Curing Stresses in an Epoxy Polymer

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Synopsis

Curing stresses in sheets of an epoxy polymer cured at 80°C, 120°C, and 135°C have been determined using the layer removal procedure. Tensile stresses were found to be present in the interior and compressive stresses near to the surface in all samples. Very low stresses were found to be present in material cured at 80°C, with a maximum compressive stress level close to 0.5 MN/m^2 and a maximum tensile stress close to 0.25 MN/m^2. Higher stress magnitudes were obtained when using higher curing temperatures, with values of more than 1 MN/m^2 (compressive) and 0.6 MN/m^2 (tensile) recorded for specimens cured at 135°C.

INTRODUCTION

The development and measurement of residual molding stresses in thermoplastics has received significant attention, as can be confirmed by the extent of the bibliography included in Ref. 1. Much of this work has been concentrated on injection moldings, in which it is usually found that tensile stresses form in the interior and compressive stresses are located near to the surface. The latter may be of benefit for they tend to inhibit crack propagation from a surface flaw, but the tensile stresses in the interior will add to any externally applied stress, so reducing the load required to promote crazing and fracture in this region. Residual stress may cause failure through the action of a crazing agent even in the absence of external tractions. If unbalanced, residual stresses may cause distortion, and this may develop at any time after molding if the article is placed in a temperature gradient.[2] Another effect of a temperature gradient is that it may cause the reversal of the sense of the stress near to one surface,[2] in which case the influence on the fracture properties of the molding may be even more detrimental than the distortion. Extrusion-molded specimens also contain residual stresses, and in the case of pipe the stress at the inner surface may be tensile unless forced cooling is applied to the bore.[3]

Curing stresses in thermosets can be expected to influence fracture in a similar way, though the dimensional stability of these materials should be superior. Another important reason for requiring information on curing stresses is that they will partly determine the fiber pullout characteristics when a fiber composite fails, so controlling one of the chief components of the fracture toughness.[4,5]

In the investigation reported here the layer removal technique, as used in the examination of residual stress in thermoplastics, has been applied to samples cut from sheets molded from an epoxy polymer.

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TABLE I
Curing Conditions

Specimen designation	Curing temp (°C)	Curing time (h)
B	80	44
A1	120	16
A2	135	14

EXPERIMENTAL

Specimen Preparation. Specimens were produced using an epoxy resin (Ciba-Geigy Araldite CT200) and phthalic anhydride (Ciba-Geigy HT901) in the ratio 100:30. The resin was heated in a beaker at 110°C for 20–25 min, becoming a free-flowing liquid. While maintaining the temperature at 110°C, the phthalic anhydride hardener was added, stirring continuously using a rotating paddle until solution was complete. Mixing was completed in 50–60 min, and the mixture was poured into an open mold preheated to 110°C. The cavity measured 250 mm × 200 mm × 25 mm and sufficient material was added to give a thickness of approximately 5 mm. The mold was transferred to a vacuum oven preset to the curing temperature (Table I). In each case a uniform parallel-sided transparent sheet with good surface finish was obtained. Test bars measuring 190 mm × 12.5 mm were cut for layer removal analysis, avoiding regions containing flaws or strong birefringence revealed when viewed between crossed polars.

Layer Removal Analysis. The method used to obtain the residual stress distribution in flat-thermoplastic moldings was described by Treuting and Read[6] and consists of removing thin uniform layers followed by the measurement of the change in curvature that is caused by the consequent imbalance in stresses. Repeated removals and curvature measurements permits the plotting of the relationship between curvature, ρ, and the depth of material removed $(z_0 - z_1)$, from which the stress distribution in the molding prior to layer removal can be computed if the Young's modulus E and Poisson's ratio ν are uniform and of known values. Measurement of the curvatures, ρ_x and ρ_y, in the two principal directions perpendicular to the z (sheet thickness) direction, permits a biaxial analysis to be performed using the equation[6]

$$\sigma_{i,x}(z_1) = \frac{-E}{(1-\nu^2)}\left[(z_0 - z_1)^2\left(\frac{d\rho_x(z_1)}{dz_1} + \frac{\nu\, d\rho_y(z_1)}{dz_1}\right) + 4(z_0 + z_1) \times[\rho_x(z_1) + \rho_y(z_1)] - 2\int_{z_1}^{z_0} [\rho_{x(z)} + \nu\rho_y(z)]\, dz\right] \quad (1)$$

where z is measured from the plane located at the center of the sheet prior to layer removals, $z = \pm z_0$ locate the surfaces before layers are removed and $z = z_1$ locates the new position of the upper surface after layers have been removed.

