of 1 rad/s and a strain of 5% in nitrogen for (a) melt-blended and (b) dry-blended PET/nylon 6,6 samples: (■) 100/0; (□) 75/25; (◇) 50/50; (○) 25/75; (●) 0/100, at 290°C.

the decrease in $|\eta^*|$ with time for the MB-25/75 and MB-50/50 is seen to be between that of the neat polymers (e.g., 3 and 7%, respectively, in 5 min), while the MB-75/25 blend complex viscosity decreases at a rate higher than that of neat PET (e.g., 14% in 5 min). On the other hand, in the case of the dry-blended samples, the complex viscosity is seen to increase slightly with time until approximately 3 min, after which no further change is observed. The increase in complex viscosity (e.g., < 4% in 5 min) with time for the dry-blended samples may be related to the incomplete relaxation of the morphology after preshearing because time sweeps were started approximately 30 s after cessation of the preshear. The results presented here are in contrast to those reported by Utracki et al.¹⁴ in which it was reported that the degradation process measured in terms of the decrease in viscosity with time were the same in both air and nitrogen atmospheres.

The role played by degradation and the two-phase morphology of the blends on $|\eta^*|$ as a function of angular frequency and steady shear viscosity as a function of shear rate was investigated. The magnitude of the complex viscosity of the MB-25/75, MB-50/50, and MB-75/25 blends as a function of angular frequency is shown in Figure 4 along with that of the neat extruded polymers (MB-PET and MB-nylon 6,6). The magnitude of the complex viscosity of the MB-75/25 and MB-50/50 blends is be-

Table II Logarithmic Decrement of Viscosity (D) in Nitrogen PET/Nylon 6,6 Blends

PET/Nylon 6,6 (w/w)	$D (\pm 2) [\ln(\text{Pa}\cdot\text{s})/\text{s}]$
Dry blends	
100/0	18.75
75/25	0 ^a
50/50	0 ^a
25/75	0 ^a
0/100	9.72
Melt blends	
100/0	20.15
75/25	34.50
50/50	20.98
25/75	19.74
0/100	9.91

^a An increase in complex viscosity was observed in these blends and may be related to a relaxing morphology following preshearing.

low that of the neat polymers. The reduced $|\eta^*|$ of the MB-75/25 and MB-50/50 blends relative to that of the neat polymers can be correlated directly to the higher rate of degradation of the blends during extrusion than that of the neat polymers. A higher value of $|\eta^*|$ for the MB-75/25 and MB-50/50 blends than the neat polymers would be observed in the absence of degradation. The MB-25/75 blend has higher values of $|\eta^*|$ than those of the neat polymers at all but the highest angular frequency

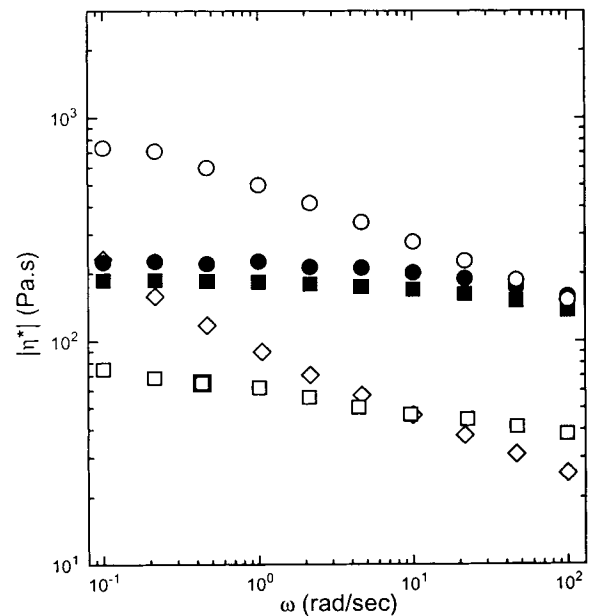


Figure 4 Magnitude of the complex viscosity as a function of frequency at 290°C for melt-blended PET/nylon 6,6 samples: (■) 100/0; (□) 75/25; (◇) 50/50; (○) 25/75; (●) 0/100.

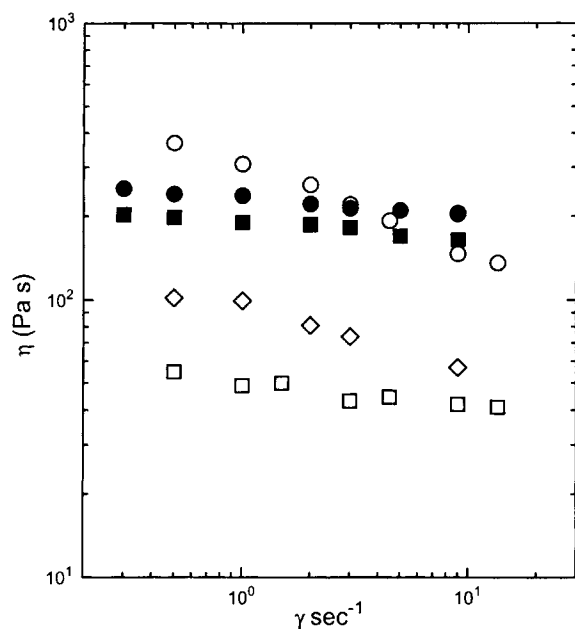


Figure 5 Steady shear viscosity as a function of shear rate at 290°C for melt-blended PET/nylon 6,6 samples: (■) 100/0; (□) 75/25; (◇) 50/50; (○) 25/75; (●) 0/100.

