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THERMAL AND MECHANICAL CHARACTERIZATION OF HIGH PERFORMANCE EPOXY SYSTEMS WITH EXTENDED CURE TIMES

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Abstract

Five epoxy resins of different chemistry and functionality were cured with DDS (4,4'-diaminodiphenyl sulfone) using 2, 8 and 14 h curecycles. Both Differential Scanning Calorimetry (DSC) and Thermomechanical Analysis (TMA) were used to characterize reaction behavior and cured properties of the resin systems. In addition, static mechanical tests and density measurements were integrated with the thermal characterization methods to correlate resin properties with process time. Flexural three-point bending experiments showed that the resins tended to have higher yield stress and toughness values at extended cure times. The improved mechanical properties could be attributed to the full development of the epoxy molecular structure, in the form of cross-linked networks and molecular rearrangement. These results suggest that extended cure times or high temperature post-curing may be required to obtain the resin's ultimate mechanical properties for high performance composites.

Keywords: characterization, epoxy, extended cure time

Introduction

While the fibers bear most of the load in a fiber-reinforced polymeric composite part, the resin matrix is responsible for transferring the load between fibers. The matrix also protects the fibers from damage and provides stability against fiber buckling and abrasion. However, the most important role of the matrix is in the control of processability and durability of the composite [1]. One of the most common thermosetting polymers for use in the aerospace/aircraft industry is epoxy resin. Epoxies hold several advantages over other matrix systems. Specifically, they do not give off volatiles when heated, exhibit low shrinkage during processing, and can have tailor made properties [2]. These

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factors help explain why epoxies find widespread use in the aerospace/aircraft industry today.

When cured at the appropriate time and temperature, epoxies polymerize into solid, cross-linked networks suitable for structural applications. The degree to which a resin is cured corresponds to the development of the resin's molecular structure in the form of cross-linking. An extensive quantitative model for describing the crosslink structure was developed by Chu and Seferis [3]. Their works were based on the probability of epoxide and amino groups reacting as a function of reactant composition and extent of secondary amine reaction. Information such as molecular weight between crosslinks and crosslink density were calculated for a TGDDM-Novolac-DDS system. Nearly all macroscopic properties of epoxies are dependent on the degree of cure [4].

In the aerospace industry, most thermoset composites are processed with standard two-hour cure cycles. However, at extended cure times various epoxy systems exhibit unexpected trends in mechanical properties. Improvements such as higher fracture toughness and failure stress are attributed to a greater degree of cross-linking. In theory, the rate of degree of cure improvement may slow down if the resin's glass transition temperature (T_g) approaches the cure temperature. Under these conditions, there is a transition from a reaction limited cure to a diffusion limited cure [5]. In addition, physical aging might occur after extended cure time for partially of fully cured epoxy systems [6]. These complex kinetic and thermodynamic effects on thermoset properties and performance are not completely understood when the T_g exceeds the cure temperature. Collectively, both thermal and mechanical analysis methods need to be integrated to characterize these systems.

Thermal analysis methods such as Differential Scanning Calorimetry (DSC) and Thermomechanical Analysis (TMA) provide thermal property changes with temperature. DSC measures heat flow to and from a sample as the temperature changes, and can be used to characterize reaction behavior, while TMA measures dimensional changes in the sample, and thus provides information about stability and transition states such as T_g. A static mechanical test can measure resin mechanical properties such as yield stress, modulus, and toughness in a three-point bend apparatus. Both thermal techniques may provide information about development in the epoxy's molecular structure, while static mechanical characterization techniques supply information about the material's performance. In unison, thermal and mechanical characterization techniques are powerful tools for understanding the properties and behavior of all thermosetting polymers.

The objective of this paper was to evaluate the thermal and mechanical properties of epoxies processed at various cure times. To conduct this study, DSC, TMA, three-point bending, and density measurement tests were performed on epoxy systems with different chemistry and functionality. Knowledge of thermal

and mechanical properties is important for successful polymeric composites processing. Several resins tested in this study are candidate matrix systems for future work in Resin Transfer Molding (RTM) and Resin Film Infusion Process (RFIP) [7].

