Rheo-optical Properties of Polymers: Relaxation and Recovery During Absorption and Desorption of Organic Liquids

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Synopsis

As part of a study in elucidating the mechanisms by which crazing is initiated in polymers, we have measured the force and birefringence decay which occurs in several polymers when placed in contact with methanol. In all cases, the force decay can be used to determine the rate of bulk diffusion of the liquid into the polymer. In contrast, the birefringence decay appears to be related to shear relaxation mechanisms which are highly dependent on the type of material. For example, in the case of simple rubbers such as polyisoprene, the rates of decay of force and birefringence are identical within experimental error. In contrast, in amorphous thermoplastics the force decay is typically an order of magnitude faster than the birefringence decay. These results are discussed in terms of distortional and orientational birefringence and with respect to the morphology of the glassy state.

INTRODUCTION

Recent work by Fellers and Kee clearly indicate that the initiation of crazing is independent of molecular weight in glassy polymers.[1] In fact, one might extend this conclusion and suggest that the initiation sites for crazing are independent of polymer structure because the evaluation of the craze structure by small-angle x-ray scattering in several polymers including poly(vinyl chloride), bisphenol A polycarbonate, and poly(methyl methacrylate), and a few samples of different MW yield average radii for the voids in crazes from 80 to 100 Å.[2,3] Thus, it would appear that the nucleation of a craze, as detected by the reflection of light, requires the formation of several voids judiciously located in a plane normal to the major stress axis such that locally a condition of plane strain exist in their environment. In contrast, the stress around a single isolated molecular void can lead to shear yielding without dilation. Studies of dynamic and equilibrium adsorption of vapors and liquids by glassy polymers suggest that in some polymers the first molecules sorbed may be distributed inside the polymer in a matter so that a large proportion are immobilized on specific sites. In others, a clustering of the penetrant molecules may take place inside the polymer matrix. Finally, a plasticitation of the matrix may take place which will cause relaxation of the polymer matrix.[47] The major conclusion to be reached is that glassy amorphous thermoplastics are inhomogeneous on a scale comparable to the di. and additives, in-

trinsic inhomogeneities in glassy polymers can occur for two basic reasons: (1) it has been shown for mixtures of several different polymers that a surface excess of some of the components can occur,[8] and (2) it is known that, as a glassy polymer is cooled from temperatures above T_g to below T_g, some of the molecules or portions of these molecules are frozen into configurations representative of higher temperature[9,10] and may be interpreted as frozen in local stresses or strains. Techniques to detect the presence of such defects have not been successful because they are random in position and orientation in the matrix and are small in comparison to macromolecular dimensions. However, it is clear that such defects should be related to both yielding and crazing because they represent high energy states. These defects can be either relieved by solvent relaxation, which would lead to molecular dilation or cavitation as in the case of crystallization, or enhanced by a stress which would lead to local yielding.

In 1948, Stein and Tobolsky published a classic paper on the relationship between the structure, mechanical properties, and birefringence of polymers and discussed in detail the various relaxation processes which can occur.[11] In this paper, we extend their work to include swelling of polymers and investigate the use of one rheo-optical technique to study the behavior of stressed glassy polymers during the absorption and desorption of organic liquids or vapors.

EXPERIMENTAL

Materials. Lexan bisphenol A polycarbonate was obtained as a powder and as thin film (Dr. D. Caird, General Electric Co., Pittsfield, Mass.). Poly(2,6-dimethylphenylene oxide) was obtained as a thin film (Dr. A. Katchman, General Electric Co., Selkirk, N.Y.). The block copolymer of bisphenol A polycarbonate and poly(dimethylsiloxane) was obtained as a powder (Dr. H. Vaughn, General Electric Co., Waterford, N.Y.). The bisphenol A polycarbonate and the copolymer were formed into sheets ranging in thickness from 1 to 20 mils by solvent casting from methylene chloride solutions. Samples were placed under vacuum over for 24 hr at 50°C in order to ensure complete elimination of the solvent. The poly-*cis*-isoprene was obtained as stock from Dr. S. Aggarwal, Goodyear Tire Co., Akron, Ohio. It was crosslinked into sheet 10–25 mils thick using the procedure described by Gent.[12] After crosslinking, the sheets were extracted several times with carbon tetrachloride in order to remove any uncrosslinked and low molecular materials. The apparatus used in these studies has been described elsewhere.[13]

