Birefringence in an Epoxy Polymer During Stress-Relaxation and Recovery

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Synopsis

Measurements of birefringence during stress–relaxation and recovery have been recorded for examples of an epoxy resin cured at three different temperatures. Birefringence remained constant during stress–relaxation even after prolonged testing during which the stress fell considerably. The stress sensitivity was found to be the same on both loading and unloading so that, immediately after unloading, the birefringence was different to that prior to the stress–relaxation test. This residual change began to decay after a prolonged period free from applied stress. No significant differences were noted in the birefringence measurements made on samples cured at different temperatures, but, when the stress–relaxation data were analyzed by the procedure of Kubát and Rigdahl, marked differences appeared.

INTRODUCTION

In a recent survey of the birefringence of thermoplastics during stress–relaxation and recovery, it was observed that, under the levels of deformation and loading commonly used in field applications, birefringence cannot be described by a time-independent stress-optical coefficient.[1] This has been known for many years,[2,3] but the time dependence is sometimes ignored. Time dependence in thermoset materials would not be expected to be as pronounced as with thermoplastics, but it is of importance to examine the extent to which it is present, especially in materials which are employed in photoelastic analysis.[4–6]

In this paper are reported the results of measurements conducted on samples of an epoxy polymer cured at different temperatures and tested in uniaxial tensile stress–relaxation.

EXPERIMENTAL

Specimen Preparation. Sheets of uniform thickness were produced from a mixture of 100 parts Ciba-Geigy Araldite CT200 and 30 parts phthalic anhydride (Ciba-Geigy HT901),[7] using three different curing temperatures (Table I). The thickness of the sheets used for the experiments reported here was approximately 5.2 mm. Test bars measuring 190 mm × 12.5 mm were cut for stress–relaxation tests.

Stress–Relaxation and Birefringence Measurements. Stress–relaxation tests were conducted and birefringence measured at intervals in exactly the same manner as in previous experiments with polystyrene and polycarbonate.[8] The rigs, described earlier,[9,10] permitted close temperature control and experiments

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TABLE I
Curing Conditions and Results of the KR Analyses

Specimen designation	Curing temp (°C)	Curing time (h)	σ_i (MN/m^2)	n
B	80	44	-2.0 ± 0.4	22.2
A1	120	16	-0.06 ± 0.02	15.8
A2	135	14	2.1 ± 0.4	24.3

were conducted mainly at 30°C with some further tests at 40°C. Initial loading was achieved at a rate of ca. 2×10^{-3} s^{-1}.

RESULTS

Birefringence in the As-Cured Condition. In the as-cured state, the sheet looked fairly uniform when reviewed between crossed polars and appeared to be isotropic in the xy plane (where z is measured in the sheet thickness direction). The relative retardation for a 5.2 mm thick sheet was less than 300 nm. When bars were cut from the sheet and the cut faces polished to give good optical clarity, it was found that xz or yz birefringence was present, giving colored fringes when viewed between crossed polars using a white light source.

Birefringence during Stress–Relaxation. The stress–relaxation-birefringence results for samples of each type (B, A1, A2) were similar and a typical example obtained from a test at 30°C is shown in Figure 1. The birefringence increased from 5.5×10^{-5} in the unstressed state to approximately 24×10^{-5} on applying the deformation, and then remained constant on prolonged testing (>3 h), even though the stress dropped by about one third of its initial value. The steady birefringence values obtained in tests obtained at different deformations on all three types of sample are shown in Figure 2, plotted against the initial stress.
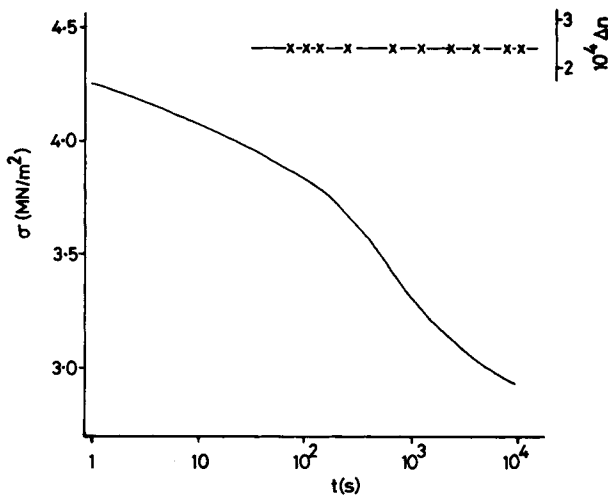