Experimental

Materials

Five commercial epoxy resins from the Shell Chemical Company were used for thermal and mechanical characterization. EPON-828 is a standard, difunctional, diglycidyl ether of Bisphenol A (DGEBA), DPS-155 is a polyfunctional epoxy phenolic novolac resin, and RSL-1895 is a candidate RTM resin, composed of several multifunctional systems. Two other Shell systems were also used: HPT-1077, a tetraglycidyl ether of methylenedianiline (TGMDA), and HPT-1071, another tetraglycidyl resin. The epoxide equivalent weights (EEW) of all the resin systems are shown in Table 1. The curing agent used was HT-976 (4,4′-diaminodiphenyl sulfone or DDS), from the Ciba-Geigy Company. The chem- ical structures of the resins and hardener have been widely reported in the literature [8, 9]. Each resin system was processed at different cure times of 2, 8, and 14 h.

Table 1 Epoxide equivalent weight (EEW) of all resin systems

Epoxy system	Epoxide equivalent/weight
EPON-828	185–192
DPS-155	174–180
HPT-1071	150–170
HPT-1077	110–125
RSL-1895	115–135

Resin plaques used for testing were cured in sample molds. The mold was made from two glass plates sealed with Teflon. Both glass plates were coated with Sulfasil release agent to prevent adhesion. The mold was then preheated at the appropriate mixing temperature. Resin was mixed stoichiometrically with melted DDS for 10 min. The resin-hardener mixture was degassed and poured into the glass mold, and then left in the oven for further degassing for about 15 min. To simulate a cure cycle used in an autoclave, the oven temperature was manually ramped 2°C min^{-1} to 150°C.

At this temperature, vacuum pressure was gradually decreased and the sample was then cured for 2 h. The isothermal cure process was suggested by Shell Development Company [10]. After 2 h, the oven temperature was ramped

$2°C\ min^{-1}$ to 177°C. These resin plaques were further cured for 2, 8, or 14 h at 177°C to investigate the cure time influence on resin property changes.

Methodology

Uncured and cured samples were obtained from each resin system, and were tested with a TA Instruments 912 DSC coupled to a TA Instruments Thermal Analyst 2100 controller to characterize the cure behavior of all systems. DSC samples (5 to 10 mg) were ramped at $5°C\ min^{-1}$ to 350°C in a nitrogen environment. DSC analysis provided total enthalpy of reaction for uncured resins, and residual enthalpies of reaction for cured resins. These enthalpies were then used to calculate the resin's degree of cure [4]. A TA Instruments TMA 2940 coupled to a Thermal Analyst 2100 controller was also used to evaluate the resin's thermal properties. Samples of about 3 mm thickness from each resin plaque were ramped at $5°C\ min^{-1}$ to 350°C in a nitrogen environment with a 0.01 N load. TMA analysis provided properties such as T_g and coefficients of thermal expansion (CTE) for glassy, relaxation, and rubbery states of the epoxy.

Mechanical analysis was performed using an Instron 4505 mechanical tester. Six samples (60 mm×10 mm×3 mm) from each resin plaque were subjected to a flexural three-point bending test, ASTM D790-86. A crosshead speed of $1\ mm\ min^{-1}$ was used for all experiments. Properties determined from this experiment included yield stress, elastic modulus, and toughness, and were calculated using the following standard relations pertaining to the ASTM D790-86 flexural test:

$$\sigma = \frac{3F_pC}{2WT^2} \tag{1a}$$

$$E = \frac{mC^3}{4WT^3} \tag{1b}$$

$$J = \frac{E_b}{CWT} \tag{1c}$$

where σ=stress at yield point, E=flexural modulus, J=toughness, m=slope (F_p/D), F_p=load at yield, D=displacement, W=sample width, T=sample depth, C=span, E_b=energy to break.

Results were averaged over six experiments, with the maximum and minimum data points excluded.

Density measurements were performed using the density-gradient technique, ASTM D1505-85. Solutions of distilled water ($\rho=1.00\ g\ cm^{-3}$) and hydrated calcium nitrate ($\rho=1.86\ g\ cm^{-3}$) were added in appropriate proportions to establish a density range of 1.16 to $1.34\ g\ cm^{-3}$ in the 70 cm high gradient column. The column was then calibrated with standard glass floats, and the resins' densities were subsequently measured.

