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Build-up of structure and viscoelastic properties in epoxy and acrylate resins cured below their ultimate glass transition temperature

Jakob Lange and Jan-Anders E. Månson*
Laboratoire de Technologie des Composites et Polymères, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

and Anders Hult
Department of Polymer Technology, Royal Institution of Technology, S-100 44 Stockholm, Sweden
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The build-up of structure and viscoelastic properties with conversion during cure below the ultimate glass transition temperature of epoxy and acrylate resins has been investigated. Using a torsional dynamic mechanical analyser, dynamic shear modulus and change in sample thickness was monitored simultaneously, thus giving information on both the physical properties (stiffness) and the progress of the reaction (shrinkage) in one experiment. Two step-wise curing epoxy systems and two chain-wise curing acrylate systems with different crosslink densities were studied and compared. The results showed that in the epoxies vitrification was a distinct event, occurring separately from gelation and ending with the end of the cure reaction. In the acrylates vitrification began immediately after gelation, the two events being indistinguishable, and lasted until the end of the reaction, leaving the sample in its transition zone. Scaling of modulus–cure time data obtained at different frequencies showed that the data for each system followed one single curve, independent of frequency over five decades. This made it possible to estimate the modulus development at low frequencies early in the reaction, which is difficult to measure directly. From the shrinkage and storage moduli approximate values of the relaxation modulus as a function of chemical conversion were calculated. The relaxation modulus curves at different conversions were then shifted along the time axis to provide a relaxation master curve. The data and understanding gained in this work provide the basis for analysing the time-dependent mechanical behaviour during cure, e.g. build-up and relaxation of residual stresses. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

The cure process plays a key role in determining the properties of a thermoset material. The way in which the changes occur during cure, when stiffness builds up and volume decreases, will determine the final structure and thereby the properties of the polymer itself. Furthermore, the system properties of the polymer in its application may be influenced by the cure cycle through process-induced residual stresses[1]. In order to use the full potential of a thermosetting material a thorough understanding of the events and changes in the material during cure is required.

One important aspect of thermoset cure is the reaction mechanism. Polymer networks may be formed by two principally different mechanisms; step-wise reaction and chain-wise reaction[2]. The step-wise mechanism, by which, for example, epoxy-amine, polyester and isocyanate systems react, is a gradual process where the structure is built up in steps throughout the system. The chain-wise mechanism, employed by, for example, acrylates, proceeds by way of active species which initiate chain polymerization reactions, each rapidly forming a large number of primary bonds on different locations in the system. The reacting system therefore becomes an inhomogeneous mixture of reacted polymer and unreacted monomer. Both the structure of the resulting network and the events during the reaction depend strongly on the reaction mechanism.

The two main events that may occur during the reaction 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. There are two main cure temperature regimes[3,4]. On curing above the ultimate glass transition temperature

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* To whom correspondence should be addressed

(T_g^∞) of the polymer only gelation will occur, whereas if the cure temperature is below T_g^∞ the polymer will first experience gelation and then vitrification. Gelation and vitrification are accompanied by changes in the physical properties of the polymer. On gelation the system is transformed from a liquid to a gel, thereby acquiring an equilibrium modulus. In the gelled state, far away from T_g, the modulus is essentially elastic, and exhibits little time-dependence[5]. During vitrification, or gel–glass transition, the mechanical behaviour then changes from elastic to viscoelastic, i.e. it becomes time-dependent. As the material proceeds further into the glassy state the time-dependence decreases, the modulus again becoming essentially elastic[5]. Modelling of the mechanical behaviour during cure is relatively simple when only gelation is involved, but becomes quite complex when vitrification has to be included[6].

The curing and the change in properties with cure of thermosets is well documented in literature both for step-wise reacting systems and for chain-wise reacting systems[2,4,7]. In most cases the physical properties and the chemical conversion have been measured in separate experiments, since few methods are capable of following both parameters. In general, chain-wise reacting systems exhibit gelation at lower degrees of conversion and yield materials with higher crosslink densities than do step-wise reacting systems. Regarding the development of viscoelastic properties upon cure little has been reported on chain-wise reacting systems, whereas step-wise systems have been investigated to a large extent. An inherent problem with studying time-dependent properties of reacting systems is that the properties often change faster than they can be measured, i.e. a significant change in properties takes place within the time needed for one measurement. This can be circumvented by synthesizing a series of networks with chemically fixed degrees of conversion between 0 and 1, e.g. by blocking a certain percentage of the reactive groups on the monomer prior to polymerization. The disadvantages with this approach, however, are that the model networks will always differ somewhat from the real, reacting systems and that it does not apply to chain-wise reacting systems, where producing networks with a fixed degree of conversion is difficult. Using the approach of synthesizing networks with different degrees of conversion Plazek and Chay[8] measured the development of the creep compliance and the retardation spectrum with conversion in an epoxy system. Adolf and Martin[9], studying epoxies, and Hodgson and Amis[10], using silanes, measured dynamic storage and loss moduli at different frequencies during cure near the gel point and showed that viscoelastic functions, e.g. the relaxation modulus, could be superposed at different extents of reaction. Raszcuk *et al.*[11] monitored dynamic storage modulus and dynamic viscosity, again at different frequencies, during cure for a urethaneurea system at different cure temperatures and curing agent concentrations.