Fig. 1. Stress–relaxation of epoxy polymer type A1, showing birefringence values recorded during the same test on the same time scale.
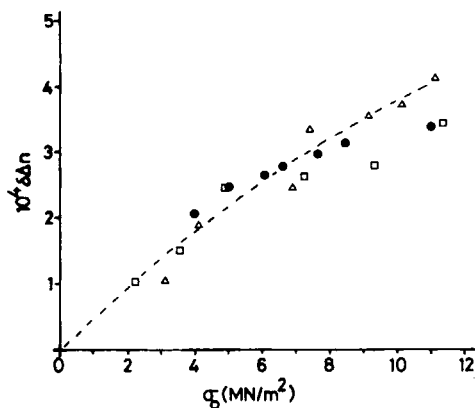
Fig. 2. Changes in birefringence ($\delta\Delta n$) obtained on deforming samples plotted against the initial stress σ_0: ($\triangle$) type B; ($\bullet$) type A1; ($\square$) type A2.

Birefringence during Recovery. On unloading, the birefringence dropped instantaneously but to a value significantly higher than the as-cured value prior to the stress–relaxation test. On prolonged storage at 30°C with no applied load, the birefringence began to fall towards the as-cured value (Fig. 3).

The stress sensitivity of the epoxy polymers was found to be the same on both loading and unloading (Fig. 4). In this figure are plotted (i) the change in birefringence magnitude on applying the deformation versus the initial stress in the stress–relaxation test and (ii) the change in the birefringence magnitude on unloading versus the stress recorded just before unloading. Both plots appear to fall on the same line.

Deformation Kinetics. The stress relaxation data was analyzed according to procedures introduced by Li[11] and by Kubát and Rigdahl (KR).[12] In the Li analysis the stress–relaxation data is plotted as σ vs. $\ln t$, the gradient is read off at several points, and a plot is made of the quantity $(-d\sigma/d \ln t)$ vs. corresponding σ values. For readings taken after the point of inflection of the σ vs. $\ln t$ curve a straight line plot of $(-d\sigma/d \ln t)$ vs. σ is normally obtained,[11,13,14] and this line is extrapolated to intersect the stress axis at a point taken to represent the internal stress, σ_1. This value will inevitably contain contributions of both deformation-induced internal stress and residual stress.[15] An example
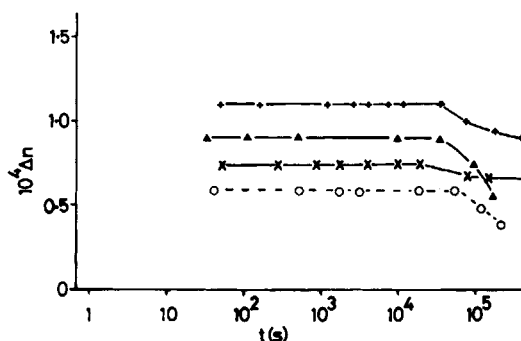

Fig. 3. Birefringence vs. time recorded during recovery following stress–relaxation: ($\blacktriangle$) type B; ($\bigcirc$) type A1; (+,x) type A2.
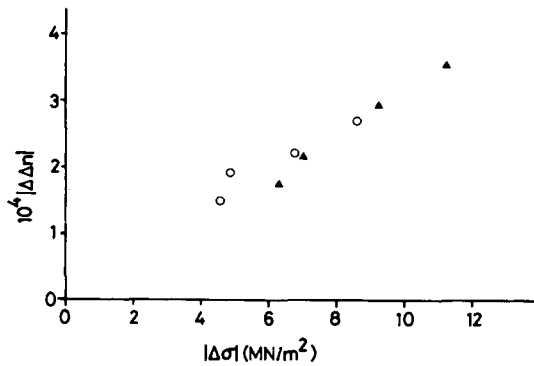
Fig. 4. Change in birefringence, $|\Delta\Delta n|$, plotted against the change in stress $|\Delta\sigma|$, for both loading (▲) and unloading (○), type B.

of a Li plot obtained from a sheet of type A1 is shown in Figure 5. Tests at different deformation levels inevitably produce different values of σ_1. By plotting σ_1 vs. the corresponding value of initial stress σ_0, it can be shown that the deformation-related component of σ_i is proportional to σ_0 (Fig. 6). A similar result was obtained with crosslinked high density polyethylene.[13]

