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

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The stress build-up during isothermal cure below the ultimate glass transition temperature of epoxy and acrylate films is investigated in detail. Four systems are studied; two acrylates and two epoxies, with different crosslink densities. Relaxation modulus and film shrinkage are measured simultaneously during cure. The stress build-up is measured independently using a bi-layer beam bending technique. A model for the build-up of cure stresses is proposed, in which stresses are generated by the cure shrinkage and decay by viscoelastic relaxation. The relaxation is described by a simple, modified Maxwell model. Owing to the absence of memory in the Maxwell model, the resulting equation is simple and numerical stress computation straightforward. The stress build-up over time is thus simulated for the four model systems based on the relaxation and shrinkage data, and the simulations compared with the experimentally observed stress build-up. The model successfully predicts the cure stresses where more standard elastic methods fail. It is found that the amount of stress build-up during cure varies greatly between the different systems. In general, a higher crosslink density results in higher stress build-up. The stress on cure ranged from less than 1% of the total stress on cure and cool-down in a lightly crosslinked epoxy to more than 30% of the total stress in densely crosslinked epoxies and acrylates. Finally simple approximations for estimating the stress levels after cure and cool-down from basic material properties, e.g. modulus and cure shrinkage, are proposed. © 1997 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

In applications such as electronic encapsulants, coatings and advanced composites where a thermoset is cured in association with a solid substrate, the shrinkage of the polymer will be partly constrained by the substrate and thus generate residual stresses at the interface between the polymer and the substrate. High levels of such stresses are unwanted since they may reduce the technical performance of the system, resulting in for instance deformation, cracking or debonding of the interface[1–3]. A thorough understanding of the process of stress build-up during cure is crucial if residual stress states are to be controlled.

The build-up of residual internal stresses is related to the evolution of shrinkage strain and mechanical stiffness during the cure process. The development of these quantities with cure for stepwise reacting epoxy and chainwise reacting acrylate resins has been extensively studied by Lange *et al.* Using the technique of dynamic mechanical analysis in torsion, the shear modulus and thickness contraction of a film were monitored simultaneously during cure[4]. Measurements at different frequencies permitted the time-dependence of the modulus to be probed[5]. The two main transitions occurring during cure are gelation and vitrification. Gelation corresponds to the formation of an infinite network, whereas vitrification occurs when the glass transition temperature (T_g) of the reacting system reaches the cure temperature. Based on if and in what sequence gelation and vitrification occur during isothermal cure one can identify two main regimes of cure temperatures. During isothermal cure above the ultimate glass transition temperature ($T_{g}\infty$) of the polymer only gelation will occur[4], whereas if the cure temperature is below $T_{g}\infty$ the polymer will first experience gelation and then vitrification[5]. On gelation, i.e. the liquid to gel transition, the system acquires an equilibrium modulus which is essentially elastic. Gelation proceeds similarly in both acrylates and epoxies. On vitrification the rubbery gel is transformed into a glassy solid. During this transformation the mechanical behaviour changes from elastic to viscoelastic, i.e. it becomes time-dependent. In the epoxies vitrification is a distinct event, occurring separately from gelation and ending with the end of the cure reaction. In the acrylates vitrification commences immediately after gelation, the two events being virtually

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indistinguishable, and lasts until the end of the reaction, leaving the sample still in the transition zone[5].

Above $T_g\infty$ the build-up of a residual stress state can be predicted from the change of volume and stiffness of the polymer as shown by Lange *et al.*[4]. The prediction is performed incrementally, where each increment of cure shrinkage causes a contribution to the residual stress and the total residual stress is obtained by a summation over the cure process. The stress increments are calculated elastically, using the relaxed modulus at the time of the increment, thus assuming that all relaxation occurs instantaneously. The actual stress levels reached during cure above $T_g\infty$ of epoxy and acrylate films were found to be proportional to the ultimate rubbery modulus and the amount of cure shrinkage after gelation[4]. Thus a polymer with low rubbery modulus and limited cure shrinkage, e.g. an epoxy, exhibited negligible stresses during cure, whereas curing a polymer with high rubbery modulus and significant cure shrinkage, such as a low molar mass acrylate, lead to higher stress levels.