measured. Because parameter D calculated from time sweep experiments and estimated for the extrusion process for the 25/75 PET/nylon 6,6 blend is between that of the neat polymers (see Table I and Fig. 1), the higher values of $|\eta^*|$ relative to those of the neat polymers can be attributed to the two-phase nature of the blend and not to degradation. The steady shear viscosity as a function of shear rate for the MB-25/75, MB-50/50, and MB-75/25 blends shown in Figure 5 displays similar qualitative behavior as the complex viscosity as a function of angular frequency for these blends. It can also be seen that both the 75/25 and 50/50 PET/nylon 6,6 blends display a greater degree of shear thinning than do the neat polymers with the highest degree of shear thinning being seen in the 75/25 blend. The observed shear thinning cannot be explained in terms of degradation occurring during the dynamic oscillatory and steady shear experiments. An apparent yield stress was observed by Utracki et al.¹⁴ in PET/nylon 6,6 blends by an upturn of the viscosity at low shear rates at 280°C but was not observed at 285 and 290°C. Utracki et al. attributed the apparent yield stress to associations of the dispersed phase at 280°C which were destroyed at 285–290°C. The higher viscosity of the MB-25/75 blend than that of the neat polymers can most likely be attributed to the two-phase morphology. The lower viscosity of the MB-75/25 and MB-50/50 blends relative to the neat polymers can be attributed to degradation.

To confirm that the lower values of viscosity for the MB-75/25 and MB-50/50 blends relative to those of the neat polymers are a result of the accelerated degradation which occurs for these blends relative to the neat polymers during extrusion, frequency sweeps were also carried out on the dry-blended samples and neat polymers without subjecting them to extrusion (see Fig. 6). The data in Figure 6 shows that all three blends display a higher viscosity than that of the neat polymers. These results show that the blend rich in PET (e.g., DB-75/25) has the highest viscosity followed by the DB-50/50 blend and, finally, the DB-25/75 blend. In contrast to the melt-blended samples, the enhanced shear thinning behavior relative to the neat polymers is not observed in the dry-blended samples which may be due to the shear thinning behavior of the neat polymers themselves.

The magnitude of the complex viscosity and the steady shear viscosity and rate of degradation of the blends relative to that of the neat polymers can also be correlated to the morphology of the blends. The higher rate of degradation and lower viscosity of the MB-75/25 and MB-50/50 blends as compared to the neat polymers corresponds to a larger dispersed phase size than is observed in the MB-25/75 blend (see Fig. 7). The dispersed phase of nylon 6,6 for the MB-75/25 and MB-50/50 blends [Fig. 7(a) and (b), respectively] has dimensions in the range of 10–30

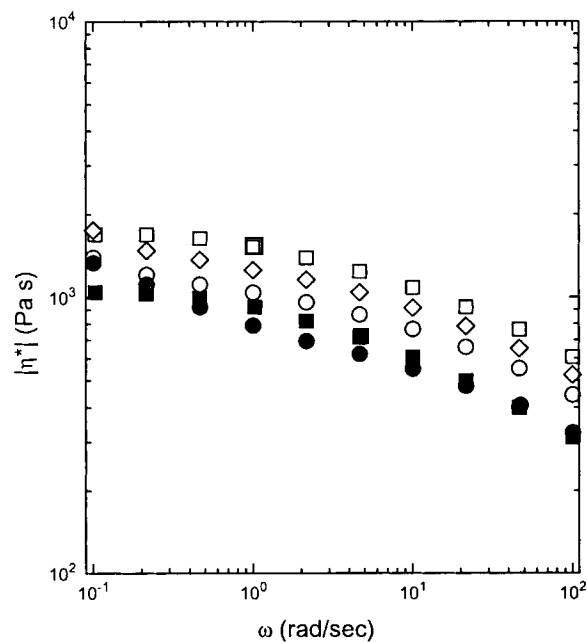


Figure 6 Magnitude of the complex viscosity as a function of frequency at 290°C for dry-blended PET/nylon 6,6 samples: (■) 100/0; (□) 75/25; (◇) 50/50; (○) 25/75; (●) 0/100.

