

# Stress Relaxation Behavior of Polyacetal–Thermoplastic Polyurethane Elastomer Blends

G. KUMAR, Mr. ARINDAM, N. R. NEELAKANTAN,\* and N. SUBRAMANIAN

Department of Chemical Engineering, Indian Institute of Technology, Madras-600036, India

## SYNOPSIS

The yield stress of polyacetal (POM) decreases monotonically with the incorporation of thermoplastic polyurethane (TPU) elastomer in POM/TPU blends as would be anticipated. However, the impact strength of the resultant POM/TPU blends increases initially up to 30% TPU and thereafter decreases with the addition of TPU. Stress relaxation measurements in simple extension were carried out for POM and its blends with 10, 20, and 30% TPU at a constant temperature (30°C). Rate of loss of the relaxation modulus was found to be a nonlinear function of time. It has been demonstrated that the stress relaxation modulus values measured at different strains can be superimposed by a shift along the logarithmic time axis to yield master curves of modulus over an extended time period. It has also been found that while it is possible to determine, at any strain, relaxation curves covering an appreciable time range, the demarcation of linear and nonlinear behavior ranges of stress could not be done for these materials as all the strain values chosen in our experiments were in the region of linear behavior. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

For components based on polymeric materials, one would seek information about the mechanical response as a function of time and temperature. It is obviously not possible to test each component for a very long time, say for 25 years. Therefore some kind of accelerated testing must be carried out whereby the effects of both time and temperature can be substantially speeded up so that meaningful data with which to predict behavior over extended time and temperature regions can be obtained but over much shorter testing intervals. Creep and stress relaxation measurements are the widely employed standard methods for this purpose. The measurement of stress relaxation is considered to be a very useful tool to predict the long-term characteristics of polymeric materials as it represents the basic time-dependent response from which other time-dependent responses such as creep can be obtained.<sup>1</sup>

A simple approximation, proposed by Denby,<sup>2</sup> is capable of relating creep, stress relaxation, and recovery and is accurate enough for all textile polymers and can also be extended successfully to other viscoelastic materials.

Stress relaxation characteristics were measured<sup>3</sup> in addition to fatigue and monotonic tension tests to help gain further insight into the deformation mechanisms for glassy polymers like polycarbonate. Malik et al.<sup>4</sup> investigated the time-dependent behavior of the liquid crystalline polyester/polycarbonate blends by performing solid-state relaxation measurements. Hawthorne<sup>5</sup> discussed in detail the experimental techniques developed to measure the stress relaxation behavior of very thin (0.145  $\mu\text{m}$ ) poly(ethylene terephthalate) (PET) films using the DuPont 943 thermomechanical analyzer (TMA) module provided with the stress relaxation accessory. Kutty et al.<sup>6</sup> have investigated the stress relaxation behavior of short Kevlar fiber-reinforced thermoplastic polyurethane (TPU) elastomer with respect to strain level, strain rate, fiber loading, and fiber orientation and temperature.

Tieghi et al.<sup>7</sup> have established that the relaxation

\* To whom correspondence should be addressed.

curves of a series of crosslinked polyester resins can be superimposed by a shift along the logarithmic time axis, with shift factors that are in a good linear relation to the initial stress, and with slope and intercept values characteristic of every material. A review of the literature by these authors also shows that master curves have been constructed from the creep or stress relaxation plots of many polymeric materials by vertical<sup>8</sup> and horizontal<sup>9</sup> superimposability and by the superimposability of both.<sup>10</sup>

The rubber toughening of high-performance plastics such as polyacetal (POM), aromatic polyesters, and nylons has provided second-generation materials that can outperform most classic construction materials.<sup>11</sup> With continuing advances in the exploration of new areas of application for these materials, a thorough study of mechanical behavior, particularly long-term properties, is of great relevance. Hence the objective of the work reported here is to provide data on the stress relaxation behavior of POM/TPU blends at various strain levels and to generate master curves with simple correlations of the relative shift factors, leading to more reliable extrapolation of the data toward considerably longer loading times.<sup>7</sup> The tensile, flexural, and impact properties of POM/TPU blends are also determined and compared.

