

# Melt Rheology of Poly(ethylene Terephthalate), Polyarylate, and Their Blends

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## Synopsis

Rheological properties of two polyesters; poly(ethylene terephthalate) (PET) and bisphenol A-50/50 isophthalic/terephthalic acid based polyarylate (PAR), and their 85/15, 50/50, and 30/70 (PET/PAR) blends were investigated using a RDS rheometer, 290–310°C. Measurements included complex viscosity and modulus. Activation energy for flow and relaxation spectrum were subsequently calculated. Results indicated that PET/PAR blends are rheologically incompatible, i.e., zero-shear viscosities of the blends showed a negative deviation from the averages of the two homopolymers with a sharp minimum at 85/15 composition. The relaxation spectrum for 85/15 blend also showed a relaxation plateau, a characteristic of rigid particle suspension. The morphology of the polymer blends was examined from cryogenically fractured and etched surface using a scanning electron microscopy (SEM). Morphological observation indicated that PAR-rich phases, order of 0.1  $\mu\text{m}$ , were finely dispersed in PET phase for 85/15 blend, whereas the dispersion of PET phase in PAR-rich phase was in spherical form, order of 0.5  $\mu\text{m}$  in diameter, for the 50/50 blend.

## INTRODUCTION

Polymer modification through blending has received rapidly growing interest during the last several decades. Nowadays a significant number of commercial blends have become available and continuous efforts are expected to further create more desirable morphologies for thermal, rheological, and mechanical properties.

The rheology of blend is important since the mechanical properties of blends, especially for multiphase blends, are greatly changed depending on deformation history. Polyester blends have extensively been studied in recent years from the practical point of view.<sup>1–6</sup> Melt rheology and transesterification for polyester blends were also studied for blends of poly(butylene terephthalate) (PBT) with polyarylate (PAR).<sup>2</sup> To the knowledge of the present authors, there are no papers devoted to the melt rheology of PET/PAR blend and this is the motivation of the present work.

The miscibilities of PET/PAR based on bisphenol A-isophthalic/terephthalic acid based blends were reported by several authors.<sup>4–6</sup> Two studies for solution-cast samples disagree<sup>4,6</sup> on the phase behavior, and later work on melt blend<sup>5</sup> reported that the mixing condition was of prime importance in determining the miscibility.

In the present paper, the rheological properties of PET/PAR (bisphenol A-50/50 isophthalic/terephthalic acid based) blends, and the two homopolymers were investigated using a RDS rheometer. The advantage of rotational type rheometer especially in oscillatory mode over capillary type is that the former has a less effect on the state of dispersion and gives better correlations between elastic properties.<sup>7-10</sup> The results obtained include shear viscosities and elastic moduli at three different temperatures, 290–310°C. The activation energies for the flow process, and the relaxation spectra from loss moduli were calculated.

Although the morphological textures do not always confirm the rheological behavior, an attempt was made to interrelate the rheological properties with morphology. That is, scanning electron micrograph (SEM) was taken from the cryogenically fractured and etched surface of the blends.

## EXPERIMENTAL

The commercial grades of polyester as received were employed for blending. The  $M_n$  and  $M_w$  of PET (Tongyang Polyester) were respectively 17,700 and 47,400. The PAR was Unitika's Arylef U-100 polyarylate of bisphenol A-50/50 isophthalic/terephthalic acid base with  $M_n = 21,200$  and  $M_w = 51,400$ .<sup>11</sup>

The blends were prepared by first mixing the dried chips thoroughly, followed by melt blending in a twin screw compounding machine (Baker Perkins) at 280–295°C. The samples were subsequently quenched in water and pelletized (Berlyn, Pelletizer PEL-2).

For RDS measurement, blend samples as well as the two homopolymers were kept in a vacuum oven overnight at 120°C, compression-molded into discs measuring 2.5 cm (dia)  $\times$  0.3 cm (thickness), and stored in a vacuum oven until the time of the test.

A cone-and-plate type rheometer (Rheometrics Dynamic Spectrometer) with the cone angle of 0.1 rad and radius of 1.25 cm was employed. The measurements were carried out isothermally, i.e., the test fixtures were preheated to the measure temperature, samples were subsequently charged, and the excess material was trimmed followed by conditioning for several minutes to relax the residual stress.

In a separate experiment, it was determined that the viscoelastic properties were kept linear up to 10% strain level, the level tested throughout. All of the experiments were carried out in nitrogen environment to avoid oxidative degradation.

The morphology of the polymer blends was studied from a SEM (JEOL, JSM-35 CF). The cryogenically (in liquid nitrogen) fractured samples were etched in methylene chloride, a selective solvent for PAR, for 1 or 30 min and then sputtered with gold before scanning.

## RESULTS AND DISCUSSION

Following earlier studies on the phase behavior of PET/PAR blends,<sup>4-6</sup> PET/ PAR blends form homogeneous phase at < 30 wt % PET, and exhibit phase separation into a nearly pure PET phase and mixed phase rich in PAR at > 30 wt % PET. However, when the blend is prepared from melt mixing above 280°C

with moderate time and temperature exposure, adequate transesterification with PET/PAR blend occurs to yield single phase behavior such as a single glass transition temperature intermediate between the two polyester constituents.

Phase morphologies of the present PET/PAR blends are given in Figure 1. SEM micrograph for 85/15 (PET/PAR) blend [Fig. 1(a)] shows fine particle suspension nature at this composition, i.e., PAR-rich phase, order of 0.1  $\mu\text{m}$  in diameter is being etched from PET continuum. In 50/50 blend [Fig. 1(d)] 0.5  $\mu\text{m}$  order of spherical PET particles which have been disposed in PAR-rich phase are seen. The blending conditions, i.e., melt mixing at 280–295°C in a twin screw extruder, should be subject to transesterifications to some extent. Present morphologies indicate limited reaction, attested from the phase separation.