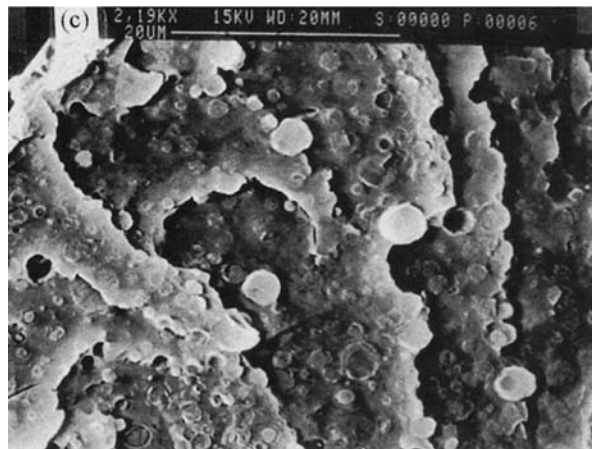
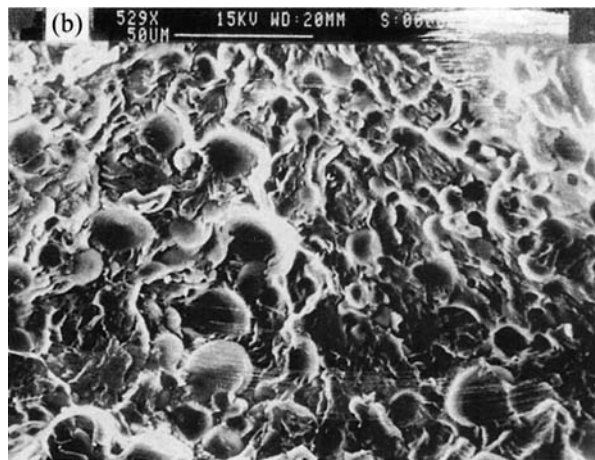
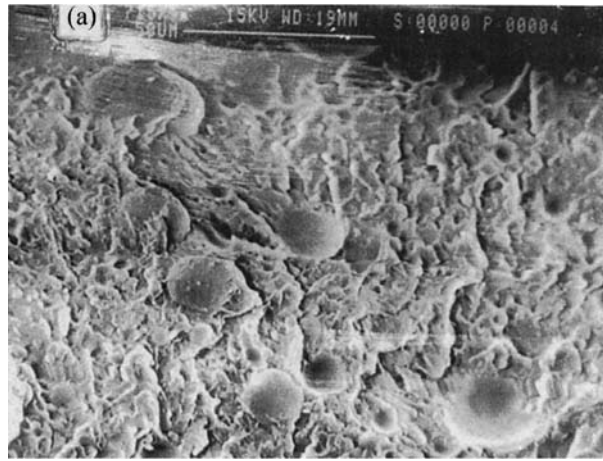


Figure 7 Scanning electron micrographs of melt-blended PET/nylon 6,6 samples: (a) 75/25; (b) 50/50; (c) 25/75.

μm in diameter. The MB-25/75 blend [see Fig. 7(c)] has a dispersed phase of PET with dimensions on the order of $5 \mu\text{m}$ in diameter. A similar dispersed

phase size for the MB-25/75 blend is seen for the dry-blended samples at all three weight ratios (see Fig. 8) and also corresponds to a viscosity which is higher than that of the neat polymers. The DB-75/25 and DB-50/50 blends [see Fig. 8(a) and (b)] have

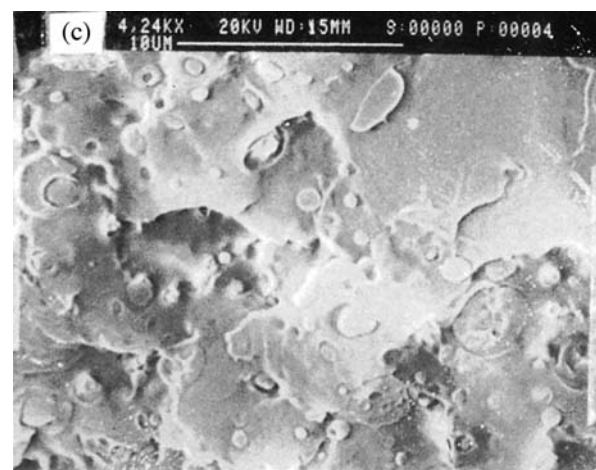
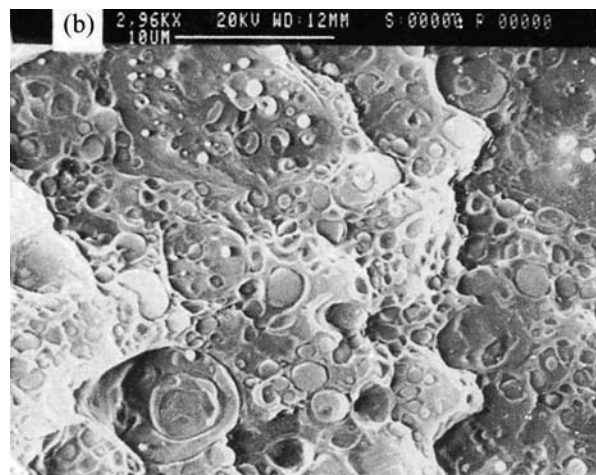
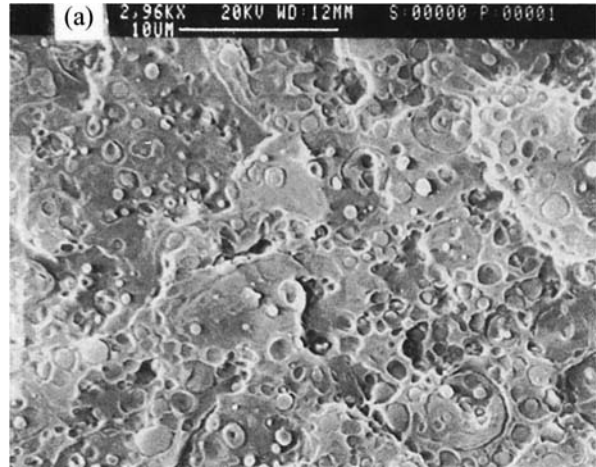


Figure 8 Scanning electron micrographs of dry-blended PET/nylon 6,6 samples: (a) 75/25; (b) 50/50; (c) 25/75.

