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Department of Chemical Engineering Polymeric Materials and Interfaces Laboratory, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061-2011

Synopsis

The theory developed by Doi and Ohta was evaluated for its ability to predict the rheology of an immiscible polymer blend. The theory describes the additional stresses arising as a consequence of interfacial tension in two phase systems in which the constituents consist of Newtonian fluids and have equal viscosities. The blend considered in this paper consisted of an immiscible mixture of poly(ethylene terephthalate) (PET) and nylon 6,6 at a composition ratio of 25/75 w/w PET/nylon 6,6. The rheological properties of this blend were found to be stable for the time frame required for the rheological experiments used in this work (e.g., < 5 min). The Doi–Ohta theory was found to be capable of qualitatively predicting the extra stresses arising as a result of the interfacial tension as observed in the steady state viscosity and steady state first normal stress difference. The transient shear stress and first normal stress difference at the start up of steady shear flow were qualitatively predicted by the Doi–Ohta theory while the recovery of the initial overshoot observed experimentally was not. The overshoot observed experimentally during step-up experiments and the undershoot observed during step-down experiments were not predicted by the theory in which it was predicted that the stresses change monotonically with a stepwise change of the shear rate to the final steady state value. While the shear thinning behavior observed for this blend was not predicted by the theory, the scaling relation for the transient stresses predicted by the theory was found to hold for the blend using stepwise changes of shear rate at a constant step ratio. © *1996 Society of Rheology.*

I. INTRODUCTION

When two immiscible polymers are mixed a complex morphology is formed. In immiscible polymer blends, one of the phases may consist of drops which during flow undergo deformation, breakup, and coalescence. Materials in which a two-phase microstructure exists are referred to as "textured fluids" [Doi (1987)]. Under an applied flow field textured fluids undergo complex structural changes and as a consequence may exhibit rheological properties which are a function of their texture and are not seen in the individual phases [Utracki *et al.* (1982); Scholz *et al.* (1989); Doi and Ohta (1991); Gramespacher and Meissner (1992)].

Investigations of the rheological behavior of polymer blends have shown a number of peculiarities that are not well understood at this time [Utracki *et al.* (1982)]. These peculiarities include, but are not limited to, a significant degree of overshoot upon start up

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[a)]Corresponding author.

of simple shear flow [Nobile *et al.* (1990)], apparent yield stresses [Utracki *et al.* (1982)], and a viscosity which relative to the log additivity of the viscosity of the neat polymers can be: (1) higher (positive deviation); (2); lower (negative deviation); and (3) higher and lower (positive–negative deviation) depending on shear stress or shear rate [Utracki (1982)].

In order to predict the rheology of immiscible polymer blends, the stresses arising as a consequence of the viscoelastic nature of the neat polymers as well as the extra stresses arising as a consequence of interfacial tension must be accounted for. During flow a complex texture is developed as a result of the mechanisms of drop deformation, breakup, and coalescence. Each of these mechanisms must be accounted for in any suitable theory. The mechanisms of drop deformation, breakup, and coalescence have each received considerable attention for purely viscous fluids by studying dilute systems [Elmendorp (1980); Utracki and Shi (1992)]. A single Newtonian drop in a Newtonian matrix was studied in the pioneering work of Taylor (1934). The velocity and pressure fields inside and outside the droplet were calculated, and it was determined that the deformation of the droplet could be expressed by means of two dimensionless parameters: (1) the capillary number; and (2) the viscosity ratio. It was shown that for a given drop diameter the smaller the viscous stresses relative to the interfacial stresses (e.g., the capillary number was small), the less the droplet deformed. As the viscous stresses became larger relative to the interfacial stress the droplet deformed more until at some critical ratio of these forces (e.g., the critical capillary number) the deformed droplet burst. While the work of Taylor has subsequently been continued for Newtonian fluids by a number of researchers [Utracki and Shi (1992)], little work has considered the deformation and breakup of drops in viscoelastic systems and even less work has been concerned with concentrated systems in which coalescence plays an important role.

A theory was developed by Doi and Ohta (1991) which attempted to predict the rheology of textured fluids. In the theory of Doi and Ohta it was predicted that viscoelastic behavior arises for two-phase fluids in which the constituents are Newtonian and have equal viscosities as a consequence of the additional stresses generated during flow due to interfacial tension. The stresses arising as a consequence of interfacial tension were assumed in the theory to change with the deformation and relaxation of the interface during flow (drop deformation, coalescence, and breakup). The relaxation of the size and shape of the interface due to interfacial tension was accounted for in the theory by two first-order kinetic equations. It was predicted by the Doi–Ohta theory that the shear stress and first normal stress difference were proportional to the shear rate and that transient stresses superimpose when the time scale associated with the flow was removed. This scaling phenomenon arises because the system was characterized by the viscosity and the interfacial tension from which a quantity with units of time could not be constructed. The scaling relation for the system as described by Doi and Ohta indicated that there was no intrinsic time constant associated with the deformation and relaxation of the interface.

The scaling relation predicted by the Doi–Ohta theory was examined experimentally using mixtures of immiscible Newtonian fluids in an investigation by Takahashi *et al.* (1994). The textured fluids considered in their investigation included mixtures consisting of polydimethylsiloxanes (a silicone oil) and hydrocarbon–formaldehyde resins at several volume fractions. The shear stress and the first normal stress difference for the mixtures were found to be nearly proportional to the shear rate, and plots of scaled transient stresses after a stepwise change of the shear rate against strain were found to superimpose on a single curve. On the other hand, the overshoot observed upon stepping up the shear rate and the undershoot observed upon stepping down the shear rate are not predicted by

the Doi–Ohta theory in which it is predicted that the stresses change monotonically to the final steady state value.

The ability of the Doi–Ohta theory in modified form to predict the rheology of a textured fluid consisting of an immiscible polymer blend was recently investigated [Lee and Park (1994)]. The system considered in the work by Lee and Park was an immiscible mixture of polystyrene (PS) and linear low-density polyethylene (LLDPE) at concentrations ranging from 10 to 90 wt % PS. The original theory of Doi and Ohta (1991) was modified to account for a mismatch in the viscosities of the polymers. This modification consisted of the contribution to the stress tensor from the viscosity ratio of the polymers as described by the theories of Schowalter *et al.* (1968) and Mellema and Willemse (1983) in which nearly spherical drops were considered. The theory was also modified with an additional kinetic equation associated with the relaxation of the interface due to droplet breakup (the original theory does not account for this mechanism explicitly). Their results showed good agreement between the experimental and predicted storage and loss moduli. Although good agreement was observed between predicted and experimental small amplitude dynamic oscillatory properties, model predictions for steady shear and transient experiments in which the mechanisms of coalescence and breakup play a large role were not reported.

The objective of this paper is to determine whether the theory proposed by Doi–Ohta can model the steady shear viscosity, steady state first normal stress difference, and transient shear stress and first normal stress difference of a textured fluid consisting of an immiscible polymer blend. This is done by comparing the predicted and observed rheological behavior for blends of poly(ethylene terephthalate) (PET) and nylon 6,6 at shear rates lower than the longest relaxation time of the neat polymers ($De < 1$). PET and nylon 6,6 were selected because they nearly meet several conditions of the system described by the Doi–Ohta theory (i.e., the PET and nylon 6,6 used have nearly equal viscosities which are Newtonian over a broad range of shear rates and each has a short relaxation time).

II. SUMMARY OF THE DOI–OHTA THEORY

In order to provide a general understanding of the basis of the theory proposed by Doi and Ohta for mixtures of Newtonian fluids, a summary of the model is presented in this section. The kinetics and rheological properties of the system are discussed, and a semi-phenomenological kinetic equation is described. Specifically, an equation for the time evolution of the size and orientation of the interface as function of interfacial tension and the macroscopic flow field is presented. In addition, the important assumptions included in the derivation are presented, and the behavior predicted by the model is described.