Shear viscosities for the two homopolymers and blends of PET and PAR at three temperatures are shown in Figures 2–6. The viscosity measured from RDS is the complex viscosity defined by

$$\eta^* = \eta' - i\eta'' \quad (1)$$

where  $\eta'$  and  $\eta''$  are in-phase and out-of-phase components of complex viscosity, respectively. Often for simplicity  $\eta'$  is called dynamic viscosity and is related to the loss modulus ( $G''$ ), whereas  $\eta''$  is related to storage modulus ( $G'$ ):

$$\eta' = G''/\omega \quad (2)$$

$$\eta'' = G'/\omega \quad (3)$$

$$\tan \delta = \eta'/\eta'' \quad (4)$$

where  $\omega$  is the frequency in rad/s, and the loss tangent ( $\tan \delta$ ) is a measure of ratio of energy lost to energy stored in a cyclic deformation.

The viscosity of prime interest in flow process is the steady viscosity ( $\eta$ ). Sometimes very good agreement between steady and dynamic viscosities was observed for certain polymer melts<sup>12–14</sup> and blends.<sup>14</sup> However, the discrepancy especially at large frequencies is generally true from eq. (2). At very low frequencies, the oscillatory deformation can be considered as nearly a steady state flow, and the very general phenomenological theory of Coleman and Markovitz<sup>15</sup> predicts a simple relationship between the two viscosities, i.e.,

$$\lim_{\omega \rightarrow 0} \eta'(\omega) = \lim_{\dot{\gamma} \rightarrow 0} \eta(\dot{\gamma}) \quad (5)$$

where  $\dot{\gamma}$  is the steady rate of shear.

The dynamic viscosities obtained at 300°C for the present system are also shown in the same figures. The results show an excellent agreement between complex and dynamic viscosities. Exception, as expected, is found at high frequencies.

Both PET and PAR homopolymers are of great thermal resistance. However, these polymers are also subject to thermal degradation under normal processing conditions. The measured viscosity for PET (Fig. 2) shows some thermal deg-

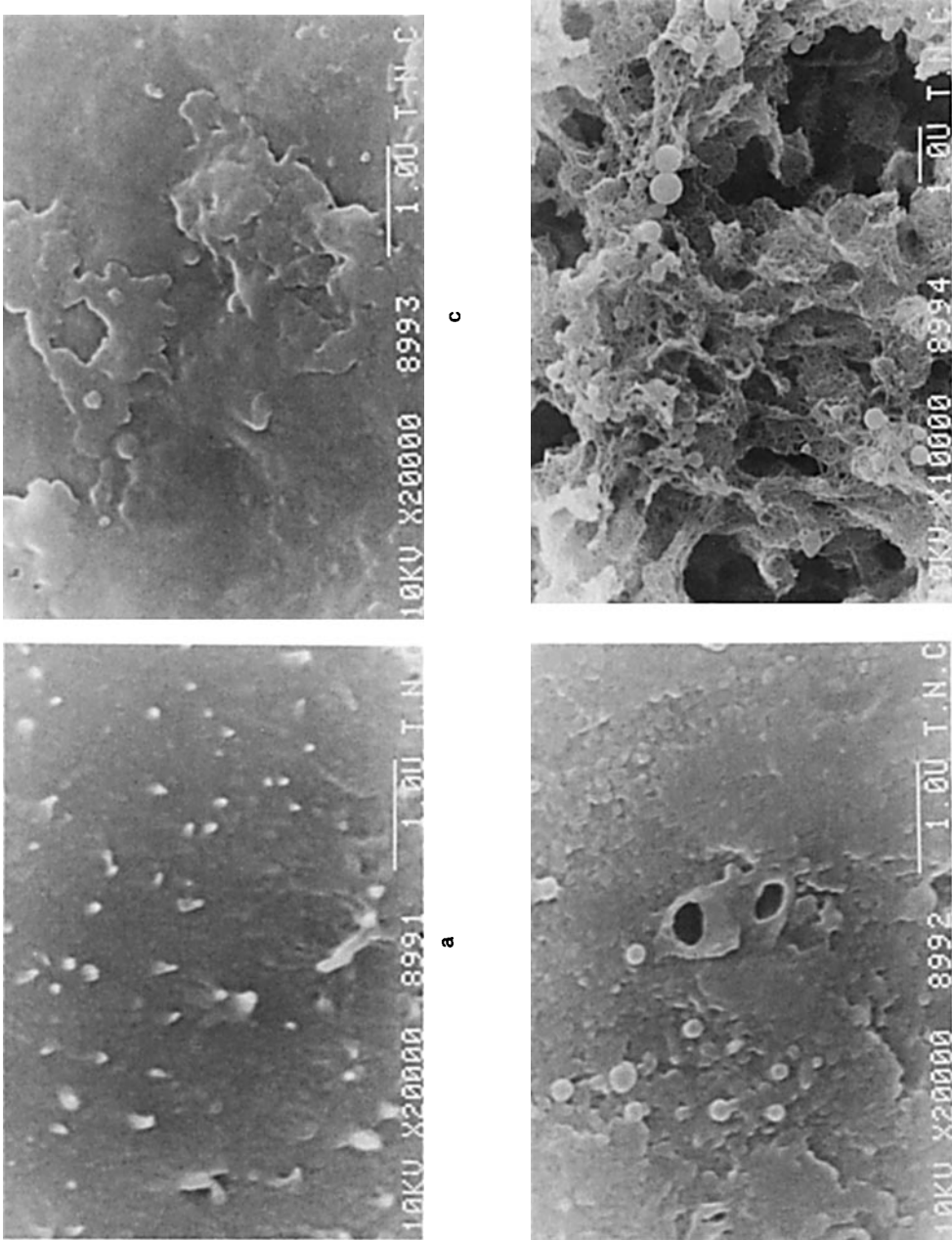


Fig. 1. Scanning electron micrographs of cryogenically fractured and etched surfaces: (a) 85/15, 1 min etching; (b) 85/15, 30 min etching; (c) 50/50, 1 min etching; (d) 50/50, 30 min etching.