In some tests the specimen was permitted to stress relax for $\sim$3 h, then was reloaded to the original stress, and stress–relaxation was allowed to continue again. In the second test the stress did not relax as much as in the first [Fig. 7(a)]. The Li analysis effectively locates the limiting value of stress after relaxation for infinite time, and the Li plots for the two curves in Figure 7(a) are consequently separated as shown in Figure 7(b). A similar result was obtained with crosslinked high-density polyethylene.[13]

It is difficult to measure the gradient of the σ vs. ln t graph with sufficient accuracy to make a Li analysis if the stress decays slowly, but the alternative procedure introduced by KR[12] can be used in such circumstances. For this method a series of stress–relaxation tests are conducted at different deformation levels on nominally identical specimens. The gradient at the point of inflection on the σ vs. ln t curve is measured for each specimen and a plot made of the magnitude $(-d\sigma/d \ln t)_{max}$ vs. σ_0, the initial stress. A straight line plot is normally obtained and can be extrapolated to intersect the σ_0 axis at a value taken as a stress–relaxation parameter σ_i. This procedure effectively extrapolates
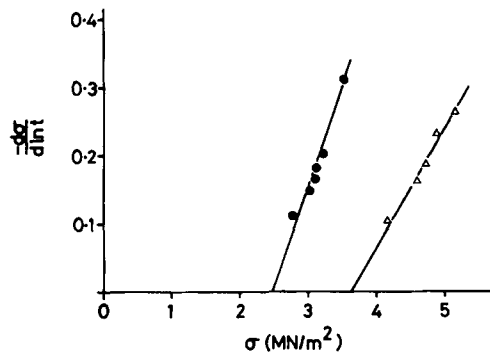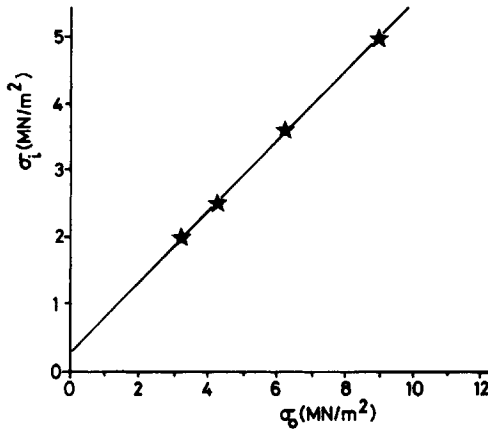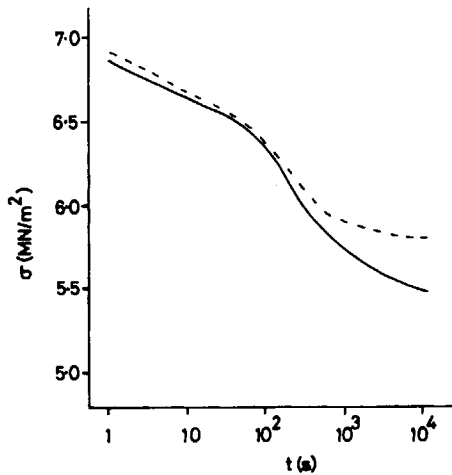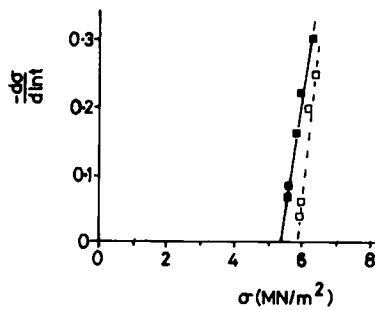

Fig. 5. Li plots for two specimens of type A1.

Fig. 6. Plot of the intercepts ("σ_i") on Li plots vs. the corresponding values of initial stress σ_0 (type B).

to zero deformation, and is therefore considered by KR to represent in some way the residual stresses in the specimens. KR plots for each of the three sheets are shown in Figure 8.

(a)

(b)

Fig. 7. (a) Stress–relaxation of an as-cured sample of type B (—) and of the same sample reloaded to approximately the same initial stress without any period of recovery (---, plotted against time elapsed from the moment of reloading). (b) Li plots corresponding to the solid line (■) and the broken line (□).
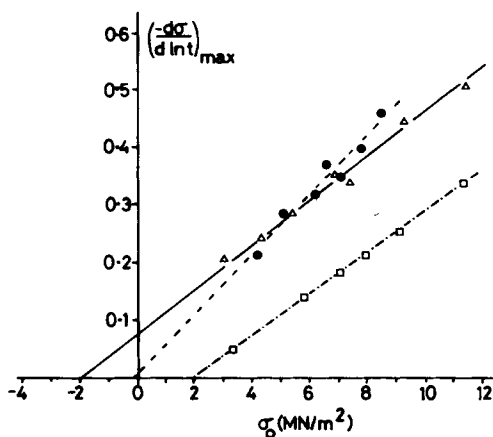
Fig. 8. KR plots for type B ($\triangle$), type A1 ($\bullet$), and type A2 ($\square$).