SWELLING OF POLYMERS

Rubbers

It has long been known that the swelling of strained rubbers can be described by equations obtained from the kinetic theory of rubber elasticity.[11,14,15] On the basis of such considerations, the birefringence and stress

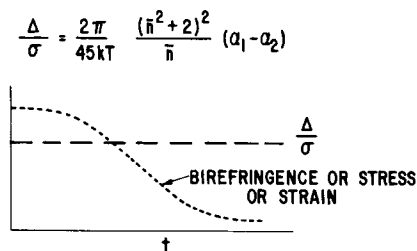$$\frac{\Delta}{\sigma} = \frac{2\pi}{45kT} \frac{(\bar{n}^2+2)^2}{\bar{n}} (a_1 - a_2)$$

Fig. 1. Variation of the stress, strain, birefringence, and birefringence–stress ratio as a function of time during swelling for strained rubber obeying kinetic theory of elasticity. Relationship between birefringence and stress is given by the equation.[14]

are expected to decay in the same way (Fig. 1) if the penetrant molecule is isotropic and the birefringence is corrected for changes in the average refractive index. The rate of decay should be related to the rate of diffusion of the penetrant molecule and, for unidirectional penetration through a thin film, is

$$X = X_0 \exp - \left\{\frac{Dt}{cl^2}\right\} \tag{1}$$

where X is either the stress or the birefringence, D is the diffusion constant, t is the time, l is the thickness of the sample, and C is a constant which is related to the geometry of the sample.

We first measured the birefringence–stress behavior of dry and swollen poly-cis-isoprene under static conditions. Carbon tetrachloride was used as the swelling agent. These results are shown in Figure 2. We then measured the decay of the stress and birefringence during the absorption of carbon tetrachloride vapors as shown in Figure 3. The ratio of the birefringence to the
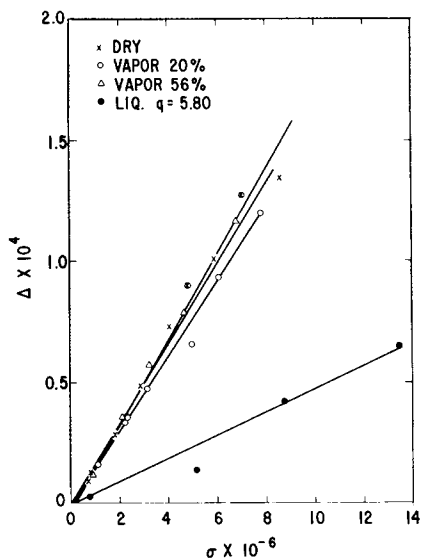

Fig. 2. Variation of birefringence with stress of poly-cis-isoprene for dry (x-x-x) and swollen samples. Carbon tetrachloride was the swelling agent.
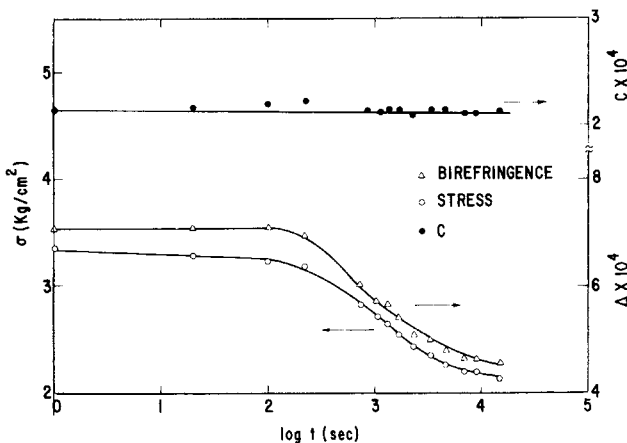
Fig. 3. Variation of force, birefringence, and birefringence–force ratio as a function of log time during the swelling of prestrained poly-*cis*-isoprene.
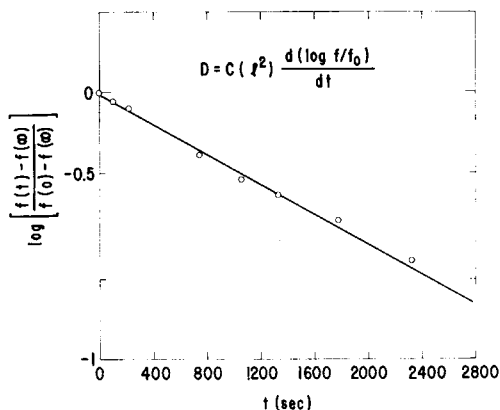