Below $T_g\infty$ the modelling of stress build-up is complicated by the vitrification process in that stress build-up and stress relaxation both proceed simultaneously. A simple elastic analysis is unable to take this time-dependence into account. As shown by Adolf and Martin[6] a thorough analysis of this situation becomes quite complex and also requires experimental data which are difficult to obtain. In order to be able to perform calculations the problem must be simplified and several assumptions made[7,8]. Stress build-up during cure of epoxy films below $T_g\infty$ has been studied by Ochi *et al.*[9] as well as by Croll[1] and Dannenberg[10]. Ochi *et al.* found that the stress level depended on the exotherm during the reaction. Thus the experiments were not truly isothermal, and the strains causing the stress were probably a mixture of cure and thermal shrinkage. In the absence of temperature variations the observed stresses were low. Croll performed his experiments under isothermal conditions, but observed an influence of water absorption. In this case the strains were thus a mixture of cure shrinkage and expansion due to water uptake. According to Croll the cure shrinkage resulted in significant stress build-up. Dannenberg cured films isothermally at room temperature without detecting any stress build-up due to the reaction.

In the present work the stress build-up during cure below $T_g\infty$ of epoxy and acrylate films is investigated in detail. Four systems are studied; two acrylates and two epoxies, with different crosslink densities. A viscoelastic stress model, taking simultaneous build-up and relaxation of stress into account, is developed. Data of dynamic shear modulus measured at several frequencies and film thickness obtained during cure of films between parallel plates in a dynamic torsional rheometer presented in a previous article[5] are then used to predict the stress build up with the model. The stress build-up is also measured independently, using a bi-layer beam bending technique. Finally simple approximations for estimating the stress build-up during cure from basic material properties are presented.

EXPERIMENTAL

Materials

The diglycidyl ether of bisphenol F (PY 306), **1**, 2,2,-di(4-aminocyclohexane)propane (HY 2954), **2**, and triglycidyl-*p*-aminophenol (MY 0510), **3**, were received from Ciba-Geigy, Switzerland. Pentaethylenehexamine, **4** 85%, and N-methyldiethanolamine, 98%, were obtained from Fluka, Switzerland. Benzopinacole, 99% was purchased from Aldrich, Germany. Di-ethoxylated bisphenol A dimethacrylate (Diacryl 101), **5**, 84% and trimethylolpropane trimethacrylate (Nuorycryl M36), **6**, 92%, were obtained from Akzo Chemicals BV, The Netherlands. All chemicals were used without further purification. The monomers are presented in *Figure 1.*

Methods

Experiments were performed on two epoxy–amine mixtures and two acrylates. The epoxy–amine mixtures were **1** + **2** and **3** + **4** in stoichiometric amounts and the two acrylates were **5** and a 1/1 mixture by weight of **5** + **6**. To the acrylate mixtures 2 mol% benzopinacole and 0.3 mol% diethanolamine was added as initiator.

The stress build-up was measured by a beam-bending technique[4,9]. Here a 100–150 μm thick layer of monomer was applied to an aluminium beam (dimensions 200× 6 × 0.3 mm^3). The beam was placed in an oven on two supports, positioned 100 mm apart, and the deflection at the centre of the beam upon curing and cooling measured. The curing was performed at a temperature of 115°C for the acrylates, 100°C for the **1** + **2** epoxy mixture and 70°C for the **3** + **4** epoxy mixture. The stress level was calculated from the measured deflection according to the expression[9]

$$\sigma(t) = d(t)\frac{4Et_1^3}{3l^2(1-\nu_s)t_2(t_1+t_2)} \tag{1}$$

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_s the Poisson's ratio of the substrate and t_1 and t_2 the thicknesses of the substrate and the polymer, respectively.