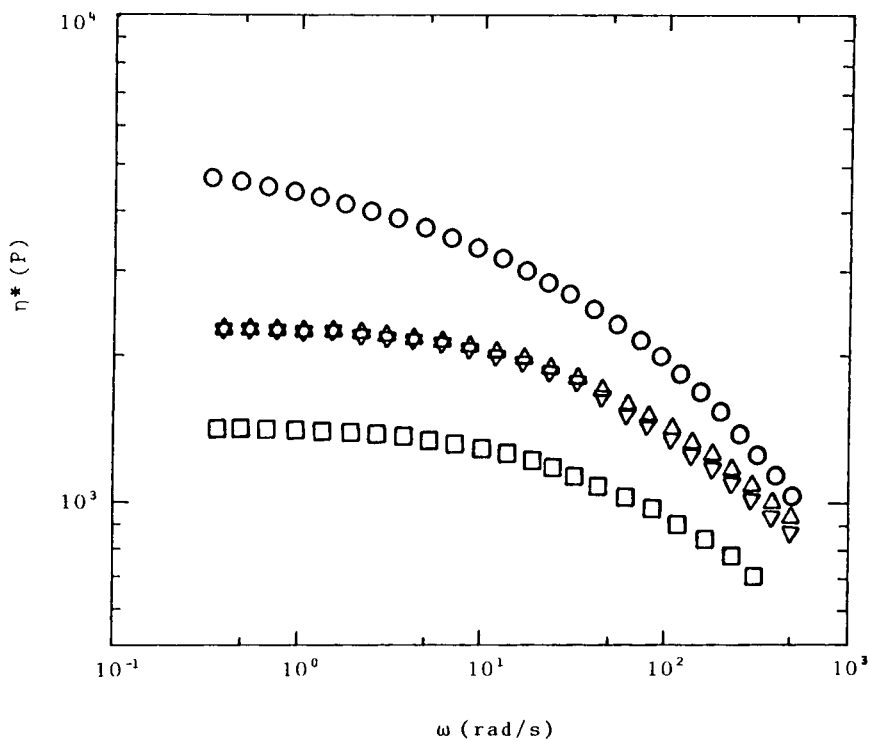


Fig. 2. Viscosities of PET: (○) 290°C, complex; (△) 300°C, complex; (□) 310°C, complex; (▽) 300°C, dynamic.

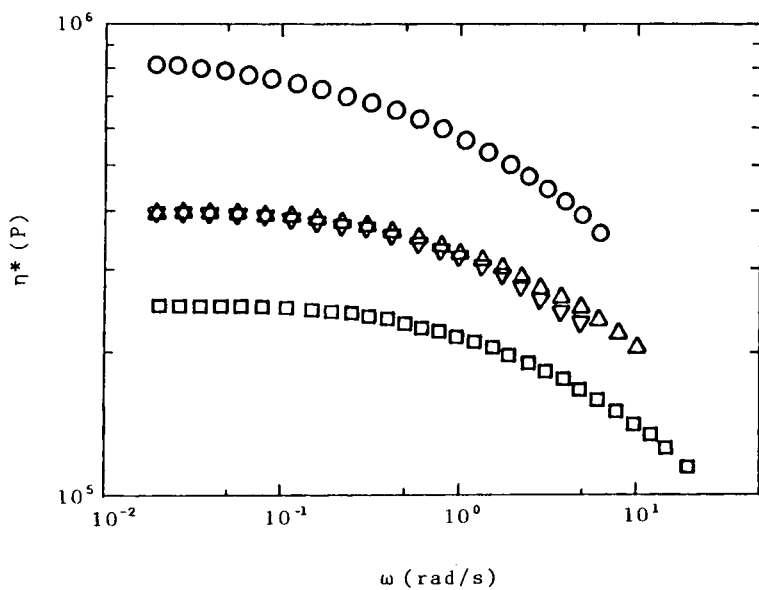


Fig. 3. Viscosities of PAR: (○) 290°C, complex; (△) 300°C, complex; (□) 310°C, complex; (▽) 300°C, dynamic.