The theory of Doi and Ohta was based on the observation that when two immiscible fluids are sheared, a rather complex interface is formed due to the coalescence, rupture, and deformation of the droplets. The system considered in the development of the theory was that of two immiscible fluids having the same viscosity. The interface of the fluid was regarded as a mathematical surface with no thickness. The theory was then based on the following formulation for the stress tensor [Rosenkleid (1967); Onuki (1987); Doi (1987)] for emulsions of two immiscible liquids having the same viscosity, η_0:

$$\pi_{\alpha\beta} = \eta_0(\kappa_{\alpha\beta} + \kappa_{\beta\alpha}) - \Gamma q_{\alpha\beta} - p\delta_{\alpha\beta}, \tag{1}$$

where $\kappa_{\alpha\beta} = \partial v_\alpha / \partial r_\beta$ is the macroscopic velocity gradient, Γ is the interfacial surface tension, $q_{\alpha\beta}$ is the interface tensor, p is the isotropic pressure, and $\delta_{\alpha\beta}$ is the Kroenecker delta. The sign convention used was such that a tensile stress is taken as a positive stress.

Equation (1) indicates that the total stress consists of contributions from the viscous stress associated with the macroscopic flow (the first term), the stress associated with the interfacial tension (the second term), and the isotropic pressure (the last term). Doi and Ohta used the formulation of the interface tensor as defined by Onuki (1987)

$$q_{\alpha\beta} = \frac{1}{V} \int \left(n_\alpha n_\beta - \frac{1}{3}\delta_{\alpha\beta} \right) dS, \tag{2}$$

where the integral is over the entire surface of the interface S and n_α are the components of the normal to the surface of the interface in the system of volume, V. The interface tensor was assumed to be determined by two factors: (1) the flow field which enlarges and orients the interface; and (2) relaxation of the interface by interfacial tension which opposes these effects. The time evolution of the interface tensor was derived by accounting for the effects of the flow and relaxation by interfacial tension separately,

$$\frac{dq_{\alpha\beta}}{dt} = \frac{dq_{\alpha\beta}}{dt}\bigg|_{flow} + \frac{dq_{\alpha\beta}}{dt}\bigg|_{relax}. \tag{3}$$

The flow term in the time evolution of the interface tensor [Eq. (3)] was derived by considering the case where the expansion and orientation of the interface was driven by the macroscopic flow field and the interfacial tension was zero. The time evolution of the interface tensor due to macroscopic flow was

$$\frac{dq_{\alpha\beta}}{dt}\bigg|_{flow} = -q_{\alpha\gamma}\kappa_{\gamma\beta} - q_{\beta\gamma}\kappa_{\gamma\alpha} + \frac{2}{3}\delta_{\alpha\beta}\kappa_{\mu\eta}q_{\mu\eta} - \frac{Q}{3}(\kappa_{\alpha\beta} + \kappa_{\beta\alpha}) + \frac{q_{\mu\upsilon}\kappa_{\mu\upsilon}}{Q}q_{\alpha\beta}, \tag{4}$$

where Q is the area of the interface per unit volume. The time evolution of the interfacial area per unit volume was

$$\frac{dQ}{dt}\bigg|_{flow} = -q_{\alpha\beta}\kappa_{\alpha\beta}. \tag{5}$$

Next, the contribution to the time evolution of the interface tensor due to relaxation by interfacial tension was derived. The interfacial tension (Γ) was assumed to drive the relaxation of the deformed interface by decreasing the area of the interface and making the system isotropic. Doi and Ohta assumed (for both lack of a better estimate and simplicity) that the relaxation process is described by first-order kinetics. Specifically, a first-order relaxation rate, r_1, was assumed for the interfacial area per unit volume, (Q), and a first-order relaxation rate, r_2, was assumed for the anisotropy ($q_{\alpha\beta}/Q$). The relaxation rates r_1 and r_2 were assumed to be determined by the viscosity η_0, the interfacial tension, Γ, and the configuration of the interface. Although the configuration of the interface was characterized by $q_{\alpha\beta}$ and Q, Doi and Ohta disregarded the dependence of the configuration of the interface on $q_{\alpha\beta}$ and assumed that relaxation rates r_1 and r_2 were determined by η_0, Γ, and Q only. Then by dimensional analysis the kinetic equations for relaxation of interfacial area (Q) and anisotropy ($q_{\alpha\beta}/Q$) were given as

$$\frac{d}{dt}(Q)\bigg|_{relax} = -r_1 Q \tag{6}$$

and

$$\frac{d}{dt}\left(\frac{q_{\alpha\beta}}{Q}\right)\Bigg|_{\text{relax}} = -r_2\left(\frac{q_{\alpha\beta}}{Q}\right), \tag{7}$$

respectively, where

$$r_1 = c\,\frac{\Gamma Q}{\eta_0}, \tag{8}$$

$$r_2 = k\,\frac{\Gamma Q}{\eta_0}, \tag{9}$$

and c and k are unknown parameters. The possibility that these unknown parameters may be related to the volume fraction, ϕ, is discussed later. Next, using Eqs. (6) and (7) the time evolution of the interface tensor due to relaxation by interfacial tension was

$$\frac{d}{dt}(q_{\alpha\beta})\Bigg|_{\text{relax}} = -(r_1+r_2)q_{\alpha\beta}. \tag{10}$$

In the absence of flow Eq. (6) indicates that the system will form a macroscopically phase separated state ($Q = 0$). While a macroscopically phase separated state could occur in systems containing equal volume fractions (which would result in co-continuous phases), in systems where the volume fractions are not equal, the final state will not reach $Q = 0$. In order to account for this aphysical feature of Eq. (6), the theory was modified so that the relaxation of the interfacial area stops when all the drops become spherical. The modified form of the kinetic equation for the relaxation of the interfacial area per unit volume was

$$r_1 = c\,\frac{\Gamma}{\eta_0}\,(\Sigma q_{\alpha\beta}^2)^{1/2}, \tag{11}$$

which assured that the relaxation stopped when the droplets of the minor phase became spherical (i.e., the summation goes to zero when $q_{\alpha\beta} = 0$ and thus r_1 goes to zero).

The time evolution of the interface tensor from the combined effects of enlargement and orientation of the interface due to macroscopic flow and relaxation of the interface due to interfacial tension were found by substituting Eqs. (4), (5), (6), and (8) into Eq. (3) to give

$$\frac{dq_{\alpha\beta}}{dt} = -q_{\alpha\gamma}\kappa_{\gamma\beta}-q_{\beta\gamma}\kappa_{\gamma\alpha}+\frac{2}{3}\delta_{\alpha\beta}\kappa_{\mu\eta}q_{\mu\eta}-\frac{Q}{3}(\kappa_{\alpha\beta}+\kappa_{\beta\alpha})$$

$$+\frac{q_{\mu\nu}\kappa_{\mu\nu}}{Q}q_{\alpha\beta}-\lambda[(1-\mu)Q+\mu(\Sigma q_{\alpha\beta}^2)^{1/2}]q_{\alpha\beta} \tag{12}$$

and the time evolution of the interfacial area was given by

$$\frac{dQ}{dt}\Bigg|_{\text{relax}} = -q_{\alpha\beta}\kappa_{\alpha\beta}-\lambda\mu(\Sigma q_{\alpha\beta}^2)^{1/2}Q, \tag{13}$$

where

$$\lambda = (c+k)\Gamma/\eta_0$$

and

$$\mu = c/(c+k). \tag{14}$$

For a given macroscopic velocity gradient tensor $\kappa(t)$ and initial values of the interfacial area per unit volume $[Q(0) = Q_0]$ and the interface tensor $(q_{\alpha\beta})$, the stresses occurring in a textured system can be calculated using Eqs. (12), (13), and (1).