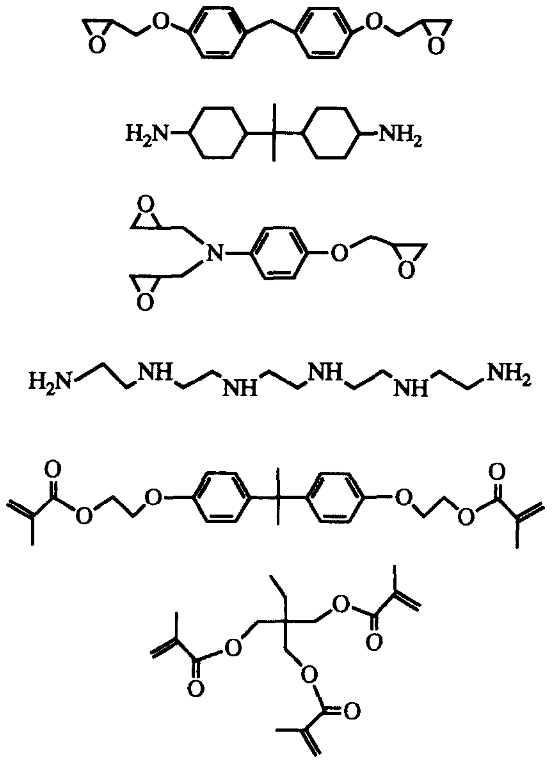

Figure 1 Epoxy (**1**, **3**), amine (**2**, **4**) and acrylate (**5**, **6**) monomers

VISCOELASTIC STRESS MODEL

In general, the rate of change of stress in a viscoelastic material can be written as a total differential

$$\frac{d\sigma}{dt} = \frac{\partial \sigma}{\partial e}\frac{de}{dt} + \frac{\partial \sigma}{\partial t} \qquad (2)$$

where e is the mechanical strain tensor. The first term is the stress production and the second the stress dissipation, or viscoelastic decay. The mechanical strain is the stress-producing strain. For example, in the presence of chemical strain, $d\varepsilon^c$, and thermal strain, $d\varepsilon^T$,

$$de = d\varepsilon - d\varepsilon^c - d\varepsilon^T \qquad (3)$$

where $d\varepsilon$ is the total (kinematic) strain.

The differential

$$\frac{\partial \sigma}{\partial e} = G_0(t) \qquad (4)$$

is the instantaneous elastic stiffness tensor.

Our analysis starts with specializing equation (2) to isothermal cure of a thin isotropic film on a rigid substrate. In this case the stress has only one non-zero component, the in-plane stress, $\sigma = \sigma_{11} = \sigma_{22}$, and $\sigma_{33} = 0$. The total strain also has only one non-zero component, the thicknesswise strain ε_{33}, while $\varepsilon_{11} = \varepsilon_{22} = 0$. For our development it will be appropriate to define the thickness contraction,

$$dc = -d\varepsilon_{33} \qquad (5)$$

which is positive upon shrinkage. For the thin film case equation (2) may thus be reduced to

$$\frac{d\sigma}{dt} = \frac{\partial \sigma}{\partial c}\frac{dc}{dt} + \frac{\partial \sigma}{\partial t} \qquad (6)$$

The first term is obtained by a purely elastic analysis of the thin film, presented in ref. 4

$$\frac{\partial \sigma}{\partial c} = 2G_0(t), \qquad (7)$$

where $G_0(t)$ is the instantaneous (unrelaxed) *shear* modulus of the polymer. Its time-dependence is here due to the chemical reaction. The second term is the viscoelastic stress decay. This is the part that usually is the most difficult to treat, due to the memory effects involved[6]. To overcome this problem we use a simple Maxwell model with a single relaxation time (no memory) and a relaxed stress σ_∞:

$$\frac{\partial \sigma}{\partial t} = -\frac{\sigma - \sigma_\infty(t)}{\tau(t)} \qquad (8)$$

where τ is the relaxation time. In this way the fact that only a part of the stress is capable of relaxing, is taken into account. Both of G_0 and τ depend on the extent of reaction and therefore time. The relaxed stress, σ_∞, is taken to be the stress built up in an infinitely slow reaction. Since this is essentially an elastic stress it is obtained in the same way as equation (7)

$$\frac{d\sigma_\infty}{dc} = 2G_\infty(t) \qquad (9)$$

Upon integration we have

$$\sigma_\infty = 2\int_0^t G_\infty(t)\frac{\partial c}{\partial t}dt \qquad (10)$$