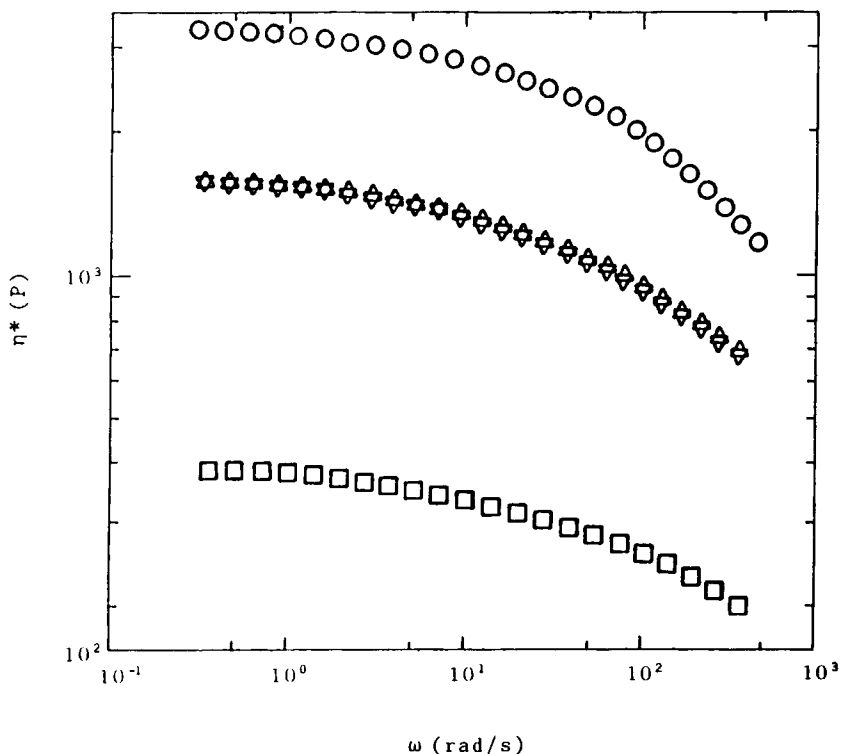


Fig. 4. Viscosities of PET/PAR (85/15) blend: (O) 290°C, complex; ( $\Delta$ ) 300°C, complex; ( $\square$ ) 310°C, complex; ( $\nabla$ ) 300°C, dynamic.

radiation of this material during the measure time, perhaps less vulnerable at lower temperature. Measurement at 290°C show shear thinning behavior from  $\omega < 1$  rad/s, whereas viscosities measured at higher temperatures extend the Newtonian flow region beyond  $\omega = 10$  rad/s.

With thermal degradation, dominated by transesterification,  $M_w$  decreases, keeping  $M_n$  constant, resulting in a narrow molecular weight distribution (MWD). The rheological response of a narrow MWD is to give an extended Newtonian region followed by a sharp drop in viscosity with frequency, and this is exactly what happened to PET, presently.

The shear viscosities for PAR (Fig. 3) also show a sign of thermal degradation during the measurements. However, the thermal degradation of PAR is not a significant factor compared to that of PET. As a matter of fact, a time-temperature superposition based on eq. (7) has been attempted. A fair superposition was possible for PAR, 290–310°C; however, such was not possibly done for PET and three blends due presumably to structural changes during the measurement.

Following the literature,<sup>4,5</sup> PET/PAR blends show two phases, i.e., a nearly pure PET phase and PAR-rich phase, at  $> 30$  wt % PET with minimum time and temperature exposure. However, with moderate time and temperature exposure, say 10 min, at 300°C, adequate transesterification leading to block copolymer occurs with PET/PAR blends, and an improved miscibility is ex-

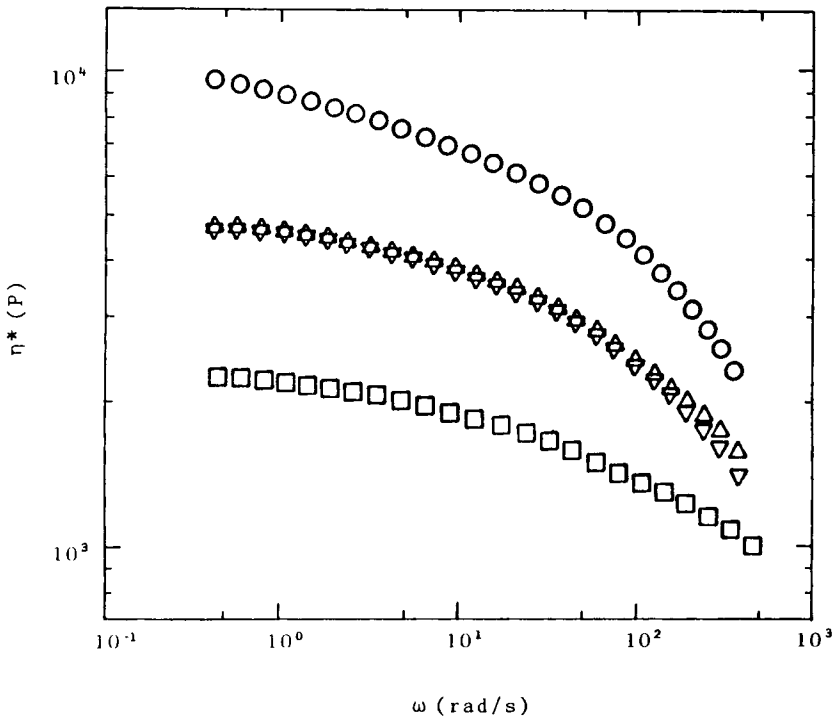


Fig. 5. Viscosities of PET/PAR (50/50) blend: (○) 290°C, complex; (△) 300°C, complex; (□) 310°C, complex; (▽) 300°C, dynamic.