There is one dimensionless parameter (μ) found in the above equations. If the system is characterized by three parameters η_0, Γ, and ϕ, then μ must be a function of the volume fraction ϕ. The dimensionless parameter, μ, represents the rate of the shape relaxation relative to the total relaxation rate. If $\mu = 0$, then the shape relaxation is rapid, and if $\mu = 1$, the shape relaxation is slow. In this case c can be considered to be a function of the volume fraction of the dispersed phase. At low volume fractions no coalescence takes place, the degree of anisotropy is low, and the interfacial area per unit volume, Q, remains constant with μ equal to zero (c is zero and r_1 is zero). Doi and Ohta regarded μ as a phenomenological parameter.

Several important assumptions were made in the derivation of the theory by Doi and Ohta. The assumptions contained in the above derivation included: (1) the viscosities of both phases were equal; (2) the relaxation of the size and shape of the interface was characterized by first-order kinetics; (3) the overall relaxation of the system during flow was assumed to be governed by only two kinetic equations when it is known that there are three mechanisms associated with the relaxation of the interface (e.g., shape relaxation, coalescence, and breakup); (4) in Eq. (6) it was assumed that the relaxation of Q was controlled by a single relaxation rate, and no distinction was made between the relaxation caused by droplet coalescence (the interfacial area decreases when two droplets coalesce to form a larger droplet) and shape relaxation driven by interfacial tension (the interfacial area of an elongated droplet decreases as the droplet becomes spherical). In dilute mixtures the shape relaxation occurs much faster than the size relaxation (the relaxation due to coalescence), which would be infinitely slow. In the case of concentrated mixtures these two mechanisms are expected to occur with similar speed.

It is predicted by the Doi–Ohta theory that viscoelastic rheological properties for textured fluids consisting of immiscible mixtures of Newtonian fluids arise as a consequence of the interfacial tension. The rheological properties which are predicted by the Doi–Ohta theory include a steady state viscosity which is independent of shear rate (Newtonian), a first normal stress difference which is proportional to the magnitude of the shear rate, a transient overshoot at the start up of shear flow, and a transient stress which scales in stress and strain. Scaling of transient shear stresses has been observed experimentally in textured fluids, which include liquid crystalline polymers [Doppert and Picken (1987); Moldenaers *et al.* (1990)] and immiscible mixtures of Newtonian fluids [Takahashi *et al.* (1994)].

The scaling relationship predicted by the theory is based on the fact that the system is characterized by η_0 and Γ from which a quantity with units of time cannot be constructed. Doi and Ohta showed that a more general scaling relation could be derived. For a given velocity gradient tensor, $\kappa(t)$, the solution of Eqs. (12)–(14) was written as

$$\sigma = \sigma(t;[\kappa(t)]) \tag{15}$$

and then it was shown that for a new velocity gradient tensor $c\kappa(ct)$ that

$$\sigma[t;c\kappa(ct)] = c\sigma(ct;\kappa(t)]), \tag{16}$$

which states that the stress at time t under the velocity gradient $c\kappa(ct)$ is c times larger than the stress at time ct under the velocity gradient $\kappa(t)$. The consequences and significance of this scaling relationship are discussed in Sec. IV as it applies to steady, transient, and oscillatory shear flow.

III. EXPERIMENT

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

A. 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 was determined to have a melting temperature of 257 °C. The recommended drying conditions for PET were 120–125 °C for 3–4 h in vacuum for a moisture content of 0.02%. The nylon 6,6 supplied by Monsanto was Vydyne 66b ($M_w = 30\,000$) and was determined to have a melting temperature of 263 °C. The recommended drying conditions for nylon 6,6 were 75–80 °C for 3–4 h in vacuum. These polymers were chosen because after extrusion, as a consequence of degradation, each neat polymer was characterized by a constant viscosity over a wide range of shear rates, and short relaxation times [Guenther and Baird (1995)]. In addition, these two polymers after extrusion had nearly equal zero shear viscosities as is required by the theory of Doi and Ohta.

A blend was prepared using the polymers described above at a composition ratio of 25/75 w/w PET/nylon 6,6 by mixing in an extruder. This composition ratio was chosen based on the results of a study by Guenther and Baird (1995) in which it was shown that the stability of the blend at a composition of 25/75 w/w PET/nylon 6,6 and the neat polymers was similar after extrusion. It was shown using rheological measurements (e.g., time sweeps) that within the time frame required for the rheological experiments used in this work (e.g., < 5 min), very little change due to degradation in the steady state and transient rheological properties of this blend occurred at 290 °C under a nitrogen atmosphere. Based on their observations the rheological properties of this blend relative to those of the neat extruded polymers were found to be a function of the morphology of the blend and not degradation.

Blending was carried out using dried polymers. 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 in order to minimize exposure time to moisture. 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 in the metering section of the extruder of 4.5 min based on the flow rate and screw dimensions. The neat polymers were subjected to the same processing histories as the blends.

B. Rheological measurements

Rheological experiments were carried out on the blends and neat polymers using a Rheometrics Mechanical 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 were obtained using start up of shear flow experiments after the sample was sheared long enough to reach steady state conditions. Time sweep experiments were carried out on all samples in which the magnitude of the complex viscosity, $|\eta^*|$, at a constant frequency of 1 rad/s and a strain of 5% was measured. All experiments were carried out at a temperature of 290 °C under a nitrogen atmosphere.

C. Microscopy

The morphology of the blend was examined by scanning electron microscopy using a Cambridge Stereoscan S200 electron microscope. Samples were cryogenically fractured after immersion in liquid nitrogen for 5 min. The fractured samples were fixed to aluminum stubs and sputter coated.

D. Interfacial tension

The value of interfacial tension, Γ, for the blend was obtained using contact angle measurements. Using two different solutions of known dispersive and polar components of surface tension, the dispersive and polar portions of the surface tension for both PET and nylon 6,6 were obtained. These values were then used to calculate the interfacial tension of the blend using the harmonic mean equation [Wu (1971)].

IV. RESULTS

The rheological and numerical results of this work are presented in this section. First, the parameters and initial conditions required in evaluating the predictions of the theory are determined. Next, the steady state viscosity, first normal stress difference, transient shear stress, and first normal stress difference of the PET nylon 6,6 blend are compared to predictions using the Doi–Ohta theory.

A. Parameters and initial conditions

In order to evaluate the Doi–Ohta theory values for the four parameters (e.g., η_0, Γ, c, and k), the initial values for Q and $q_{\alpha\beta}$ had to be determined. Of the four parameters required by the theory only η_0, Γ, and k could be determined experimentally. The last unknown parameter, c, was determined by fitting the Doi–Ohta theory [Eqs. (12), (13), and (1)] to start up of shear flow data. The initial conditions required by the equations, which included the initial values of the interfacial area per unit volume, $Q(0) = Q_0$ and the interface tensor, $q_{\alpha\beta}(0)$, were determined using the results obtained from scanning electron microscopy. The values of the parameters and initial conditions used in this work are listed in Table I.

The value of the system zero shear viscosity, η_0, was obtained in this work using the viscosity of the neat polymers after extrusion. The viscosity of the neat polymers before and after extrusion is shown in Fig. 1. The neat polymers after extrusion have a viscosity which is both lower in magnitude and more Newtonian over the shear rates measured than the neat polymers which have not been subjected to extrusion. Although the magnitude of the viscosity and the degree of shear thinning observed in the neat polymers before extrusion are substantially reduced by extrusion, the neat extruded polymers are still slightly shear thinning, and a small mismatch in their magnitudes is observed. The value of the viscosity parameter η_0 used in this work was calculated by taking the

TABLE I. Model parameters and initial conditions for the 25/75 PET/nylon, 6,6 blend.