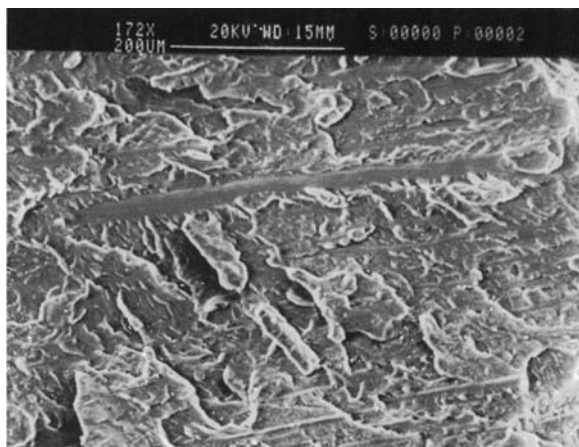


Figure 9 Scanning electron micrographs of melt-blended 25/75 PET/nylon 6,6 sample quenched after shear flow.

a dispersed phase of nylon 6,6 with drop sizes ranging from 1 to 5 μm in diameter and the DB-25/75 blend [see Fig. 8(c)] has a dispersed phase of PET with drop sizes also ranging from 1 to 5 μm . A higher rate of degradation of the blend relative to the neat polymers corresponds to a larger dispersed phase size and a blend viscosity which is lower than that of the neat polymers. The dispersed phase size is small and the viscosity of the blend is higher than that of the neat polymers when the rate of degradation of the system during blending is similar to that of the neat polymers (e.g., MB-25/75 blend) or when the extent of degradation is low (i.e., dry-blended samples). The larger dispersed phase size of the MB-75/25 and MB-50/50 blends may be related to the fact that PET degrades more during blending and, hence, it is more difficult to reach the critical Weber number (i.e., ratio of viscous stresses to interfacial stresses) at which a droplet will burst.

The effect of large strains and deformation on the dispersed phase during shear flow was examined by comparing η and $|\eta^*|$ for the blends to those of the neat polymers. The magnitude of the complex viscosity of the blend relative to that of the neat polymers (see Fig. 4) is higher than the steady shear viscosity of the blend relative to that of the neat polymers (see Fig. 5). This may be due to the deformability of the dispersed phase during shear flow. The deformability of the dispersed phase of the MB-25/75 blend is demonstrated in Figure 9 in which the sample was quenched following shear flow. It can be seen that the drops of the dispersed phase (PET) readily deform during shear flow and result in a texture consisting of both drops (with diameters on the order of 5 microns) and deformed drops or fibrils (with diameters ranging from 5 to 25 microns)

oriented in the flow direction. At a shear rate of 0.5 s^{-1} , the value of η of the MB-25/75 blend is 1.7 times higher than η based on the weighted average (by weight fraction) of η of the neat polymers. At $\omega = 0.46 \text{ rad/s}$, the value of $|\eta^*|$ of the MB-25/75 blend is three times higher than $|\eta^*|$ based on the weighted average (by weight fraction) of $|\eta^*|$ of the neat polymers. These results indicate that the contribution from the two-phase morphology is lower when the dispersed phase is oriented in the flow direction than when the dispersed phase is in the form of drops.

Steady-state First Normal Stress Difference and Storage Modulus

Next, we turn our attention to the elastic properties of the blends as determined by N_1 and G' . The elastic properties of the PET/nylon 6,6 blend system measured in terms of N_1 and G' display similar deviation from those of the neat polymers as was observed in the viscous properties at 290°C. It can be seen in Figures 10 and 11 that the MB-75/25 blend shows a negative deviation of both N_1 and G' from those of the neat polymers. The MB-50/50 blend displays N_1 and G' values which are similar in magnitude to those of the neat polymers. In the case of the MB-25/75 blend, a positive deviation of N_1 and G' from those of the neat polymers is observed. The lower values of N_1 and G' of the MB-75/25 and MB-50/

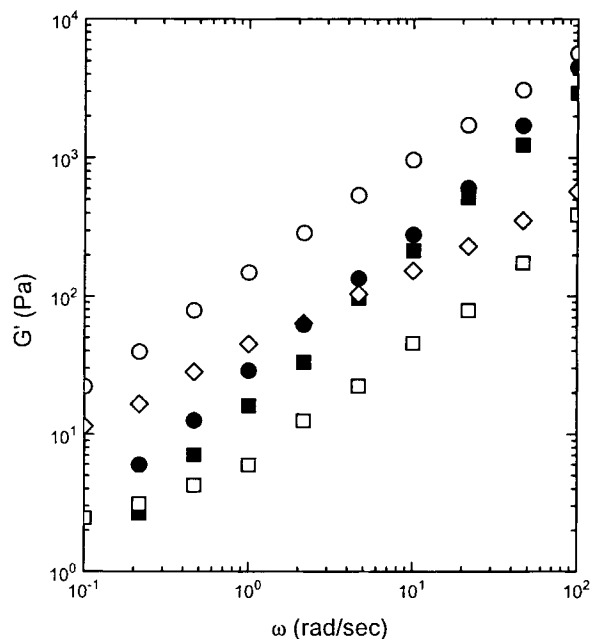


Figure 10 Storage modulus as a function of frequency at 290°C for melt-blended PET/nylon 6,6 samples: (■) 100/0; (□) 75/25; (◇) 50/50; (○) 25/75; (●) 0/100.