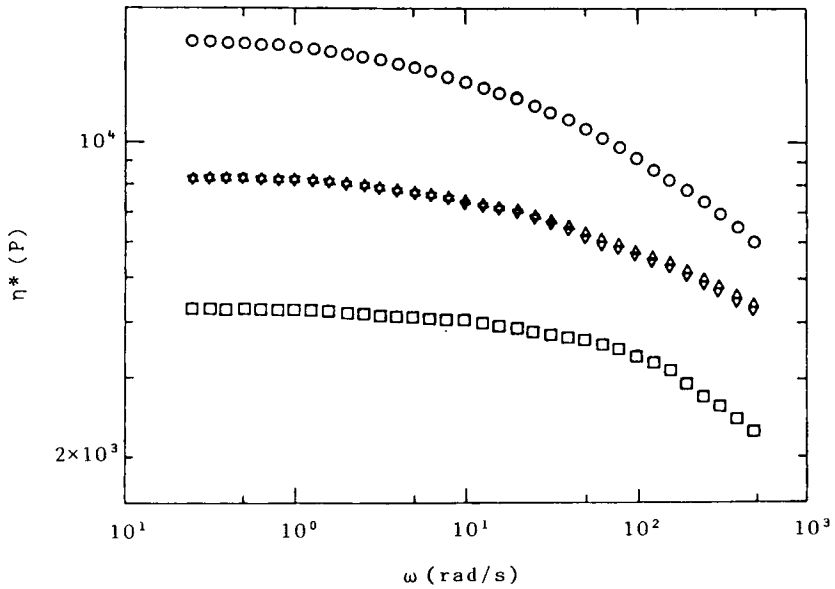


Fig. 6. Viscosities of PET/PAR (30/70) blend: (○) 290°C, complex; (△) 300°C, complex; (□) 310°C, complex; (▽) 300°C, dynamic.

pected as predicted by Meier<sup>16</sup> and Krause.<sup>17</sup> Miscibility in most cases<sup>18</sup> leads to additivity of properties.

Therefore, blend viscosities as a function of composition were examined from ones measured at the lowest rate of shear, start of measurement in rate sweep. These data correspond to minimum time exposure and are least vulnerable to thermal degradation and transesterification as well. Presently, the lowest shear viscosities correspond to Newtonian viscosity ( $\eta_0$ ) and were practically determined from low shear data using Ferry's equation<sup>19</sup>:

$$1/\eta = 1/\eta_0 + b\tau \quad (6)$$

In this equation,  $b$  is a constant and  $\tau$  is the shear stress corresponding to  $\eta$ . Such plots gave reasonably good straight lines, and the results are given in Figure 7 as a function of composition. The composition dependence of zero shear viscosity goes through a minimum at 15% PAR, indicative of incompatible state of the blend due probably to the insufficient extent of transesterification. The viscosity minimum appeared at 15% PAR should come from the fine suspension of PAR in PET matrix at this concentration, observed from SEM micrographs.

The above observation was also found for PET/polyamide,<sup>14</sup> ABS/polyamide,<sup>20</sup> polystyrene/PMMA<sup>10</sup> blends, and is generally known to apply for incompatible polymer blends.<sup>10,14</sup> Following Ref. 14 in which polyamide was dispersed into continuous PET phase, the initial dispersion of polyamide droplets generates a series of shear-dependent structures, each with its own value of characteristic zero-shear viscosity. As the concentration of the dispersed phase increases, so does the structural deformation of this phase up to a point where the droplets are interconnected and this concentration was approximately 30% polyamide in PET/polyamide blends.

For the PET/PAR blends, this concentration seems higher than 15%; however, it should be lower than 50% PAR (Fig. 7). It is also obvious that the structural deformation is easier at higher temperature, and this is seen in the same figure, i.e., the shallow minimum of viscosity becomes sharp as the temperature increases. Identically same tendency was observed in the references cited above.

The dependence of viscosity on temperature was calculated from the Arrhenius equation:

$$\eta = A \exp(E/RT) \quad (7)$$

where  $E$  is the activation energy for flow process,  $R$  is the gas constant,  $T$  is the absolute temperature (K), and  $A$  is a constant. The results are given in Figure 8. The present activation energy for PAR (38.6 kcal/mol) agrees well with those obtained by others (37–39.5 kcal/mol).<sup>1,2</sup> The activation energy for PET obtained in this experiment (40.2 kcal/mol) is higher compared to those cited in Ref. 13 (9–34 kcal/mol); however, it is essentially the same with Ref. 21 (40 kcal/mol). This is probably due to the difference in the molecular weight and its distribution of the sample. The activation energies for the blends (69.5, 50.1, and 45.3 kcal/mol for 85/15, 50/50, and 30/70 blends, respectively) are higher than the homopolymer values. This may support the particulate-in-