Parameter	Value
η_0 (Pa s)	205
$\eta(\dot{\gamma})$ (Pa s)	227 at $\dot{\gamma} = 0.3 \text{ s}^{-1}$
	185 at $\dot{\gamma} = 9.0 \text{ s}^{-1}$
Γ (mN/m)	0.397 ± 0.06 0.513^a
k	0.07
c	0.6
Initial	Value
Q_0 (m^2/m^3)	300 000
$q_{\alpha\beta}(0)$	0

[a]Published [Owens and Wendt (1969)].
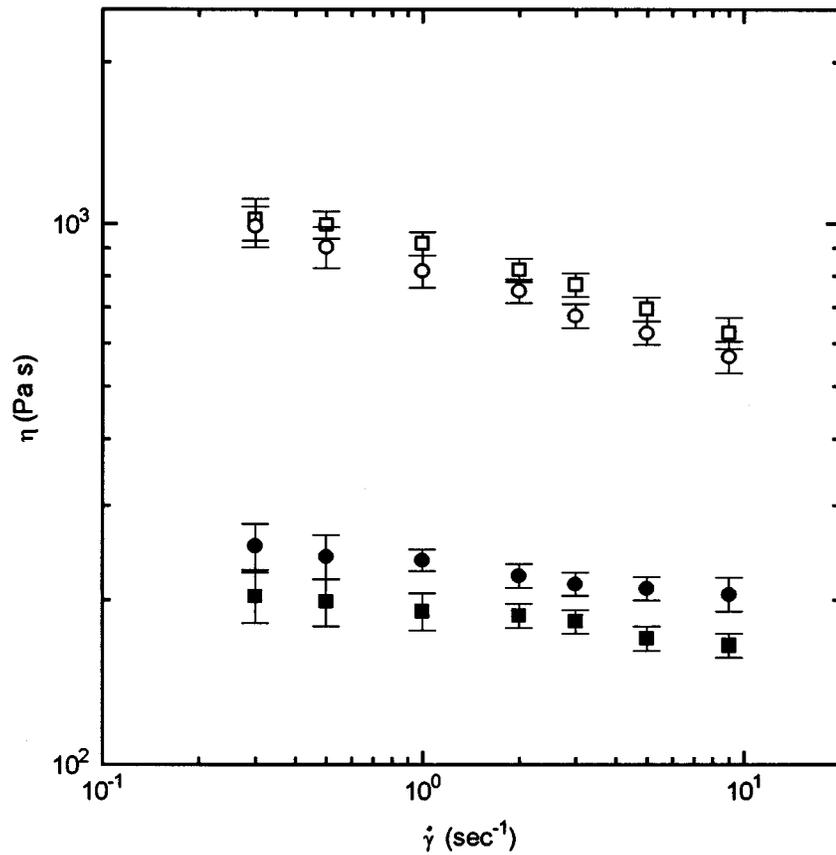
FIG. 1. Viscosity vs shear rate at 290 °C before and after extrusion: (□) PET; (○) nylon 6,6; (■) extruded PET; and (●) extruded nylon 6,6.

weighted average (based on the weight fractions of the neat polymers in the blend) of the mean viscosity of each polymer over shear rates ranging from 0.3 to 9.0 s^{-1}. In order to account for the shear thinning behavior of the neat polymers in the predictions of the Doi–Ohta theory, shear-rate-dependent values of the viscosity [e.g., $\eta(\dot{\gamma})$] were used in place of the constant viscosity parameter, η_0 in Eqs. (1), (9), and (11). The values of $\eta(\dot{\gamma})$ were calculated at shear rates ranging from 0.3 to 9 s^{-1} using the weighted average of the viscosities (based on the weight fraction of the neat polymers in the blend) of the neat polymers after extrusion.

In order to determine the stability of the samples during the rheological measurements used in this work, time sweeps were performed on the samples under a nitrogen atmosphere at 290 °C. The time frame for the rheological measurements used in this work was less than 3 min for the steady shear (η and N_1 vs $\dot{\gamma}$) and transient experiments [$N_1^+(t)$ and $\sigma^+(t)$]. The change in $|\eta^*|$ with time at a frequency of 1 rad/s for the blend and the neat polymers is shown in Fig. 2. The magnitude of the complex viscosity of the PET is seen to decrease by 7.5% in 3 min while that of the extruded nylon 6,6 remains essentially constant for 4 min. The decrease in $|\eta^*|$ with time for the blend is seen to be between that of the neat polymers (e.g., 2.5% in 3 min). Based on these results, rheological data obtained for the blend and neat polymers will be assumed to be not significantly affected by the degradation occurring during the rheological experiments.

The initial values of Q and $q_{\alpha\beta}$ required in the evaluation of the Doi–Ohta theory were determined using scanning electron micrographs of the blend. A micrograph of a sample which had been held at a temperature of 290 °C for 1 min to allow for relaxation of the morphology and then quenched is shown in Fig. 3. It can be seen that the blend has a dispersed phase of PET in the form of unoriented drops with diameters on the order of 5 μm. Based on an average drop diameter of 5 μm obtained from the scanning electron micrograph shown in Fig. 3 and the volume fraction of the blend, the initial value Q_0 was calculated to be 300 000 m^2/m^3. The initial values of the components of the interface tensor were assumed to be $q_{\alpha\beta}(0) = 0$ which is the case for isotropic conditions.

The last two parameters c and k required by the theory are the unknown constants in the kinetic equations for relaxation of the size [Eq. (11)] and shape [Eq. (9)] of the interface, respectively. The parameter, k, in Eq. (9) was obtained from a constitutive equation developed by Choi and Schowalter (1975) which describes the role played by interfacial tension on the rheological behavior of concentrated emulsions of two Newtonian fluids. Scholz $et\ al.$ (1989) have used this constitutive equation (neglecting nonlinear terms) to derive the storage and loss moduli, which are given as follows:

$$G'(\omega) = \frac{\eta}{\tau_1}\left(1 - \frac{\tau_2}{\tau_1}\right)\frac{\omega^2\tau_1^2}{1 + \omega^2\tau_1^2}, \tag{17}$$

$$G''(\omega) = \frac{\eta}{\tau_1}\left(1 - \frac{\tau_2}{\tau_1}\right)\frac{\omega\tau_1}{1 + \omega^2\tau_1^2} + \omega\eta\frac{\tau_2}{\tau_1}, \tag{18}$$

where

$$\eta = \eta_{\text{matrix}}\left[1 + \phi\,\frac{(5h + 2)}{2(h + 1)} + \phi^2\,\frac{5(5h + 2)^2}{8(h + 1)^2}\right], \tag{19}$$

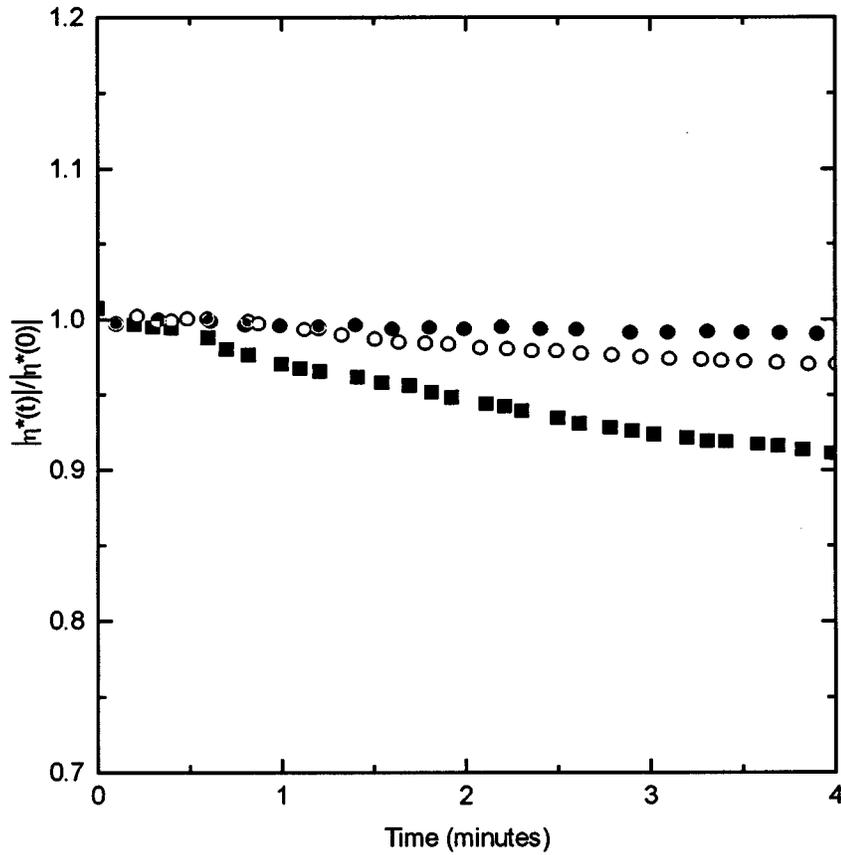$$\tau_1 = \tau_0\left[1 + \phi\,\frac{5(19h + 16)}{4(h + 1)(2h + 3)}\right], \tag{20}$$