Substitution of equations (7), (8) and (10) into equation (6) now gives the result

$$\frac{d\sigma}{dt} = 2G_0(t)\frac{dc}{dt} - \frac{\sigma}{\tau(t)} + \frac{2}{\tau(t)}\int_0^t G_\infty(t)\frac{dc}{dt}dt \qquad (11)$$

The choice of a memory-less relaxation model has the main advantage of requiring a minimum of numerical integration (history). More general viscoelastic models with memory require multiple time integrals and become computationally complex. In the limit of long relaxation times, corresponding, e.g. to very rapid cure, relaxation is negligible and equation (11) becomes equivalent to

$$\frac{d\sigma}{dt} = 2G_0\frac{dc}{dt} \qquad (12)$$

In the limit of short relaxation times, i.e. slow cure or cure above $T_g\infty$, relaxation is instantaneous and equation (11) becomes

$$\frac{d\sigma}{dt} = 2G_\infty\frac{dc}{dt} \qquad (13)$$

It is also worth noting that the thickness contraction, c, is a characteristic not of the polymer but of the system, i.e. polymer and substrate together[4]. It is related to the free linear shrinkage s of the polymer through

$$dc = \frac{1+\nu_p}{1-\nu_p}ds \qquad (14)$$

where ν_p is the Poissons' ratio of the polymer.

RESULTS AND DISCUSSION

Four different materials were studied, two epoxies and two acrylates. The first epoxy system, the diglycidyl ether of bisphenol F, **1**, reacted with 2,2-di(4-aminocyclohexane)propane, **2**, produces a network with low crosslink density by a step-wise mechanism. The second epoxy system, triglycidyl-*p*-aminophenol, **3**, reacted with pentaethylenehexamine, **4**, gives a highly crosslinked network by a step-wise route. The first acrylate, pure di-ethoxylated bisphenol A dimethacrylate, **5**, reacts in a chain-wise manner yielding a moderately crosslinked network. The second acrylate system, di-ethoxylated bisphenol A dimethacrylate mixed with trimethylolpropane trimethacrylate, **6**, produces a network with very high crosslink density, also by a chainwise mechanism. The characteristics of the four systems are given in *Table 1*. The curing of the four systems has been studied using a torsional dynamic mechanical analyser. The evolution of the shear modulus at five different measurement frequencies as well as the cure shrinkage expressed as sample contraction perpendicular to the film thickness (thickness contraction) has been reported previously[5]. Presented in the same work are also calculations and data transformations permitting the reconstruction of the early part of the modulus–cure time curve at low measurement frequencies, where the properties change faster than measurements can be performed[5].

Implementation of the viscoelastic model

Equation (11) can be integrated numerically using the following algorithm:

$$\sigma_\infty^{n+1} = \sigma_\infty^n + (G_\infty^{n+1} + G_\infty^n)(c^{n+1} - c^n) \qquad (15a)$$

Table 1 Characteristics of the studied systems, obtained from dynamic mechanical analysis

System	Ultimate glass transition temperature, $T_g\infty$ [°C]	Cure temperature, T_c [°C]	Modulus at end of cure (at T_c) [MPa]	Glassy modulus, G_g [MPa]	Rubbery modulus, G_r [MPa]	Cure shrinkage after gelation[a], c_c
Lightly crosslinked epoxy, **1** + **2**	120	100	330	340	4	0.017
Densely crosslinked epoxy, **3** + **4**	180	100	590	610	130	0.029
Moderately crosslinked acrylate, **5**	150	115	210	570	30	0.043
Very densely crosslinked acrylate, **5** + **6**	160	115	310	510	240	0.050

