Stress relaxation of poly(1,4-dimethylene-trans-cyclohexyl suberate)

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Stress relaxation experiments were conducted on poly(1,4-dimethylene-*trans*-cyclohexyl suberate) (MCS) as a function of preparation condition and temperature. Deconvolution of the stress relaxations provides relaxation times, which can be plotted as a function of temperature to obtain an activation energy for the relaxation process. For an MCS sample of $M_n = 24.8$ K, $MWD = 2$, the activation energy varies from 12.7–5.0 kcal mol^{-1} with forming temperatures varying from 45–90°C. These activation energies are associated with different populations of tie molecules between lamellae. We believe that these activation energies reflect the reorientation process in the amorphous segments of the polymer during stress relaxation.

INTRODUCTION

Stress relaxation has been used as an experimental tool to investigate the effects of polymer morphology[1-4], structure[5], ambient conditions[6,7] and dopants[8] on the viscoelastic response of polymers.

Our interest in stress relaxation stems from recent work on crack propagation in the semicrystalline polymer poly(1,4-dimethylene-*trans*-cyclohexyl suberate)[9,10] (MCS), where a logarithmic dependence of propagation energy with temperature was observed between T_g ($\sim -20°C$) and T_m (97°C). In this temperature regime the deformation character of the polymer changed from plastic deformation to *trans*-spherulitic or interspherulitic fracture with increasing temperature. We thought that the large changes in energy observed during those experiments could be correlated with stress relaxation in the polymer. Then the following experiments were undertaken.

EXPERIMENTAL

Samples for stress relaxation experiments were made by melting MCS in a mould at $\sim 130°C$, quenching the samples in a water bath at the desired annealing temperatures, and annealing them in a convection oven at the annealing temperature for 21 h (growth studies have shown this time to be sufficient for complete crystallization of the polymer except at temperatures very near the melt temperature[9]). The sample size was $10 \times 1 \times \sim 0.25$ cm. The MCS used in these experiments had a polystyrene equivalent $M_n = 24.8$ K and a molecular weight distribution = 2.

Stress relaxation experiments were conducted on an Instron tensile tester (model 1113). Samples were extended to strains of 4 and 6%, although all data presented here were taken at a strain of 6% as they were almost indistinguishable from the 4% data. Stress relaxation was carried out as a function of temperature with samples

formed at three annealing temperatures (45, 65 and 85°C). These annealing temperatures provided degrees of crystallinity of $45 \pm 3\%$ and average spherulitic radii of 8, 13 and 300 μm, respectively[9]. Average lamellar thickness varied from ~ 150–180 Å in this annealing range[9].

Some stress relaxation experiments were performed at temperatures higher than the forming temperature of the sample. In these cases, lamellar thickening of the polymer occurred during the experiment[11]. In the time frame of these experiments (~ 1 h) lamellar thickening does not appear to have affected our results significantly and may be adding only to the error in their reproducibility.

DATA ANALYSIS

Stress relaxation is many times related to a multicomponent Maxwellian model where

$$E(t) = \sum_{n=1}^{a} E_n(0)\exp(-t/\tau_n) \qquad (1)$$

where E_n represents the stress relaxation modulus of the individual components and τ_n is their relaxation time. Such a representation of the data would imply that a plot of $\log E(t)$ vs. t could provide a curve that can be deconvoluted into a series of relaxation times and that the temperature dependence of such times would provide an activation energy for the processes involved in the relaxation.

A typical stress relaxation curve for MCS is shown in *Figure 1*. The relaxation is similar to that of many polymeric systems and shows a finite stress at long times. With the asymptotic value of stress defined as $E(\infty)$, the data can be deconvoluted to provide a measure of a portion of the relaxation time distribution function. Thus, the first deconvolution would provide a plot of $\log[E(t) - E(\infty)]$ vs. time and would appear as in *Figure 2*. Further deconvolutions of data would provide ad-
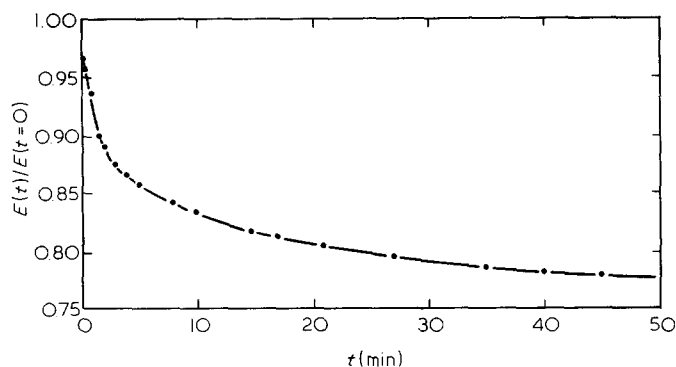
Figure 1 Reduced relaxation modulus vs. time. Experimental temperature is 59°C. Annealing temperature is 45°C
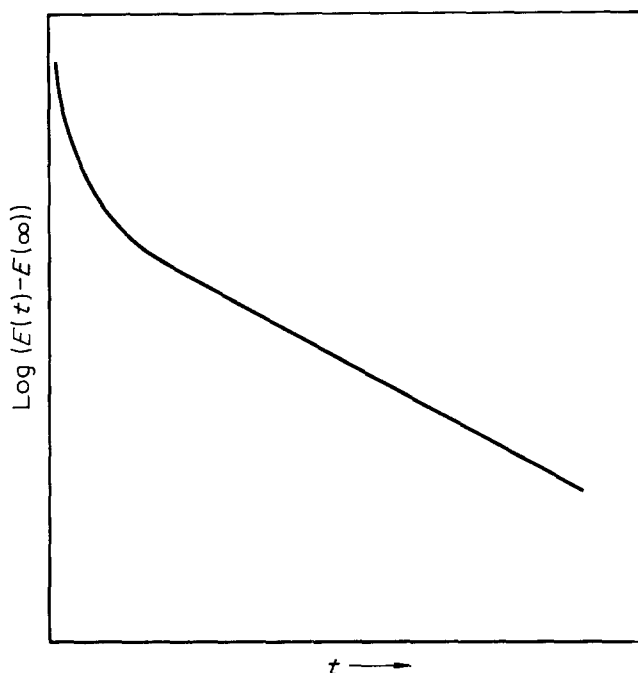