Results and discussion

DSC analysis

DSC was primarily used to measure heats of reaction and relaxation in the epoxy systems. By comparing the exothermic peak for the unreacted resin with the residual heat of reaction in the cured sample, the degree of cure may be calculated [4]. Figure 1a shows the DSC thermogram for uncured RSL-1895 as an example. The epoxy reaction begins at about 130°C and continues to a maximum temperature of 224.5°C, with a heat of reaction of 573.1 J g^{-1}. The heats of reaction for all the uncured systems are shown in Table 2. Figure 1b shows the results of a DSC experiment performed on RSL-1895 that had been cured for 2 h. As expected, the exothermic peak was considerably smaller at 144.3 J g^{-1}, which corresponded to a degree of cure of 0.75. The reaction initiation temperature increased from 130 to 150°C for the 2-hour cured sample. Since cure occurs after the resin enters the rubbery state, changes in T_g would directly influence the reaction initiation temperature. As will be shown later, the T_g increases with longer cure times.

Table 2 Heat of reactions of all uncured resin systems, determined by DSC (5°C min^{-1} heating rate)

Epoxy system	Heat of reaction of uncured resin/J g^{-1}
EPON-828	165.8
DPS-155	175.0
HPT-1071	434.6
HPT-1077	567.6
RSL-1895	573.1

Degrees of cure were determined for all resin systems in this work, and are summarized in Fig. 2. Figure 2 shows several different phenomena when the degree of cure is plotted as a function of cure time. The EPON-828 and DPS-155 systems both undergo complete reaction after 14 h under the current process method. Systems such as RSL-1895, HPT-1071, and HPT-1077 all show higher degrees of cure from 2 to 8 h, meaning that the cross-linking reaction continues. However, after 14 h the degree of cure either increased only slightly, or remained constant. This implies that further cure had become diffusion limited, and that the extent of cross-linking was not longer appreciable [5].

DSC was also used to investigate relaxation mechanisms for one of the resin systems, DPS-155. Figure 3 shows for the 14 h cured DPS-155 resin, an endothermic peak of 6.2 J g^{-1} beginning at around 180°C. This endotherm corresponds to the energy absorbed by the polymer chains as they are released

