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Residual stress build-up in thermoset films cured above their ultimate glass transition temperature

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The build-up of in-plane stress over time during curing and on cooling of thermoset films is investigated. The stress in a thin contracting film on a rigid substrate is analysed, and obtained as an integral of essentially the shear modulus and thickness of the curing film. Films are cured and cooled between parallel plates in a dynamic torsional rheometer, which allows dynamic shear modulus and film thickness to be monitored simultaneously. Stress predictions are compared with independent stress observations, obtained using a bilayer beam bending technique. A conventional epoxy system and a low molar mass difunctional acrylate are studied and compared. The epoxy, in agreement with the literature, exhibits no detectable stress during the curing reaction, nor during cooling to the glass transition temperature (T_g), but develops stress on cooling below T_g. The acrylate, by contrast, generates considerable stress throughout the reaction and cooling, with the major part of the stress originating above T_g. The observed stress build-up agrees well with the theoretical calculations based on the time-evolution of shear modulus and film thickness. Finally, approximate formulae for the estimation of residual stress are given. It is shown how the overall residual stress, as well as the contributions from the different parts of the cure process in a wide variety of systems, can be estimated from the mechanical and thermal properties of the polymer and the substrate.

(Keywords: residual stress; curing stress; thermal stress)

INTRODUCTION

Advanced composite materials, surface coatings and electronic circuit encapsulants are examples of applications involving the cure of a thermoset in contact with a solid substrate. In such processes the shrinkage of the polymer will be partly constrained by the substrate, thereby generating stresses at the interface between the polymer and the substrate. High stress levels may greatly reduce the technical performance of the system; for example, cracking, interface debonding and dimensional instability may result[1–3]. Appropriate residual stress states may on the other hand be favourable; for example, positive hoop stresses around a reinforcing fibre may augment the pull-out energy dissipation and thus increase toughness[4]. To be able to control residual stress states, a fundamental understanding of the process of stress build-up during cure is imperative.

The build-up of a stress state over time is governed by the course of change of volume and stiffness of both the polymer and the substrate. A typical curing process involves two steps: (1) curing at a constant elevated temperature during which the polymer simultaneously shrinks and builds up stiffness and the substrate remains unchanged; (2) cooling from the cure temperature during which both polymer and substrate shrink but by different amounts, and at least the polymer may drastically change its stiffness.

It is generally hypothesized that an increment of chemically or thermally induced strain de causes a contribution dσ to the stress after completion of the process according to Hooke's law. Thus, in the case of uniaxial stress

$$d\sigma = E\,de \qquad (1)$$

where E is the elastic modulus at the time of the strain increment. The total stress σ is obtained by integration of equation (1) throughout the process:

$$\sigma = \int E\,de \qquad (2)$$

Of course general stress states require an additional elastic modulus, e.g. the bulk modulus, in which case this integral includes two terms and two moduli which have to be followed through the process. In many cases, however, one modulus can be made to suffice either by choosing a geometry in which the effect of one modulus

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is minimized, or by assuming that the bulk modulus is constant throughout the process[5].

Plepys *et al.*[6] used impulse viscoelasticity to measure the pertinent parameters in an equation similar to equation (1) and thereby obtained the expected stress level as a function of cure time in a bulk epoxy. Lagasse *et al.*[5] measured the modulus and the cure shrinkage as a function of time during cure of a bulk epoxy in different experiments and then calculated the expected stress level. A sphere geometry was used, which made it necessary to include the bulk modulus, but by experimentally showing it to be reasonably independent of the degree of conversion it could be eliminated from the stress integral, yielding an expression of the same type as equation (2).

A rough estimate of the cooling stress can be obtained by assuming that the modulus rises as a step function at T_g and then stays constant below T_g, in which case the stress is simply the product of the final modulus and the hindered thermal contraction of the polymer below its T_g. In this manner the cooling stresses in epoxy films were estimated by Dannenberg[7] as well as by Shimbo *et al.*[8].

Direct measurement of the stress can be done using a bilayer system where the polymer is cured or cooled in association with a metal substrate and the stress evaluated either using a strain gauge or in terms of global deformation or deflection of the substrate. The most commonly used technique employs a slender beam coated with polymer on one side (beam-bending), as described by Dannenberg[7].

