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STRAIN, BIREFRINGENCE, AND VOLUME RELAXATION AND RECOVERY IN POLYMER GLASSES *

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ABSTRACT

Stress and volume relaxation, creep, strain recovery and thermally activated strain recovery measurements have been made on bisphenol-A polycarbonate, a polyetherimide, and poly(2,6-dimethyl-1,4-phenylene oxide) as functions of thermal history, room temperature aging, strain, hold time and temperature. It was observed that as the temperature was increased, the amount of persistent strain not only increased, but also affected the stress relaxation behavior, and was observed to be partially recoverable at the test temperature. These data are interpreted in terms of a network model wherein it is proposed that the motion of defects between and past entanglements, their loss at chain ends, and the disentanglement of chain ends from other segments serve as the primary mechanisms of relaxation in the glassy state.

INTRODUCTION

The use of amorphous thermoplastics such as bisphenol-A polycarbonate (PC), polyetherimide (PEI) and poly(2,6-dimethyl-1,4-phenylene oxide) (PXO) is a consequence of their high heat distortion temperatures. However, it is well known that such materials undergo physical aging at room temperature and thermal aging at elevated temperatures. For example, in the case of polycarbonate, it has been shown that thermal aging leads to embrittlement as measured by notched Izod impact tests, and that the phenomenon is sensitive to the molecular weight, the molecular weight distribution, and the annealing temperature [1].

The present work focuses on the anelastic and plastic response of such materials as functions of thermal history, temperature and strain/stress level, with the objective of trying to define the underlying mechanisms that contribute to mechanical behavior. The results are interpreted in terms of

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various possible motions of conformational defects within the chain structure as well as at chain ends.

THEORY

In previous works, we have proposed that the mechanical response of polycarbonate can be interpreted in terms of the motion of defects within a network [2–4]. In particular, it was proposed that (1) the motion of defects between entanglements would give rise to an anelastic response of the material, (2) the passage of a defect past an entanglement would cause a persistent strain, and (3) the loss of a defect at the end of a chain would cause a second type of persistent strain. These processes were assumed to occur in a consecutive rather than a parallel manner. As in the case of consecutive chemical reactions (e.g. A going to B, B going to C, and C going to D), the overall rate is a complex function of the individual rate constants. A dashpot model for this behavior is shown in Fig. 1, where the springs and dashpots are numbered. If one assumes that η_3 and η_4 are infinite, then one obtains the following equation for the stress relaxation:

$$\sigma(t) = \epsilon(E_r + \Delta E \exp(-t/\tau)) \qquad (1)$$

where E_r is the relaxed modulus, ΔE is the difference between the unre-

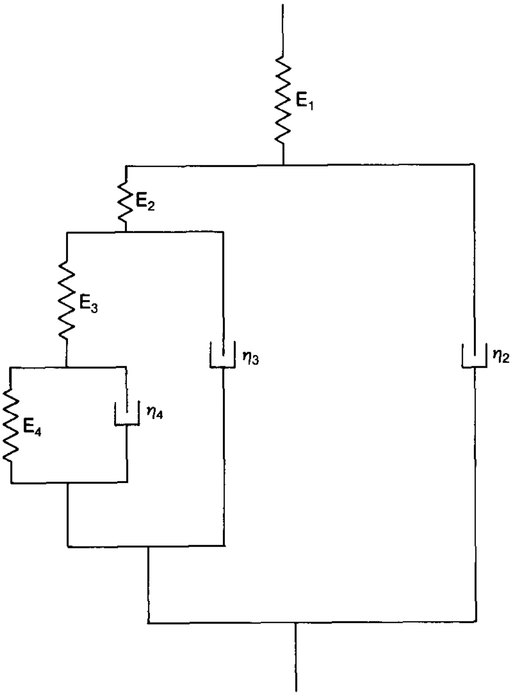

Fig. 1. A dashpot model for stress relaxation.