Fig. 4. Variation of log $[f(t) - f(\infty)/f(0) - f(\infty)]$ with time during swelling of prestrained poly-*cis*-isoprene.

stress C is also plotted in Figure 3 and is found to be independent of time as predicted. If this decay is diffusion controlled, then a plot of these data, as presented in Figure 4, should yield a straight line whose slope can be used to obtain the diffusion coefficient.* From our data, the diffusion coefficient for carbon tetrachloride in *cis*-polyisoprene is evaluated as 5.06×10^{-8} cm^2/sec. Thus, we can conclude for this system that the decay is diffusion controlled. An important aspect of this is the thickness dependence which can be used to shift this relaxational phenomena in order to distinguish it from other intrinsic relaxational mechanisms which are independent of thickness.

Glassy Thermoplastics

In contrast to rubbers, the swelling of glassy thermoplastics is expected to be more complex because of the reduction of segmental mobility and the het-

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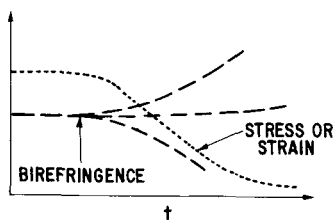* The author wishes to acknowledge a discussion with Dr. H. L. Frisch about this procedure.

Fig. 5. Variations in stress strains and birefringence of prestrained glassy thermoplastics as a function of time during swelling.

erogeneous nature of the glassy state. In the glassy state, the stress can decay because the modulus is reduced by plasticization of the penetrant molecule, the strain is reduced by swelling due to dimensional changes (the same as in rubbers), and the distortional strains are relieved by orientation of segments of the chains.

However, the birefringence of the sample may increase, decrease, or remain constant, as shown in Figure 5. An increase in the birefringence may occur if the penetrant molecule is oriented during penetration with its major optic axis along the stress axis or if the relaxation of distortions occurs as a result of orientation of larger segments of the molecules. A decrease can occur if the penetrant molecules plasticize the material or if the penetrant molecule is oriented with its major optic axis perpendicular to the major stress axis. Simple isotropic expansion from swelling should not affect the birefringence except for variations in the average refractive index.

Finally, if we are dealing with diffusion-controlled relaxation, application of eq. (1) to the stress time data should yield a method of linearization and an evaluation of the diffusion coefficient.

We first measured the birefringence–stress curve for dry and swollen bisphenol A polycarbonate as shown in Figure 6, under static conditions. For the observed degree of swelling, the glass transition of the polymer is predict-
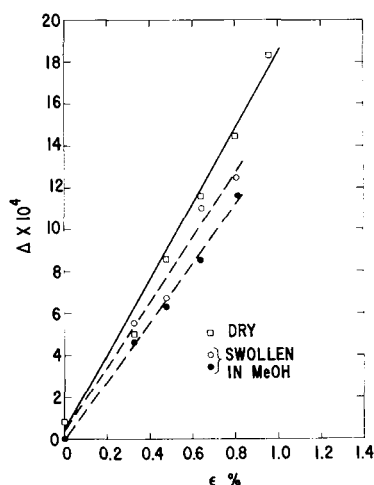