Measurement of internal stress build-up in thermosets has mainly been reported for epoxy-type materials. Stress build-up due to curing has been studied in epoxies by Lagasse *et al.*[5] and by Shimbo *et al.*[8], and in bismaleimides by White and Hahn[9]. In all cases the observed stress due to curing above the ultimate glass transition temperature (T_g^{∞}) of the material was negligible. The stress due to cooling after cure has also been investigated by the above[5,8,9], as well as by other workers[1,7]. Generally no stress was detected in the initial phase of the cooling, i.e. above the T_g of the polymer. As soon as the temperature descends below T_g, however, the stress starts to build up and then increases linearly with decreasing temperature. Thus, the general observation is that epoxies and similar resins are unable to build up stress above T_g, which is explained by the low rubbery modulus of the materials.

In the present work the detailed relationship between volume change, modulus and stress build-up when curing or cooling a thermoset film on rigid substrate is investigated. Based on the above principles, equations (1) and (2), the internal stress is derived for the thin film case in terms of the measurable change of film thickness. A technique allowing simultaneous measurements of modulus and thickness change is described. The calculated stress levels are then compared with results obtained using the beam-bending technique. Using these techniques two quite different systems are investigated: a conventional epoxy, comparable to the systems discussed above, and a low molar mass difunctional acrylate. Similar systems have already been compared in investigations of network formation[10]. The large differences in reaction mechanism, amount of cure shrinkage and crosslink density between the two systems suggest potential differences also in their stress build-up. Finally, an attempt is made to find a simplified, general expression for the stress build-up during the entire cure process, affording residual stress estimates based on easily measured properties of the material.

STRESS ANALYSIS

The stress integral in equation (2) is valid only if a modulus $E(t)$, signifying the stress response at a time t_∞ after completion of the process due to a unit change of strain at time t during the process, can be defined. Since any relaxation taking place between t and t_∞ would depend on the evolution of state (volume and viscoelastic properties) over that period, and $E(t)$ makes no account of that evolution, $E(t)$ cannot allow for any relaxation other than immediately after t. In other words, the relaxation time must be either very short or very long compared to the time of the experiment. Stress build-up well above and well below T_g are thus governed by the relaxed rubbery and the unrelaxed glassy modulus, respectively. However, on passing from the rubbery into the glassy state, through the glass transition region, the rate of change of the relaxation time is for a moment of the order of unity. This means that the relaxation time changes during the relaxation process, and $E(t)$ is no longer independent of the rate of change of state. To overcome this problem one must make sure that the dominating part of the process takes place outside such transitions and that the moduli chosen in the transition region are measured at an appropriate frequency, say $f\tau \approx \mathrm{d}\tau/\mathrm{d}t$, where f is frequency and τ is a characteristic relaxation time of the material.

The counterpart of equation (1) for a general stress state is

$$\mathrm{d}\sigma_{ij} = K\delta_{ij}\,\mathrm{d}e_{kk} + 2G(\mathrm{d}e_{ij} - \tfrac{1}{3}\delta_{ij}\,\mathrm{d}e_{kk}) \tag{3}$$

The moduli G and K are the shear and bulk moduli, respectively, and $\mathrm{d}e_{ij}$ is the elastic strain increment or, equivalently, the hindered strain

$$\mathrm{d}e_{ij} = \mathrm{d}\epsilon_{ij} + \delta_{ij}\,\mathrm{d}s \tag{4}$$

where $\mathrm{d}\epsilon_{ij}$ is the total (measurable) strain increment and $\mathrm{d}s$ is the free linear shrinkage, e.g. due to a chemical reaction or a change in temperature in the absence of the constraint of a substrate. The free shrinkage is thus assumed to be isotropic.

The in-plane stress in a thin film

Consider the thin-film geometry in *Figure 1*. Equation (3) predicts the stress build-up at a point in the material given the history of the moduli and the elastic part of the strain tensor e_{ij}. We thus need to relate e_{ij} to a measurable quantity, e.g. the film thickness. Matters will be considerably simplified by the thin-film assumption of plane stress, $\sigma_{33} = 0$. Writing equation (3) for one