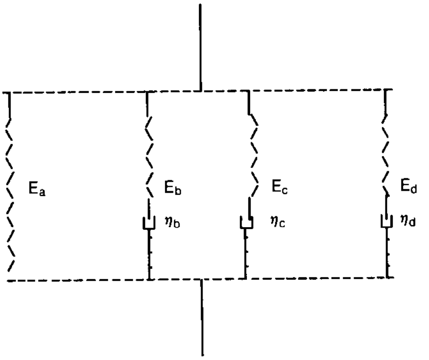

Fig. 2. A Maxwell model which is equivalent to the model in Fig. 1.

laxed and relaxed moduli, and τ is the relaxation time. If one assumes that only η_4 is infinite, then the new equation is given as

$$\sigma(t)=\epsilon(E_r+\exp(-Dt/\tau)(A\sinh(Qt/2)+B\cosh(Qt/2))) \tag{2}$$

where D, A and Q are parameters that are defined in terms of the various E_i and η_i quantities. As shown by Alfrey, if one redefines the various coefficients appropriately, then eqn. (2) can be rewritten as

$$\sigma(t)=\epsilon(E_r+\Delta E_1\exp(-t/\tau_1)+\Delta E_2\exp(-t/\tau_2)) \tag{3}$$

which is mathematically equivalent to a generalized Maxwell model of the type shown in Fig. 2 [5].

It was assumed in the above models that either one or two relaxation times could be used to describe the stress relaxation behavior. In reality, it has been repeatedly shown that a distribution of relaxation is necessary to describe this behavior. Recent work has focused on the use of the stretched exponential (SE), and it has been shown that a solution of the Boltzmann integral equation for stress relaxation using the SE for the memory leads to

$$\sigma(t)=\epsilon\left(E_r+\Delta E\exp\left(-(t/\tau)^{\alpha}\right)\right) \tag{4}$$

where α is the fractional exponent and can vary from 0 to 1 [6]. If the material exhibits a bimodal distribution of relaxation times with different values of α and τ, then eqn. (4) becomes

$$\sigma(t)=\epsilon\left(E_r+\Delta E_1\exp\left(-(t/\tau_1)^{\alpha}\right)+\Delta E_2\exp\left(-(t/\tau_2)^{\beta}\right)\right) \tag{5}$$

The same Boltzmann equations can be solved for the strain recovery following stress relaxation, and the result is

$$\epsilon_r=\epsilon\left(1-\frac{E_r+\Delta E\exp\left(-((t+t_h)/\tau)^{\alpha}\right)}{E_r+\Delta E\exp\left(-(t/\tau)^{\alpha}\right)}\right) \tag{6}$$

where t_h is the time that the sample was held during stress relaxation. When t_h is large, eqn. (6) reduces to one used previously by the present authors

[2,3]. Inversion of the Boltzmann equation to predict creep compliance has been reported by Hussain, Noble and Bendler [8].

EXPERIMENTAL

The various materials were obtained in the form of large sheets, injected molded plaques or dogbones. All samples were annealed at 20 ° C above their glass transitions for several hours and then quenched in ice water. The samples were allowed to remain in the ice water for at least 30 min, and in most cases for 1 h. The residual birefringence was measured using a polarized polychromatic light source and a Babinet compensator that had been calibrated with a mercury light source at 546 nm. The nominal amount of birefringence was of the order of 10^{-6}.

Stress relaxation, creep and strain/birefringence recovery measurements were performed on a screw-driven Instron Model 6025. The thermally activated strain recovery measurements were performed on in-house apparatus that has been described elsewhere [9].

RESULTS

Typical relaxation modulus data for thermally quenched samples of the different materials at 50 ° C and at a strain of 1% are shown in Fig. 3. Stress relaxation on the same materials after aging at room temperature for periods of up to 3 months falls within experimental error. However, the creep compliance behavior, as shown in Figs. 4 and 5 for PC and PXO, was

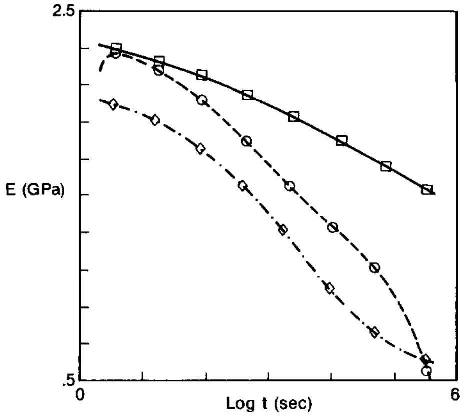

Fig. 3. Typical stress relaxation moduli for bisphenol-A polycarbonate, polyetherimide and poly(2,6-dimethyl-1,4-phenylene oxide) at a strain of 1%. The top curve is for PC at 50 ° C. The middle and bottom curves are for PEI and PXO, respectively, at 145 ° C.