In the present work the build-up of structure and viscoelastic properties during cure below T_g^∞ of step-wise and chain-wise reacting materials is investigated in detail. Two epoxy systems and two acrylate systems with different crosslink densities are studied and compared. Using a torsional dynamic mechanical analyser samples are cured between parallel plates, which allows dynamic shear modulus and sample thickness to be monitored simultaneously[1]. This method offers information both on the development of physical properties (stiffness) and the progress of the cure reaction (shrinkage) in one experiment. Measurements are carried out at multiple frequencies, which makes it possible to probe the time-dependence of the mechanical properties during cure. A reconstruction technique for estimating the modulus at low frequencies early in the reaction–data otherwise difficult to obtain–is demonstrated. The modulus and shrinkage data are analysed and converted into curves of relaxation modulus vs conversion. The modelling of mechanical behaviour during cure is beyond the scope of this paper, but should be kept in mind as being an important objective also for the present work.

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 obtained from Ciba, 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 trimethylopropane 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 **5** and a 1/1 mixture by weight of **5** + **6**. To the acrylate mixtures 2 mol% benzopinacole and 0.3 mol% diethanolamine were added as initiators.

Samples were cured in a rotational parallel plate

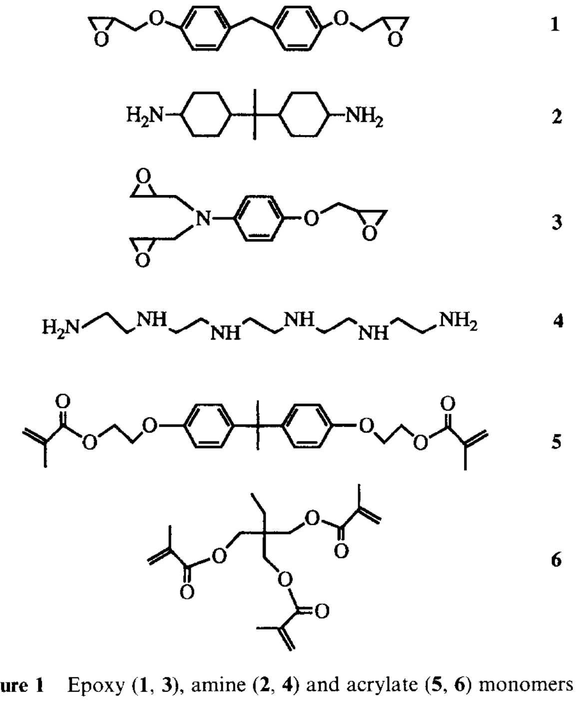

Figure 1 Epoxy (**1**, **3**), amine (**2**, **4**) and acrylate (**5**, **6**) monomers

rheometer (Rheometrics RDA 2 dynamic mechanical analyser, DMA). Aluminium plates of diameter 8 mm were used. The dynamic shear modulus was measured, at regular intervals, at five frequencies between 0.001 and 10 Hz and at zero normal force, while simultaneously monitoring the change in plate distance. The strain was varied automatically by the instrument and was between 0.05 and 0.001. In a typical experiment the liquid monomer was applied between the plates of the rheometer and the distance set to 1 mm. The sample was then heated to the cure temperature, 115°C for the acrylates, 100°C for the first epoxy (**1** + **2**) and 70°C for the second (**3** + **4**), and the dynamic shear modulus and the change in plate distance measured as a function of cure time. During one run measurements were performed at three frequencies simultaneously by superposition of the strain input signal and decomposition of the stress output signal. A complete set of five frequencies thus required two runs. After completion of the cure, temperature scans were performed. The samples were heated to a temperature well above T_g^∞, thus enabling full cure, and then cooled to the cure temperature while measuring the shear modulus at 1 Hz and a strain between 0.05 and 0.001.

RESULTS AND DISCUSSION

Modulus and shrinkage vs cure time

Four different materials were studied, two epoxies and two acrylates. The samples differ with respect to reaction mechanism and crosslink density. The first epoxy system, the diglycidyl ether of bisphenol F (**1**), reacted with 2,2-di(4-aminocyclo-hexane)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 dimethyacrylate (**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 chain-wise mechanism. The cure temperatures, 100°C for the first epoxy, 70°C for the second and 115°C for the acrylates, were chosen to be well below the T_g^∞ of the systems. The characteristics of the four systems are given in *Table 1*.

As described in a previous publication, simultaneous measurement of modulus and thickness contraction using DMA permit the change in structure with cure to be monitored[1]. The thickness contraction or change in sample thickness (c) is a characteristic not of the polymer alone but of the system, i.e. the polymer and the substrate together. Under isothermal conditions it is related to the free linear shrinkage(s) of the polymer, through

$$dc = \frac{1+\nu}{1-\nu}\, ds \qquad (1)$$

where ν is the Poisson's ratio of the polymer. Since the amount of shrinkage is proportional to the degree of conversion, c gives an indication of the progress of the cure reaction.

Table 1 Characteristics of the studied systems, obtained from dynamic mechanical analysis. The bold numbers refer to the materials (see *Figure 1*)

System	T_g^∞ (°C)	Modulus at end of cure (MPa)	G_g (MPa)	G_r (MPa)
Lightly crosslinked acrylate, **1** + **2**	120	330	340	4
Densely crosslinked acrylate, **3** + **4**	190	590	610	130
Moderately crosslinked acrylate, **5**	150	210	570	30
Very densely crosslinked acrylate, **5** + **6**	160	310	510	240

Figures 2 and *3* show typical evolutions of shear modulus and thickness contraction with cure time for the epoxy and acrylate materials. In order to characterize not only the elastic but also the viscoelastic behaviour, the modulus was measured at five different frequencies (of which three are shown in *Figures 2* and *3*). The measurements at the lowest frequencies could not be carried out at the beginning of the reaction since the properties of the system changed faster than the measurement could be performed. There are some common features to the cure reaction in all systems. At first, in the liquid state, the modulus and the thickness contraction are negligible. Then, as the sample passes gelation, the modulus starts to rise and the thickness contraction becomes detectable. This is followed by vitrification, accompanied by a further increase in modulus and decrease in volume. Finally the modulus and thickness contraction level out at their final values as the reaction comes to an end.