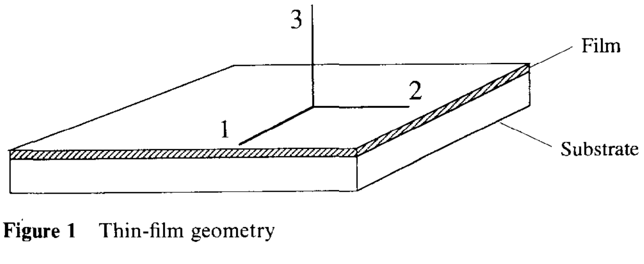

Figure 1 Thin-film geometry

in-plane stress component and the zero out-of-plane stress:

$$d\sigma_{11} = K\,de_{kk} + 2G(de_{11} - \tfrac{1}{3}de_{kk}) \tag{5}$$

$$d\sigma_{33} = K\,de_{kk} + 2G(de_{33} - \tfrac{1}{3}de_{kk}) = 0 \tag{6}$$

and subtracting gives

$$d\sigma_{11} = 2G(de_{11} - de_{33}) \tag{7}$$

The bulk modulus is thus automatically eliminated in the plane stress case, and only the evolution of the shear modulus and the in-plane and out-of-plane elastic strains as the state of the material changes need to be known. To find these elastic strains as functions of the measurable total strain ϵ_{ij}, equation (4) is written for one in-plane and the out-of-plane strain

$$de_{11} = d\epsilon_{11} + ds \tag{8}$$

$$de_{33} = d\epsilon_{33} + ds \tag{9}$$

Subtraction gives

$$de_{11} - de_{33} = d\epsilon_{11} - d\epsilon_{33} \tag{10}$$

The in-plane stress is thus obtained in terms of the total strains parallel and perpendicular to the film

$$d\sigma_{11} = 2G(d\epsilon_{11} - d\epsilon_{33}) \tag{11}$$

Of course, a similar equation holds for $d\sigma_{22}$. In the following, no distinction will be made between the directions 1 and 2 and the in-plane stress in the film will be denoted $\sigma = \sigma_{11} = \sigma_{22}$. Similarly, the in-plane strain $\epsilon = \epsilon_{11} = \epsilon_{22}$.

The stress integral

To obtain the total stress at any given time it is sufficient to integrate equation (11) up to that time. Thus the total in-plane stress in the film is given by

$$\sigma = 2\int G\,d\epsilon - 2\int G\,d\epsilon_{33} \tag{12}$$

The overall stress will be built up in two stages; the isothermal reaction and the cooling from the cure temperature down to the ambient temperature. The substrate will be assumed to be much stiffer than the polymer film, and thus deforms only by its own thermal dilatation. During the isothermal reaction this implies the condition

$$d\epsilon = 0 \tag{13}$$

and the corresponding stress contribution σ' in the film is obtained as

$$\sigma' = 2\int_{t_0}^{t_c} G\frac{\partial c}{\partial t}\,dt \tag{14}$$

where $c = -\epsilon_{33}$ denotes the thickness contraction of the film, which is measurable. The limits t_0 and t_c are the times at gelation and completion of cure, respectively. Similarly during cooling

$$d\epsilon = \alpha_s\,dT \tag{15}$$

where α_s is the linear thermal expansivity of the substrate, and the cooling stress in the film is

$$\sigma'' = 2\int_{T_c}^{T_f} G\left(\alpha_s + \frac{\partial c}{\partial T}\right)dT \tag{16}$$

Here T_c and T_f are the temperatures of cure and at the end of the cool-down, respectively. The total internal stress, $\sigma = \sigma' + \sigma''$, is

$$\sigma = 2\left[\int_{t_0}^{t_c} G\frac{\partial c}{\partial t}\,dt + \int_{T_c}^{T_f} G\left(\alpha_s + \frac{\partial c}{\partial T}\right)dT\right] \tag{17}$$

It should be recognized that the thickness contraction $c(t)$ is a characteristic not of the polymer alone but of the system, i.e. the polymer and the substrate together. It is related to the substrate dilatation $\alpha_s\,dT$ and the free linear shrinkage ds of the film, through

$$dc = 2\frac{\nu}{1-\nu}\alpha_s\,dT + \frac{1+\nu}{1-\nu}\,ds \tag{18}$$

where ν is the Poisson's ratio of the film.

In conclusion, any material characteristics affecting the stress level, e.g. network structure, glass transition temperature and cure process parameters, will manifest themselves as changes in the shear modulus and/or the thickness contraction. Thus, if the quantities can be monitored through the cure process for different materials and related to the characteristics of the systems, a general understanding of the stress build-up in a wide range of systems may be gained.