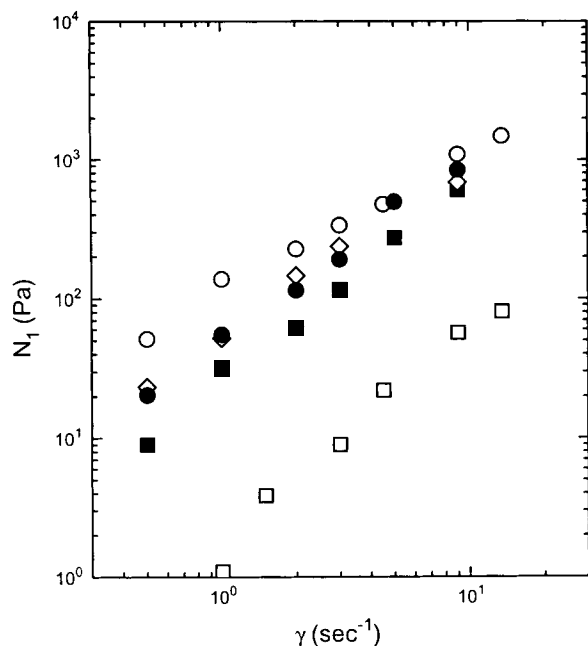


Figure 11 Steady-state first normal stress difference as a function of shear rate at 290°C for melt-blended PET/nylon 6,6 samples: (■) 100/0; (□) 75/25; (◇) 50/50; (○) 25/75; (●) 0/100.

50 blends relative to those of the neat polymers may be related to the higher rate of degradation of the samples during melt blending.

To determine the role played by the two-phase morphology obtained by blending PET and nylon 6,6 in the absence of significant degradation on G' , the storage modulus of the dry-blended samples was also measured and is shown in Figure 12 along with that of the neat polymers. It can be seen that a positive deviation is observed at all three weight ratios, with G' for the DB-75/25 blend being the highest.

A comparison of the relative deviation of the values of N_1 and G' of the blends at all three concentrations from that of the blend constituents reveals the effect of the different textures present during each rheological test (e.g., drops, elongated drops, and fibrils in steady shear experiments and only drops in small amplitude dynamic oscillatory experiments). At a shear rate of 0.5 s^{-1} , the value of N_1 of the MB-25/75 blend is 3.2 times higher than N_1 based on the weighted average (by weight fraction) of N_1 of the neat polymers. At $\omega = 0.46 \text{ rad/s}$, the value of G' of the MB-25/75 blend is 6.5 times higher than is G' based on the weighted average (by weight fraction) of G' of the neat polymers. These results indicate that the elastic contribution from the two-phase morphology relative to the neat polymers decreases with orientation of the dispersed phase in the flow direction.

Transient Shear Stress and First Normal Stress Difference

The transient shear stress and first normal stress difference of the blends are discussed in this section. The transient experiments performed include start up of shear flow, stepwise changes of shear flow, and interrupted stress growth experiments. Using these experiments, the role of interfacial tension and degradation on the transient rheology of the PET/nylon 6,6 blend was examined.

The transient shear stress at the start up of steady shear flow for the melt-blended and dry-blended samples at all three weight ratios is shown in Figures 13 and 14, respectively. The shear stress at the start up of shear flow for the extruded neat polymers (see Fig. 13) is seen to increase monotonically to the steady-state values. The MB-25/75 blend displays a large overshoot at the start up of shear flow followed by a monotonic decrease to a steady state value which is higher than that of the neat polymers. The presence of an overshoot may be associated with the two-phase morphology of the blend, because this behavior is not observed in either neat polymer. While the MB-50/50 blend also displays an overshoot at start up of shear flow, the peak value of stress is small relative to the steady-state value. In the case of the MB-75/25 blend, no overshoot is observed at the start up of shear flow. The reduction in the magnitude of the overshoot relative to the

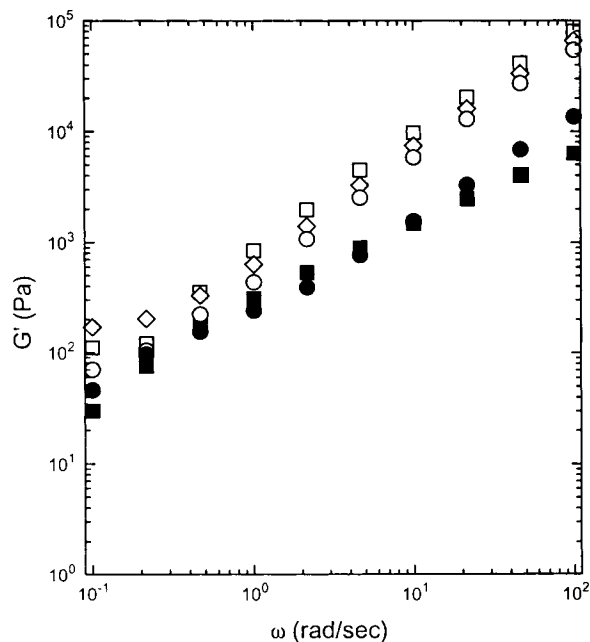


Figure 12 Storage modulus as a function of frequency at 290°C for dry-blended PET/nylon 6,6 samples: (■) 100/0; (□) 75/25; (◇) 50/50; (○) 25/75; (●) 0/100.