[a] Defined as thickness contraction and related to the free linear shrinkage s through equation (14)

$$\sigma_*^{n+1} = \sigma_*^n + (G_0^{n+1} + G_0^n)(c^{n+1} - c^n) - 2\frac{t^{n+1} - t^n}{\tau^{n+1} + \tau^n}(\sigma_*^n - \sigma_\infty^n) \qquad (15b)$$

$$\sigma^{n+1} = \max(\sigma_*^{n+1}, \sigma_\infty^{n+1}) \qquad (15c)$$

where the relaxed and unrelaxed shear moduli, G_∞ and G_0, may or may not be functions of time. Equation (15c) ensures that the lower bound $\sigma \geq \sigma_\infty$ is not violated when the relaxation time is of the same order as the timestep used or less (at the beginning of cure). Calculations are considerably simplified by setting

$$\sigma^{n+1} = \sigma_\infty^{n+1}$$

until $\tau > \Delta t$. The numerical integration will be accurate only if the timestep is sufficiently shorter than the relaxation time τ. Otherwise it will overestimate relaxation and thus underestimate stress. This is of course of no consequence at short relaxation times when $\sigma \approx \sigma_\infty$. The appropriate requirement is that $\Delta t/\tau$ becomes small while $\sigma \approx \sigma_\infty$ is still valid. This is easily checked by varying the timestep.

In order to use equations (15) an expression for the relaxation time as a function of cure time is needed. To find this, the data of modulus vs cure time obtained at different frequencies presented in ref. 5 can be used. Each frequency, f, can be taken to correspond to a certain relaxation time, $\tau = 1/f$. A criterion determining when the modulus at a particular frequency becomes high/enters into the glassy region can then be defined. At the cure time at which this criterion is fulfilled for a given frequency, the system is then assumed to have the mean relaxation time corresponding to that frequency. In this way each measurement frequency will provide a point on the curve of relaxation time *versus* cure time. It is important of course to choose the criterion properly. In the first part of this work, where a similar criterion was needed to make curves at different frequencies comparable[5], the point where the modulus reaches 3/4 of its final value was shown to work well for all four systems. Relaxation time vs cure time for all systems obtained using the same criterion is depicted in *Figure 2*. As can be seen the plots can in all cases be taken to be linear as a first approximation. The relaxation time is thus given by the expression

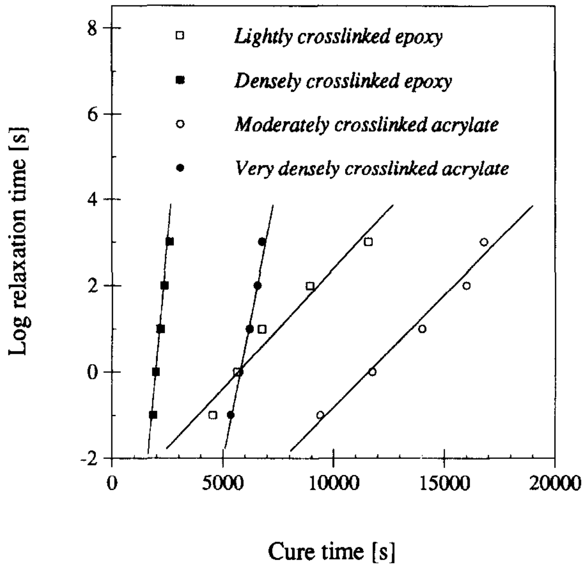

Figure 2 Development of relaxation time with cure for all systems. The lines indicate linear approximations of the experimental data

$$\tau^{n+1} = 10^{(At^{n+1}+B)} \qquad (16)$$

with the constants A and B derived from linear curve fits to the data in *Figure 6*. Similar expressions have also been suggested in literature[11]. The constants for the four systems are presented in *Table 2*.

To use equations (15) values must be assigned to the unrelaxed and relaxed moduli. In the calculations the unrelaxed modulus, G_0, is taken as constant and equal to the modulus of the fully cured material measured at room temperature. The relaxed modulus, G_∞, is taken as the modulus measured at the lowest possible frequency up to G_r and constant from that point onwards. A timestep of 30 s was used throughout the calculations. Sensitivity studies showed that varying the time step between 1 and 100 s did not significantly change the results.