A comparison of *Figures 2* and *3* points to some fundamental differences between the epoxy and the acrylate systems. One such difference is that the overall thickness contraction after gelation is higher for the acrylates than for the epoxies. This is due to the combined influence of the structure of the monomers and the reaction mechanism; the ring-opening polymerization of the epoxy in combination with the step-wise reaction mechanism leading to a low overall shrinkage and the late gelation on one hand and the vinyl polymerization of the acrylate in combination with the chain-wise reaction mechanism leading to a high overall shrinkage and early gelation on the other[2,7]. Another difference is that while gelation and vitrification are separate events in the epoxies, as indicated by the tendency towards a knee in the modulus curves before it rises to its final glassy value, vitrification seems to begin immediately after gelation in the acrylates. There the modulus rises evenly from gelation towards the final value. This behaviour, i.e. the separation of gelation and vitrification during cure below T_g^∞ in step-wise reacting systems but not in chain-wise reacting systems has been reported by Babayevsky[4]. It is worth mentioning that step-wise reacting systems also are known to exhibit simultaneous gelation and vitrification, but then only at one specific cure temperature[3]. The fact that *all* investigated chain-wise curing systems (the two

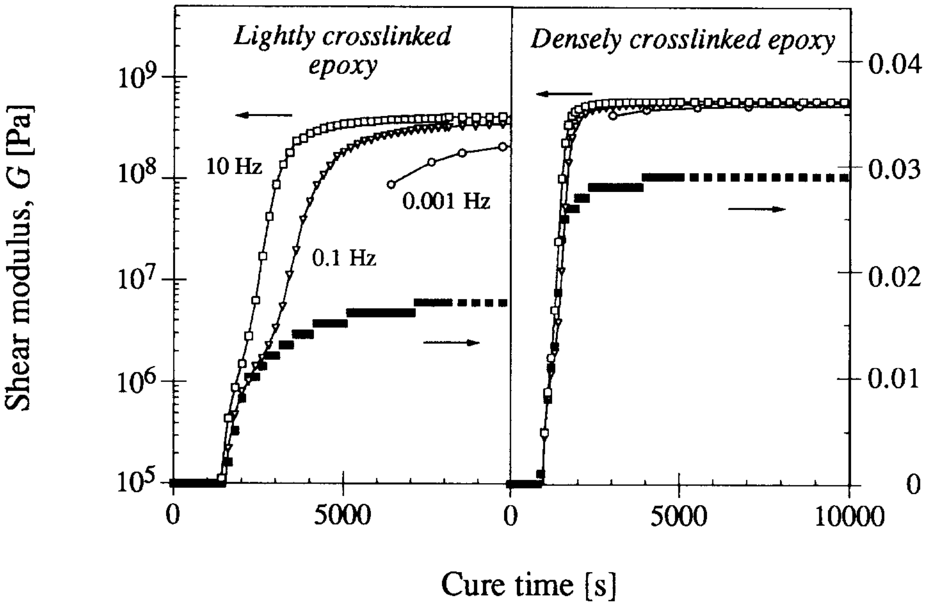

Figure 2 Experimental dynamic shear modulus at 10 (□), 0.1 (▽) and 0.001 (○) Hz, and thickness contraction (■) during cure of the epoxy systems

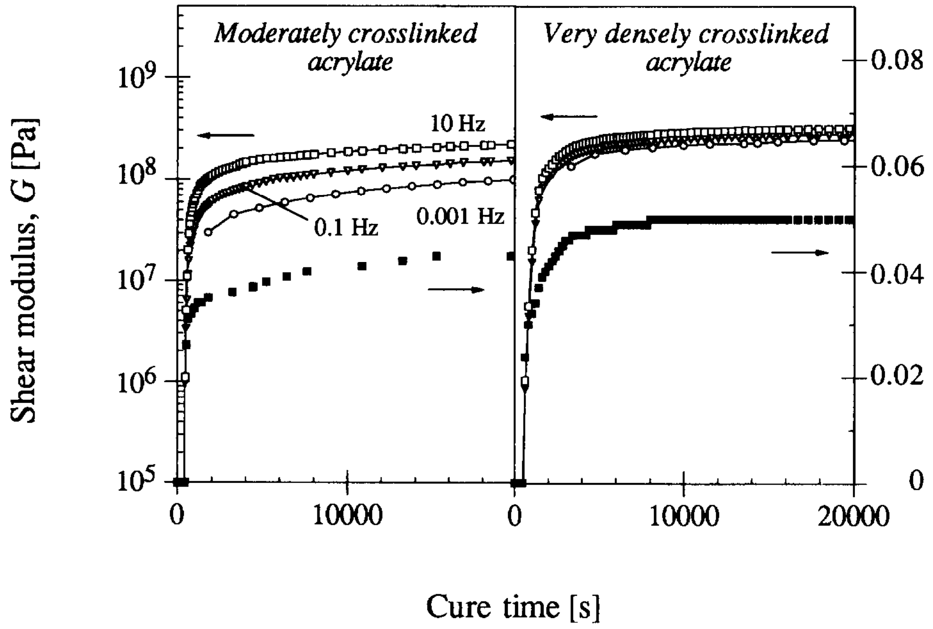

Figure 3 Experimental dynamic shear modulus at 10 (□), 0.1 (▽) and 0.001 (○) Hz, and thickness contraction (■) during cure of the acrylate systems

acrylates in the present study as well as several others not reported here) behaved the same way indicates that the simultaneous gelation and vitrification could be a general characteristic of chain-wise reacting systems. As can be seen in *Figures 2* and *3* the influence of crosslink density is, for both epoxies and acrylates, more a difference of degree than of nature, at both crosslink densities the curves have the same shape, although the curves at different frequencies are closer together in the highly crosslinked samples.