EXPERIMENTAL

Materials

Tripropylene glycol diacrylate (**1**) and benzopinacole, 99%, were obtained from Aldrich, Germany. *N*-methyldiethanolamine, 98%, was obtained from Fluka, Switzerland. 2,2-Di(4-aminocyclohexane)propane (**2**) and the diglycidyl ether of bisphenol F (**3**) were received from Ciba-Geigy, Switzerland. All chemicals were used without further purification. The monomers are presented in *Figure 2*.

Methods

Samples were cured in a torsional parallel-plate rheometer (Rheometrics RDA 2 Dynamic Mechanical Analyser), using aluminium plates of 8 mm diameter. The dynamic shear modulus was measured, at regular intervals, at a frequency of 1 Hz and at zero normal force, while simultaneously monitoring the change in plate distance. In a typical experiment the liquid monomer, either a stoichiometric amine/epoxy mixture or the acrylate with 2 mol% benzopinacole and 0.3 mol% diethanolamine, was applied between the plates of the rheometer and the distance between the plates set to 1 mm. Benzopinacole and diethanolamine

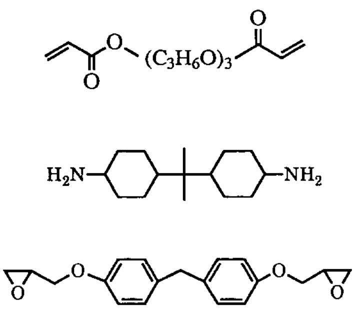

Figure 2 Acrylate (**1**), amine (**2**) and epoxy (**3**) monomers

were used as initiators since they are less sensitive to oxygen than common radical initiators. The sample was then heated to the cure temperature, 115°C for the acrylate and 140°C for the epoxy, and the dynamic shear modulus and the change in plate distance measured as a function of cure time. When the cure was completed the sample was cooled to room temperature while still measuring the same parameters. Repetitions of the experiments showed the reproducibility to be very good for the measurements of modulus, a variation of less than 5% was observed. The variation between the contraction measurements was up to 20%.

The stress build-up was measured independently by a beam-bending technique[7]. Here a 100–150 μm thick layer of monomer, mixed as in the rheometer experiments, was applied to an aluminium beam (dimensions $200 \times 6 \times 0.3$ mm). The beam was placed in an oven on two supports, positioned 100 mm apart, and the deflection at the centre of the beam measured upon curing and cooling. The curing was performed at a temperature of 115°C or 140°C. The stress level was calculated from the measured deflection according to the following expression[7]:

$$\sigma(t) = d(t)\,\frac{4Et_s^3}{3l^2(1-\nu)\,t_p(t_s+t_p)} \qquad (19)$$

where σ is the stress, d the deflection, E the elastic modulus of the substrate, l the length of the beam between the supports, ν the Poisson's ratio of the substrate and t_s and t_p the thicknesses of the substrate and the polymer film, respectively.

RESULTS AND DISCUSSION

The curing reaction of a thermoset involves dramatic changes in the properties of the resin[11]. After heating up of the initially liquid monomer the reaction commences, the molecular weight and the degree of crosslinking increase and the volume of the system decreases. As the reaction proceeds two phenomena may occur independently: gelation and vitrification. Gelation corresponds to the formation of an infinite network and can be regarded as the point after which the system can sustain stress. Vitrification occurs when the T_g of the reacting system reaches the cure temperature. On vitrification the system, either a rubbery network, or, if vitrification precedes gelation, a viscous liquid, is transformed into a glass. In the present experiments vitrification was avoided altogether by curing at a temperature well above the ultimate glass transition temperature, T_g^{∞}.

Upon cooling a thermoset from a curing temperature above T_g^{∞} to room temperature it goes from a rubbery material to a glassy solid. The glass transition is accompanied by changes in modulus as well as in thermal expansivity. The relaxation time of the polymer rises by several orders of magnitude, and the unrelaxed modulus becomes important.

Evolution of shrinkage and elastic modulus

It has already been established that the stress build-up is governed by the shear modulus and the thickness change. Using dynamic mechanical analysis these two quantities could be monitored simultaneously through both cure and cool-down.