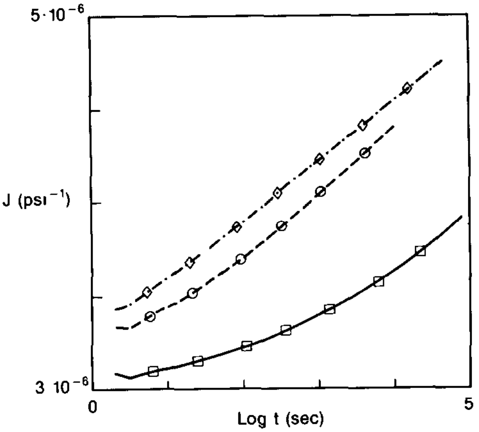

Fig. 4. Creep compliance of poly(2,6-dimethyl-1,4-phenylene oxide) at room temperature as a function of aging at room temperature. The top curve is for a thermally quenched sample, the middle curve for a thermally quenched sample which has aged at room temperature for 120 h, and the bottom curve for a sample which was thermally annealed at 198° C for 14 h.

significantly altered even after only 1 h of aging at room temperature. Volumetric changes during stress relaxation of PC are shown in Fig. 6, and it is apparent that upon straining, one induces a dilation which subsequently relaxes. Similar changes are observed in both PEI and PXO. For some samples the density actually becomes greater during relaxation than the initial density. During recovery, as shown in Fig. 7, while the longitudinal strain is recovering, the volume is actually smaller than its initial volume, i.e. the sample density has increased. It is observed that shapes and degrees of recovery for the various materials are not the same, i.e. the amount of plastic

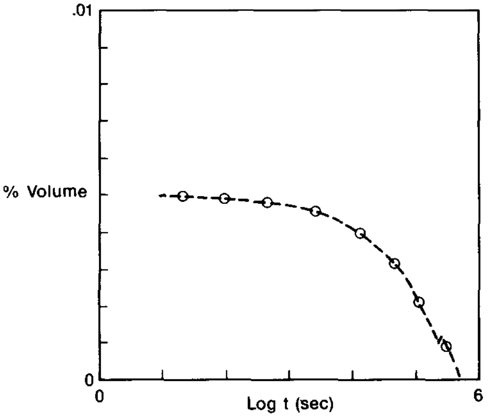

Fig. 5. Creep compliance of bisphenol-A polycarbonate at room temperature as a function of aging time at room temperature. The top curve is for a sample which was aged for 3 h, the middle curve is after aging for 19 h, and the bottom curve is after aging for 49 days.

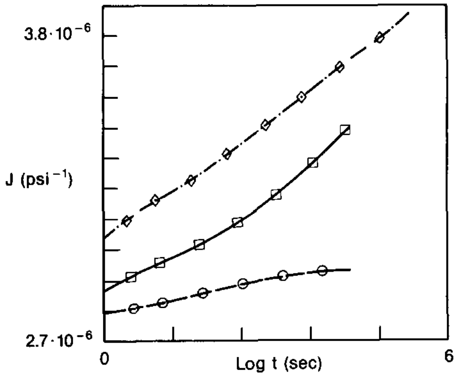

Fig. 6. Volumetric relaxation during stress relaxation for bisphenol-A polycarbonate at a strain of 0.5% and a temperature of 50 ° C.

strain is different even though the samples were tested under the same test conditions in terms of strain, temperature and hold time. These differences are similar to those observed between the stress relaxation curves shown in Fig. 3. Thermally activated strain recovery for PC samples after standing at the test temperature for several days varies, as shown in Fig. 8. Further, the temperature at which the samples start to recover is dependent on both the test temperature and the material.

DATA ANALYSIS

Over the years, a number of different equations and procedures have been used to analyze stress relaxation and creep data. In general, these were

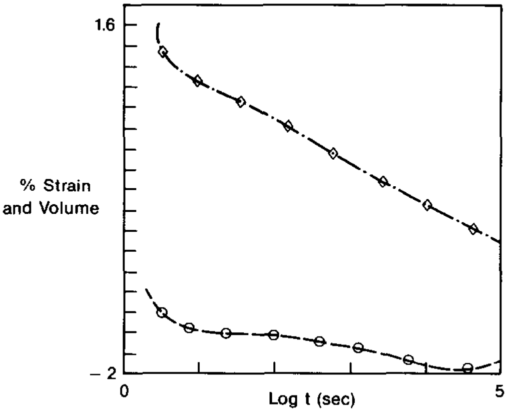

Fig. 7. Strain and volume recovery for bisphenol-A polycarbonate after stress relaxation at a strain of 3% and at room temperature. The hold time was 398948 s. The top curve is for the strain and the bottom for the volume. Note that the volume is negative.