FIG. 2. Magnitude of the complex viscosity vs time at 290 °C for: (■) PET; (○) nylon; and (●) 25/75 PET/nylon 6,6 blend.

$$\tau_2 = \tau_0 \left[1 + \phi \frac{3(19h+16)}{4(h+1)(2h+3)} \right], \tag{21}$$

$$\tau_0 = \frac{\eta_{\text{matrix}} D}{2\Gamma} \frac{(19h+16)(2h+3)}{40(h+1)}, \tag{22}$$

$$h = \frac{\eta_{\text{dispersed phase}}}{\eta_{\text{matrix}}}, \tag{23}$$

and where ϕ is the volume fraction of the dispersed phase and D is the diameter of the dispersed phase. The relaxation time τ_1 calculated using Eqs. (20) and (22) was found in the work by Gramespacher and Meissner (1992) to be equal to the relaxation time associated with the interface for immiscible polymer blends consisting of polystyrene and poly(methylmethacrylate). The relaxation time associated with the interface was obtained experimentally by Gramespacher and Meissner from the relaxation spectrum of the blend in which three peaks were observed. The relaxation times at which the first two peaks occurred were attributed to the relaxation times of the two neat polymers and the relaxation time at which the third peak occurred was attributed to the relaxation time associ-
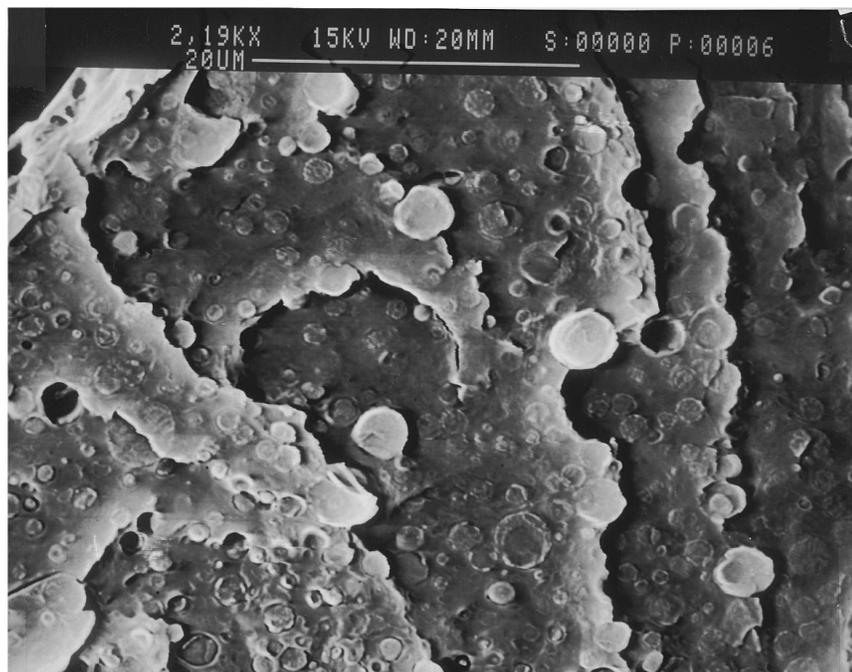
FIG. 3. Scanning electron micrograph of 25/75 PET/nylon 6,6 blend.

ated with the interface. Hence, assuming that the relaxation time associated with the interface, τ_1 in Eq. (20), is equal to $1/r_2$ in Eq. (9) in small deformations, the parameter, k, was calculated directly using Eqs. (20), (22), and (9). The value of τ_1 calculated using Eqs. (20) and (22) was 6 s. Using the relaxation time τ_1 determined in the manner described above, the parameter k was calculated to be 0.07. Justification for the use of this method to determine the parameter k is based on the assumption that in small deformations the change in the area of the interface is negligible ($\Delta Q \cong 0$ and $r_1 \cong 0$), and, therefore the only contribution from the interface is that from the anisotropy ($Q/q_{\alpha\beta}$) of the interface. The method for determining k based on the use of small strain dynamic oscillatory data is certainly questionable. In small deformations it is reasonable to assume that there is no change in the interfacial area. However, in steady shear the deformations are finite, and one might expect the interfacial area to be changing. Hence, using small strain dynamic data to predict the behavior in steady shear might be questionable. The method that we chose here, however, has some theoretical basis and leads to a value of k which is very similar to that which is obtained by fitting the start up of shear data by the Doi–Ohta theory and adjusting both c and k until one obtains the desired fit. It may be completely fortuitous that the values of k are so similar using two different methods or it may be that the rotational nature of shear flow leads to deformation similar to that developed in oscillatory shear flow. In any event, for lack of a better method we chose to use dynamic oscillatory data to obtain k.

The remaining parameter required in the evaluation of the model, c, was determined using the shear stress at the start up of shear flow. The transient data used to fit the parameter were obtained by preshearing the sample for 1 min at a shear rate of 1 s^{-1} and then allowing the sample to relax for 1 min before the start up of shear flow experiment
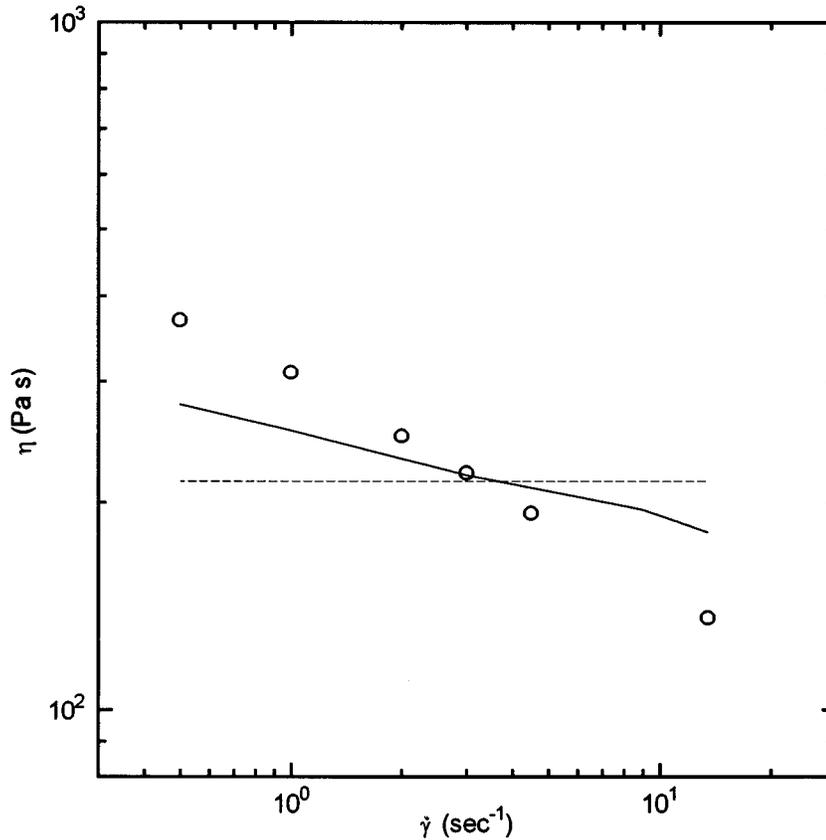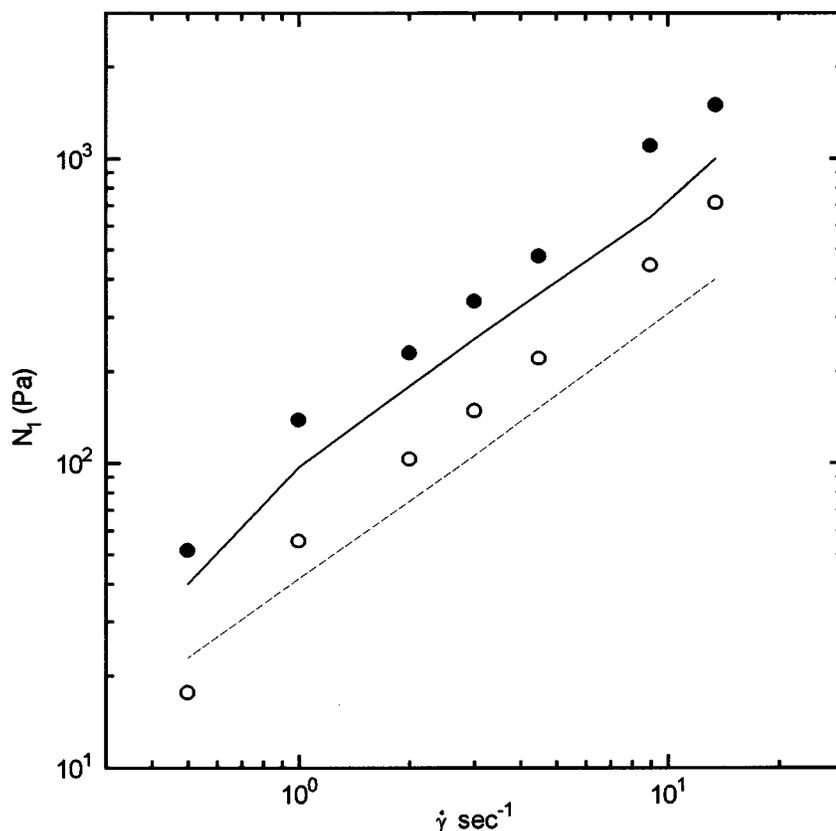
FIG. 4. Viscosity as a function of shear rate at 290 °C for 25/75 PET/nylon 6,6 blend: (○) experimental; (---) predicted by the Doi–Ohta theory using η_0(constant); and (—) predicted by the Doi–Ohta theory using $\eta(\dot\gamma)$.