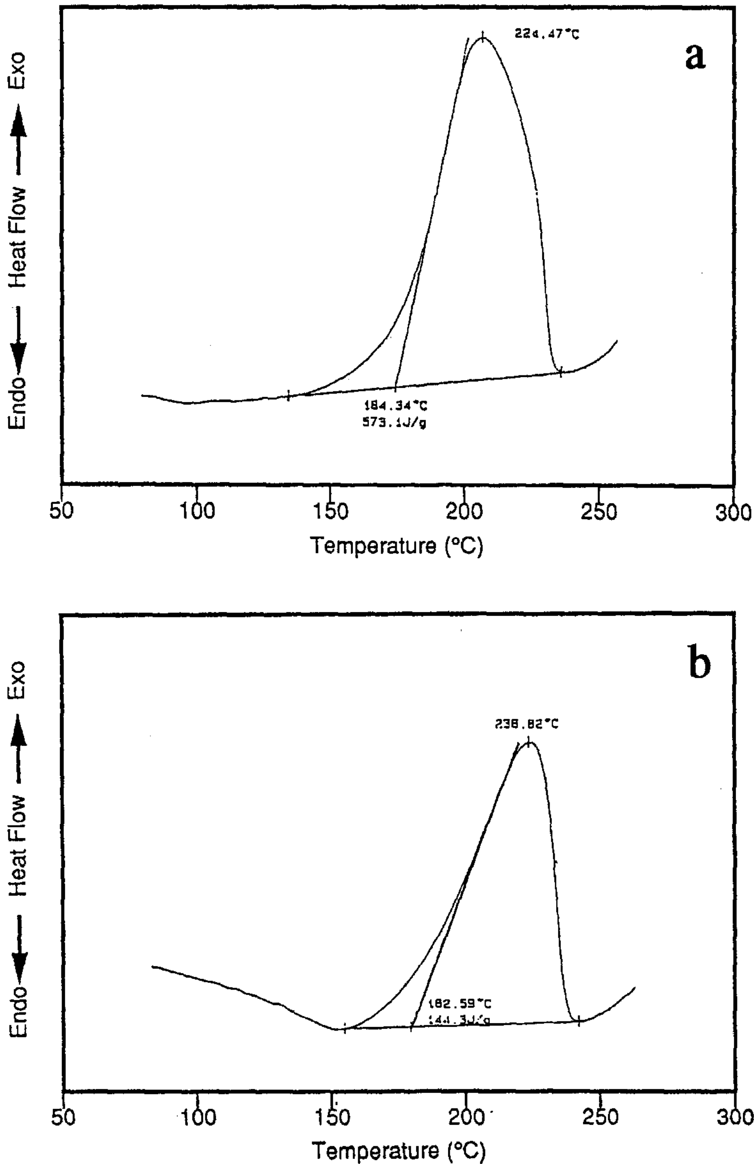

Fig. 1 DSC curve of (a) uncured RSL-1895 epoxy (5°C min^{-1} heating rate) (b) DSC curve of 2 h cured RSL-1895 epoxy (5°C min^{-1} heating rate)

from their frozen molecular structures (i.e., enthalpy of relaxation). The DPS-155 system is unique in that its T_g after 2 h approximately coincides with the isothermal cure temperature (177°C), as will be shown in Fig. 6. Under this condition, the resin vitrifies from the rubbery to the glassy state [1], and thus

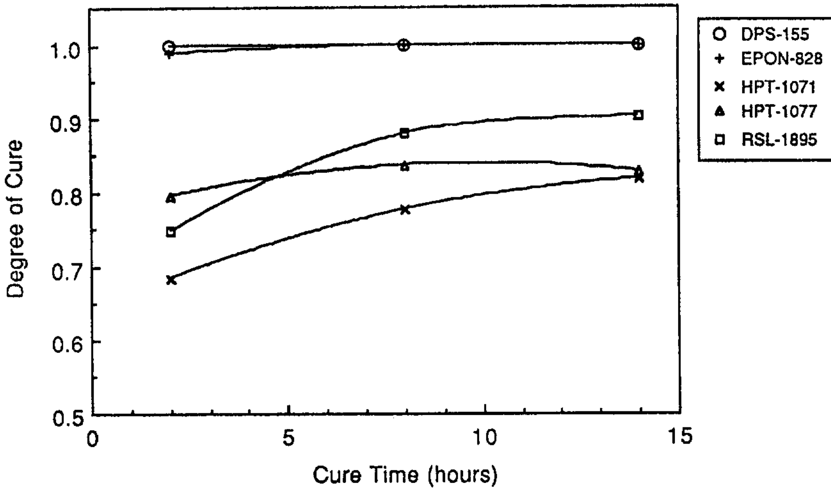

Fig. 2 Degree of cure for the epoxy systems as a function of cure time

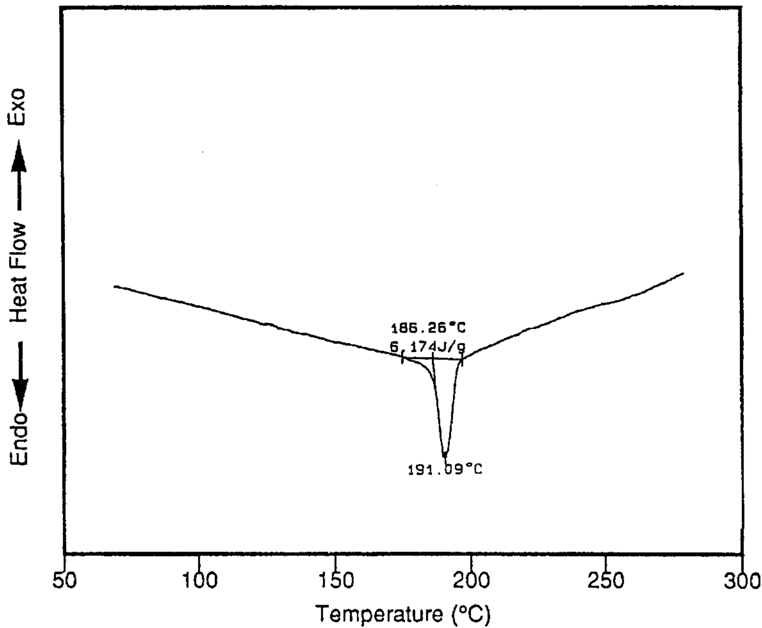

Fig. 3 DSC curve of 14 h cured DPS-155 (5°C min^{-1} heating rate), showing heat of relaxation endotherm

the polymer chains are immobilized in a non-equilibrium state [6]. This results in a relaxation endotherm when the material is heated above its T_g. Although EPON-828 also showed almost complete cure at all cure times, its T_g ranged