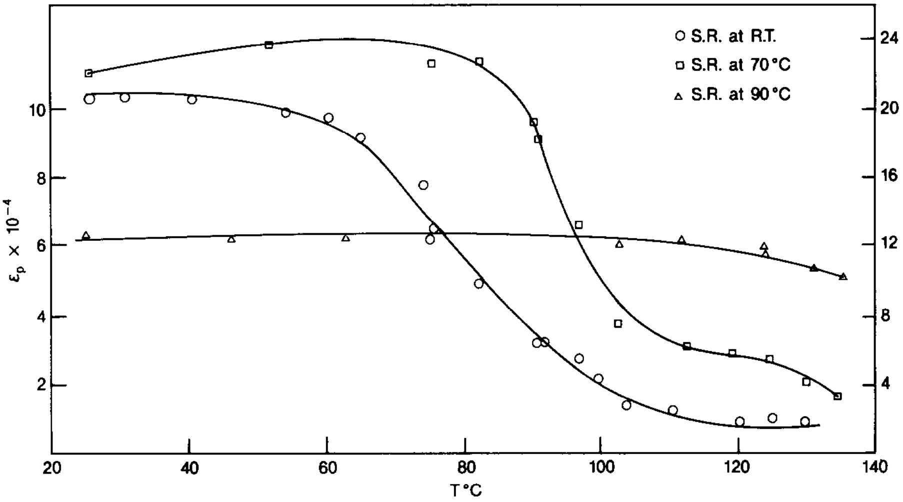

Fig. 8. Thermally activated recovery for bisphenol-A polycarbonate following stress relaxation and strain recovery and then holding at room temperature for 18 months.

empirical in nature, and had the goal of providing simple constitutive expressions that could be used in the design of parts. In more recent times, emphasis has shifted to trying to interpret the data in terms of various models of how polymeric glasses respond on a molecular or submolecular basis. Our methods of analyzing stress relaxation, creep and initial strain recovery data are based on the use of the KWW function, i.e. the stretched exponential function, along with the Boltzmann superposition equation, leading to expressions for stress relaxation, creep and strain/birefringence recovery, as discussed above. The equations for volume relaxation and thermally activated recovery are empirical but are expected to be closely related to those for stress relaxation, creep and strain recovery. Equations (5) and (6) are used to evaluate the stress relaxation and strain recovery data, while the following equations are used for the volume relaxation, creep and thermally activated recovery data.

Volume relaxation

$$V(t) = V_0 + \Delta V_1 \exp\left(-(t/\tau_v)^{\zeta}\right) + \Delta V_2\left(1 - \exp\left(-(t/\tau_a)^{\eta}\right)\right) \tag{7}$$

Creep

$$J(t) = \frac{1}{E_r + \Delta E_1 \exp\left(-(t/\tau_1)^{\alpha} + \Delta E_2 \exp\left(-(t/\tau_2)^{\beta}\right)\right)} \tag{8}$$

Thermally activated recovery of the residual strain

$$\epsilon(T) = \epsilon_{p3} \exp\left(-(t/\omega_3)^{\beta}\right) + \epsilon_{p4} \exp\left(-(t/\gamma_4)^{\beta}\right) \tag{9}$$

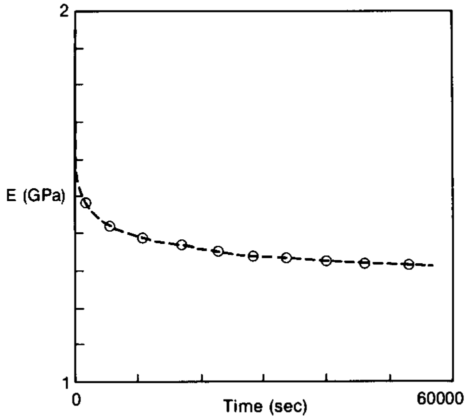

Fig. 9. Stress relaxation on a linear time scale.

where ω and γ are temperature-dependent relaxation times and are given by

$$\omega(T) = 3.2 \times 10^{-18} \exp(36000/RT) \tag{10}$$

and

$$\gamma(T) = 2.7 \times 10^{-20} \exp(36000/RT) \tag{11}$$

and β is assumed to be 0.33.