was performed. This procedure provided for reproducible data with an error which was within a 5% range and was used to fit the parameter, c, in the theory using the values of η_0, Γ, k, Q, and $q_{\alpha\beta}$ determined above. The value for the parameter which provided for the best fit for the shear stress at the start up of simple shear flow was $c = 0.6$.

B. Steady shear flow predictions

A comparison of the predicted and experimental steady shear rheology of the 25/75 PET/nylon 6,6 blend is presented here. Under steady state conditions the texture of the system is in a constant state of droplet deformation, breakup, and coalescence in which the droplets have a distribution of sizes and orientations of their interfaces which are constant. At steady state the area of the interface per unit volume and the components of the interface tensor are predicted to be constant in the theory of Doi and Ohta. The steady state viscosity is predicted to be independent of shear rate and the first normal stress difference is proportional to the shear rate. These results should hold because they are a result of dimensional analysis, and the steady state viscosity should be determined by Γ, η_0, and $\dot\gamma$.

A comparison of the predicted viscosity using the Doi–Ohta model to experimental values is shown in Fig. 4. In this figure the predicted blend viscosity using both a constant value of viscosity (η_0) and a shear-rate-dependent viscosity $\eta(\dot\gamma)$ is shown. It can be seen
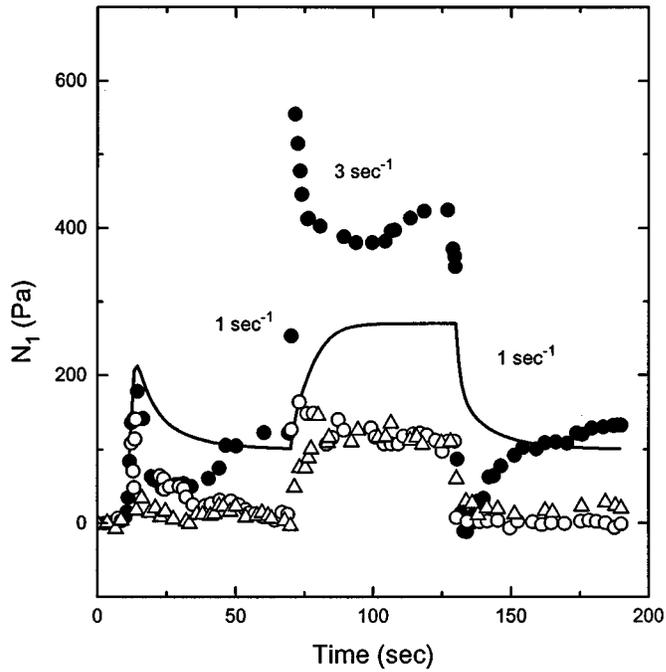
FIG. 5. First normal stress difference as a function of shear rate at 290 °C: (○) weighted average (by weight fraction) of the values for PET and nylon 6,6; (●) experimental 25/75 PET/nylon 6,6 blend; (---) predicted by Doi–Ohta theory; and (—) predicted using the weighted average values of neat polymers added to the values predicted.

that when a constant value for the viscosity parameter is used the predicted viscosity for the blend is Newtonian. The use of a shear thinning viscosity function, $\eta(\dot{\gamma})$, calculated from the weighted average (based on the weight fractions of the neat polymers in the blend) of the measured viscosity for the neat polymers in Eqs. (1), (9), and (11) results in a predicted blend viscosity which is more shear thinning than observed experimentally for the neat polymers. The shear thinning behavior of the blend suggests that a characteristic time scale associated with the interface exists for the blend [e.g., Eq. (16) does not hold] because it could not be accounted for by the shear thinning behavior of the neat polymers.

A comparison of predicted and observed steady state first normal stress difference behavior as a function of shear rate is shown in Fig. 5. A finite normal stress that is proportional to $|\dot{\gamma}|$ is predicted to arise as a consequence of interfacial tension because even at infinitely small shear rates the texture changes. In order to determine if the contribution to the first normal stress difference from the interface is accurately predicted by the theory, the contribution to N_1 from the neat polymers was added to the normal stress predicted by the theory, since in the theory the fluids are Newtonian. The N_1 contribution of the blend constituents at each shear rate was calculated using the weighted average (based on the weight fractions of the neat polymers in the blend) of the
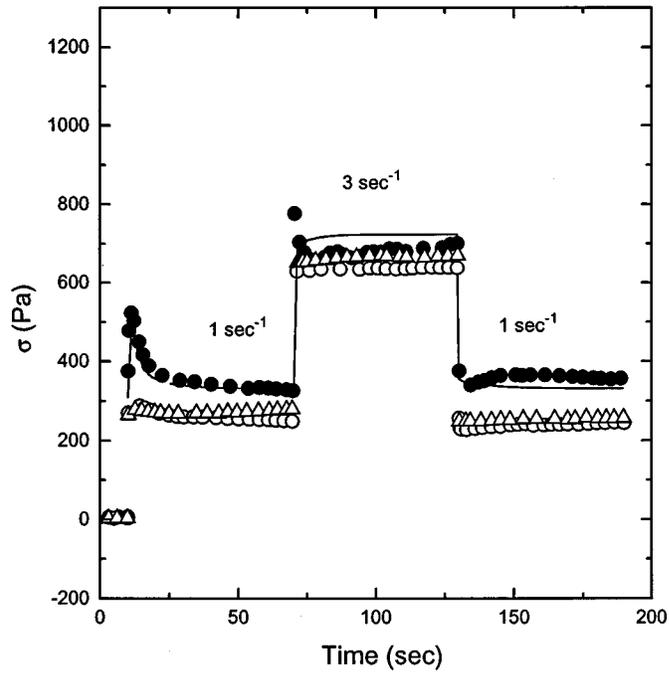
FIG. 6. Transient shear stress vs time at 290 °C: (○) PET; (△) nylon 6,6; (●) 25/75 PET/nylon 6,6 blend; (—) predicted by Doi–Ohta theory.