from 130 to 160°C, which is below the process temperature. EPON-828 is therefore already relaxed in the rubbery state and the heat of relaxation is not observed for this system. Figure 4 shows that the heat of relaxation for DPS-155 increases with cure times. The linear increase suggests that the relaxation phenomenon is time-dependent and related to physical aging of the resin. With longer cure times, the polymer chains become more compacted, and a greater amount of energy is required for relaxation. Although DSC was able to characterize the reaction and relaxation behaviors of the resin systems, it was not sufficiently sensitive to determine the T_g. Another thermal characterization method, TMA, was required to identify the T_g change with process time.

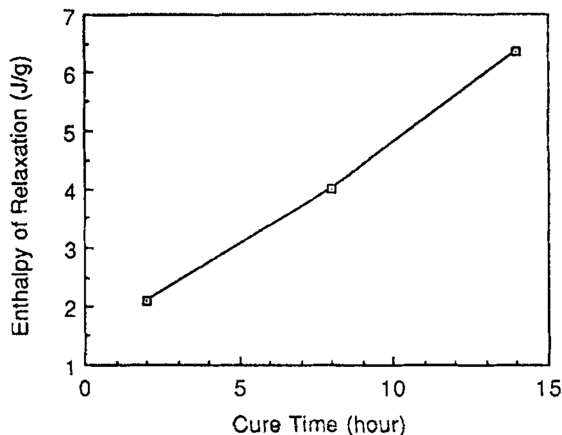

Fig. 4 Enthalpy of relaxation for DPS-155 as a function of cure time

TMA analysis

The TMA is useful for analyzing glass transitions and stability in polymers. Specifically, this analysis concentrated on determining the T_g and the CTE at relaxation. The relaxation region is of special interest because the CTE may provide information about the compaction of development of the molecular network structure. The CTE at relaxation measured in this study may represent those at specific conditions such as load and heating rate. However, if the measurement condition is specified, the CTE at relaxation would be an indication regarding material property change. Figure 5 shows a TMA curve for DPS-155 cured at 14 h. The three viscoelastic regions (glassy, relaxation, and rubbery) are represented as three linear segments in the TMA profile. This sample shows a T_g of 199.1°C, a relaxation CTE of 496 μm/m°C, and glassy and rubbery state CTEs of 56.1 μm/m°C and 91.5 μm/m°C respectively. The rubbery state occurs after the relaxation state, and has a CTE higher than the glassy state because the polymer chains have greater freedom to move. If greater load is ap-

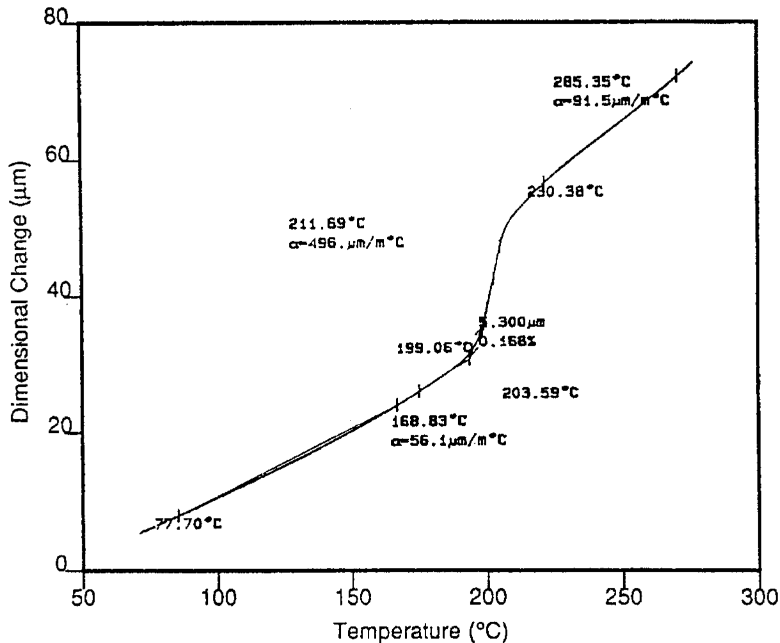

Fig. 5 TMA curve of DPS-155 (5°C min^{-1} heating rate, 0.01 N load)

plied, the relaxation CTE will have a negative slope in the TMA curve [11]. With the additional exception of EPON-828, all other resin systems had non-linear rubbery regions in the TMA curves, since the cure reaction was still proceeding.