## EXPERIMENTAL

### Materials

Polyacetal (POM) (Celcon M 140) used was procured from Hoechst Celanese, USA. Celcon M 140 is a polyoxymethylene-based copolymer with a melt flow index value of 14.0 g/10 min. The TPU elas-

tomer (Estane 58311) ( $M_w = 1.5 \times 10^5$ ;  $T_g = -21^\circ\text{C}$  as determined by dynamic mechanical analysis<sup>6</sup>) is a polyether-based TPU supplied by B. F. Goodrich Co., Belgium.

### Procedure

Blends of POM and TPU were prepared by melt blending in the temperature range 170 to 200°C using a single-screw extruder ( $L/D = 20$ ), equipped with a mixing head at the screw end. The pellets obtained were utilized for determining the melt flow index (MFI) values as per ASTM D1238 with a Rosand Precision Melt Flow Index system. Compositions and the denominations with the corresponding MFI values are given in Table I. Test samples for impact testing (ASTM D256), flexural testing (ASTM D790), and dumbbell-shaped samples for tensile testing and stress relaxation measurements (ASTM D638) were prepared by injection molding method. Standard notches were made in some impact test samples for Izod impact tests and the remaining samples were used for Charpy impact tests. Samples were conditioned at the test temperature for about 24 h prior to testing. The tensile and flexural tests were carried out at a crosshead speed of 5 and 2.1 mm/min, respectively, at 30°C, with a Zwick Universal Testing Machine (UTM/model 1465).

The same UTM was also employed for relaxation measurements in uniaxial tension at 30°C. The temperature was controlled by using an environmental chamber and the temperature stability was of the order of  $\pm 1^\circ\text{C}$ . The test specimens were pulled to required strain levels, viz. 2, 3, 4, and 5% for all the materials using a crosshead speed of 10 mm/min; after the appropriate strain was reached, the strain was held constant and the decay in stress was

**Table I** Composition and Properties of the Blends

Sample Code	%TPU	MFI <sup>a</sup> (g/10 min)	Yield Stress (MPa)		Impact Strength (J/m) <sup>b</sup>	
			Tensile	Flexural	Izod (Notched)	Charpy (Unnotched)
POM	0	14.14	59.81	66.54	73.70	292.86
AU91	10	10.24	45.69	57.31	123.15	489.13
AU82	20	7.44	42.21	49.26	153.46	622.43
AU73	30	7.50	34.88	39.83	190.85	760.21
AU64	40	7.46	30.75	33.57	168.14	668.13
AU55	50	7.40	24.02	27.31	153.28	608.86
AU46	60	7.52	21.69	25.12	140.00	524.51

<sup>a</sup> Determined at 190°C; load 2.16 kg; die dia. 2.00 mm.

<sup>b</sup> To convert J/m to ft-lb/in, divide by 53.39.

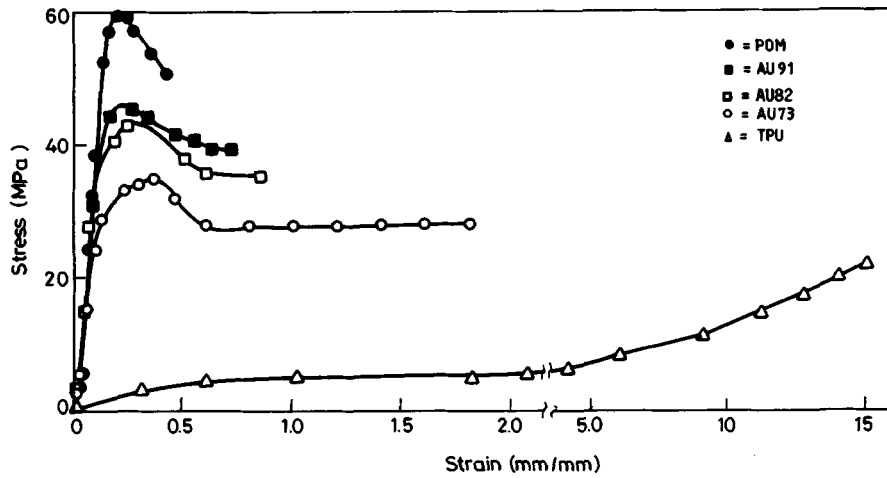


Figure 1 Tensile stress-strain curves of POM/TPU blends.

recorded as a function of time for a time span covering about 1000 min. The tensile strain was always kept within the limit of linear viscoelasticity. The stress value was converted to the corresponding modulus,  $E_r(t)$  by dividing the stress,  $\sigma(t)$  by the appropriate strain,  $\epsilon_0$ . As the instantaneous application of strain affects the early period of the relaxation behavior, the stress data have been recorded

starting 30 s after the predetermined constant strain was attained.