With injection moldings, the recoil of molecules oriented when the melt flows into the mold may cause the stresses parallel and perpendicular to flow to be significantly different,[7] and the full biaxial treatment is required.[8] On the other

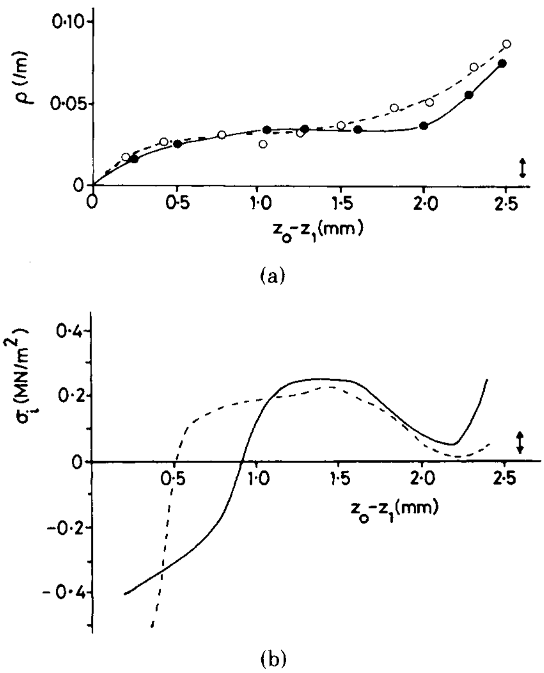

Fig. 1. (a) Curvature ρ vs. depth removed, $(z_0 - z_1)$, for two specimens cut from a type B sheet; (b) residual stress profiles computed from the plots shown in (a). The vertical arrow marks the bar center.

hand, if shrinkage takes place isotropically in the xy planes, then $\rho_x = \rho_y (= \rho)$, and eq. (1) reduces to

$$\sigma_i(z_1) = \frac{-E}{(1-\nu)}\left((z_0 + z_1)^2 \frac{d\rho(z_1)}{dz_1} + 4(z_0 + z_1)\rho(z_1) - 2\int_{z_1}^{z_0} \rho(z)\, dz\right) \quad (2)$$

This is the form used in the present work.

Layers were removed on a milling machine using a single point cutter with the point rotating in a horizontal plane. Approximately 0.2 mm was removed at each stage using a single pass. The specimen was secured to an accurately leveled steel slab on the machine bed by means of double-sided adhesive tape. The curvature was measured using a noncontact method in which a laser beam is directed in turn at mirrors attached to two different sites along the curved bar and the positions of the reflections noted.[1,9]

RESULTS

The results of the layer removal analyses are shown in Figures 1–3. The values $E = 3.0$ GN/m^2 and $\nu = 0.35$ used in the computations were obtained from Ciba-Geigy literature. Good reproducibility was found for specimens A1 and A2 but bars from type B sheet showed less agreement in the computed stress profiles [Fig. 1(b)]. This illustrates the sensitivity of the process of transformation from the curvature plot to the residual stress distribution, for the cur-