As Fig. 6 shows, the T_g for each resin system followed a similar trend to the degree of cure. For the most part, the T_g increased with cure time. This result is expected because as the extent of cross-linking is greater in a polymer, the molecular network is more developed. More energy is thus required for the chains to move relative to one another. The molecular weight dependence on the T_g was represented by the following stoichiometric model for DGEBA-MDA from Bell [12]:

$$M_c = \frac{3.9\times10^4}{T_g - T_{g_o}} \tag{2}$$

where M_c=number average molecular weight between crosslinks, T_g=glass transition temperature, T_{g_o}=glass transition temperature of unreacted resin.

This equation means that the epoxy's T_g shift increases as the molecular weight between crosslinks decreases, a phenomenon that occurs with increasing degree of cure. For the system that was completely cured (DPS-155) at 2 h, the T_g increase with cure time may be attributed to physical aging at the 177°C cure temperature [6].

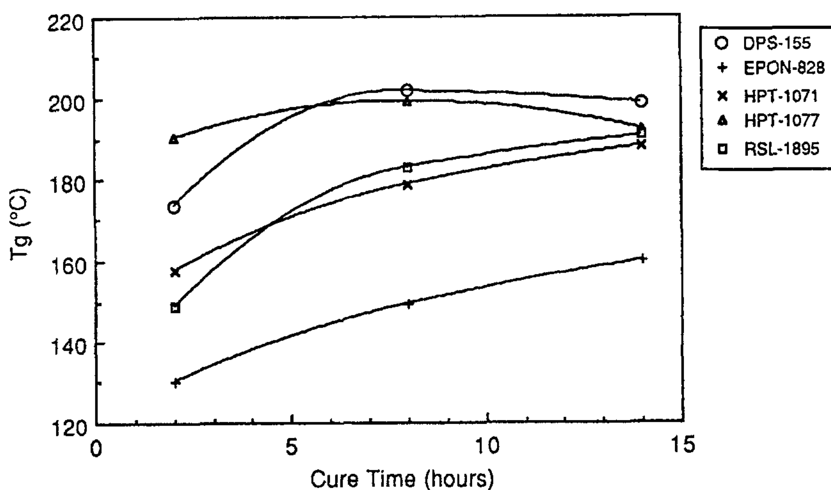

Fig. 6 Glass transition temperature for the epoxy systems as a function of cure time

Many researchers have described the relationship between degree of cure and T_g. Jordan *et al.* discussed the validity of the theoretical equation developed by DiBenedetto as [13]:

$$\frac{(T_g - T_{g_0})}{(T_{g_\infty} - T_{g_0})} = \frac{\lambda X}{1 - (1 - \lambda)X} \tag{3}$$

where T_{g_∞} is T_g of the fully cured network, X is a degree of cure, and λ is an adjustable parameter which is the isobaric heat capacity ratio between fully reacted network and unreacted epoxy. The DiBenedetto equation is widely accepted as a quick and viable model to relate T_g with degree of cure. The experimental results in Fig. 2 and Fig. 6 could be analyzed by the DiBenedetto model. However, our results, viewed only as preliminary, have only three data points for each epoxy system and a very limited range of degree of cure. Thus, further analysis or calculations from these data will require additional experiments which will be generated as our work continues.

Figure 7 shows the relaxation CTE plotted against the cure time for all resin systems. Most systems exhibit an increase in CTE with longer cure times. At longer cure times, there is an increased cross-link density and compaction of polymer chains. This means that at the T_g, the sample as a whole will experience greater expansion when all of these polymer chains attempt to relax. For the fully cured DPS-155 resin, the increased CTE is consistent with physical aging effects and increasing enthalpy of relaxation from Fig. 4. The resin system that did not follow the main trend was EPON-828, which showed a decrease in relaxation CTE with cure time. Like DPS-155, this system was almost