If one plots stress relaxation, creep or strain recovery data on a linear time scale, as shown in Figs. 9–11, then one notes a rapid leveling-off of the variable as a function of time, and as a first approximation the variable represents a limiting value of the parameters E_r, J_r or ϵ_r. This is not meant to imply that the value may not at some future time change, but rather that within the laboratory time frame it is approximately constant. Fitting to nonlinear equations such as

$$X(t) = X_r + \Delta X_1 \exp((-t/\tau)^{\chi}) + \Delta X_2 \exp(-(t/\tau)^{\pi}) \tag{12}$$

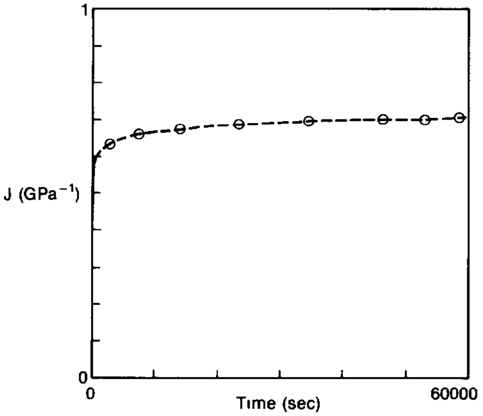

Fig. 10. Creep on a linear time scale.

TABLE 1

Typical values of the coefficients and of α and τ, evaluated for the different materials and experimental methods using eqns. (5)–(11)

I. Stress relaxation

Material	Thermal	Strain	T (°C)	E_r	ΔE_1	ΔE_2	α	β	τ_α	τ_β
PC	Quenched	0.5	50	1.38	0.72	0.49	0.15	0.33	400	90000
PEI	Quenched	0.5	145	0.8	0.55	1.40	0.15	0.33	400	30000
PXO	Quenched	0.5	145	0.5	1.45	0.2	0.33	0.33	3000	10^6
	Annealed	0.5	145	2.3	0.3	–	0.15	–	400	–

II. Strain recovery

Material	Thermal	T (°C)	E_p	δE_1	δE_2	α	β	τ_α	τ_β
PXO	Quenched	30	0.1	0.3	0.2	0.33	0.15	16000	400
	Annealed	30	0	0	0.118	–	0.15	–	400

III. Volume relaxation

Material	Thermal	T (°C)	$\%V$	α	τ	$\%V_2$	β	τ_β	$\%V_0$
PC	Quenched	50	0.8	0.35	350000	0.15	0.15	400	−0.35

IV. Thermal activated strain recovery

Material	Thermal	T (°C)	ϵ_1	ϵ_2	ϵ_p
PC	Quenched–SR	50	3.0	4.0	1.0
		70	11	2.0	0.1
		90	11	2.2	0.1

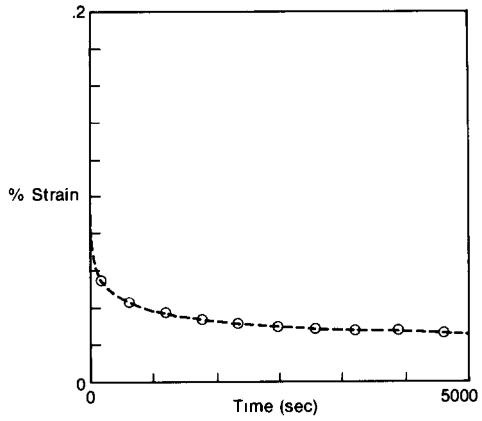

Fig. 11. Strain recovery on a linear time scale.

is possible using nonlinear mathematical regression routines available on a number of computers, or empirically via graphical comparison between observed and simulated data. It should be noted that the parameters which are obtained will be model dependent. But if they can be used in predicting the response of other experiments or obtained from other experiments, and at the same time are physically reasonable, then they can be used in advancing our understanding of the behavior of such materials as well as in developing alternative models.