The isothermal curing is illustrated in *Figure 3*, which

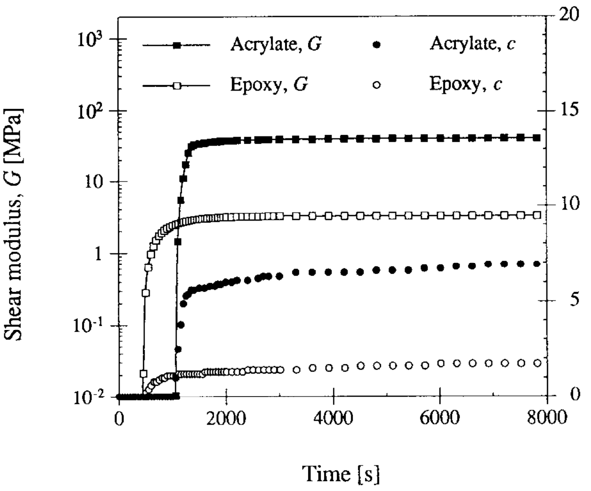

Figure 3 Experimental dynamic shear modulus and thickness contraction during cure

Table 1 Comparison of observed, predicted and approximated stress levels during the different parts of the cure process

Sample	Modulus, G (MPa)	Thickness contraction, c	Stress, observed (MPa)	Stress, predicted[a] (MPa)	Stress, approximated[b] (MPa)
Cure					
Epoxy	3.2	0.017	–	0.06	0.05
Acrylate	39	0.069	1.8	1.7	2.7
Cooling above T_g					
Epoxy	3.2	0.014	–	0.26	0.09
Acrylate	39	0.027	2.3	2.1	2.0
Cooling below T_g					
Epoxy	260	0.013	5.8	6.0	5.7
Acrylate	300	0.005	2.4	2.6	2.4
Total					
Epoxy			5.8	6.3	5.8
Acrylate			6.5	6.4	7.1

[a] Numerical integration according to equation (17)
[b] Approximation according to equations (20)–(22)

shows typical evolutions of shear modulus and thickness contraction with cure time for the two materials. It should be noted that only the contraction after gelation was measured; prior to gelation the liquid sample between the plates is unable to exert any attractive force on the plates and accommodates to the shrinkage by flowing. At first, during the heating up and reaction until gelation, the modulus is virtually zero. At gelation the modulus begins to rise rapidly and the system may start to build up stress. At the same instant the shrinkage becomes detectable. Finally the reaction goes to completion, accompanied by a slight increase in modulus and decrease in volume. *Figure 3* shows that the acrylate and the epoxy are qualitatively similar but quantitatively quite different. The values of final rubbery modulus and total thickness contraction on cure are presented in *Table 1*. The acrylate exhibits a much higher rubbery modulus and a much larger shrinkage than the epoxy. This discrepancy is not unexpected. Indeed, considering the structure of the monomers and their reaction mechanism it is evident that they will behave differently. The epoxy–amine system reacts by a stepwise mechanism, connecting two epoxide groups to every amine, whereas the acrylate system reacts in a chainwise manner, forming carbon–carbon bonds between the vinyl groups. The result is that the acrylate network becomes much denser than the epoxy network. Since the modulus for a rubber, i.e. a crosslinked material above T_g, depends strongly on the crosslink density, the acrylate should thus have a higher rubbery modulus than the epoxy. Regarding the difference in volume change, it is well known that the ring-opening reaction of epoxies is accompanied by a low shrinkage whereas acrylates normally exhibit a considerable shrinkage. Furthermore, it is important to recognize that stresses are produced, not by the total shrinkage, but by the shrinkage after gelation. The chainwise reaction of the acrylate yields an early gelation, typically at below 5% conversion[12]. As opposed to this an epoxy, reacting by a stepwise mechanism, experiences gelation later, normally at about 60% conversion[11]. Consequently, the volume change after gelation will for the acrylate be >95% and for the epoxy approximately 40% of the total volume change.

The subsequent cool-down of the two materials is shown in *Figure 4*. The difference in behaviour between the two systems is clearly visible. While the epoxy exhibits a narrow glass transition, as shown by the sharp step in modulus, and a definite change in thermal expansion coefficient, the acrylate shows a broad, more or less continuous transition. This is expected, since it is well known that the width of the transition increases with increasing crosslink density[13]. The glass transition temperatures are roughly 60°C for the acrylate and 120°C for the epoxy, thus confirming that the curing temperatures were well above T_g for both systems.