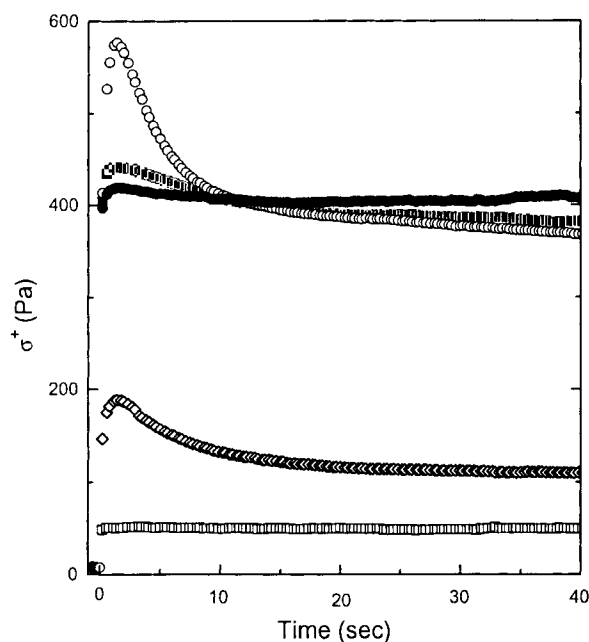


Figure 13 Transient shear stress at the start up of shear flow at 290°C and a shear rate of 1 s^{-1} for melt-blended PET/nylon 6,6 samples: (■) 100/0; (□) 75/25; (◇) 50/50; (○) 25/75; (●) 0/100.

steady-state shear stress with an increase in PET content may be correlated to the increase in the extent of degradation occurring during extrusion. The enhancement of the overshoot is seen clearly in the dry-blended samples at all weight ratios (see Fig. 14). Although the neat polymers which have not been degraded by extrusion show an overshoot, the overshoot for the dry-blended samples is larger than that of the neat polymers, and much larger strains are required to reach the steady state. The presence of the overshoot in the melt-blended samples and enhancement of the overshoot in the dry-blended samples may be associated with the two-phase morphology because these phenomena are not seen in the rheological behavior of the neat polymers. The transient first normal stress difference for the MB-25/75 blend at the start up of shear flow displays enhanced behavior due to the two-phase morphology when compared to data for the neat polymers (see Fig. 15). This behavior consists of an overshoot which is not seen in the neat polymers, the MB-75/25, or the MB-50/50 blends.

The overshoot observed in the start up of shear flow experiments for the MB-25/75 blend was investigated further using interrupted stress growth experiments. Interrupted stress growth experiments were carried out by first shearing the samples at a shear rate of 1 s^{-1} for 45 s and then allowing the samples to recover for increasing amounts of time

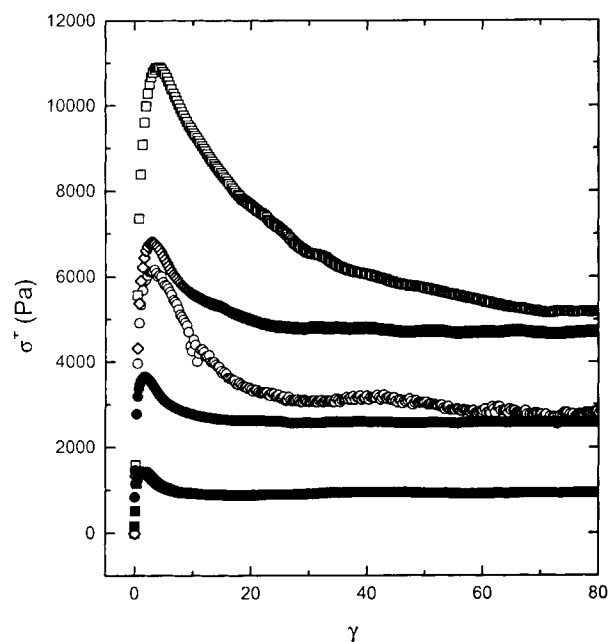


Figure 14 Transient shear stress at the start up of shear flow at 290°C and a shear rate of 1 s^{-1} for dry-blended PET/nylon 6,6 samples: (■) 100/0; (□) 75/25; (◇) 50/50; (○) 25/75; (●) 0/100.

before performing start up of shear flow again. The recovery of the overshoot associated with a recovery of the equilibrium texture can be seen in Figure 16 for the MB-25/75 blend where the shear stress is

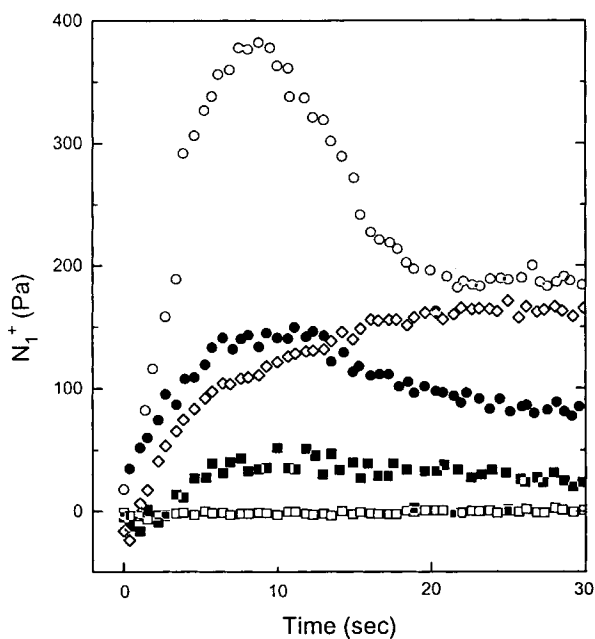


Figure 15 Transient first normal stress difference at the start up of shear flow at 290°C and a shear rate of 1 s^{-1} for melt-blended PET/nylon 6,6 samples: (■) 100/0; (□) 75/25; (◇) 50/50; (○) 25/75; (●) 0/100.