RESULTS AND DISCUSSION

The tensile stress-strain curves of POM, TPU, and their blends are given in Figure 1. The addition of

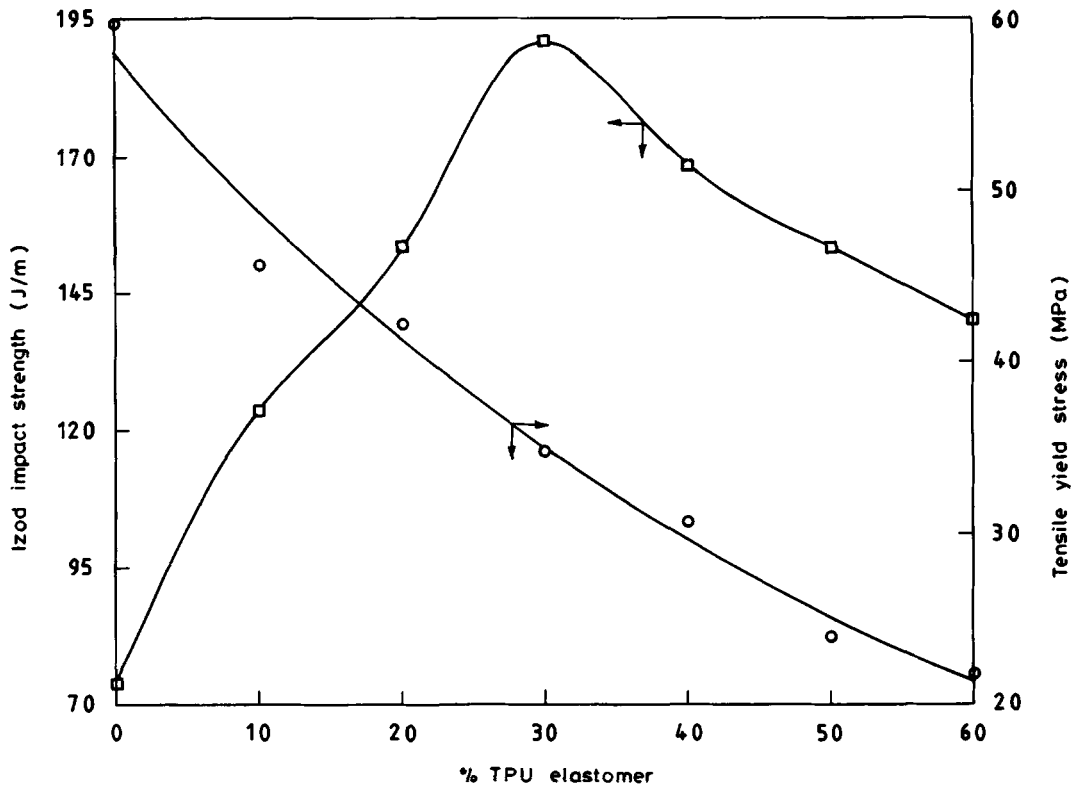


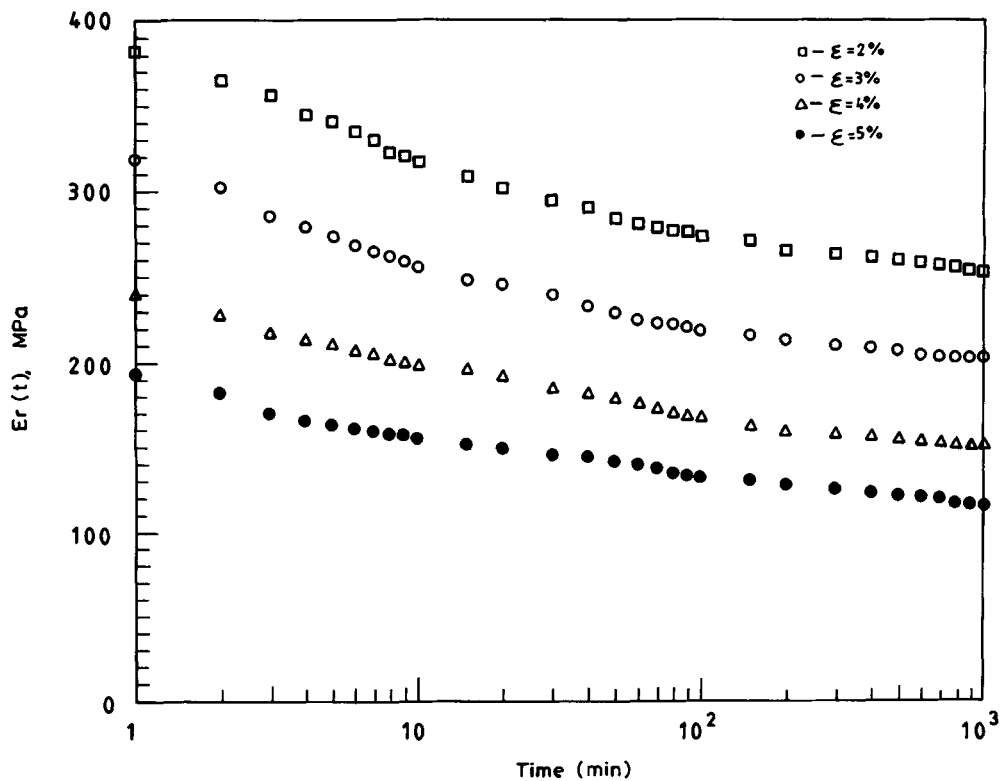
Figure 2 Effect of TPU elastomer on Izod impact strength (□) and tensile yield stress (○) of POM/TPU blends.

TPU in POM results in a decreased tensile strength and tensile modulus and increased elongation-at-break. Figure 2 shows the effect of TPU content on the tensile yield stress and the Izod impact strength of POM. The incorporation of rubbery TPU in POM/TPU leads to POMs with consistently decreasing yield stresses (Table I) as is the case with any other brittle plastics being toughened. The impact strength value of blends increases initially and reaches maximum with 30% TPU. The further addition of TPU shows a decrease in impact strength and does not, in any way, result in progressive toughening of POM. The blend AU73 exhibits a 150% increment in impact strength, and this observation is in consonance with that of Chang et al.<sup>12</sup> who have made studies with POM blends containing up to 30% TPU. It appears that addition of TPU exceeding 30% TPU does not improve the impact strength but decreases it.

Figures 3 to 6 are the stress relaxation curves of POM, AU91, AU82, and AU73, respectively, illustrating the stress relaxation behavior as a function of time. A closer examination of the stress values recorded at different strains with time reveals that the percent of stress relaxation that occurs increases

with initial strain irrespective of the composition of the material. This is consistent with the fact<sup>3</sup> that as stress increases, the probability of a chain segment possessing enough energy to flow increases and more viscous flow takes place. The nonlinear character of every material is readily discernible going by the different shapes of the modulus-time curves.

In this study an empirical horizontal shift of the  $E_r(t)$  versus time curves is made and the horizontal shift factors are computed as per a procedure similar to the one reported.<sup>13</sup> The master curves are constructed for all the compositions with respect to the lowest strain value (2%) and are shown in Figure 7. All the stress relaxation curves of the blends could be satisfactorily superimposed and smooth master curves have been obtained, barring POM and AU73 wherein a few stray points were spotted and later removed in order to get a smooth curve. The construction of master curves actually enables one to predict the long-term mechanical behavior of the blends. A superficial look at the master curves reveals an interesting observation that the initial (negative) slope values decrease with the addition of TPU, suggesting that the initial rate of stress relaxation process is slowed down because of the