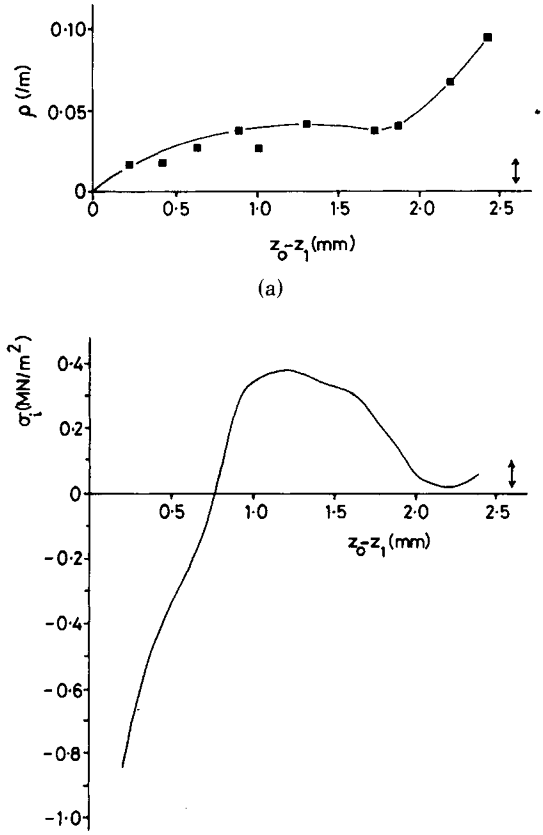

Fig. 2. (a) ρ vs. $(z_0 - z_1)$ for a specimen cut from a type A1 sheet; (b) the corresponding residual stress profile.

vature plots shown in Figure 1(a) from which the plots shown in Figure 1(b) were derived are not very different. The stresses in sheet B were quite modest, the levels indicated being of the order of 0.5 MN/m^2 (compressive) near to the surface and 0.25 MN/m^2 (tensile) in the interior. Higher stress magnitudes were recorded with samples taken from type A1 [Fig. 2(b)], and the reproducibility was much better; a second sample gave a ρ vs. $(z_0 - z_1)$ plot almost indistinguishable from Figure 2(a). Type A2 samples showed good reproducibility (Fig. 3) and showed still higher stresses rising to more than 1 MN/m^2 (compressive) near to the surface and more than 0.6 MN/m^2 (tensile) near the center [Fig. 3(b)].

In all the tests performed in this study the bars contained stress profiles of the same sense, with compressive stresses near to the surface and tensile stresses in the interior. In each case the maximum magnitude of the compressive stress was much greater than the maximum tensile stress. In some thermoplastics the residual stress profile is parabolic or nearly parabolic,[10] in accordance with theories for the solidification of glassy materials.[11–17] A quite marked departure from a parabolic profile is seen to correspond to the specimens investigated here. A curious feature of the profiles obtained with types B and A1 is that the maximum occurs not at the bar center but approximately midway between the center