Predicted and observed stresses

Observed and predicted stress levels are presented for all systems in *Figures 3–6*. As can be seen the viscoelastic model performs well in all cases. In order to investigate the importance of taking relaxation into account, linear

Table 2 Parameters for relaxation time, $\log \tau = At + B$

System	A	B
Lightly crosslinked epoxy	5.53×10^{-4}	3.14
Densely crosslinked epoxy	5.45×10^{-3}	10.87
Moderately crosslinked acrylate	5.12×10^{-4}	5.96
Very densely crosslinked acrylate	2.71×10^{-3}	15.6

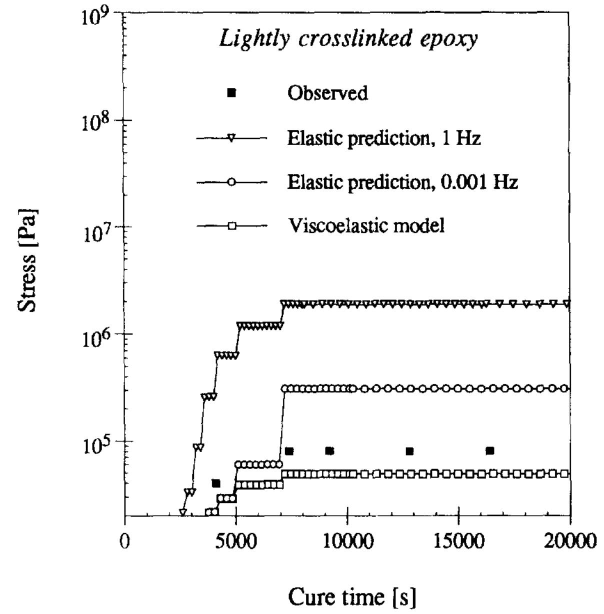

Figure 3 Predicted and observed stress build-up during isothermal cure of the lightly crosslinked epoxy system

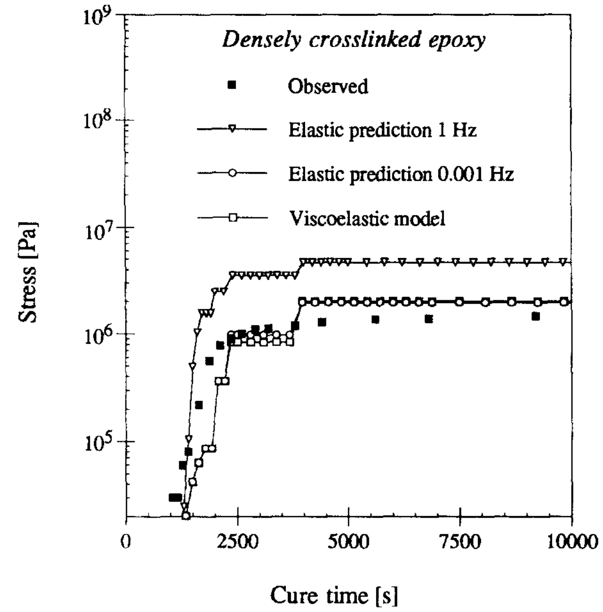

Figure 4 Predicted and observed stress build-up during isothermal cure of the densely crosslinked epoxy system

elastic predictions were also performed. The elastic predictions were made using the same analysis as was used for cure above $T_g\infty$, i.e. equation (15a) with G_∞ as the modulus measured at one single frequency throughout the reaction. Values of shear modulus obtained at two different frequencies, 1 Hz and 0.001 Hz, were used. 1 Hz is the frequency at which successful predictions were performed for cure above $T_g\infty$ and during cool-down. Using G at 0.001 Hz, the lowest frequency where experiments could be performed, is a simple attempt at gearing the analysis towards the relaxed, long-time response, since a lower frequency corresponds to longer times.