**Figure 3** Tensile stress relaxation modulus against time for POM at 30°C at various strain values.

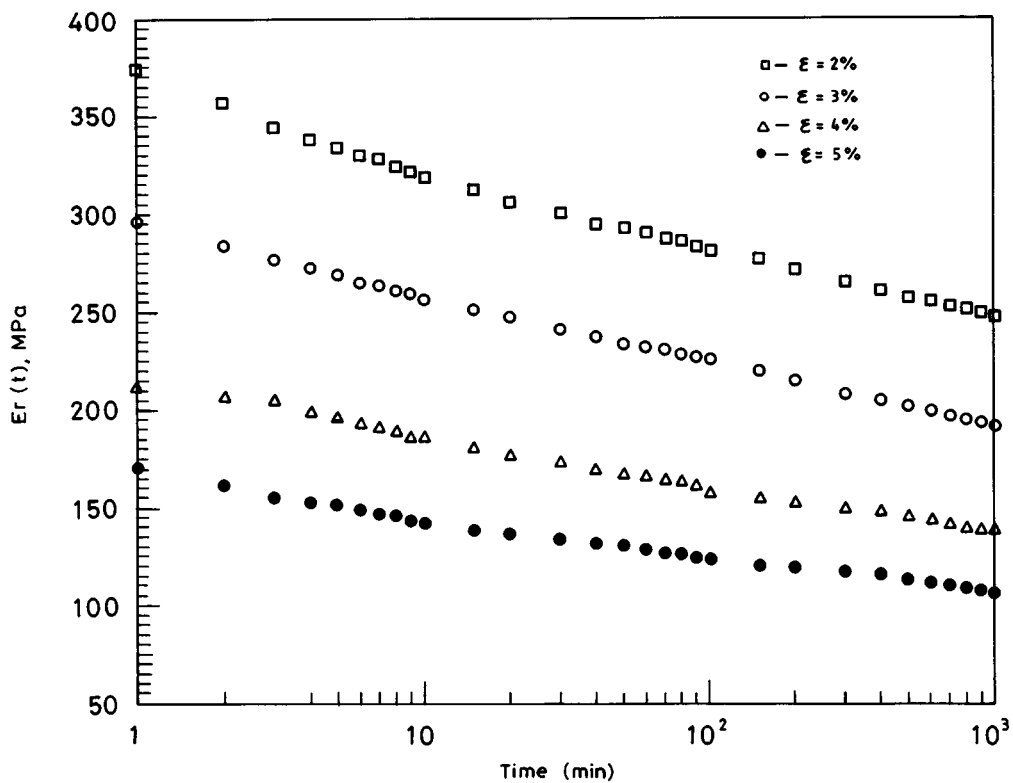


Figure 4 Tensile stress relaxation modulus against time for AU91 at 30°C at various strain values.

