

Effect of shear stress on viscoelastic properties of a phase-separated multiblock thermoplastic elastomer

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Shear experiments on a molten thermoplastic elastomer (TPE) show that, above a critical stress level, the viscoelastic properties are severely affected by the flow. The TPE is a microphase-separated multiblock copolymer of poly(4-methyl-1,3-dioxolane) (PMDOL) with a copolymer of dioxolane and trioxane (PDT). The amorphous PMDOL undergoes glass transition at about -60°C , and the crystalline PDT phase melts at about 105°C . When sheared in a creep experiment at a shear stress below a critical value, the transient shear viscosity, $\tau/\dot{\gamma}(t)$, grew by two orders of magnitude without coming close to reaching steady state in the first 1000 s, and 40–80% of the total strain was recovered upon release of the shear stress. At higher shear stresses, $\tau/\dot{\gamma}(t)$ passed through a maximum and then levelled off to a low plateau (steady shear viscosity), i.e. the TPE changed into a viscoelastic fluid of low viscosity. In oscillatory shear, linear viscoelasticity was limited by a critical shear stress amplitude, τ_0 , which was independent of frequency and in agreement with τ_c of the creep experiment. τ_c dropped from 800 to 100 Pa as the temperature was increased from 120 to 160°C . Polarizing microscopy showed that the shear-induced transition is accompanied by the disruption of PDT domains which otherwise would act as physical crosslinks in the TPE melt.

(Keywords: shear stress; viscoelastic properties; thermoplastic elastomer)

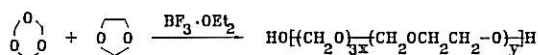
INTRODUCTION

The rheological behaviour of microphase-separated block copolymers have been studied extensively^{1–14}. Compared with homopolymers of similar molecular weight, phase-separated block copolymers often exhibit very high viscoelastic properties, which, however, are sensitive to shear modification. This character of phase-separated block copolymers is attributed to two-phase domain structuring. In the present work, phase separation and shear-induced structuring in a multiblock thermoplastic elastomer melt were studied as a function of shear stress and temperature, using rheometers and a polarizing microscope.

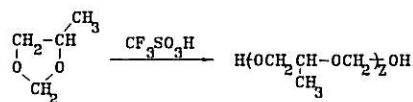
EXPERIMENTS

Materials

The crystalline block consisted of dioxolane and trioxane (PDT):

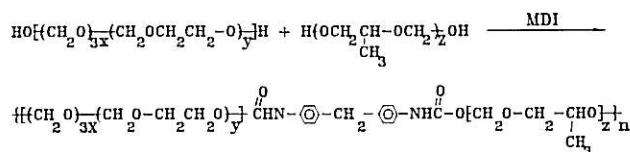


The \bar{M}_n as estimated by determination of active hydrogen was 3000 and melting temperature was about 105°C . The amorphous block was poly(4-methyl-1,3-dioxolane) (PMDOL).



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with an \bar{M}_n of 6000 and a glass transition temperature of about -60°C . The multiblock thermoplastic elastomer (TPE) was prepared from PDT and PMDOL with mole ratio 1:4, using 4,4-diphenylmethane diisocyanate (MDI) as coupling agent:



In the molecular formulae above, x , y , z and n are distributive parameters.

Apparatus

Steady and dynamic shear flow measurements were performed, respectively, on a Rheometrics stress rheometer (RSR) and a Rheometrics dynamic spectrometer (RDS), using cone/plate geometry. Samples were moulded in the rheometers at 120°C , then annealed at the experimental temperature for 30 min before the measurement. The crystallinity and the microphase-separated structure of the multiblock TPE were examined on a Leitz polarizing microscope.