FIG. 7. Transient first normal stress difference vs time at 290 °C: (○) PET; (△) nylon 6,6; (●) 25/75 PET/ nylon 6,6 blend; (—) predicted by Doi–Ohta theory.
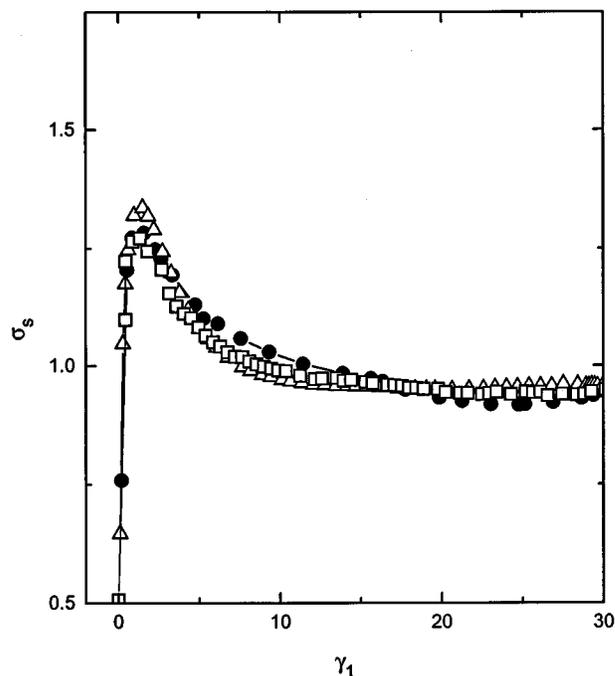
FIG. 8. Transient scaled shear stress $\sigma_s = [\sigma^+(t, \dot{\gamma}_1) - \sigma(\dot{\gamma}_0)]/[\sigma(\dot{\gamma}_1) - \sigma(\dot{\gamma}_0)]$ vs γ_1, where $(\dot{\gamma}_1/\dot{\gamma}_0 = 3)$ and where $\dot{\gamma}_1$ is; ($\triangle$) 1.5 s^{-1}; ($\bullet$) 3.0 s^{-1}; and ($\square$) 4.5 s^{-1} for 25/75 PET/nylon 6,6 blend at 290 °C.

measured first normal stress difference for the neat polymers. The contribution to N_1 from the neat polymers was simply added to the extra stress calculated using the model at each shear rate. It can be seen in Fig. 5 that the first normal stress difference calculated in this manner very nearly approximates the first normal stress difference observed for the blend both in magnitude and rate dependence.

C. Transient shear flow predictions

The transient shear stress and first normal stress difference predicted using the Doi–Ohta theory and the experimental results for the 25/75 PET/nylon 6,6 blend are shown in Figs. 6 and 7, respectively. These two figures show the results of transient experiments consisting of the start up of steady shear flow, a step up of the shear rate, and a step down of the shear rate. As a consequence of the short relaxation times of both neat polymers, the transients for the shear stress and first normal stress difference for the neat polymers do not show the overshoot at the start up of shear flow and upon a stepwise increase of the shear rate or the undershoot upon a stepwise decrease of the shear rate which is observed for the blend. It can be seen that both the shear stress and first normal stress difference are qualitatively modeled by the theory at the start up of shear flow. As the shear rate is stepped up in the experiment, the overshoot in shear stress and first normal stress difference are not predicted by the theory. As the shear rate is stepped down in the last part of the experiment, the undershoot in both shear stress and first normal stress difference is not predicted by the theory. Failure of the theory to predict the overshoot and undershoot observed in step changes of shear rate indicates that the kinetic equations do not accurately model the relaxation behavior of both the shape and size of the interface which may occur in this flow.
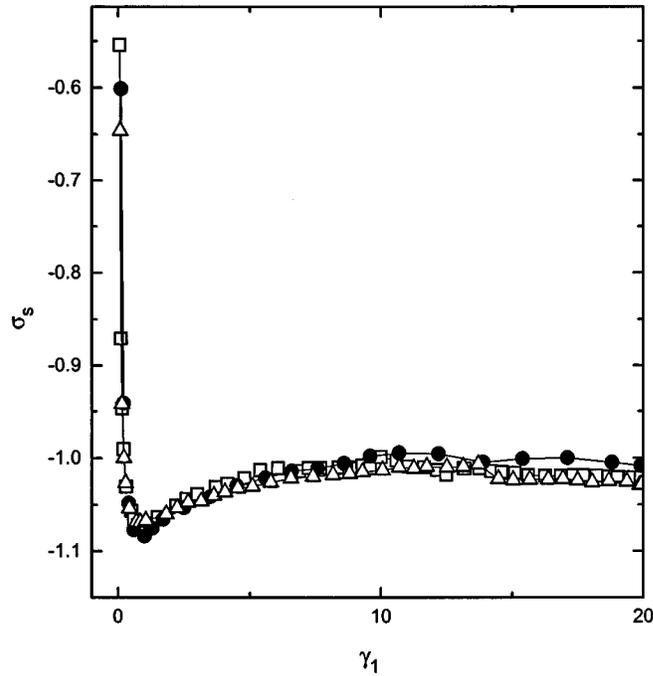
FIG. 9. Transient scaled shear stress $\sigma_s = [\sigma^+(t,\dot{\gamma}_1) - \sigma(\dot{\gamma}_0)]/[\sigma(\dot{\gamma}_1) - \sigma(\dot{\gamma}_0)]$ vs γ_1 where $(\dot{\gamma}_0/\dot{\gamma}_1 = 3)$ and where $\dot{\gamma}_1$ is; ($\triangle$) 0.5 s^{-1}; ($\bullet$) 1.0 s^{-1}; and ($\square$) 1.5 s^{-1} for 25/75 PET/nylon 6,6 blend at 290 °C.

The scaling relationship predicted by the Doi–Ohta equations for transient shear flows was investigated using the transient shear stress data obtained from stepwise changes of the shear rate. Consider the transient experiment where the shear rate is changed from $\dot{\gamma}_0$ to $\dot{\gamma}_1$ at time $t = 0$. The Doi–Ohta theory predicts that the stress growth or relaxation curve plotted in terms of scaled stress (σ_s),

$$\sigma_s = \frac{\sigma^+(t,\dot{\gamma}_1) - \sigma(\dot{\gamma}_0)}{\sigma(\dot{\gamma}_1) - \sigma(\dot{\gamma}_0)}, \tag{24}$$

and strain (γ_1),

$$\gamma_1 = \dot{\gamma}_1 t, \tag{25}$$

can be superimposed at constant step ratios of $\dot{\gamma}_0/\dot{\gamma}_1$ regardless of the final shear rate, $\dot{\gamma}_1$. This scaling relationship can be observed using step-up and step-down experiments with a constant step-up and step-down ratio ($\dot{\gamma}_0/\dot{\gamma}_1$ = constant) and plotted as function of the scaled stress (σ_s) for the blend as shown in Figs. 8 and 9. Although the overshoot and undershoot are not predicted by the theory, the transient shear stress of this blend does in fact scale. This is a special case of the more general scaling relation described by Eqs. (15) and (16).