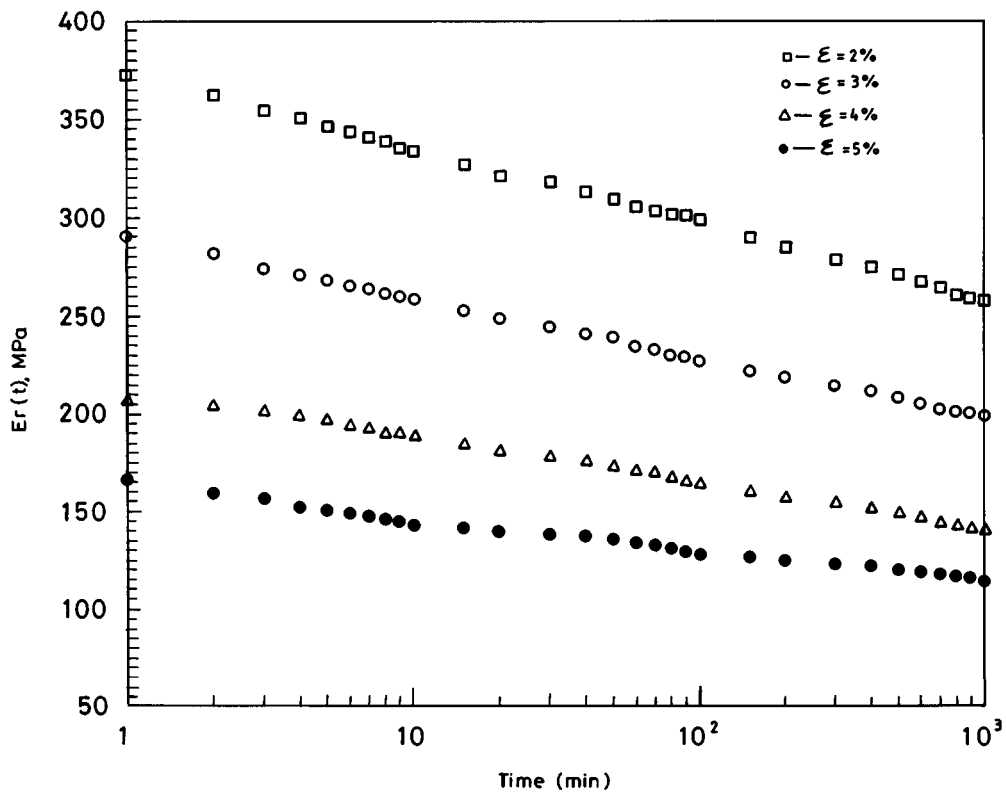
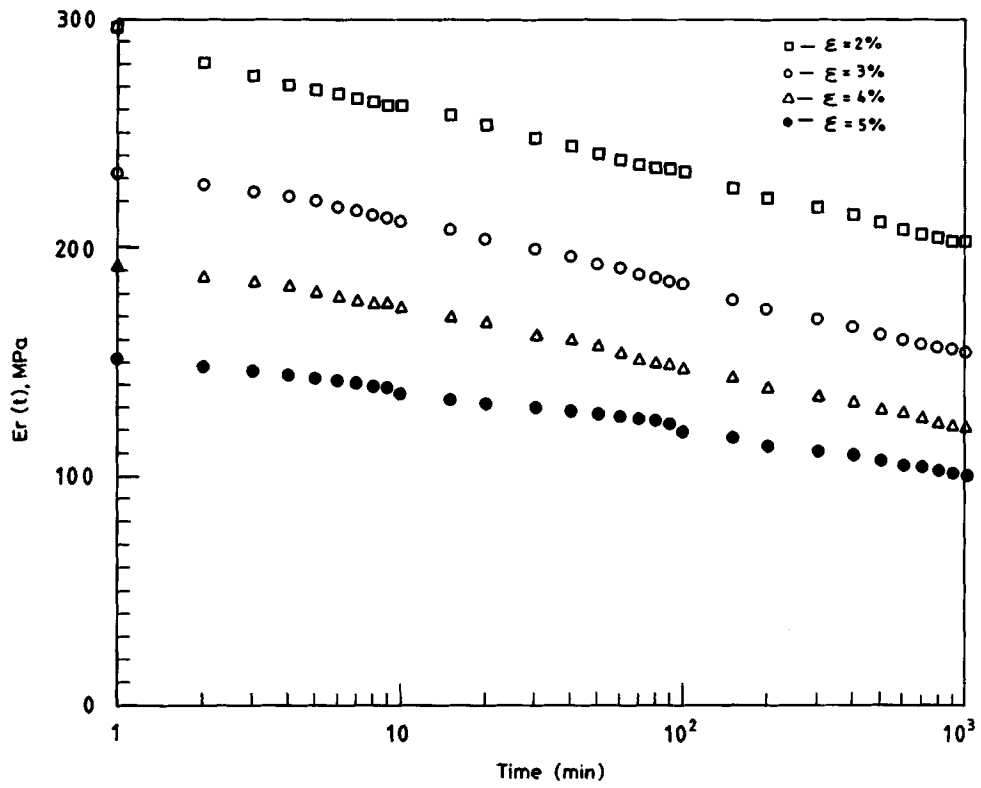