RESULTS AND DISCUSSION

In a temperature sweep (Figure 1), the PDT and the TPE showed the same melting temperature of about 105°C . This indicates that the TPE phase separated into domains^{15,16} and that the crystalline structure of PDT

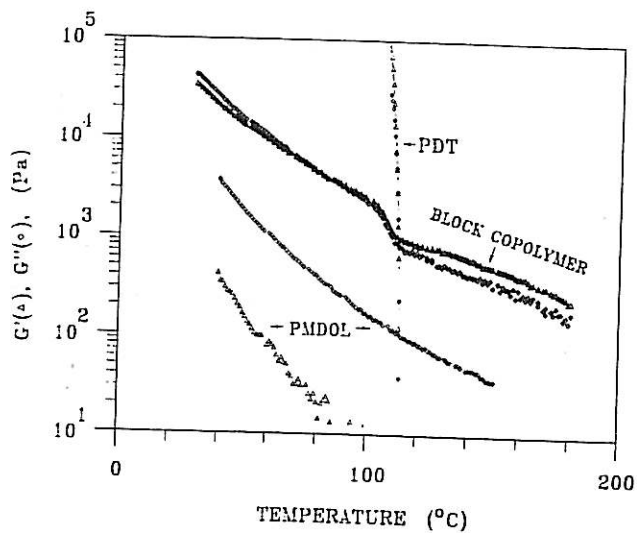


Figure 1 Temperature sweep on RDS at frequency $\omega=1 \text{ rad s}^{-1}$, heating rate 1 K min^{-1} , and small strain amplitude within linear viscoelastic region. G' and G'' are the storage modulus and the loss modulus respectively

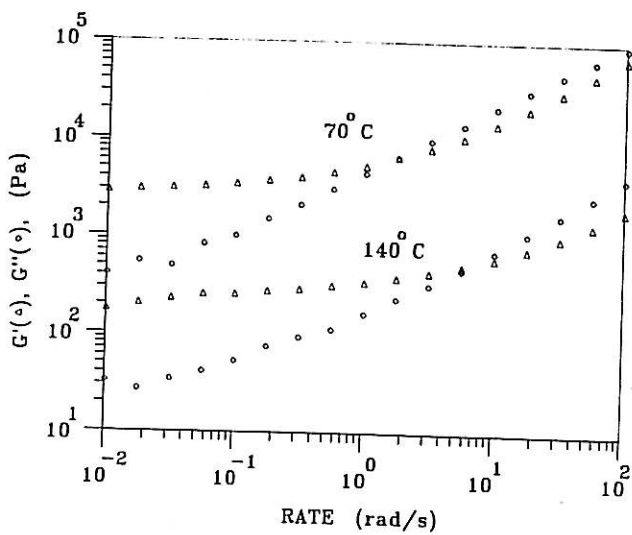


Figure 2 Rate sweep for the TPE below or above the melting temperature of the PDT phase

phase is not significantly modified by the presence of surrounding PMDOL amorphous phase. The strongly phase-separated system forms a physical network in which the PDT domains act as multifunctional junction points and the PMDOL chains act as flexible connectors. Below the melting temperature of PDT, the PDT blocks register into crystalline order. Note that in the TPE the weight ratio of PDT/PMDOL is only about 1:8, but the TPE showed a storage modulus 100 times and a loss modulus ten times that of the PMDOL homopolymer of similar molecular weight.

Above the melting temperature of the PDT phase, polarizing microscopy showed the absence of crystallinity in the TPE. However, the TPE melt still exhibited much higher mechanical properties than PDT and PMDOL homopolymers (Figure 1). On the other hand, a frequency sweep in the linear viscoelastic region showed that melting of the PDT phase did not modify significantly the shape of mechanical spectra (Figure 2). The G' plateau at low frequencies indicates solid behaviour even above the T_m of PDT. The decreasing modulus with increasing

temperature may be attributed first to the increased mobility of the PMDOL chains as the PDT domains become amorphous and secondly to the finite lifetime of the PDT network junctions. Time-temperature superposition of the curves would require a vertical as well as a horizontal shift.