Both the epoxies and the acrylates exhibit frequency dependencies that vary as the reaction proceeds. Regarding the epoxies (*Figure 2*) the liquid state and the initial part of the gelled state exhibit no frequency dependence, but as the sample approaches vitrification a strong influence of measurement frequency is observed. The rise in modulus accompanying the glass transition is detected earlier at higher frequencies. Finally, at the end of the reaction, well into the glassy state, the frequency dependence again decreases. The slight increase in modulus with increasing frequency at this stage is typical of all viscoelastic materials in the vicinity of the glass transition [5]. In the acrylates (*Figure 3*) the frequency-dependent region extends from just after gelation to the end of the reaction. As in the epoxies, the higher the measurement frequency, the higher the modulus. The width of the frequency-dependent region indicates that in the acrylates vitrification commences just after gelation and that the glass transition is wide, particularly in the very densely crosslinked acrylate.

Frequency–cure time superposition

A difficulty encountered when measuring at lower frequencies is the previously mentioned problem of obtaining data in the first part of the reaction, i.e. where the properties of the system change rapidly. The time of measurement is proportional to the inverse of the measurement frequency. For example, if a measurement is to be taken at 0.001 Hz the time required will be at least 1000 s. *Figures 2* and *3* show that early in the reaction the properties of the system change rapidly, making measurements lasting more than about 10 s (0.1 Hz) unrealistic. One way of addressing this problem would be to extrapolate high frequency data into the desired range, since measurements at higher frequencies can be performed over the whole range of conversions.

As first reported by Plazek for natural rubber and later by Chan and Aklonis for polyurethanes there is an interchangeability between crosslink density and time, where a change in crosslink density corresponds to a change in response time of the material. From observations that curves of creep compliance for materials with different crosslink densities could be made to superpose by vertical and horizontal shifts, they concluded that as the crosslink density changes it is mainly the relaxation time that is affected, not the shape of the relaxation time spectrum[12,13]. Thus, it is mainly the characteristic response time of the viscoelastic behaviour that changes with crosslink density, not the behaviour itself. The time–cure superposition in the vicinity of the gel-point proposed by Adolf and Martin for epoxies as well as by Hodgson and Amis for silanes also indicates that there is an interchangeability between measurement frequency and crosslink density (cure time in this case)[9,10]. It should be noted that these studies all concerned materials far away from their glass transition, close to the gel point or very lightly crosslinked, where the characteristic relaxation time *decreases* with increasing crosslink density. The properties of the materials used in the present work are instead dominated by the glassy state where the relaxation time *increases* with increased degree of crosslinking[14]. The basic time-dependence of the properties, i.e. the interchangeability between cure time and measurement frequency should, however, be the same.

Studying the sets of curves at different frequencies for each material in *Figures 2* and *3* a certain resemblance in shape within each set is visible. Postulating that the gelation occurs at one single time (t_{gel}), independent of frequency [9], and assuming the time to rise in modulus (t_{rise}) to be a characteristic of the behaviour at each frequency, two characteristic values on the cure time scale for each modulus curve are obtained. If the time is set to zero at gelation and the time-scale for each modulus curve is then divided by the time to rise (defined as the time to reach 3/4 of the final modulus at that frequency) a scaling, or normalization, along the time axis is obtained. The time is thus normalized according to $t_{\mathrm{norm}} = (t - t_{\mathrm{gel}})/t_{\mathrm{rise}}$, where $t_{\mathrm{rise}} = t$ at $G = 0.75G_{\mathrm{final}}$. The result of such a scaling of time, together with a normalization of the modulus with respect to final value; $G_{\mathrm{norm}} = G/G_{\mathrm{final}}$, applied to the five experimental frequencies is shown in *Figure 4*. As can be seen the scaling

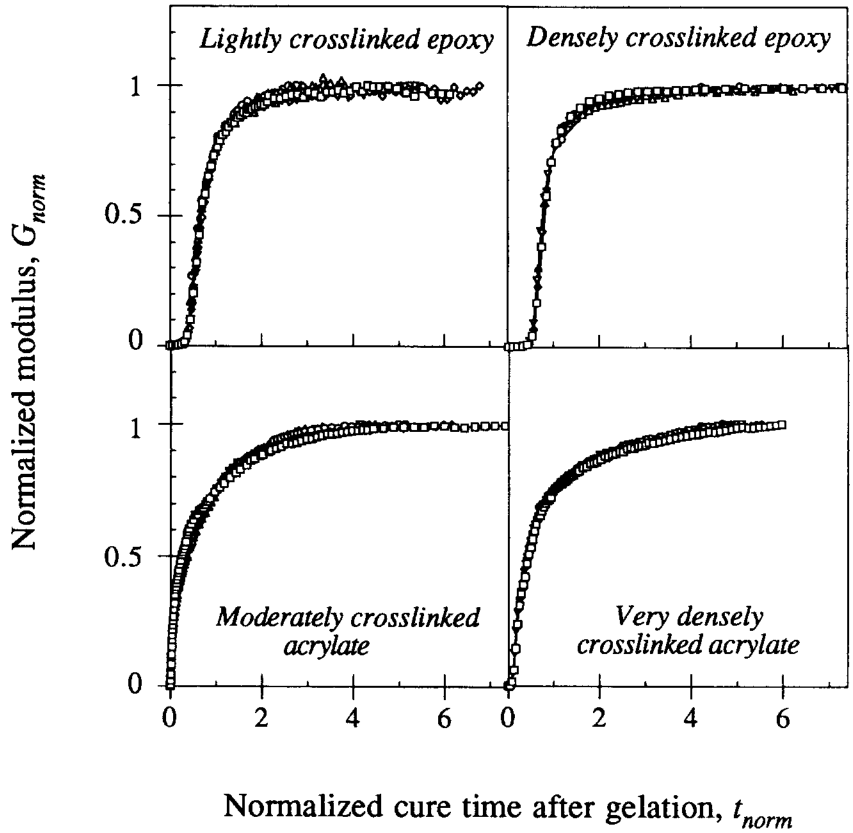

Figure 4 Normalized dynamic shear modulus ($G_{\mathrm{norm}} = G/G_{\mathrm{final}}$) at 10 (□), 1 (◇), 0.1 (▽), 0.001 (△) and 0.001 (●) Hz *versus* normalized cure time after gelation ($t_{\mathrm{norm}} = (t - t_{\mathrm{gel}})/t_{\mathrm{rise}}$) for all systems