Typical results of such analysis for various materials are presented in Table 1. Comparisons of experimental and simulated data for a polycarbonate sample are given in Figs. 12–14. The estimated experimental error for the measurements is of the order of ±1%, and the % difference between

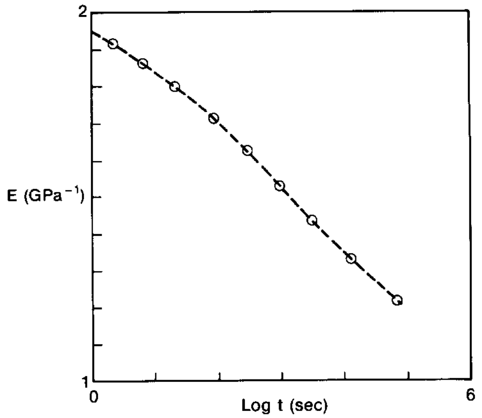

Fig. 12. Comparison of a simulated and experimental stress relaxation curve for a sample of bisphenol-A polycarbonate using $E_r = 1.07$, $\Delta E_1 = 0.8$, $\Delta E_2 = 0.37$, $\alpha = 0.15$, $\tau_1 = 400$, $\beta = 0.33$ and $\tau_2 = 6800$. The test temperature was 70 °C and the strain 1%.

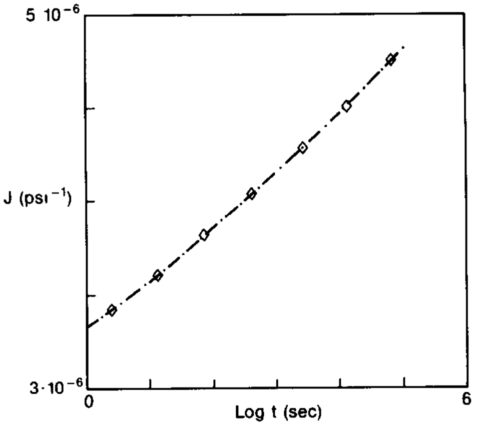

Fig. 13. Comparison of simulated and experimental creep compliance curves.

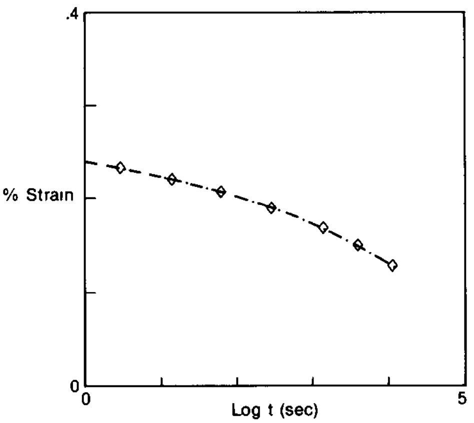

Fig. 14. Comparison of simulated and experimental strain recovery curves for PC.

the experimental and the simulated data is, in general, less than this difference. Further, the values of the fractional exponents, the τ, and the coefficients can be changed by small amounts without altering this degree of correlation, though attempts to make major changes in their values clearly give deviations outside of the experimental error.

If one attempts to fit the data in Fig. 12 using eqn. (4) rather than eqn. (5), it is found that a fit can be obtained at short times but not at long times.