The rheological behaviour of the TPE melt was found to be very sensitive to stress. Figure 3 shows the transient viscosity, $\tau/\dot{\gamma}(t)$, in a shear creep experiment on the RSR rheometer at 140°C . When the shear stress was $< 300 \text{ Pa}$, the transient viscosity increased by two orders of magnitude in the first 1000 seconds, and the resulting strain did not exceed 5 shear units. After the cessation of shear stress, 40–80% of the total shear strain recovered. The TPE melt behaved in a highly elastic manner. However, with shear stresses above 600 Pa, $\tau/\dot{\gamma}(t)$ passed through a maximum and then levelled off to a low plateau which can be regarded as steady shear viscosity. Then, the recoverable shear strain was negligibly small, i.e. the TPE melt was transformed to a viscoelastic fluid of low viscosity and low elasticity. There appears to exist a critical shear stress which is needed to reduce the connectivity of the microphase-separated structure.

The value of critical shear stress was checked by oscillatory shear on the RDS rheometer. At a constant frequency ($\omega=0.1, 1, 10$ or 100 rad s^{-1}), the viscoelastic properties of the TPE melt changed as the strain amplitude increased, especially at low frequencies (Figure 4). However, the TPE melt did not show a frequency-independent critical strain amplitude (as one usually finds when working with homopolymers). In a search for a critical stress amplitude, the data of Figure 4 was replotted versus measured stress amplitude (Figure 5). At all experimental frequencies, the viscoelastic properties of the TPE melt seem to change at a critical stress amplitude of 700 Pa.

For the critical stress amplitude $\tau_0=700 \text{ Pa}$, the average shear stress in oscillatory shear

$$\bar{\tau}_d = \omega/2\pi \int_0^{2\pi/\omega} |\tau^0 \sin(\omega t + \delta)| dt = 2\tau_0/\pi$$

is calculated as $\bar{\tau}_d=450 \text{ Pa}$. This value is in good agreement with the results of the creep experiment shown in Figure 3.

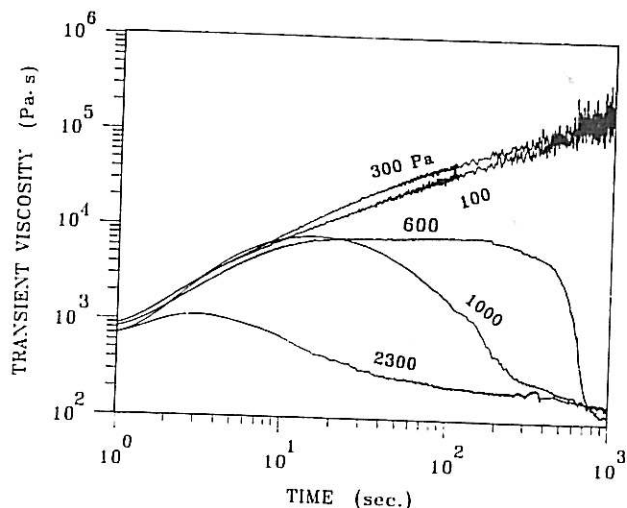


Figure 3 Shear creep on RSR at 140°C for various values of shear stress

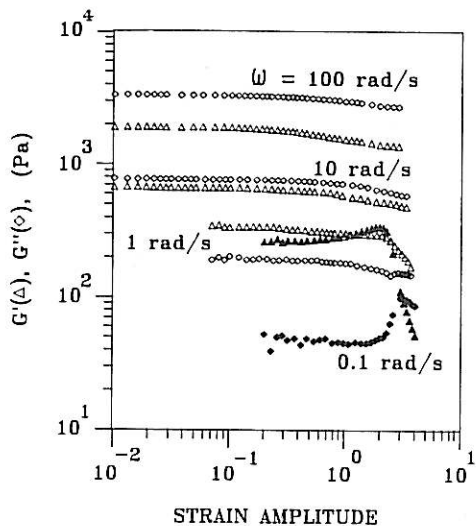


Figure 4 Strain sweep on RDS at 140°C and indicated frequencies, ω

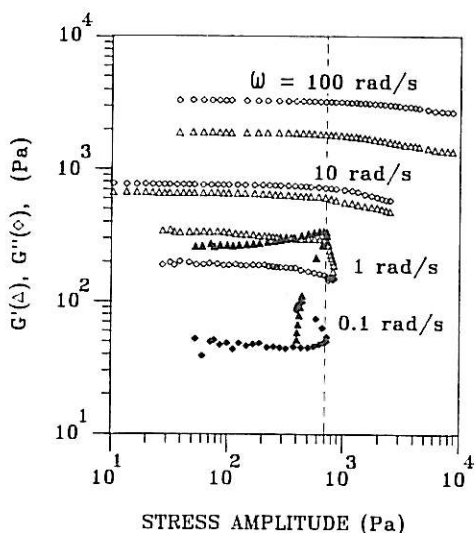


Figure 5 Storage modulus and loss modulus as a function of measured shear stress amplitude. Data are from Figure 4