works well, and the curves are superposed. The choice of 3/4 of the final value as point of reference is of course arbitrary. What is required is a characteristic time for the rise in modulus. The two epoxies and the very densely crosslinked acrylate were not sensitive to the choice of the second reference time, all tested values between 0.2 and 0.8 produced a good superposition. The moderately crosslinked acrylate was more sensitive, however, and 0.75 gave the best correlation.

One single curve thus describes all the modulus–cure time data obtained over five decades of measurement frequencies. As a consequence, once the relationship between modulus and cure time is established, it is sufficient to know the characteristic time and final modulus value at any frequency to reconstruct the full curve at that particular frequency. Since these values can also be obtained at low measurement frequencies, in spite of the difficulties in observing the early stages of the reaction, this makes it possible to reconstruct the initial part of the curve.

Relaxation behaviour

The long-time response to deformation, i.e. the relaxation behaviour, is an important characteristic of a reacting polymer system. It will determine how residual stresses build up during cure[1]. The relaxation behaviour

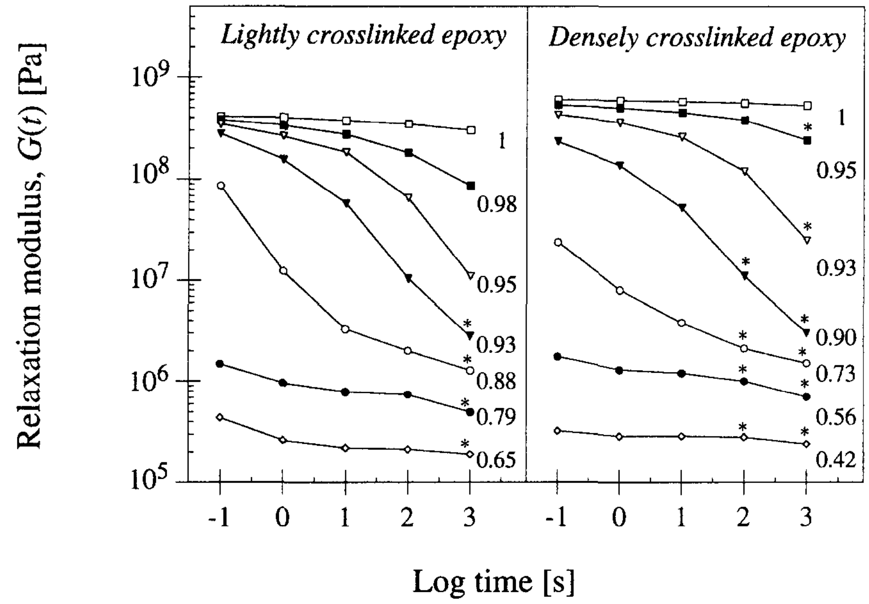

Figure 5 Relaxation modulus calculated from dynamic shear modulus (time = 1/frequency) at different degrees of conversion for the epoxy systems. Points obtained using the reconstruction technique are indicated by asterisks

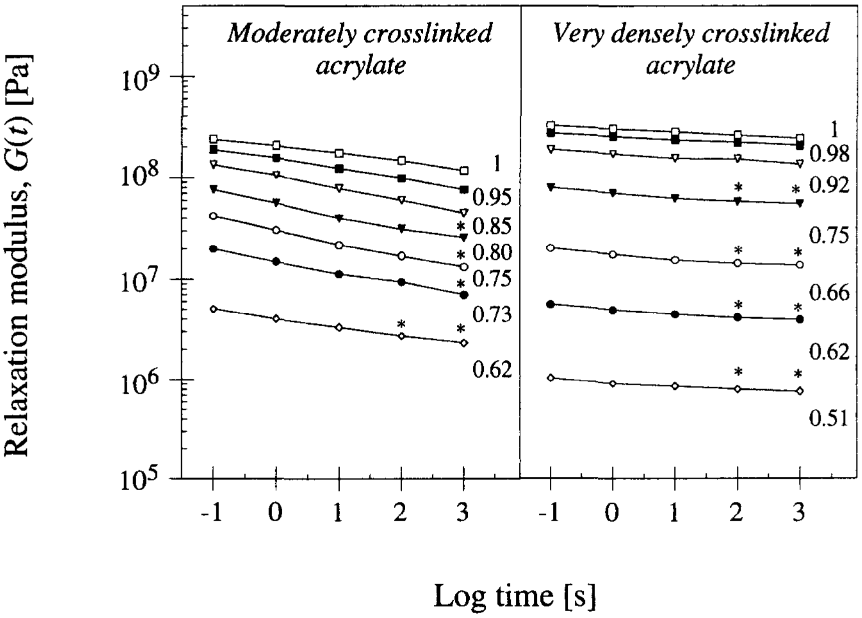

Figure 6 Relaxation modulus calculated from dynamic shear modulus (time = 1/frequency) at different degrees of conversion for the acrylate systems. Points obtained using the reconstruction technique are indicated by asterisks

of a viscoelastic material is described by the relaxation modulus, $G(t)$. Directly measuring the relaxation modulus, i.e. observing the decay in stress following a step strain, is difficult during a reaction due to the progressive change in properties with cure time. $G(t)$ can instead be approximated from the storage modulus, by substituting the relaxation modulus at a certain time with the storage modulus measured at a frequency corresponding to the inverse of that time: $G(t) \approx G'(1/t)$[15]. In this manner the data in *Figures 2* and *3* can be converted into estimates of the evolution of $G(t)$ with cure.