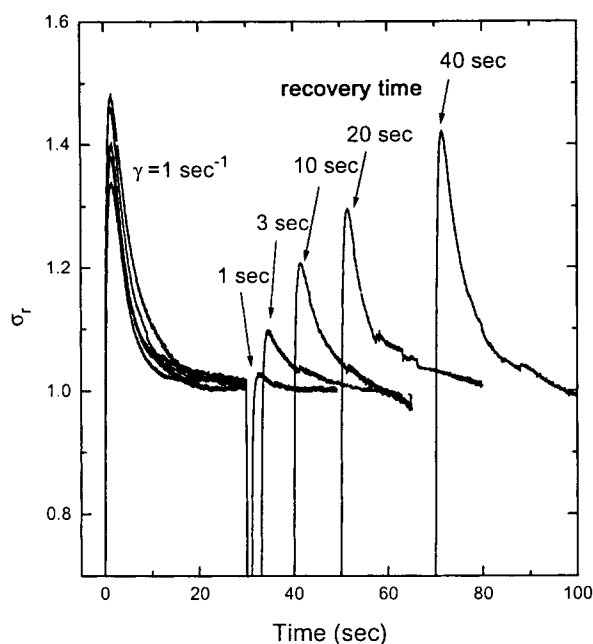


Figure 16 Transient reduced shear stress $\sigma_r = \sigma^+(t, \dot{\gamma}_0)/\sigma(\dot{\gamma}_0)$ vs. time using interrupted stress growth experiments as function of recovery time for the melt-blended 25/75 PET/nylon 6,6 sample at 290°C.

reduced by the steady state shear stress [e.g., $\sigma_r = \sigma^+(t, \dot{\gamma}_0)/\sigma(\dot{\gamma}_0)$]. In this figure, it can be seen that 40 s are required to achieve approximately 90% recovery of the overshoot for the MB-25/75 blend.

The transient shear stress from step-up and step-down experiments for all three melt-blended samples and the extruded neat polymers is shown in Figures 17 and 18. Step-up experiments were carried out using a constant step-up ratio ($\dot{\gamma}_1/\dot{\gamma}_0 = 3$), and the data are plotted as function of the scaled stress (σ_s):

$$\sigma_s = \frac{\sigma^+(t, \dot{\gamma}_1) - \sigma(\dot{\gamma}_0)}{\sigma(\dot{\gamma}_1) - \sigma(\dot{\gamma}_0)} \quad (3)$$

and strain (γ_1):

$$\gamma_1 = \dot{\gamma}_1 \cdot t \quad (4)$$

In the case of the neat polymers [Fig. 17(a) and (e)] and the MB-75/25 blend [Fig. 17(b)], the stress is seen to increase monotonically to steady-state values while an overshoot is observed in the MB-50/50 and MB-25/75 blends [Fig. 17(c) and (d), respectively] with the overshoot of the MB-25/75 blend being higher. It can also be seen that the transients for the blends when plotted in the above-mentioned manner superimpose to form a single curve regardless of the shear rate, $\dot{\gamma}_1$. The transient shear stress from step-down experiments for all three melt-

blended samples and the extruded neat polymers is shown in Figure 18. The step-down experiments were carried out at a constant step-down ratio ($\dot{\gamma}_0/\dot{\gamma}_1 = 3$), and the data are plotted in reduced form as described above in eqs. (3) and (4). In the case of the neat polymers [Fig. 18(a) and (e)] and the MB-75/25 blend [Fig. 18(b)], the shear stress is seen to decrease monotonically to the final steady-state value while an undershoot is observed in the MB-50/50 and MB-25/75 blends [Fig. 18(c) and (d), respectively] with the undershoot of the MB-25/75 blend being greater. It can also be seen that the transients from the step-down experiments for the blends when plotted in the above-mentioned manner also superimpose to form a single curve regardless of the shear rate, $\dot{\gamma}_1$. This scaling relationship has been observed in some liquid crystalline polymers^{30,31,32} with a polydomain texture and has recently been found to hold for immiscible mixtures of Newtonian fluids consisting of oils at all volume ratios tested.³³ These results indicate by removal of the time scale associated with the applied flow that there appears to be no intrinsic time constant for these blends. This result only holds when the shear rate used is less than the reciprocal of the longest relaxation time of the neat polymers. Similar scaling of the shear stress for the samples prepared by dry blending was not observed and may be due to in-