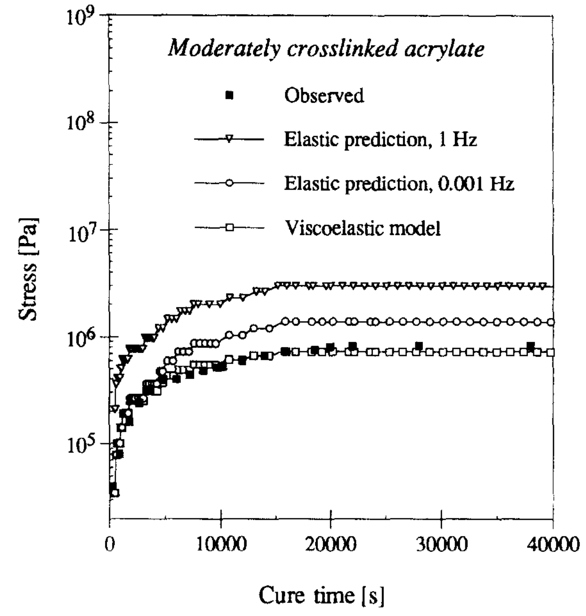

Figure 5 Predicted and observed stress build-up during isothermal cure of the moderately crosslinked acrylate system

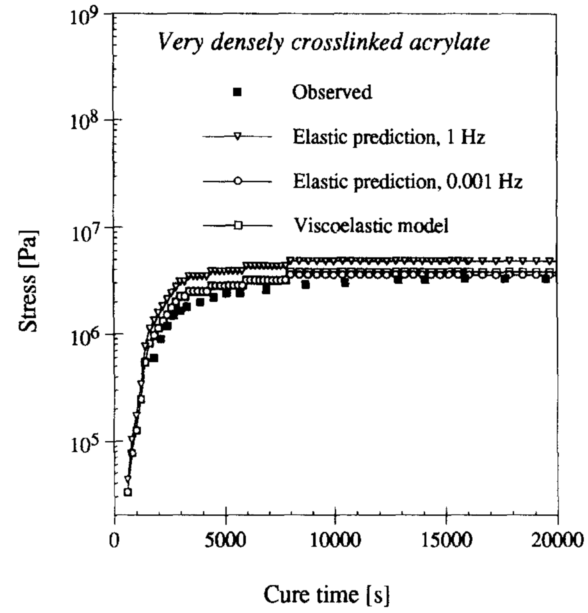

Figure 6 Predicted and observed stress build-up during isothermal cure of the very densely crosslinked acrylate system

The elastic predictions at the two frequencies are shown in *Figures 3–6*. It can be seen that not taking relaxation into account leads to an overestimation of the stress levels in all cases. Using G measured at 1 Hz over-predicts the stresses by a factor of 1.5–20, whereas using G at 0.001 Hz leads to an overprediction of up to four times. These overestimates are generally smaller for the more crosslinked materials. The elastic predictions at 0.001 Hz are quite acceptable for the densely crosslinked epoxy and the very densely crosslinked acrylate. The purely elastic analysis fails, however, to predict the stress build-up in the less crosslinked materials. Here only the viscoelastic model succeeds in predicting the low but measurable stress build-up. It may thus be concluded that in general it is indeed necessary to consider the viscoelastic effects when modelling the stress build-up during cure below $T_g\infty$. A comparison of the stress levels after cure predicted by the different models, as well as observed stress levels after cure and cool-down are given in *Table 3.*

Regarding the stress levels reached after cure and cool-down of the different systems some observations can be made. In general the amount of stress build-up during cure is higher for systems with high rubbery modulus and significant cure shrinkage after gelation. The cure stress ranges from about 1% of the total stress in the lightly crosslinked epoxy and over 10% in the moderately crosslinked acrylate to up to above 30% in the heavily crosslinked epoxy and the very heavily crosslinked acrylate. It is interesting to note that when the lightly crosslinked epoxy system is cured above $T_g\infty$ the cure stress is around 50% lower than when it is cured below $T_g\infty$[4]. The increase in stress observed on cure below $T_g\infty$ is most likely due to inhibition of relaxation towards the end of the reaction leading to a 'freezing-in' of stress above the equilibrium level. Some results in literature on stress build-up in lightly crosslinked epoxies also indicate that cure below $T_g\infty$ increases the stress levels[1].

In general it may be observed that, as in the case of cure above $T_g\infty$, there are great variations in the amount of cure stress between the materials. This indicates that the commonly used assumption of no stress build-up during isothermal cure is not always applicable, and must be verified in each individual case.