Figure 2 Schematic of deconvolution of stress relaxation data

ditional relaxation times. Naturally, each consecutive deconvolution would provide for less reliable values of the relaxation time; thus the smaller values of τ will be much more inaccurate.

These data were deconvoluted by a linear regression of the linear portion of the data in *Figure 2*. The data were then replotted as $\log[E(t)-E_1(t)]$ vs. t. The maximum number of deconvolutions for any experiment was three, providing four relaxation times. Data for a single temperature experiment (*Table 1*) show almost an order of magnitude changes in τ. *Figure 3* shows a plot of the deconvoluted relaxation time data for an MCS sample formed and annealed at 45°C; the activation energies calculated from the best fit of the data as shown. Average activation energies (the average of those shown in the figure) for samples formed at various temperatures are given in *Table 2*.

DISCUSSION

The activation energies derived from the relaxation data are lower than those observed for shear relaxation in polyethylene[4]. Their dependence on annealing temperature is similar to that observed in crack propagation

studies on MCS, i.e. they decrease with increasing annealing temperature. For an identical molecular weight, they are about half the value observed for crack propagation. Yamada et al.[4] related their relaxation activation energy to the molecular structure of the sample being studied (branched polyethylene). For MCS, the temperature region of interest is between T_g and T_m. No evidence for any molecular relaxation taking place in the crystalline regions of MCS has been found in this region (dynamic mechanical, dielectric experiments), so it must be assumed that the activation energy obtained is due to some stress induced reorientation barrier in the amorphous regions. The fact that these activation energies are smaller than those observed in crack propagation studies could be due to either of two effects: (1) The activation energy could be a function of the absolute strain and of the strain rate of the material, which would make the two experiments (stress relaxation and energy to propagate) significantly different. (2) The two experiments could be sampling different time scales in the relaxation distribution function that have quite different values of τ and activation energy.

Table 1 Relaxation times (sec) for an MCS sample prepared at 45°C. Stress relaxation done at 60°C

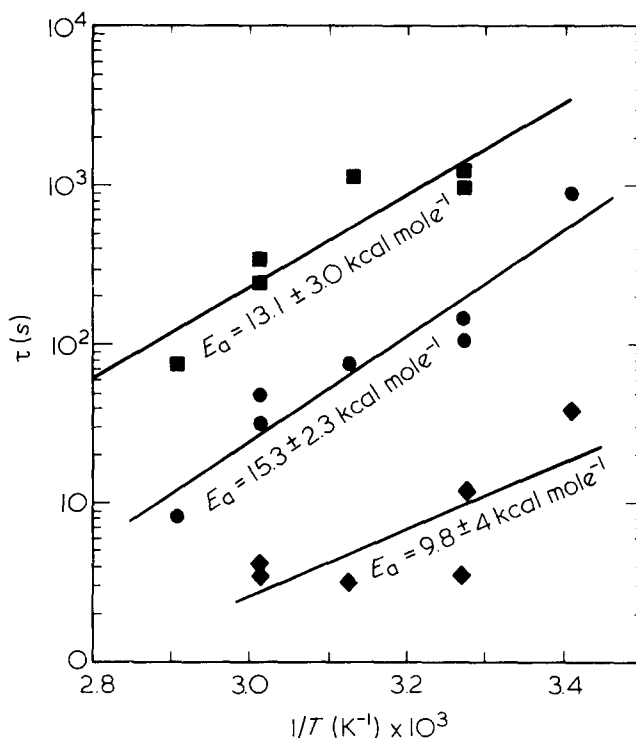| τ_1	τ_2	τ_3	τ_4
2125 ± 530	300 ± 70	39 ± 13	3.8 ± 0.4

Figure 3 Stress relaxation time vs. inverse temperature for MCS sample formed and annealed at 45°C

Table 2 Average stress relaxation energy as a function of forming temperatures for MCS

Forming temperature (°C)	E_a (kcal/mol)
45	12.7 ± 3.1
65	9.9 ± 1.9
85	5.0 ± 1.5

One might expect this to be true, as the energy to propagate specifically contains a strain-rate dependence, which could sample faster relaxation times than the stress relaxation measurement. Thus it is not surprising that the measured activation energies do not coincide. The decrease in activation energy with increased annealing temperature can be ascribed to the change in tie-molecule population with increased annealing temperature. Producing semicrystalline samples at temperatures near T_m increases lamellar thickness, increases spherulite size, and decreases the number of interlamellar tie molecules[12]. Decreasing the number of tie molecules (with the degree of crystallinity remaining constant) will result in less energy being required to reorient the molecules during the stress relaxation experiment. Thus it might be expected that higher annealing temperatures would produce lower activation energies for the stress relaxation.

It is tempting to compare relaxation times from the various experiments (annealing conditions); however, there is no way of ascertaining what portion of the relaxation time spectra is being sampled in each case, and as such, no direct comparison of the relaxation time can be made.

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