The degree of conversion as a function of cure time can be calculated from the thickness contraction, if the conversion at the gel point is known, and by assuming that the thickness contraction is zero until gelation and then directly proportional to the conversion. The change in Poisson's ratio with cure is thus neglected. The gel-point conversion can be calculated theoretically for step-wise reacting systems using the classical theory of gelation[15], but has to be measured or estimated for chain-wise systems. For the two epoxies the gel-point conversions were calculated to be 0.6 and 0.3 for the low and high crosslink systems respectively. The gel-point conversion was taken to be 0.05 for both acrylates[7]. The degree of conversion (x) was calculated from the thickness contraction (c), the gel point conversion (x_{gel}) and the total thickness contraction after gelation (c_{total}) according to the following expression:

$$x(t) = \frac{c(t)}{c_{\mathrm{total}}}(1 - x_{\mathrm{gel}}) + x_{\mathrm{gel}} \qquad (2)$$

It should be noted that the degree of cure as calculated here is relative to full cure (end of reaction) and the cure temperature, thus not taking any residual reactivity into account.

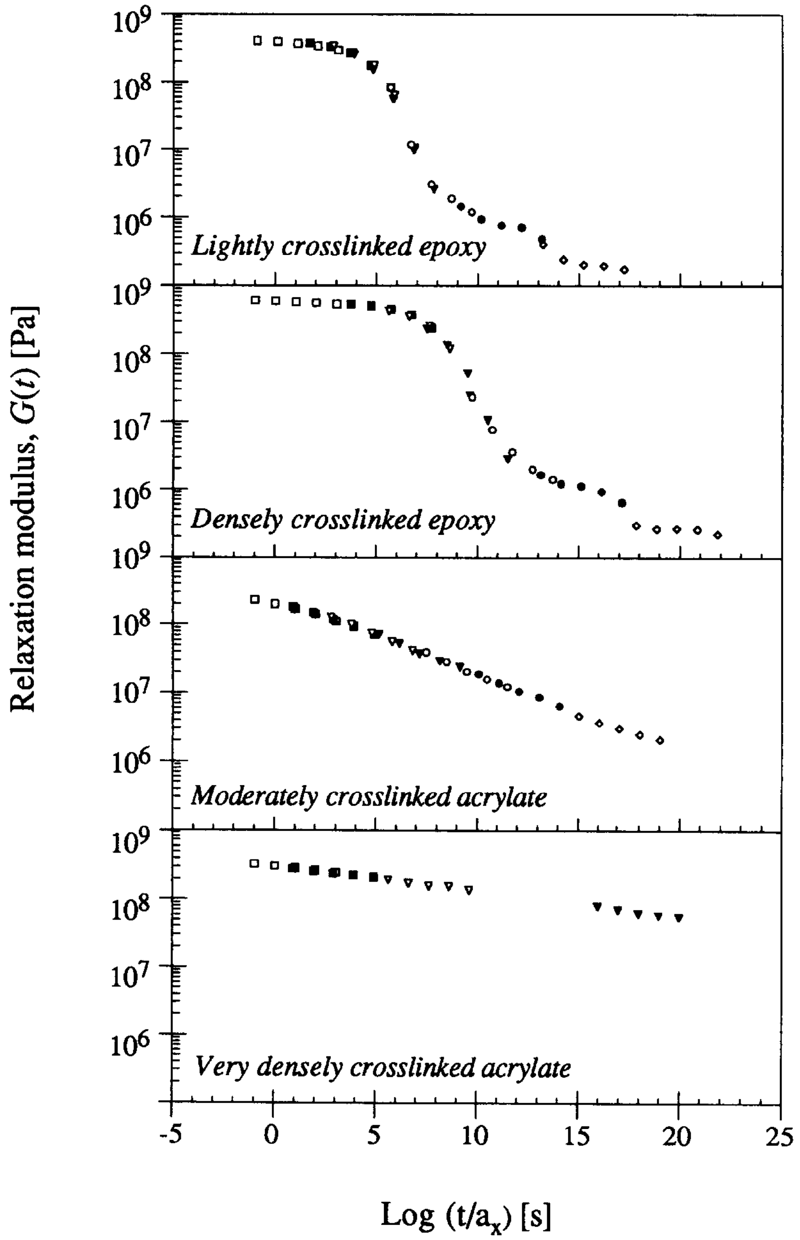

Figure 7 Master curves of relaxation modulus obtained by empirical shift of the curves in *Figures 5* and *6* along the time axis using the top curve (full conversion) as reference state

Curves of relaxation modulus *versus* conversion calculated from the data in *Figures 2* and *3* are shown in *Figures 5* and *6*. It may be noted that some points (indicated by asterisks) at low frequencies and low conversions have been obtained using the reconstruction technique described in the previous section. The behaviour of the two epoxy systems (*Figure 5*) agrees well with the traditional description of the glass transition in a viscoelastic solid[5]. Early in the reaction, just after gelation, the modulus is at its relaxed or equilibrium value, which is independent of time. The level of the relaxed modulus increases as the sample cures, however, as indicated by the vertical change with conversion. As the cure proceeds and the material vitrifies, the modulus then rises to the glass value, beginning at short times. Finally, the behaviour over the whole experimental window is governed by the unrelaxed, glassy modulus, which is largely independent of time as well as of conversion[3,5]. The same behaviour is observed for both epoxy systems.