The transition from elastic to viscous behaviour upon shearing above the critical shear stress is considered to be a result of the breaking of physical crosslinks, i.e. of disrupting the PDT domains. To provide evidence for that, a thin layer of the TPE was placed between two glass slides, heated to 140°C for 30 min, severely sheared, and then quickly cooled to room temperature. For comparison, a second sample was prepared with the same thermal treatment but without shearing. Polarizing microscopy showed that the crystalline PDT domains of the sheared sample were much smaller (Figure 6). This supports the hypothesis that a high stress shear at 140°C disrupts the PDT domains.

The critical shear stress varied with temperature. With the creep experiment, we took the ratio $\tau/\dot{\gamma}$ ($t=1000$ s) and plotted it as a function of shear stress (Figure 7). It can be seen that the critical shear stress decreased as the temperature increased. This decrease is attributed to the approach to the coexistence temperature. However, coexistence could not be achieved due to starting degradation above 160°C.

Figure 8 shows the reversibility of high stress induced

structuring in the TPE melt. On the RDS rheometer, a sample was sheared at a frequency of 0.1 rad s⁻¹. When the strain amplitude was stepped up to $\gamma_0 = 3$ (τ_0 changed to 1000 Pa in the first cycle), the dynamic moduli gradually decreased. After returning to a small strain amplitude ($\gamma_0 = 0.3$) so that the resulting shear stress amplitude was much below the critical value, both the

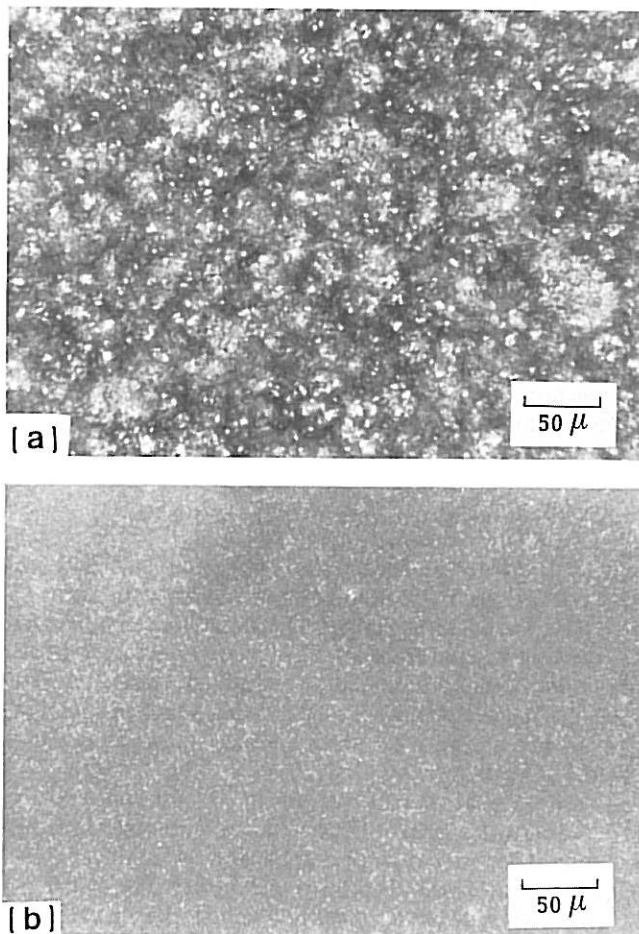


Figure 6 Polarising microscopy photographs taken at room temperature. The samples were quickly cooled from 140°C. (a) Unsheared sample; (b) sample which had been severely sheared at 140°C