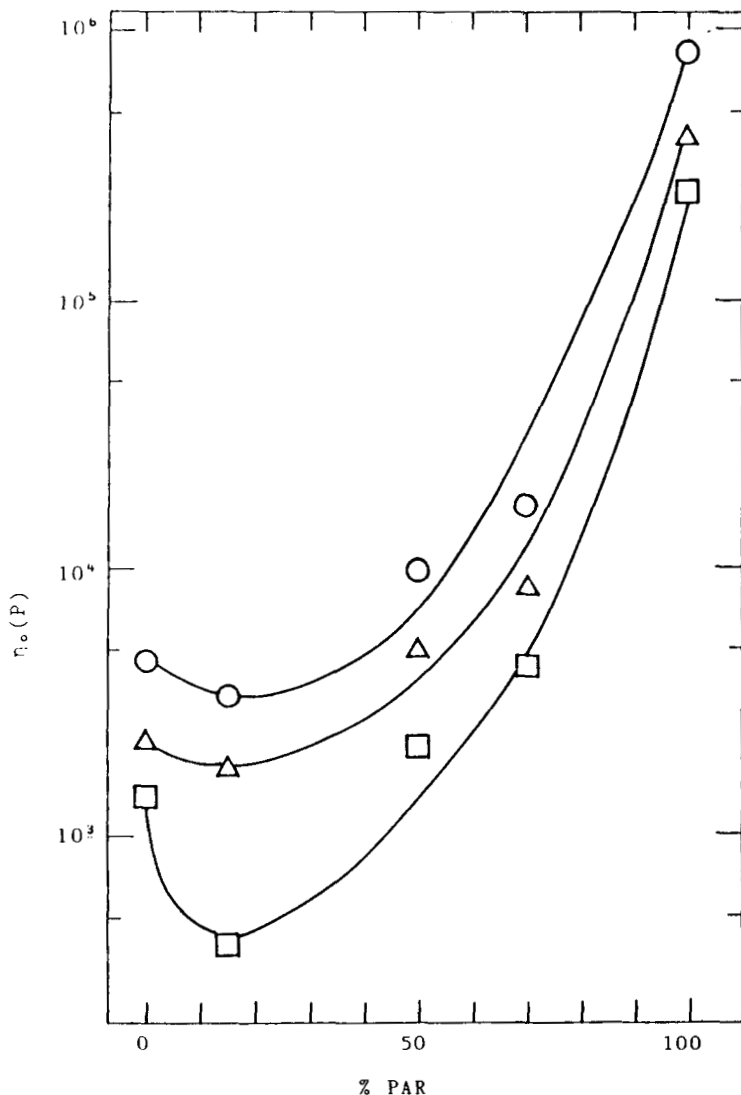


Fig. 7. Zero-shear viscosities as a function of composition: (○) 290°C; (△) 300°C; (□) 310°C.

matrix nature for the flow of blend melts, mentioned above. The rapid initial increase of activation energy with dispersed phase content is an indication of sharp growth of the flow volume.<sup>14</sup>

The elastic responses in oscillatory flows for the two homopolymers and blends are shown in Figures 9 and 10. The loss modulus ( $G''$ ) as well as the storage modulus ( $G'$ ) decreased as the temperature increased. To save the space, only data obtained at 300°C are given here. The storage modulus for PAR is by far the highest when compared at the same frequencies. This primarily reflects the chain rigidity of this material and should imply an energetic relaxation involved. Factors contributing to relaxation time include the stiffness of polymer backbone, extent of entanglement, molecular weight, and molecular

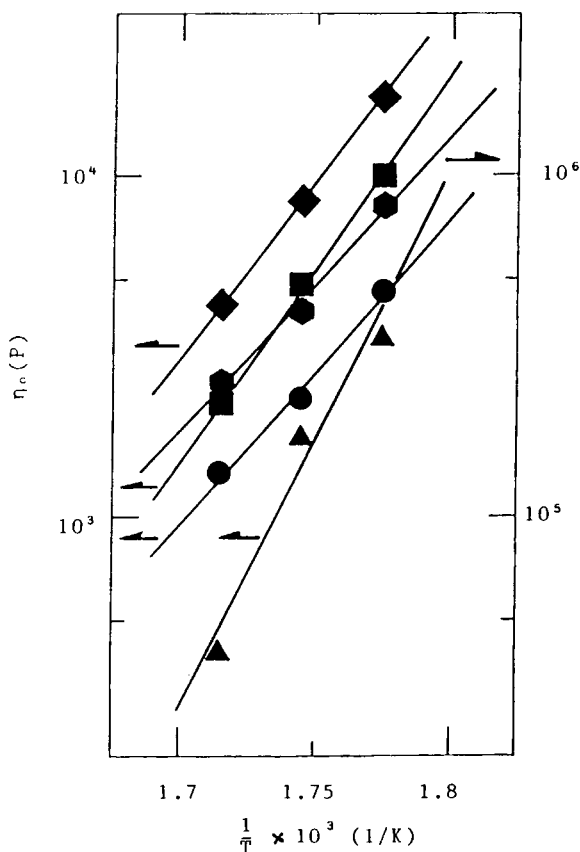


Fig. 8. Activation energies for the flow process ( $E_a$ ): (●) PET, 40.2; (◼) PAR, 38.6; (▲) 85/15 blend, 69.5; (■) 50/50 blend, 50.1; (◆) 30/70 blend, 45.3 kcal/mol.

weight distribution. It is also worth noting that the storage modulus for the 85/15 blend is even lower than the PET value. This should be related to the viscosity minimum at this composition, addressed above.

The loss tangent, i.e.,  $\tan \delta$  (Fig. 11) also shows some interesting features. The loss tangent, as mentioned earlier, is simply the ratio of energy stored to energy dissipated for an oscillatory deformation. The loss tangents for blends are higher compared to those for homopolymers, and this certainly sheds a light on the deformation mechanism. With a dispersed phase in continuum, the interface creates additional free volume for slippage, resulting in a reduced viscosity, and additional friction as well due to the heterogeneity of the mixture.<sup>14</sup>

The relaxation spectra for the two homopolymers and blends are shown in Figure 12. The relaxation spectrum for each material was calculated using loss modulus data. The approximate method of Ninomiya and Ferry<sup>19</sup> was employed to calculate these spectra. This calculation involves three values of  $G''$ , equally spaced on the logarithmic frequency scale with a spacing of  $\log a$ :

$$H(\tau) = (2/\pi)G''(\omega) - a/(a-1)[(G''(a\omega) + G''(\omega/a) - 2G''(\omega))] \quad (8)$$

where  $\tau = 1/\omega$  and  $a$  was set to 1.259.