Stress build-up

Plots of modulus vs. thickness contraction for the epoxy and the acrylate during the cure reaction are presented in *Figure 5*. The normalized scales display a certain similarity in shape between the two curves. This will be discussed later. The expected stress build-up as a function of cure time is proportional to the area under this curve according to equation (14). It should be noted, of course, that the proportionality constants are quite different for the two materials. The stress build-up, calculated by numerical integration of equation (14) on the data in *Figure 3*, is shown in *Figure 6*. A considerable stress is predicted in the acrylate, whereas the epoxy should exhibit a much lower stress level. Experimental

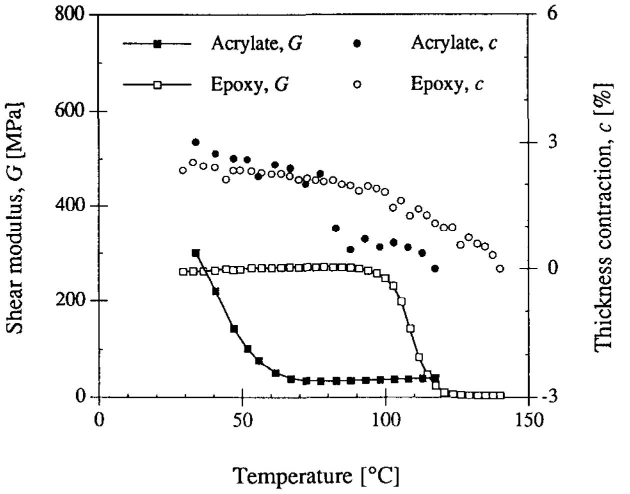

Figure 4 Experimental dynamic shear modulus and thickness contraction during cool-down

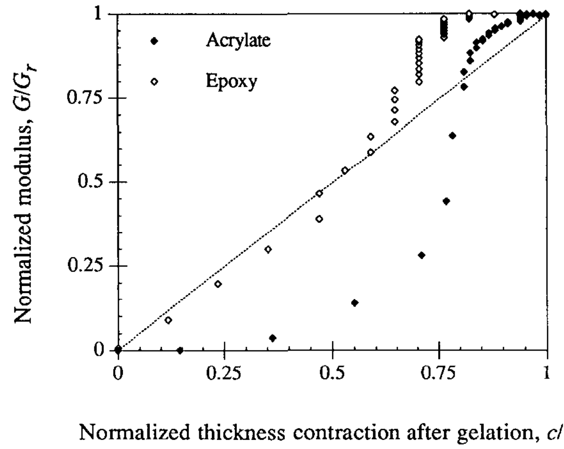

Figure 5 Experimental dynamic shear modulus *versus* thickness contraction during cure after gelation. The residual stress is proportional to the area under the curve. The area approximation is indicated by the dotted line

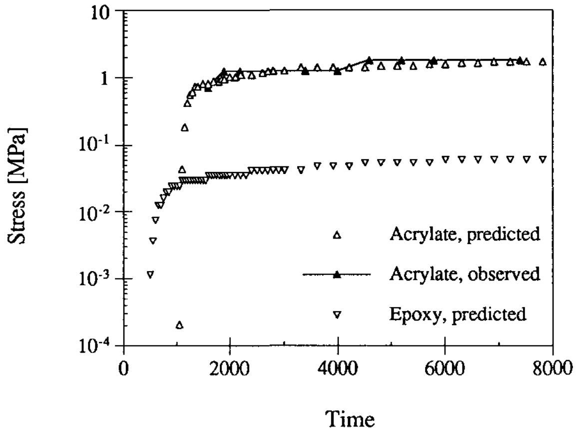

Figure 6 Predicted and observed stress build-up during cure

observations, using the beam-bending technique, confirm the predictions (*Figure 6*), in spite of the difference in film geometry between the rheometer and the beam-bending experiment. In the case of the acrylate the predicted and observed stress follow each other closely. For the epoxy no stress was observed, due to the limited sensitivity of the experimental technique. The smallest distinguishable deflection of the beam is about 50 μm. The stress predicted in the epoxy, 6×10^4 Pa, corresponds to a deflection of 20 μm, and is thus not detectable. As previously mentioned, other workers using similar techniques have reported that no stress build-up was observed when curing epoxies under the same conditions[1,8]; again the stress would have been below the detectable level.