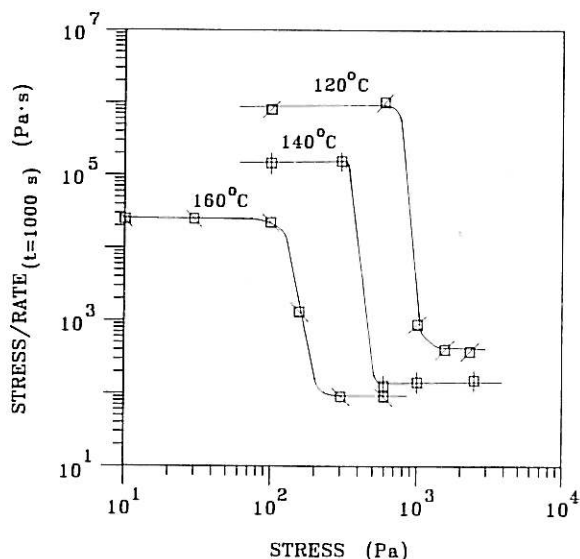


Figure 7 Temperature dependence of critical shear stress

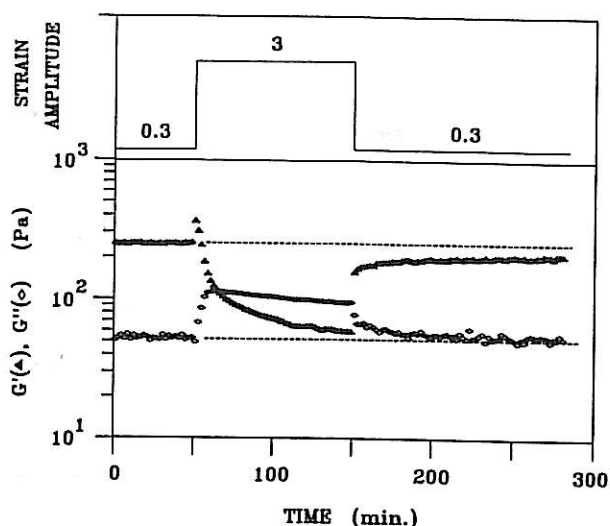


Figure 8 Recovery after large strain amplitude shear, with $T = 140^{\circ}\text{C}$, and $\omega = 0.1 \text{ rad s}^{-1}$

storage modulus and the loss modulus returned gradually to the initial values. This indicates a slow recovery of the PDT domains.

CONCLUSIONS

The TPE forms a microphase-separated structure in which PDT domains connect the continuous, low T_g PMDOL chains into a three-dimensional network. Below the melting temperature of PDT, the crystalline PDT junctions are of permanent nature and the whole material is an elastomer. Above T_m , the PDT junctions are of non-permanent nature. Their lifetime depends on the applied stress.

At low stresses, the relaxation time of the junctions is so large that the network seems to be permanent in the dynamic mechanical experiment (G' plateau at low frequencies) and in short creep experiments. The transient nature of the junctions reveals itself in the incomplete recovery after shear and in the lack of time-temperature superposition of the linear viscoelastic data. The mechanism of flow at low stresses is not yet known.

As the stress increases beyond a critical value τ_c , a drastic reduction of the dynamic moduli and of the transient shear viscosity (creep) is observed. This may

be attributed to the breaking of PDT domains as the mechanical energy density $\tau\gamma$ exceeds the phase separation energy $N\chi kT$, and the PDT blocks will be pulled out from the PDT domains. After flow at a high shear stress, the two-phase network structure of the TPE melt recovers slowly, as observed in the polarizing microscope, and hence the low viscosity behaviour can be temporarily maintained for processing.

The existence of a critical shear stress for the onset of nonlinear viscoelasticity will be important for the formulation of rheological constitutive equations for TPEs. This observation is especially interesting in comparison with the behaviour of conventional homopolymers, for which the onset of nonlinear viscoelasticity seems to occur at a critical strain, independent of the associated stress.

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