Fig. 6. Variation of birefringence with stress for dry and preswollen bisphenol A polycarbonate. Methyl alcohol is swelling agent.
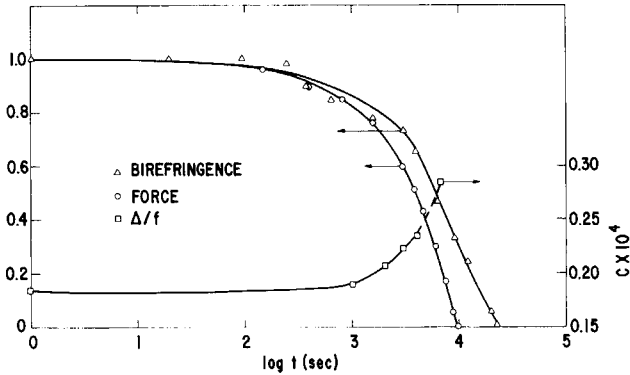
Fig. 7. Variation of the normalized birefringence and force and the birefringence–stress ratio as a function of log t for prestrained bisphenol A polycarbonate during swelling with methyl alcohol.

ed by the Kelley-Bueche equation to be approximately 128°C, and measurements of the sonic modulus indicate the overall degree of plasticization of the polymer to be minimal. While a reduction occurred in the stress-optical coefficient as a result of swelling, the magnitude is not enough to explain the result to be presented below.

In Figure 7, we plot the behavior of the normalized stress and birefringence as a function of log time. Normalization was performed by dividing the value of the parameter at time t by the initial value. The ratio of the birefringence to the stress, denoted by C, is also presented. In contrast to rubbers, it is observed that the stress and the birefringence do not decay at the same rate as indicated by the increase of C.

It is important to point out that in order to perform these experiments, the initial stress on the sample had to be small in order to avoid crazing and/or yielding during the swelling portion of the experiment. This condition leads to a negative swelling stress at long times (equilibrium swelling). In order to determine if any permanent plastic flow had occurred, we removed the chamber containing the swelling agent and observed the force and birefringence recovery of the sample during desorption. It was observed that the stress recovery occurred more rapidly than the birefringence and that they both returned within experimental error to their initial values. These data clearly indicate the reversibility of the phenomena.

By replotting the data in Figure 7 on the basis of eq. (1), similar to that in Figure 4, it is found that both the stress and birefringence decay are diffusion controlled. However, the slopes indicate the differences in their rates of decay. Determination of the diffusion coefficient by the mass loss technique described by McCall[16] yields the value given in Table I. We studied both the effect of the level of stress and the effect of thickness of the sample on these phenomena and found that sample-to-sample variation was a more significant parameter than either of the above.

A third type of experiment was to preswell the sample under no stress for either ½ hr or 1 hr, and then to apply a small stress and then follow the decay of the stress and birefringence during swelling. The results of these experiments were the same as those observed with the unswollen samples. Several

TABLE I
Average Diffusion Coefficient Obtained by Force Decay and Mass Loss Techniques

Sample	D, cm^2/sec	Condition	Method[a]
Poly-cis-isoprene	5.06×10^{-8}	as prepared	F
Bisphenol A polycarbonate	7.45×10^{-10}	as received	W
	9.1×10^{-10}	as received	F
	5.5×10^{-10}	annealed	F
Poly(2,4-dimethylphenylene oxide)	5.8×10^{-9}	as received	W
	$5.6-8.8 \times 10^{-9}$	as received	F
	2.2×10^{-9}	annealed	
Block copolymer of bisphenol poly- carbonate and poly(dimethylsiloxane)	$1.2-1.8 \times 10^{-7}$	as received	F

[a] F designates the force decay method described in text, and W designates method described by McCall.[16]

attempts were made to examine samples which were allowed to swell for 24 hr prior to being stressed. Stressing of these samples invariably led to crazing or yielding either at the start of the experiment or at later times.