As can be seen in *Figure 6* the acrylates exhibit a different behaviour. Instead of the three distinct regions present in the epoxies a set of parallel curves is observed. The difference between the two acrylates is that the slope of the curves is less steep for the more crosslinked material. When interpreting these curves the characteristics of chain-wise reacting systems should be kept in mind. The absence of separation between gelation and vitrification has already been discussed. In other words vitrification is expected to commence at gelation, which would explain the absence of the first flat region observed in the epoxies. Furthermore, the transition region is known to be wide in highly crosslinked systems, such as the materials produced by chain-wise crosslinking of highly functional acrylate monomers[16]. At the end of the reaction, the epoxies seems to have left the transition zone and moved well into the glassy state, as indicated by the low time-dependence of the final relaxation modulus values. The acrylates, in contrast, still exhibit a significant time-dependence of the modulus values at the end of the reaction indicating that the materials are still in the transition region. The rise in level of the relaxation modulus with increasing conversion in the acrylates is related to the change in the equilibrium modulus with cure. In conclusion, whereas three distinct regions are observed in the epoxies, i.e. gel state, transition region and glassy state, the acrylates exhibit essentially the central part of the relaxation curve, i.e. the transition region, together with a rise in equilibrium modulus.

It is worth noting that the curves in *Figures 5* and *6* are quite unique. They are only available through the simultaneous measurement of conversion and modulus at several frequencies in combination with the extrapolation technique described previously. To the authors' knowledge this is the first time that the change in relaxation behaviour during cure of rapidly reacting systems has been characterized in this manner. These curves are helpful in understanding and modelling the mechanical behaviour during cure, which is essential for the prediction of process-induced internal stresses.

Modulus–conversion master curves

Plazek and Chay have shown that curves of creep compliance measured at different extents of cure for an epoxy system could be made to superpose by shifting along the time axis[8]. They did this in analogy with the time–temperature superposition (Williams–Landel–Ferry, WLF) principle[17], using the change in T_g with conversion rather than the measurement temperature as the variable. Thus, instead of shifting a set of curves obtained at different temperatures they shifted curves obtained at different T_gs, i.e. different degrees of conversion. Their superposition worked well at short times (in the glassy region) but failed at longer times. This is not surprising since the glassy modulus is quite insensitive to changes in chemical conversion whereas the equilibrium modulus increases dramatically with conversion, especially early in the reaction[1,2].

The shape of the curves in *Figures 5* and *6* suggest that master curves could be created by shifting along the time axis. Choosing the end of cure as reference state yields the master curves presented in *Figure 7*. For the two

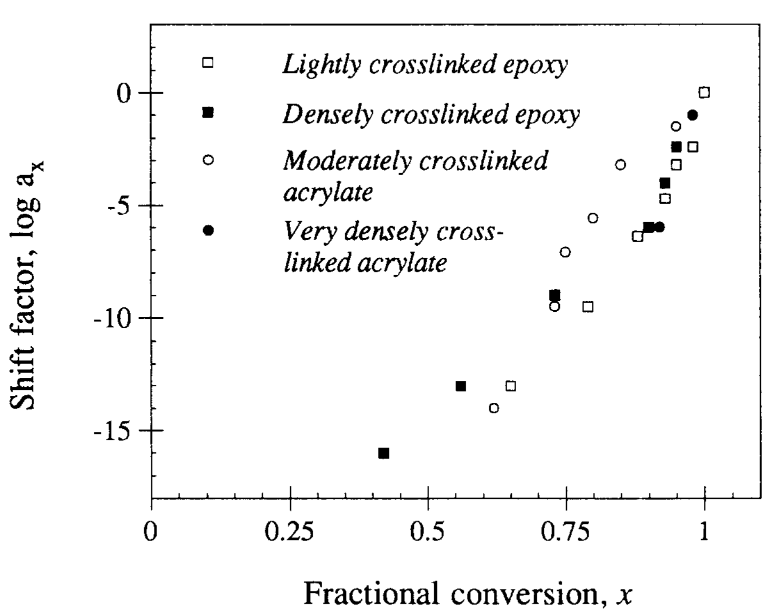

Figure 8 Shift factors used to create the master curves in *Figure 7* vs degree of conversion for all systems

epoxies the time–conversion shifting works well, particularly at higher conversions. The shifting produces master curves showing all parts of the transition and it is only at longer times and lower conversions that the curves become slightly ambiguous. The absence of a well-defined relaxed plateau is presumably due to the large changes in equilibrium modulus early in the reaction. In the case of the acrylates the time–conversion shifting produces mater curves exhibiting a very wide transition. In addition the master curves will also here become ambiguous at lower conversions, where the curve segments have to be shifted quite far along the time axis in order to fall on the master curve. Again the reason is presumably the change in equilibrium modulus during the earlier parts of the reaction.

The master curve can be taken to be a view of the material behaviour at the reference state. It gives an idea of how fast the material would have to be deformed in order to behave in a fully glasslike manner, as well as the time required for substantial relaxation to occur. By choosing a different point during cure as reference, the time scale is shifted, and another view of the properties is obtained. The difference between this time–cure master curve and a conventional time–temperature master curve is that the latter describes the properties of a fully cured material, whereas the former includes information from several degrees of conversion. The main advantage with the time–cure master curve is that it permits the extrapolation into long and short time ranges, areas which are inaccessible to DMA. The short time range might be possible to reach using dielectric or acoustic methods, but these techniques impose other problems. The long time range is difficult to investigate since the properties of the material change drastically during the measurement.