DISCUSSION

The changes in birefringence during stress relaxation and recovery observed with the epoxy polymer studied here are similar to those found previously with polycarbonate at 60°C.[8] Although there are strong similarities in the structure, the high crosslink density in the epoxy polymer might be expected to produce a quite different time dependence when compared to the thermoplastic poly-carbonate. Once again it is observed that the birefringence remains unchanged during stress–relaxation even when stress relaxes by a significant amount. The immediate recovery of a large fraction of the deformation birefringence on un-loading also follows the behavior of polycarbonate, but the time-dependent component begins much later, showing a time constant much greater than that for stress relaxation. The stress sensitivity on loading and unloading is the same. We must conclude from these results that, as with polycarbonate, the confor-mational changes which cause stress–relaxation must at the same time contribute to the orientational component of birefringence an amount equal to that lost on account of the reduction of stress on the chemical bonds. The results after un-loading show that these conformational changes are not easily reversed, but do eventually recover at least partially. No significant differences in the time-dependent birefringence behavior has been found with resins cured at different temperatures. The KR analysis has been used before in many studies of ther-moplastics and has been shown to be sensitive to the thermomechanical his-tory.[10,12,16–18] A broad scheme for the interpretation of the results of the KR procedure has been proposed by Kubát and Rigdahl in another paper,[19] but it has not been developed in sufficient detail to permit prediction of the trends in σ_i or n (the power law index) expected when a processing parameter is changed. Therefore, it has not been possible to attach a meaning to the variations in σ_i reported in the literature. The implication of the KR papers is that the value of the stress–relaxation parameter σ_i obtained by their procedure is determined primarily by the residual stress levels. They acknowledge that the average value of the residual stress must be zero over the cross section of a bar free from external constraints, but propose that variations in modulus or relaxation behavior at different depths can give rise to nonzero values of the stress–relaxation param-

eter. Such depth-varying properties are known to be present in injection-molded thermoplastics,[20-22] the form most widely studied for these effects.

We are not aware of previous applications of this technique to thermosets, nor are we aware of any reports of depth variations in modulus or relaxation behavior on thermosets which have been carefully prepared, as described here. In previous publications,[23,24] it has been shown that the site model theory can be used to describe the deformation behavior as an alternative to the power law upon which Kubát and Rigdahl base their analysis. We are currently attempting to extend this approach to correlate the residual stress parameter measurements with the residual stress profiles and will report at a later date. It is encouraging to note that the KR plots from samples cured at different temperatures showed marked differences, even though the birefringence behavior was similar, indicating that this analysis might be quite sensitive to variations in the sate of the material. The value of σ_i is seen to increase with curing temperature, but the value of the power law index n, which is computed from the gradient of the KR plot,[12] does not show a monotonic trend (Table I).

The Li analyses have shown a deformation dependence similar to that observed previously with thermoplastics with the derived value of σ_i proportional to the initial stress σ_0. The plot of σ_i vs. σ_0 did not pass through the origin, a result which indicates a second, deformation-independent, component presumed to be connected with residual stress. This also follows the result obtained with a crosslinked high-density polyethylene.[13] The deformation-independent component is given by the intercept with the σ_i axis ($\sigma_0 = 0$) and in Figure 6 is ~0.3 MN/m². This assumes that the value of σ_i can be expressed in the form $\sigma_i = \sigma_{i,r} + p\sigma_0$, where $\sigma_{i,r}$ is the residual stress contribution. It might be expected that $\sigma_{i,r}$ obtained in this way should equate to the σ_i parameter obtained by the KR analysis which for type B specimens was -2.0 ± 0.4 MN/m². The lack of agreement emphasizes the need for a more rational interpretation of the parameters derived from the KR and the Li analyses.

CONCLUSIONS

The change in birefringence during a stress–relaxation and recovery cycle is similar to that obtained previously with polycarbonate, but different to the behavior observed with several other thermoplastics.[1] The stress sensitivity was found to be the same for resins cured at three quite different temperatures and was the same for unloading as for loading. Differences in the stress relaxation behavior of the same resins was detected using the Kubát and Rigdahl procedure. This procedure has not been applied to thermosets before, and we have not yet explained these observations.

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