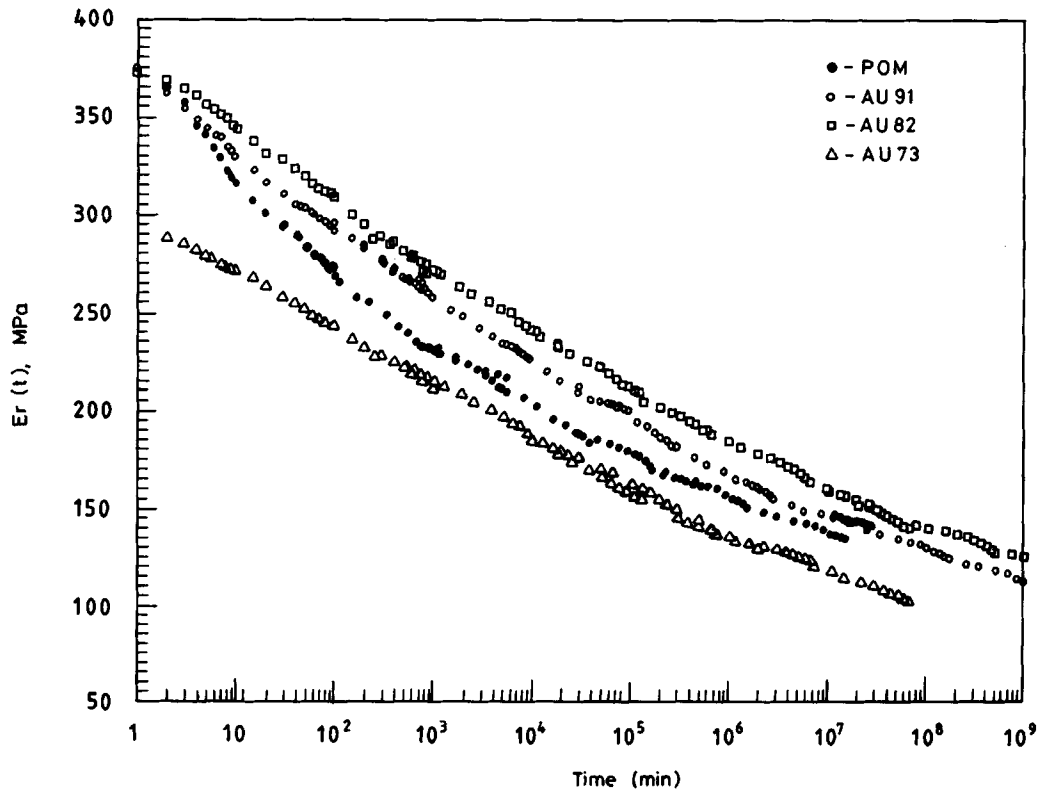