In *Figure 8*, the shift factors used to generate the master curves in *Figure 7* are shown as a function of fractional conversion. As can be seen the relationship

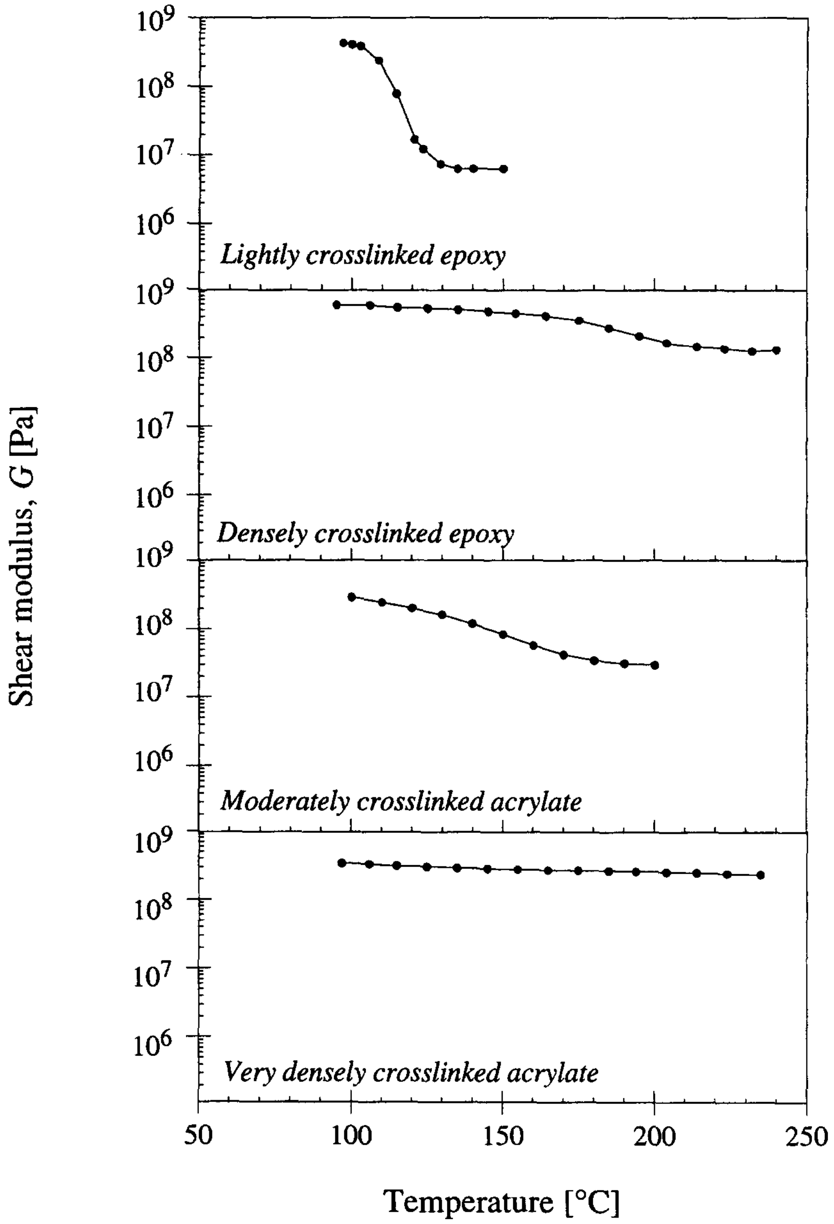

Figure 9 Experimental dynamic shear modulus at 1 Hz vs temperature measured on cooling

between the shift factors and conversion is approximately linear for all systems. Furthermore, the relationship is similar for both the epoxies and the acrylates in spite of the great differences in cure behaviour.

The shear modulus as a function of temperature was measured for all materials after cure. In order to avoid further cure during the temperature scans, the samples were first heated to a temperature well above T_g^∞. The modulus was then measured on cooling down to the cure temperature. In principle the modulus–temperature curve should resemble the relationship between modulus and time (or frequency), according to traditional viscoelastic theory[5]. It is therefore useful to compare these curves, presented in *Figure 9*, with the master curves in *Figure 7*. It can be seen that in all cases the equilibrium (or rubbery) moduli are higher in the temperature scans than in the master curves. It thus further points to the difficulties in shifting the curves at lower conversions without taking the increase in equilibrium modulus into account. In general the high conversion and low temperature parts of each set of curves resemble each other quite well, the region of resemblance being wider in the less crosslinked systems.

CONCLUSIONS

The evolution of structure and viscoelastic properties with conversion during cure of thermosets can be conveniently monitored using DMA. Comparing the behaviour of stepwise curing epoxies and chainwise reacting acrylates points to differences in the sequence of events during cure. In the epoxies vitrification is a distinct event, occurring separately from gelation and ending with the end of the cure reactions. In the acrylates vitrification commences immediately after gelation, the two events being indistinguishable, and continues until the end of the reaction, leaving the sample still in the transition zone.

Modulus–cure time curves obtained at different frequencies for a certain material may be superposed, provided that each curve is scaled along the modulus and time axes. As a consequence, if the full relationship between modulus and cure time is established at one frequency, it suffices to know the scaling parameters at any other frequency to reconstruct the full curve at that other frequency. This makes it possible to estimate the modulus development at low frequencies early in the reaction, which is difficult to measure directly.

From the dynamic storage modulus measured at different frequencies correlated with shrinkage data the development of the relaxation modulus with chemical conversion during cure can be calculated. The relaxation modulus curves at different conversions can then be shifted along the time axis to provide a relaxation modulus–conversion master curve.

The data and understanding gained in this work provides the basis for modelling the time-dependent mechanical behaviour, e.g. build-up and decay of residual stress, during isothermal cure where vitrification occurs.

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