Approximations

Using the full time evolutions of thickness contraction and shear modulus at different frequencies the stress build-up during cure of a thermoset film below $T_g\infty$ on a rigid substrate can be modelled. In many cases, however, the complete data are difficult to obtain. It is therefore desirable to find more approximate expressions, permitting the cure contribution to the total stress build-up to be estimated from more accessible data. On cure above $T_g\infty$, where equation (15a) is applicable, the expected stress can be represented graphically by the curve of G_∞ vs c. From the shape of such curves for epoxy and acrylate systems it was shown that the stress level after completed isothermal cure can be estimated from

$$\sigma^{\text{cure}} = G_r c_c \tag{17}$$

where G_r is the rubbery modulus and c_c the thickness contraction after gelation until end of cure[4]. The time-dependence and relaxation present when curing below $T_g\infty$ make graphical representation difficult. Nevertheless, results presented in *Table 3* indicate that the approximation is also useful for cure below $T_g\infty$. Here cure stress levels for the two epoxies and the two acrylates estimated according to equation (17), using data from *Table 1*, are presented. As can be seen in *Table 3* the approximated values are good for the lightly crosslinked epoxy and the moderately crosslinked acrylate, acceptable for the densely crosslinked epoxy but much too high for the very densely crosslinked acrylate. It should be remembered that the four systems are very different with respect to reaction mechanism and crosslink density. Furthermore, it should be noted that the crosslink density of the last acrylate is extremely high, far above what would be found in materials for commercial applications. It may thus be concluded that the approximation in equation (17) applies to cure both above and below $T_g\infty$ of a wide range of materials, i.e. that it should cover most of the cure conditions commonly encountered.

The shrinkage after gelation, s_c, can be estimated from the total cure shrinkage, s_{tot} and the conversion at the gel-point: $s_c = s_{\text{tot}}(1 - x_{\text{gel}})$. Using equation (14) and the approximation $\nu_p = \nu_r$, where ν_r is the rubbery Poissons' ratio of the polymer, the system-dependent thickness contraction in equation (17) can now be replaced by

$$\sigma = 2G_r \frac{1+\nu_r}{1-\nu_r}(1 - x_{\text{gel}})s_{\text{tot}} \tag{18}$$

In this manner the stress level after cure can be estimated from basic material properties. To estimate the full stress, i.e. after cool-down, it suffices to add a term as described previously[4]

$$\sigma = 2G_r \frac{1+\nu_r}{1-\nu_r} s_{\text{tot}}(1 - x_{\text{gel}}) + 2G_g \frac{1+\nu_g}{1-\nu_g}(\alpha_s - \alpha_p)\Delta T \tag{19}$$

Table 3 Observed, predicted and approximated stress levels

System	Stress build-up during cure (MPa)					Total observed stress after cool-down (MPa)
	Observed	Elastic prediction, 1 Hz	Elastic prediction, 0.001 Hz	Viscoelastic model	Approximation	
Lightly crosslinked epoxy	0.08	1.9	0.3	0.05	0.07	6.2
Densely crosslinked epoxy	1.7	4.7	2.0	2.0	3.8	5.5
Moderately crosslinked acrylate	0.8	3.0	1.4	0.7	1.3	8.3
Very densely crosslinked acrylate	3.3	4.9	3.6	3.8	12	9.3

where α_s and α_p are the coefficients of thermal expansion of the substrate and the polymer, respectively, ν_g the glassy Poissons' ratio of the polymer, and ΔT the temperature difference between the cure temperature and room temperature. Using equation (19) the contributions from the cure and cool-down 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 amount of stress build-up during isothermal cure varies greatly between different materials. In general, the higher the crosslink density, the higher the stress build-up. In the materials investigated, it ranged from below 1% of the total stress in a lightly crosslinked epoxy to above 30% in densely crosslinked epoxies and acrylates.

The stress build-up during cure of thermoset materials below $T_g\infty$ can be modelled using a very simple memoryless Maxwell description of stress relaxation using a single conversion-dependent relaxation time. The resulting model is readily implemented numerically, and succeeds in predicting the stress build-up in epoxy and acrylate films where standard linear elastic models fail.

Using simple approximations it is possible to estimate the amount of stress built up during cure and cool-down in a wide range of systems from material characteristics, i.e. cure shrinkage and elastic properties.

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