Finally, in a fourth series of experiments, samples were annealed at 125°C for 4 hr prior to the measurement. The rate of decay of the force and birefringence were both decreased as a resulting of annealing. These results are similar to those observed by Chen.[17]

Another series of experiments were performed on poly(2,4-dimethylphenylene oxide) in order to determine the generality of our observations. Typical curves for the stress and birefringence decay during swelling are presented in Figure 8. Using the data from these measurements and eq. (1), diffusion coefficients were calculated and are presented in Table I. The general conclusion to be drawn from the experiments on the bisphenol A polycarbonate and the poly(2,4-dimethylphenylene oxide) is that the rate of decay of the birefringence is slower than the force.

Two alternate models can be postulated to explain these observations. In the first model, a two-step process for relaxation is invoked.[11] The first step involves the relief of distortional strain and birefringence by an orientation of segments of the chains. However, as a result of this segmental orientation, an orientational birefringence is produced which adds to the total birefringence in the system. In the second step, either as a result of time or further
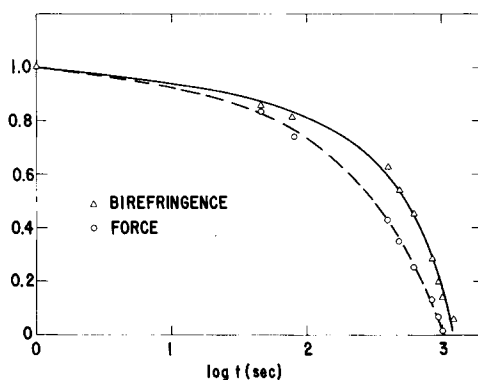

Fig. 8. Variation of normalized birefringence and force as a function of log time for prestrained poly(2,4-dimethylphenylene oxide).
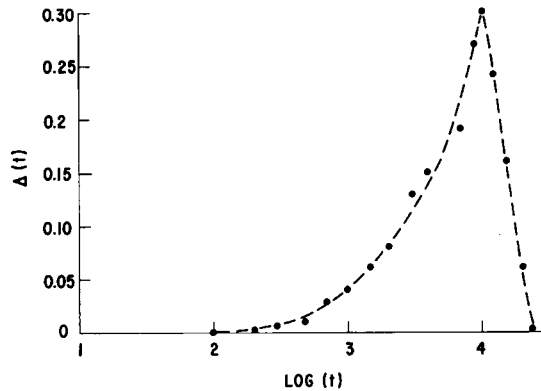
Fig. 9. Variation of quantity $\Delta_0(t) - \Delta_0^0$ as a function of log time for prestrained bisphenol A polycarbonate during swelling with methyl alcohol.

swelling, the orientational birefringence decreases as a result of a loss in orientation by relaxation. In contrast, the entropic contributions to the force as a result of segmental orientation in the glassy state are extremely small and, thus, the force decay reflects only the distortional strains.

For this model, the total birefringence of the system can be given by

$$\Delta_T = \Delta_D + \Delta_0 \tag{2}$$

where Δ_D and Δ_0 are distortional and orientational birefringence. If we assume that the decay of the distortional birefringence is linearly related to the force, then equation 2 may be rewritten as

$$\Delta_0 = \Delta_T^0\, e^{t/\tau^1} - \Delta_D^0\, e^{t/\tau^2} \tag{3}$$

where τ_1 and τ_2 are the relaxation times for the total and distortional birefringence, Δ_T^0 and Δ_D^0 are the birefringence values at zero time. If we substitute

$$\Delta_D^0 = \Delta_T^0 - \Delta_0^0 \tag{4}$$

into eq. (3), then

$$\Delta_0(t) - \Delta_0^0 = \Delta_T^0(e^{-t/\tau_1} - e^{-t/\tau_2}). \tag{5}$$

Substituting the values of τ_1 and τ_2 obtained from the decay of the birefringence and the force and τ_{T_0} into eq. (5), we obtain the curve presented in Figure 9. This curve indicates that a maximum orientation of segments occurs at the point when τ equals t. In order to more clearly demonstrate this, we have evaluated a hypothetical system where we have kept τ_1 constant and allowed τ_2 to assume different values. These results are presented in Figure 10.