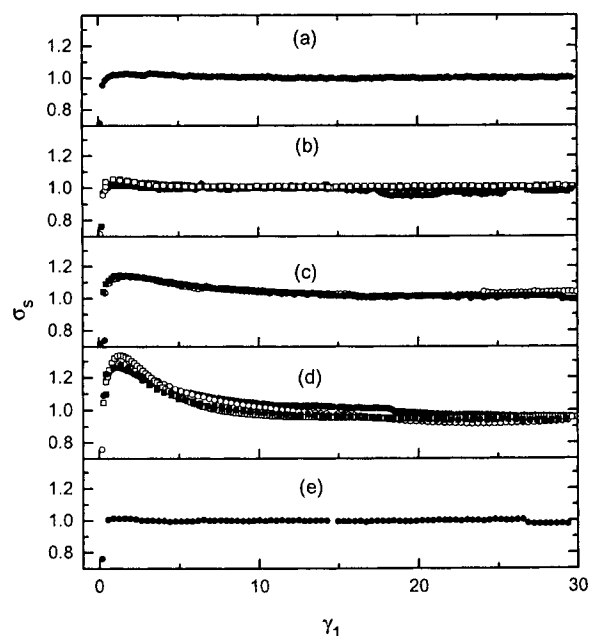


Figure 17 Transient scaled shear stress $\sigma_s = [\sigma^+(t, \dot{\gamma}_1) - \sigma(\dot{\gamma}_0)]/[\sigma(\dot{\gamma}_1) - \sigma(\dot{\gamma}_0)]$ vs. γ_1 , where $\dot{\gamma}_1/\dot{\gamma}_0 = 3$ and $\dot{\gamma}_1$ is (○) 0.5 s⁻¹, (●) 1.0 s⁻¹, (■) 1.5 s⁻¹, and (□) 3 s⁻¹ for melt-blended PET/nylon 6,6 samples: (a) 100/0; (b) 75/25; (c) 50/50; (d) 25/75; (e) 0/100 at 290°C.

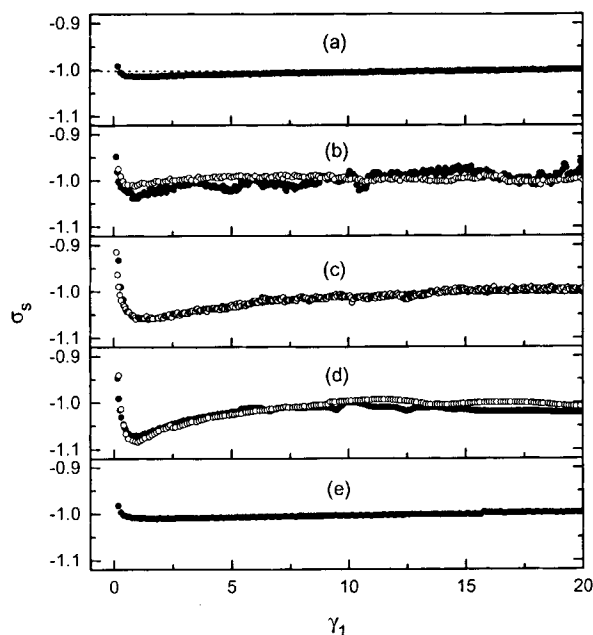


Figure 18 Transient scaled shear stress $\sigma_s = [\sigma^+(t, \dot{\gamma}_1) - \sigma(\dot{\gamma}_0)] / [\sigma(\dot{\gamma}_1) - \sigma(\dot{\gamma}_0)]$ vs. $\dot{\gamma}_1$, where $\dot{\gamma}_0/\dot{\gamma}_1 = 3$ and $\dot{\gamma}_1$ is (O) 1 s^{-1} and (●) 0.5 s^{-1} for melt-blended PET/nylon 6,6 samples: (a) 100/0; (b) 75/25; (c) 50/50; (d) 25/75; (e) 0/100 at 290°C .

complete mixing and the long relaxation times of the neat polymers which were not degraded by extrusion.

CONCLUSIONS

The rheological properties of PET/nylon 6,6 blends were found to be a strong function of polymer degradation during melt blending and while making rheological measurements. A high rate of degradation for PET, nylon 6,6 and PET/nylon 6,6 blends was found to occur during melt blending in an extruder due to the exposure of the materials to moisture. The rate of degradation for the blend at a weight ratio of 25/75 PET/nylon 6,6 was between that of the neat polymers and was higher than that of the neat polymers for the blends at weight ratios of 75/25 and 50/50 w/w PET/nylon 6,6. The lower values of $|\eta^*|$, η , G' , and N_1 of the blends relative to those of the extruded neat polymers were found to be a consequence of the accelerated rate of degradation occurring for the 75/25 and 50/50 w/w PET/nylon 6,6 blends relative to the neat polymers during melt blending in an extruder.

The role played by the two-phase nature on the rheological properties of 75/25, 50/50, and 25/75 w/w PET/nylon 6,6 blends was observed using samples prepared by dry blending and mixing in

cone-and-plate fixtures under a nitrogen atmosphere and the melt-blended 25/75 w/w PET/nylon 6,6 system. The 25/75 PET/nylon 6,6 blend prepared by mixing in an extruder exhibited rheological properties which had to be a function of its two-phase nature because they were not seen in the rheological properties of the neat polymers. The two-phase nature of the dry-blended samples and the extruded 25/75 w/w PET/nylon 6,6 blend resulted in values of $|\eta^*|$, η , G' , and N_1 which were higher than those of the neat polymers. The effect of the two-phase nature of the blends was also observed in enhanced transient shear and first normal stress difference behavior relative to that of the neat polymers. The enhanced transient behavior consisted of a large overshoot at the start up of shear flow which was found to recover upon cessation of shear flow using interrupted stress growth experiments. In addition, an overshoot was observed using step-up experiments and an undershoot was observed using step-down experiments. The transients observed using stepwise changes of shear rate were found to superimpose when plotted in reduced form, indicating that at rates lower than the reciprocal of the longest relaxation time of the neat polymers there was no intrinsic time constant associated with the deformation of the interface in the blends.

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