DISCUSSION

The first point to address is the creep compliance behavior of the different materials when aged at room temperature. It is clear from the data in Figs. 4 and 5 that a process is occurring at room temperature causing a change in the long time compliance of PC and PXO. This is also observed with PEI, and is similar to the results of other investigators. We have previously proposed that this process is associated with the loss of defects at the ends of the claim. However, this room temperature process, in contrast to that which occurs during thermal annealing of PC and PXO below T_g, does not cause embrittlement, or increase the yield stress, or alter the stress relaxation behavior. As a result, the effect of thermal annealing, i.e. near T_g, may be due to one or more processes. For example, it has been suggested that the random migration of defects within the chain network to the ends of the chain with their subsequent loss at the ends could be one mechanism, and that this process should scale as M_w^6 or so [7]. Two other mechanisms are possible. The first follows an argument proposed by Bendler and Shlesinger, which assumes that defect clusters are formed during thermal quenching below T_g. It is possible that thermal annealing causes these clusters to break up so that the defects are more homogeneously distributed throughout the network, rather than being destroyed or lost at chain ends. The third mechanism involves the disentanglement of chain ends from other chain ends or segments. The basic question is, can one do experiments that can distinguish between these different mechanisms, and/or what predictions can be made in terms of the different types of experiments in view of these mechanisms? For example, there appear to be two types of persistent strains which recover on different time scales and/or at different temperatures, as shown in Fig. 8. The magnitudes of these persistent strains are clearly dependent upon a number of different parameters, such as thermal history, strain, temperature, and most importantly, molecular weight. At the same time, the time to embrittle is dependent on both molecular weight and temperature; however, the thermal recovery of the persistent strain on high and low molecular weight samples indicates that the magnitude of the second type of persistent strain for the same thermal and mechanical history is larger for the low molecular weight materials, and that the first type of persistent strain is larger for high molecular weight materials. If the predominant mechanism involved in thermal annealing was the random migration of defects to the ends of chains, then one would have to associate the loss of the second type of persistent strain with it. However, the second type of persistent strain appears to be larger for the lower molecular weight material, wherein the number of defects at the ends of chains is larger because of the lower molecular weight. Since the activation energies for recovery of the persistent strains are nominally the same and are independent of molecular weight, it is tempting to conclude that the effect of thermal annealing involves homogenization of chain defects and chain disentanglement, rather than the loss of defects at chain ends. It is obvious that thermal annealing will also accelerate the loss of defects at chain ends, which are already at chain ends. This type of physical picture is consistent with the stress relaxation and strain recovery data *.

Another complication is that eqns. (5) and (8), which are solutions to the Volterra equation for constant strain and stress conditions, indicate that one should be able to predict the creep behavior from the stress relaxation, or vice versa. This is not observed, which is in agreement with a statement made by Ferry. He indicates that

$$J(t) \neq \frac{1}{E(t)}$$

The primary differences are that plastic flow is more readily observed during creep than in stress relaxation, and that the volume changes do not follow the same path. This observation suggests that one needs to introduce other relaxation mechanisms into the constitutive equation, and to solve it for both stress relaxation and creep. The former is rather straightforward, while the latter is currently being examined [9].

The second point to address is the difference in the stress relaxation, initial strain recovery and thermally activated recovery data for the samples. If one uses the argument that defect motion between entanglements is responsible for the anelastic response, while motion past entanglements is responsible for persistent strain, then it would appear that the ability for defects to go past entanglement points is slower in polycarbonate than in the other materials. This may reflect either a different energy barrier or local packing fluctuations, i.e. the motion of a defect past an entanglement may be a co-operative phenomenon involving the opening up of a hole for the defect to pass through. A alternative possibility is that chain ends entangled with other chain ends or chain segments may undergo disentanglement, giving rise to relaxation. Since one also observes that strain recovery behavior tends to reflect stress relaxation behavior, one expects that this latter process could only be activated by temperature, and thus would only be activated during thermally activated recovery.

The last point to address is that of the volumetric relaxation and densification of the samples during stress relaxation and creep. This process appears to be more dependent on thermal history and strain than on the type of material. Densification is obviously a more complex process because it requires a three-dimensional change in the sample to produce a volume change. The observation that the relaxation time for this process is slower than the anelastic and first plastic process suggests that it is associated with a macroscopic repacking of the chains and/or local repacking of chain

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* Recent stress relaxation and strain recovery measurements on a densely crosslinked epoxy which had been thermally quenched show the presence of an anelastic as well as the first type of persistent strain. These results offer further support for a network model.

segments. This type of process would be expected to require a more co-operative interaction. Its magnitude is similar to what is observed during thermal annealing, and it may therefore be due to the same phenomenon suggested earlier, i.e. homogenization of defects, loss at chain ends, or disentanglement of chain ends. If these processes are the same, then one would predict that mechanical aging could cause embrittlement.

CONCLUSIONS

The anelastic and plastic responses of different amorphous thermoplastics have been measured as a function of strain, thermal aging and other factors. Creep measurements after aging at room temperature for thermally quenched samples and the measurements made at room temperature indicate that these materials are undergoing physical changes that decrease the long time compliance. Stress relaxation, strain/birefringence recovery and thermally activated strain recovery measurements suggest that the materials undergo relaxation and recovery by a disentanglement of chain ends as well as by the motion of defects between entanglements as evidenced by the shape of the relaxation and recovery curves.

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