The second model invokes the concept of nonhomogeneous swelling. Local variations in the density and morphology, which represent in part frozen-in thermal fluctuations, give rise to nonuniform adsorption and diffusion at low penetrant concentrations. (This is not to be confused with the concentration gradient to be observed in unidirectional diffusion.) These have been discussed in the early adsorption work of Zimm and Lundberg, in studies of diffusion by Rogers, and in the swelling of filled rubbers by Sternstein and
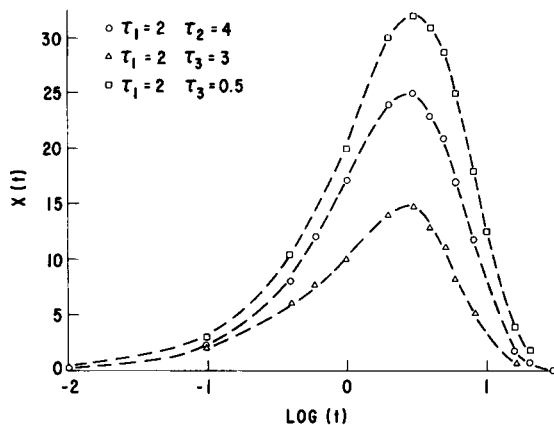
Fig. 10. Variation of function $(e^{-t/\tau_1} - e^{-t/\tau_2})$ with log time for a hypothetical situation; τ_1 is assumed to be constant and τ_2 is varied.

Stein.[4,7,12,19] It is envisioned that in such systems some of the penetrant molecules can diffuse faster along certain unspecified paths toward the center of the sample. However, due to the fact that regions immediately adjacent to these paths contain no penetrant molecules, a radial flow of the penetrant around the path will occur. Thus, the force decreases as a result of transverse penetration while the birefringence decays as a result of the radial flow.

For this model, the same phenomenological equations can be used, and we arrive at the same conclusion in terms of the contributions of distortional and orientational birefringence during swelling.

In order to prove that this second model would behave in the same manner, we investigated a block copolymer of bisphenol A polycarbonate and poly(dimethylsiloxane) whose morphology would simulate two interpenetrating matrices such that the diffusion would occur rapidly within one and then slowly into the other. Typical data during adsorption are presented in Figure 11. Evaluation of the diffusion coefficient yields the value presented in Table I. Comparison of this diffusion coefficient with that found for the glassy ther-
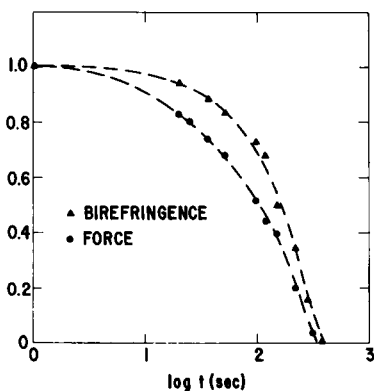

Fig. 11. Variation of birefringence and force with log time for prestrained block copolymer of bisphenol A polycarbonate and poly(dimethylsiloxane) during swelling with methyl alcohol.

moplastics and for poly-*cis*-isoprene indicates that the penetrant diffuses faster in the copolymer than in the glassy polymers but slower than in the rubber. The distinct difference in the time dependence of the birefringence and the force during adsorption certainly models the behavior of a glassy polymer.

Both models can be used to explain the stress and birefringence data because our observations represent an average or a sum of the events occurring at the macromolecular level. In view of this, we measured the wide- and small-angle x-ray scattering from dry and swollen stressed thermoplastics. No difference could be found for the two glassy thermoplastics. We believe that neutron scattering utilizing deuterated methanol would be much more sensitive than x-ray scattering and could provide a detailed picture of the morphological rearrangements which occur during swelling.

CONCLUSIONS

Swelling of stressed thermoplastics causes the stress and birefringence to decrease. It is found that the rate of the decay of the stress is faster than that of the birefringence, and both appear to be diffusion controlled. Two models are proposed to explain the data. Neutron-scattering experiments are proposed.

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