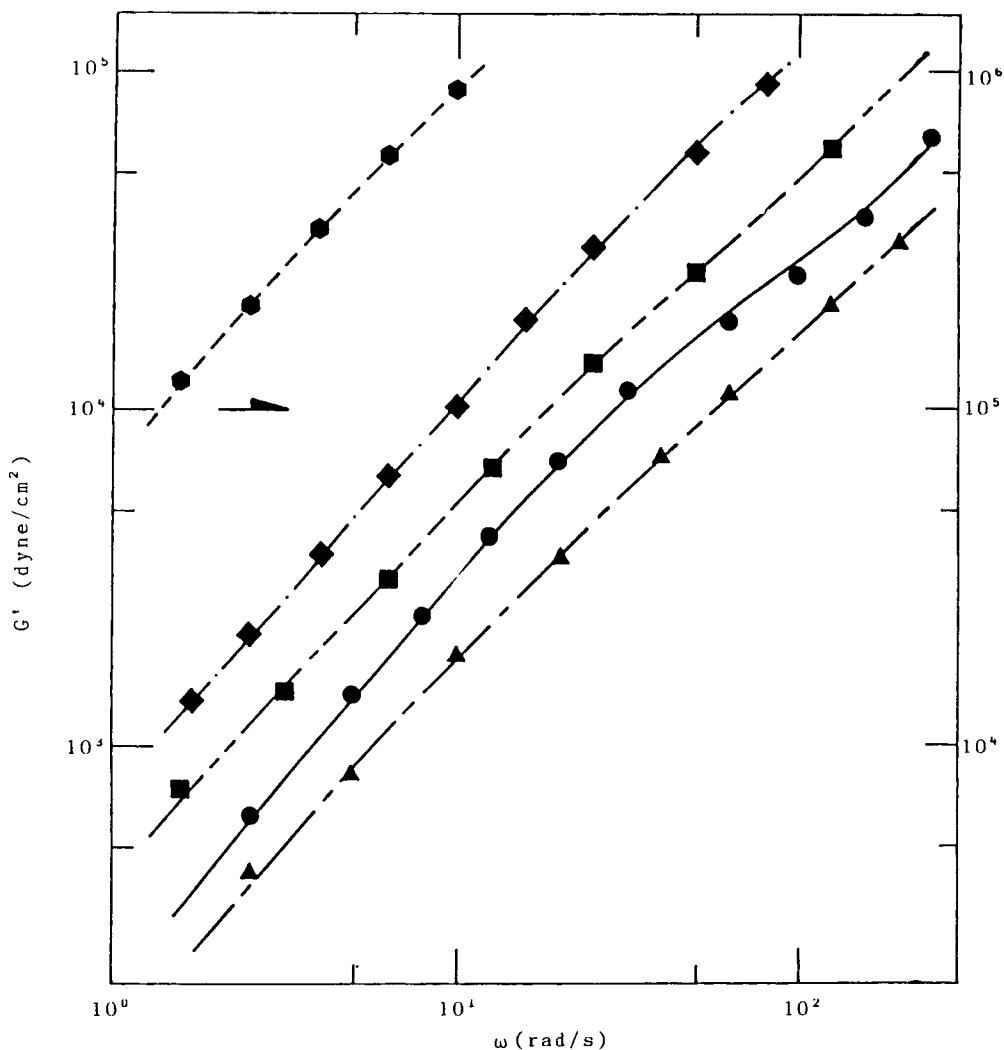


Fig. 9. Storage moduli of PET, PAR, and their blends at 300°C; Symbols are the same as Figure 7.

The relaxation spectrum refers to deformation in shear and is useful to check the internal consistency of experiment. Moreover, it is useful qualitatively in gauging the distribution of relaxation in different regions of time scale.<sup>19</sup>

The scatter in spectral points at long relaxation time is from relatively large errors in the modulus data at low frequencies where the torque is very small. As one can expect from low-frequency data, PAR extends much longer relaxation time compared to others. This is most likely due to the main chain rigidity of PAR and hence the translation of segmental motion experiences more complex flow and relaxation mechanisms than those involved in others.

The relaxation plateau, or at least a tendency to approach it, is seen only for the 85/15 blend, and the value should be lower than those of other samples. The rubbery plateau is often observed for rigid particle suspension. A sharp