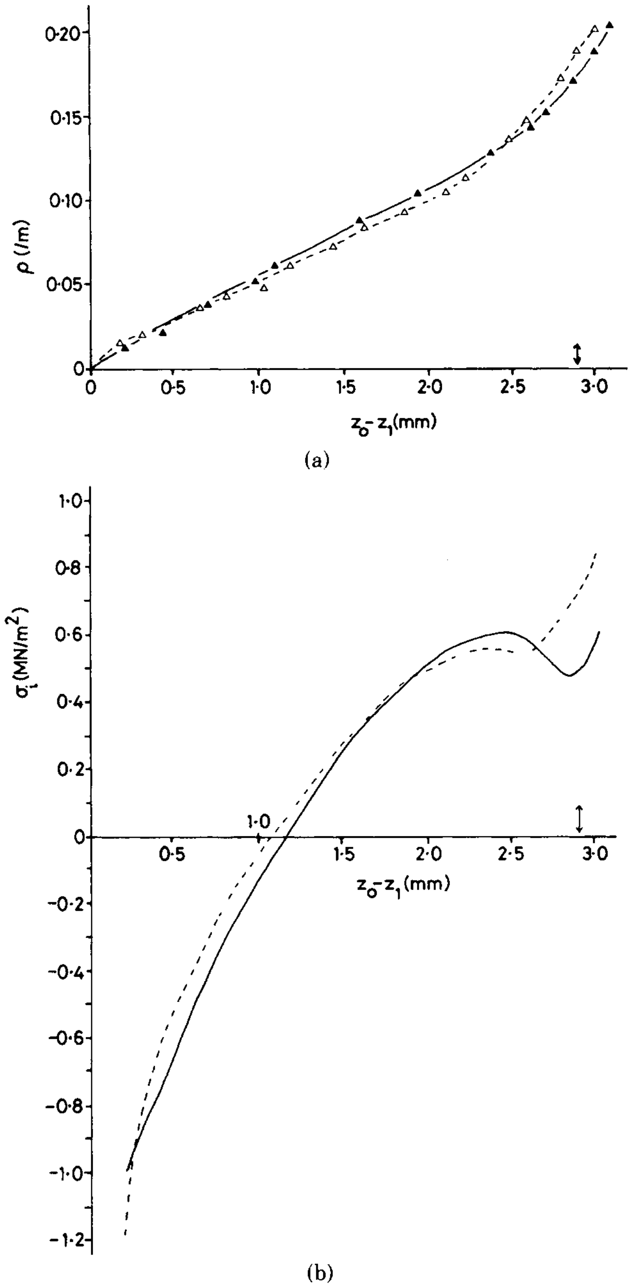

Fig. 3 (a) ρ vs. $(z_0 - z_1)$ for two specimens cut from a type A2 sheet; (b) the corresponding residual stress profiles.

and the surface. For type A2 the maxima occur much closer to the bar center, and the dip is much less pronounced than that obtained with the samples cured at lower temperatures. The presence of maxima displaced from the bar center has been observed before with some poly(methyl methacrylate) injection-molded bars.[18]

DISCUSSION

Curing stresses are often acknowledged to be present in cast thermosets but are rarely measured. Strain gauge techniques are sometimes employed, but these cannot reveal the depth variations measured by the layer removal technique. Although this technique is time-consuming, taking several hours for each analysis, it is probably quicker than the birefringence method described by Koroneos.[19] The latter method provides more information, however, giving a point-by-point stress distribution, but is confined to transparent materials. Furthermore, it has been found that the birefringence remains unaltered during stress–relaxation under an externally applied deformation with these materials.[20] Hence it might be expected that any post-cure relaxation of molding stresses will leave the birefringence unchanged, so that the birefringence data will at best reveal the stress distribution at some time soon after curing and room temperature equilibrium has been completed, but may not give information appropriate to the aged state even after storing for a period at room temperature. The layer removal procedure is shown here to be a most suitable method for measuring stresses in flat castings. The milling method gives a good finish and permits the removal of uniform layers, retaining uniform thickness at all stages. We recommend this method in preference to removal by sandpaper as cited by Miyano et al.,[17] though the results they present look plausible and show good agreement with their theoretical predictions.

The results obtained with specimens cured under different conditions show marked differences. In all cases the stresses near the surface were compressive, and those in the interior tensile. The stresses in the plate cured at 80°C were very small, and the stress magnitudes rose monotonically with curing temperature. The stresses were much smaller than those obtained by Miyano et al.[17] with rapidly quenched specimens, which is consistent with their view that a large component of the measurements they recorded was contributed by thermal stresses generated by differential cooling through the thickness of the molding.

We have not yet extended our studies to include the influence of water infusion, but we anticipate significant changes to be promoted on exposure to conditions in which water is taken up in significant quantity.

CONCLUSIONS

Curing stresses have been found to be sensitive to the curing temperature in an epoxy polymer. They have been found to be tensile in the interior and compressive near to the surface. Using a curing temperature at the lower end of the range of curing temperatures recommended by the resin manufacturer gave a sheet with very small curing stresses. A much higher curing temperature gave significant curing stresses, though these were still an order of magnitude smaller than those observed by other workers in quenched sheets of a different resin.[17] It appears that there are good prospects for exercising some control over the residual stress distribution in these thermoset materials, though other properties, including the stress relaxation behavior, may also be sensitive to the fabrication conditions which influence the residual stresses.[20] Therefore, it will be important to take into consideration these effects when attempting to adjust the curing stress distribution to give the best distortion properties or, in the case of a fiber composite, the best fiber friction characteristics.

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