The stress build-up during cool-down is calculated in a similar manner. *Figure 7* shows the evolution of modulus as a function of thickness contraction on cooling of the epoxy and the acrylate. *Figure 8* shows the predicted stress during cool-down, according to equation (16), as a function of temperature. The difference between the two systems at the point of departure, i.e. at the curing temperatures, has been discussed above. As for what happens during the cooling itself it is clear that the materials should behave differently. In the case of the epoxy the stress developed above T_g should be insignificant. As the transition is passed the stress should start to grow linearly with decreasing temperature. This is also the behaviour reported by other workers[7,8]. In the acrylate case stress should already start to build up above T_g and then continue to grow at an increasing rate as the temperature decreases. In both cases the predictions agree well with the stress levels observed with the beam-bending technique (*Figure 8*).

The overall stress level, i.e. due to cure as well as cooling, is about the same for the two materials. However, the contributions from the different parts of the cure process, presented in *Table 1*, differ markedly between the materials. It can be seen that in the epoxy stress builds up primarily during cool-down below T_g as described in the literature[7,8], whereas in the acrylate considerable stress builds up not only during the curing reaction, but also during cooling above T_g. In fact as much as two-thirds of the total stress originates above T_g. This shows that the assumption often made when modelling build-up of stress in thermosets, that no stress occurs above T_g, is not generally applicable; the characteristics of the material have to be examined before any assumptions can be made.

Approximations

We have shown that the full time-evolution of the internal stress in a thin film can be accurately described by the integral in equation (17), provided that the shear modulus and film thickness are known functions of time and temperature. However, in most practical situations the available data are far more limited. First, the full time evolution of material properties is seldom known. Instead they are known only at certain points of the process, such as at the beginning and the end of the curing reaction, and above and below T_g for the fully cured system. Secondly, shrinkage is usually known only as total free shrinkage in the polymer during cure, and as rubbery and glassy thermal expansivities during cool-down. In order to estimate residual stresses based on such more limited data, approximations are necessary.

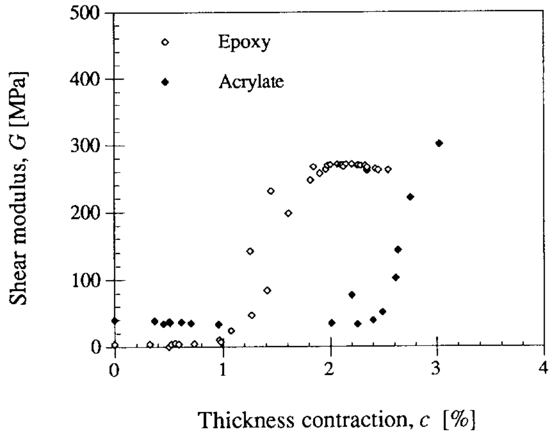

Figure 7 Experimental dynamic shear modulus *versus* thickness contraction during cool-down

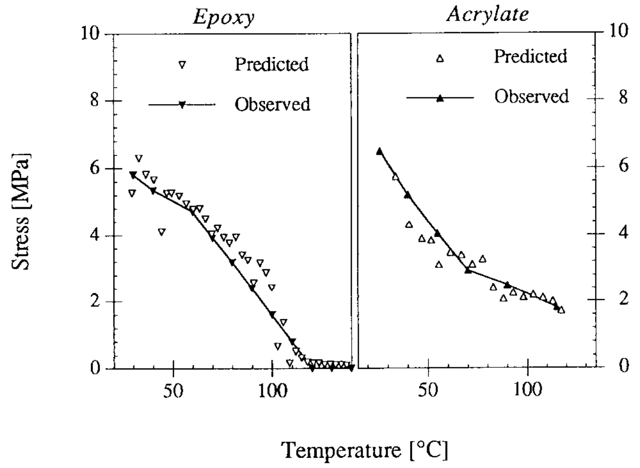

Figure 8 Predicted and observed stress during cure and cool-down

The first step in the approximation is to eliminate the need to know the full time or temperature evolutions of shear modulus and film thickness. Regarding the contribution from the cure reaction, the similarity in shape of the curves of modulus vs. shrinkage for the two systems indicated in *Figure 5*, may be used. It should be noted that while the final point, i.e. the end of the reaction, is quite unambiguous, the starting point is less well defined. We have here chosen the point at which the material exhibits a measurable ($>10^3$ Pa) elastic modulus as starting point. This choice is somewhat arbitrary and may be possible to improve on. As already discussed, the acrylate and epoxy systems are quite different. In fact they can be said to represent two extremes in terms of reaction mechanism, gel point, crosslink density and cure shrinkage. It is therefore believed that the similarity observed in *Figure 5* will extend to a wide range of systems. The S-shape of the curves suggests the following approximation:

$$\int_{t_0}^{t_c} G \frac{\partial c}{\partial t}\,\mathrm{d}t \approx \tfrac{1}{2} G_r c_c \qquad (20)$$

where G_r is the rubbery modulus and c_c the film thickness contraction between the gel point and the end of the reaction. This approximation is exact if the curves are antisymmetric about their inflection points. Regarding the cool-down, the shape of the curves of shear modulus vs. thickness contraction obtained for the corresponding processes (*Figure 7*), as well as suggestions in the literature[8], indicate that the moduli can be assumed constant above and below T_g and the area thus approximated by squares as follows:

$$\int_{T_c}^{T_g} G\left(\alpha_s + \frac{\partial c}{\partial T}\right) \mathrm{d}T \approx G_r(\alpha_s \Delta T_1 + c_1) \qquad (21)$$

$$\int_{T_g}^{T_f} G\left(\alpha_s + \frac{\partial c}{\partial T}\right) \mathrm{d}T \approx G_g(\alpha_s \Delta T_2 + c_2) \qquad (22)$$

where c_1 and c_2 are the thickness contractions and G_g denotes the glassy modulus of the polymer. ΔT_1 and ΔT_2 are the temperature differences when cooling from the cure temperature to T_g and from T_g to the final temperature, i.e. $T_g - T_c$ and $T_f - T_g$. *Table 1* shows stress approximations calculated using equations (20)–(22), together with the values obtained from the exact expression, equation (17). As can be seen the approximations hold well for the cool-down of both materials as well as the cure of the epoxy. Regarding the cure of the acrylate the approximation is less accurate but still acceptable. The approximations of overall stress levels, i.e. cure and cool-down together, are good for both materials.

The second step in the approximation is to replace the system-dependent values of film contraction with free volumetric shrinkages, measured independently. The thickness contractions in equations (20)–(22) must be substituted by equation (18), and the Poisson's ratio of the polymer must be estimated. Here, a useful approximation is to put ν to 0.5 above T_g (elastic incompressibility) and use the glassy Poisson's ratio ν_g below T_g. The shrinkage after gelation can be estimated if the total cure shrinkage and the conversion at the gel point are known: $s_c = s_{tot}(1 - \xi_{gel})$ where ξ_{gel} is the conversion at the point of gelation. The shrinkage due to the cool-down may be calculated from the thermal expansivity of the polymer above and below T_g. In this way, the residual stress can be calculated based entirely on material properties: the free cure shrinkage and the conversion at gelation, the rubbery and glassy thermal expansivities and shear moduli of the polymer, the thermal expansivity of the substrate, the glassy Poisson's ratio of the polymer, and T_g. The total internal stress is thus estimated by the equation:

$$\sigma = 3G_r s_{tot}(1 - \xi_{gel}) + 6G_r(\alpha_s - \alpha_r)\Delta T_1 + 2G_g \frac{1 + \nu_g}{1 - \nu_g}(\alpha_s - \alpha_g)\Delta T_2 \qquad (23)$$

It may be noted that whereas the terms representing the cool-down, the second and third terms, constitute mere variations upon what has already been suggested in the literature, the first term, representing the cure reaction, is new.

Using equation (23) the contributions from the different parts of the cure process may be estimated in a wide range of systems. The required material characteristics may be obtained either from literature or from simple experiments. The estimates can then be used as a basis for changing the cure process and/or the characteristics of the system in order to reduce the residual stress levels.

CONCLUSIONS

The structural changes during the cure process (reaction and cooling) were monitored using a parallel-plate torsional dynamic mechanical analyser. Based on simultaneous measurements of shear modulus and thickness change the stress build-up during all parts of the cure process was predicted. The predictions agreed well with stresses observed using a beam-bending technique.

In a conventional epoxy system no stress was detected during the reaction and during the first part of the cooling, i.e. above T_g. It was only when cooling below T_g that stress started to build up. In a difunctional acrylate considerable stress developed during the reaction and the initial part of the cooling. As much as two-thirds of the total stress could be ascribed to the parts of the cure process occurring above T_g.

Using simple approximations based on the observed characteristics of the materials and the cure process it is possible to predict the contributions from the different parts of the cure process, curing as well as cooling above and below T_g, to the overall residual stress build-up.

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