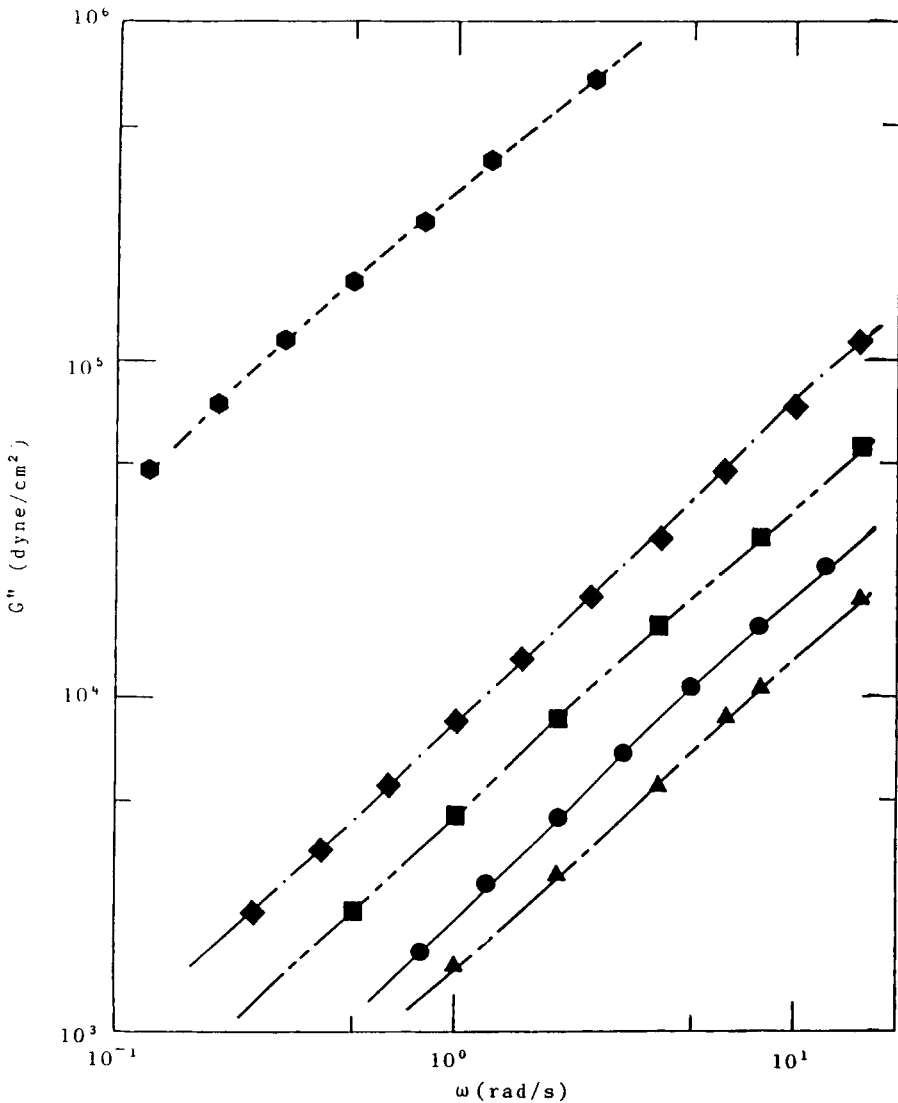


Fig. 10. Loss moduli of PET, PAR, and their blends at 300°C; Symbols are the same as Figure 7.

minimum in viscosity as well as the fine particle suspension of the dispersed phase seen at this concentration (Fig. 7) should be responsible for the existence of relaxation plateau. Present rheological measurements suggest two phase morphologies for PET/PAR blends, especially for the 85/15 blend.

### CONCLUSION

The rheological behavior of PET/PAR melt blends generally follow the two-phase incompatible system. A viscosity minimum, flow activation energy maximum, and the existence of relaxation plateau suggest a particulate-in-matrix,

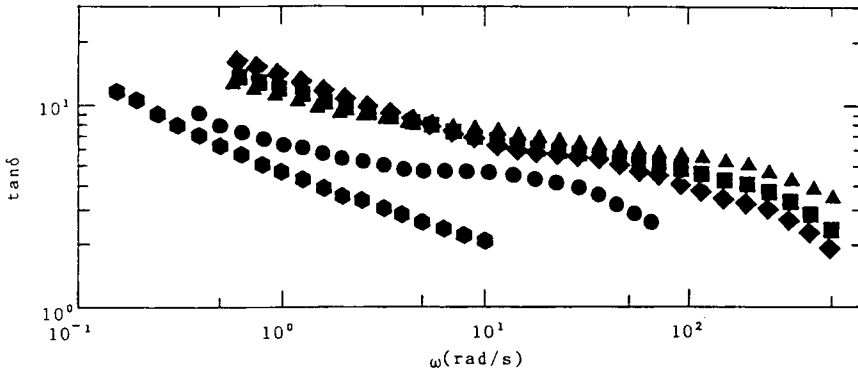


Fig. 11. Loss tangent of PET, PAR, and their blends at 300°C; Symbols are the same as Figure 7.

or a fine particle suspension nature for 85/15 (PET/PAR) composition. SEM micrographs again confirmed a fine dispersion of PAR-rich phase in PET matrix at this composition. Relatively larger dispersions of PET particles in PAR-rich matrix were observed for 50/50 blend composition.

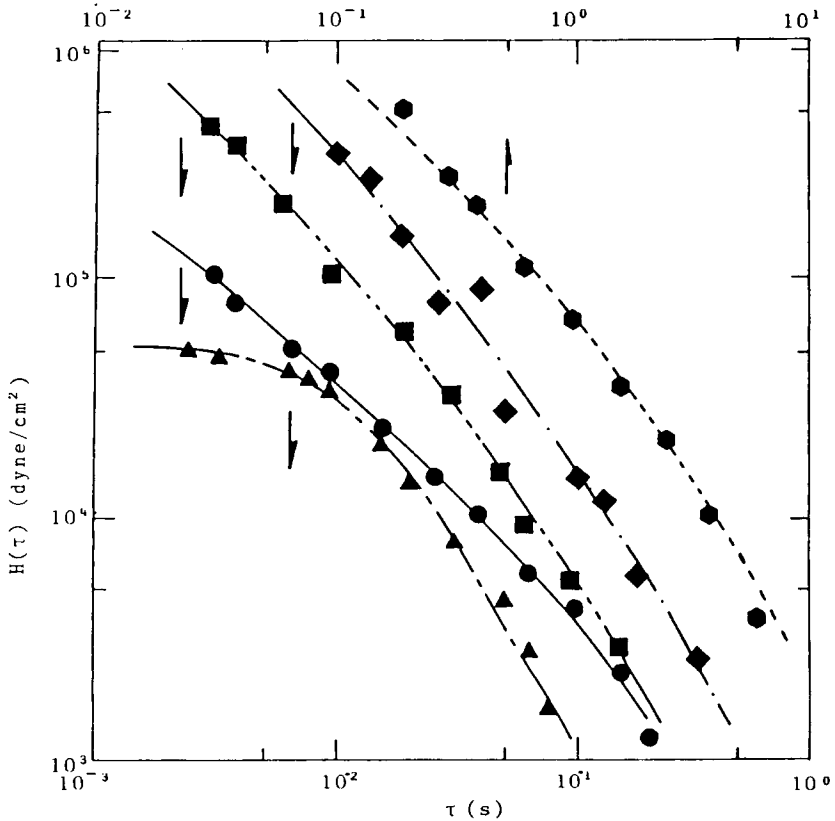


Fig. 12. Relaxation spectra from loss modulus data at 300°C; Symbols are the same as Figure 7.

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