Figure 5 Tensile stress relaxation modulus against time for AU82 at 30°C at various strain values.



**Figure 6** Tensile stress relaxation modulus against time for AU73 at 30°C at various strain values.



**Figure 7** Master relaxation modulus curves vs. log (time), with respect to the lowest strain value (2%) of POM/TPU blends.

presence of TPU. However, the rate of stress relaxation later is by and large the same for POM and the blends.

It is found in the literature that the stress-induced decrease of the viscoelastic relaxation times should be related to the increase of free volume produced by the dilation accompanying a uniaxial tensile deformation. Such an effect might be explained by the Williams, Landel, and Ferry equation.<sup>10</sup> However, Struik<sup>14</sup> has, in his experiments, observed that a nonlinear strain-dependent behavior similar to that of tensile tests can also be found in shear tests where dilational effects are absent. Moreover, Tieghi et al.<sup>7</sup> stated that in classical viscoelastic terms the effect of strain is to shift the whole relaxation spectrum by a constant amount  $\alpha$ , which depends only on the value of the applied strain. Hence they proposed two simple relationships:

$$E_r(\epsilon_0, t) = E_r(\epsilon'_0, \alpha t) \quad (1)$$

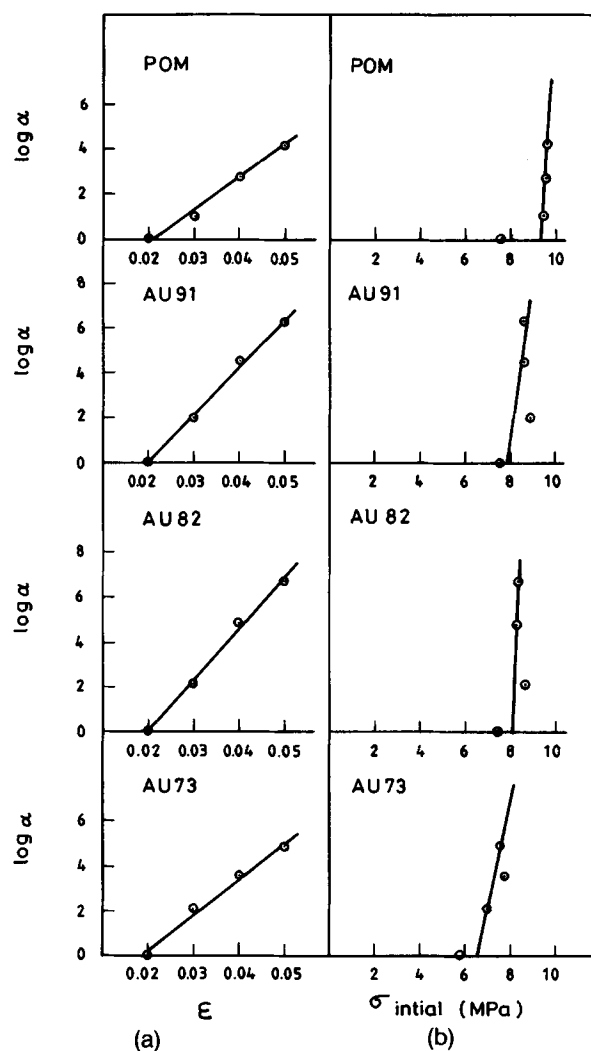
at constant temperature

$$\log \alpha = \beta(\sigma - \sigma_{lin}) \quad (2)$$

where  $E_r$  is the relaxation modulus,  $\epsilon_0$  and  $\epsilon'_0$  two different strains,  $\alpha$  the shift factor,  $\beta$  the slope of the representative straight line, and  $\sigma_{lin}$  the value of  $\sigma$  as upper limit of the linear behavior region. They have also suggested that the applicability of these relationships should be verified with other materials having different structural and morphological characteristics so as to have a generalization. As we were able to get smooth master curves covering a time range about  $10^8$  min, the first relationship appears to hold good for all the compositions of POM/TPU blends.

The computed shift factors  $\log \alpha$  versus percent strain are shown graphically in Figure 8(a). An important point to be noted here is that while Tieghi et al.<sup>7</sup> have chosen different strain levels for each material, we have selected the same set of strain values for all the materials. A linear relationship is obtained in all cases irrespective of the TPU contents in the blend.

The semilogarithmic plot of  $\log \alpha$  versus initial stress is presented in Figure 8(b). It exhibits linear characteristics. The intercept values are found to decrease with the addition of TPU elastomer as have been observed by Tieghi et al.<sup>7</sup> on a series of unsaturated polyester resins. But we could not predict the upper limit of the linear region due to the fact that all strain values selected in our case fall within the linear behavior range of the materials. Another de-



**Figure 8** Semilogarithmic plots of (a) the strain dependence and (b) the stress dependence of the horizontal shift factors determined by forming master curves of Figure 7.

viation noted in our studies is that there is a uniform fall in the slope with the addition of elastomer. This observation is actually at variance with that of the Tieghi et al.<sup>7</sup> who reported a progressive rise in slope as the flexibilizers are added to the thermoset polyester resins. The reason for this deviation may partially be attributed to the thermoplastic nature of the blends with different structural and morphological characteristics.

## CONCLUSIONS

The inclusion of up to 30% TPU results in effective toughening of POM whereas its subsequent addition proves to be otherwise. However, the yield stress of POM decreases continuously even with the further

addition of TPU elastomer. All the stress relaxation curves for the POM and POM/TPU blends could be satisfactorily superimposed and smooth master curves constructed. Future stress relaxation studies with a few more strain values chosen in the nonlinear behavior region and some additional studies at various temperatures may be required for a thorough understanding of the long-term behavior of these blends.

## REFERENCES

1. R. F. Fedors, S. Y. Chung, and S. D. Hong, *J. Appl. Polym. Sci.*, **30**, 2551 (1985).
2. E. F. Denby, *J. Text. Inst.*, **65**, 239 (1974); *Rheol. Acta*, **14**, 591 (1975).
3. T. K. Mattioli and D. J. Quesnel, *Polym. Eng. Sci.*, **27**, 843 (1987).
4. T. M. Malik, P. J. Carreau, and N. Chapleau, *Polym. Eng. Sci.*, **29**, 600 (1989).
5. J. M. Hawthorne, *J. Appl. Polym. Sci.*, **26**, 3317 (1981).
6. S. K. N. Kutty and G. B. Nando, *J. Appl. Polym. Sci.*, **42**, 1835 (1991).
7. G. Tieghi, L. A. Fallini, and F. Danusso, *Polymer*, **32**, 39 (1991).
8. R. Bloch, W. V. Chang, and N. W. Tschoegl, *J. Rheol.*, **22**, 1 (1978).
9. E. Passaglia and H. P. Koppehele, *J. Polym. Sci.*, **33**, 281 (1958).
10. S. Matsuoka, *Polym. Eng. Sci.*, **21**, 907 (1981).
11. C. K. Riew, *Rubber Toughened Plastics*, American Chemical Society, Washington, D.C., 1989.
12. F. C. Chang and M. Y. Yang, *Polym. Eng. Sci.*, **30**, 543 (1990).
13. P. M. Ogibalov, N. J. Malinin, V. P. Netrebko, and B. P. Kishkin, *Structural Polymers*, Vol. 2, Wiley, New York, 1974, p. 284.
14. L. C. E. Struik, *Physical Ageing in Amorphous Polymers and Other Materials*, Elsevier, Amsterdam, 1978.

Received February 11, 1993

Accepted March 3, 1993