Additional evidence of the wrong form or order of the relaxation equations is revealed by the inability of the Doi–Ohta theory to predict a recovery of the initial overshoot observed experimentally for the blend using start up of shear flow experiments. The recovery of the overshoot associated with a recovery of the equilibrium texture can be seen in Fig. 10 where the shear stress is reduced by the steady state shear stress [e.g.,
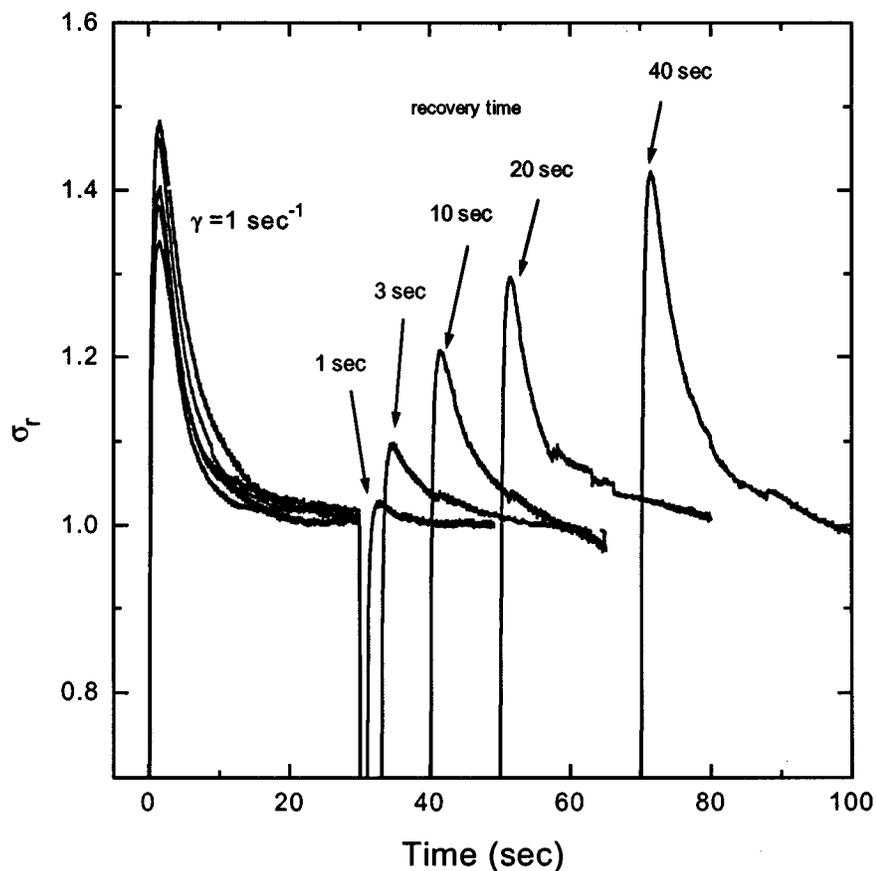
FIG. 10. Recovery of overshoot as a function of recovery time using interrupted stress growth experiments for the 25/75 PET/nylon 6,6 blend at 290 °C.

$\sigma_r = \sigma^+(t,\dot{\gamma}_0)/\sigma(t)]$. In Fig. 10 it can be seen that at a recovery time of 40 s, approximately 90% of the overshoot is recovered. The inability of the Doi–Ohta theory to predict this recovery may be explained using a quantitative analysis of the predicted area of the interface per unit volume (Q) which shows that the recovery of the texture observed experimentally is not predicted. This can be seen by the change in Q predicted for a transient shear flow consisting of a start up of shear flow, step up of shear rate, and cessation of shear flow as shown in Fig. 11. It can be seen that the theory predicts a decrease in the area of the interface at start up of shear flow and an increase in the area upon stepping up the shear rate. However, the theory inaccurately predicts that upon cessation of shear flow the area of the interface will decrease. It was observed using scanning electron microscopy (but not shown here) that the dispersed phase size of a blend which had been subjected to a shear flow between cone and plate fixtures for 1 min at a shear rate of 5 s^{-1} and then allowed to relax for 1 min before quenching was the same as that of a sample which had not been sheared (as shown in Fig. 3). This result indicates that the kinetic equations should be of a form and order which would predict that the equilibrium texture prior to shear flow is recovered upon cessation of shear flow.
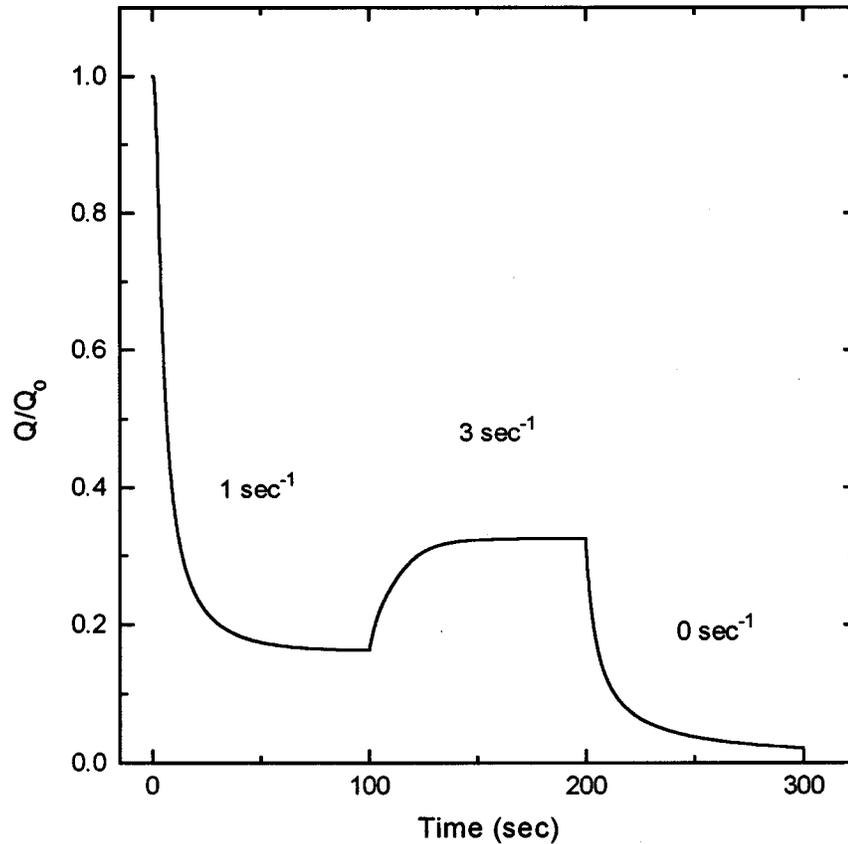
FIG. 11. Predicted normalized interfacial area per unit volume using the Doi–Ohta theory as a function of time at the start up of shear flow, step up of the shear rate, and cessation of shear flow.

V. CONCLUSIONS

At this time several limitations of the Doi–Ohta theory are apparent. Although the Doi–Ohta theory predicts an increase in blend viscosity over that of the blend constituents, as is seen experimentally for the 25/75 PET/nylon 6,6, the theory does not predict the shear thinning behavior seen experimentally in this blend. The steady shear values of η and N_1 of the 25/75 PET/nylon 6,6 blend system can be approximately estimated using the Doi–Ohta theory if the shear thinning and elastic properties of the blend constituents are taken into account. This represents a failure of the theory for systems which are made up of materials each with their own non-Newtonian properties. By definition the theory is not able to account for these contributions. On the other hand, the contributions or extra stresses which occur as a result of the texture or two-phase nature of the system appear at least in magnitude to be predicted by the theory using parameters determined experimentally and by fitting the prediction of the model to start up of shear flow experiments from an isotropic system.

The shear stress and first normal stress difference are qualitatively modeled by the theory at the start up of shear flow. On the other hand, the inability of the theory to predict the overshoot and undershoot observed experimentally using stepwise changes of shear rate indicates that the kinetic equations do not accurately model the relaxation

behavior of both the size and shape of the interface which may occur in this experiment and may also be a consequence of the relaxation behavior of the neat polymers. While the shear thinning behavior of the 25/75 w/w PET/nylon 6,6 blend is not predicted by the Doi–Ohta theory (stress is predicted to be proportional to shear rate), the scaling relationship for the transient stresses does appear to hold for the blend using step-up and step-down experiments.

ACKNOWLEDGMENT

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