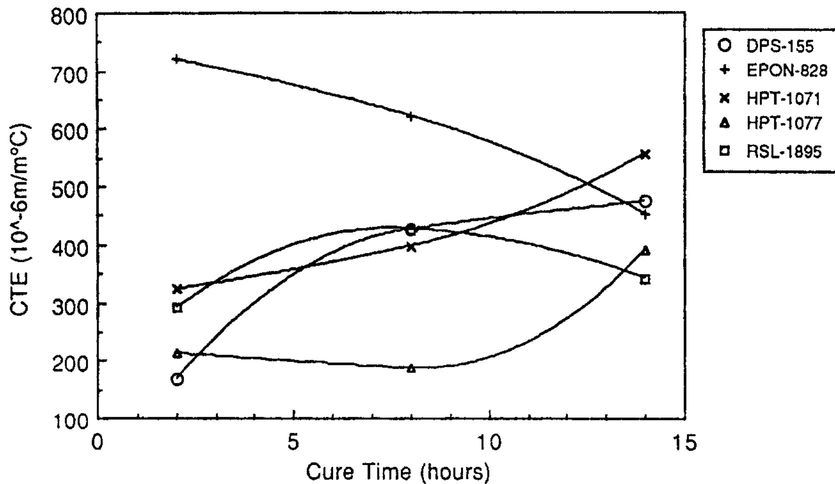

Fig. 7 Coefficient of thermal expansion at relaxation for the epoxy systems as a function of cure time

fully cured at extended cure process times; however, EPON-828 had the lowest T_g at 130°C, as shown in Fig. 6. This low T_g (relative to the cure temperature of 177°C) indicates that the polymer chains are in the rubbery state during processing, and are already relaxed. This is consistent with the increase in T_g observed in Fig. 6 and the decrease in CTE observed in Fig. 7 which also indicates that the final diffusion-controlled cross-linking may take place in the final degree of cure, although the final degree of cure can not be accurately measured by the DSC because of its lack of sensitivity [13]. CTE decreases in low T_g materials (T_g<T_{cure}) were also observed in post-cured LXT-binder systems [11]. So far, thermal analysis techniques have illustrated the impact of cross-link density and cure time on resin properties. As will be shown, these factors also play an important role when characterizing the mechanical properties of these epoxy systems.

Mechanical analysis

Three-point bending experiments with an Instron mechanical tester correlated the mechanical properties of the epoxy systems with the cure time. Figure 8 shows that most resin systems exhibited higher yield stress at longer cure times. The increase in yield stress is observed as cross-linking becomes more extensive with longer cure times. Fully reacted systems such as EPON-828 and DPS-155 also showed improved yield stress at extended cure times. This phenomenon may be related to the elimination of localized molecular defects in the epoxy network structure through molecular rearrangement [11]. EPON-828 had some deviations from the main trend in Fig. 8, but the errors are within the experimental tolerance. Although yield stress generally improved, the changes

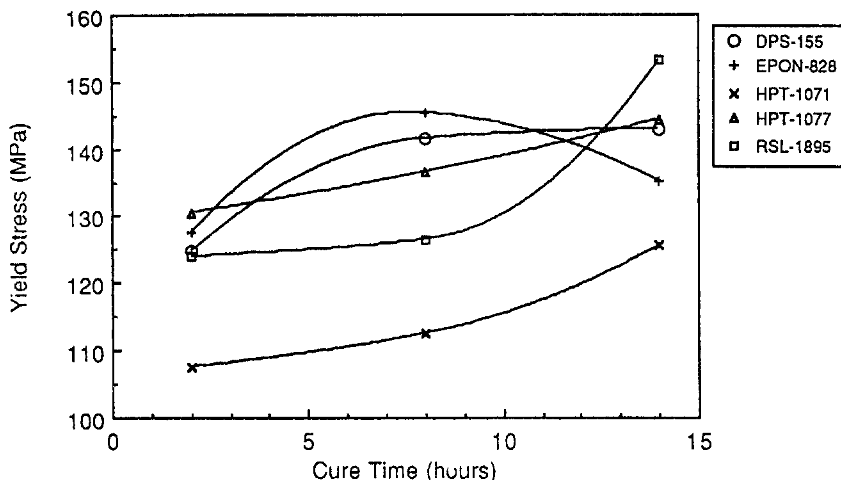

Fig. 8 Yield stress for the epoxy systems as a function of cure time

after 2 h cure were small and not of any significance. For RSL-1895, great improvement in yield stress was observed, and may be attributed to the elimination of localized molecular defects as cure reaction continues.

Figure 9 shows that the modulus tended to decrease with cure time. The decrease in modulus is best explained by the transition from linear elasticity to nonlinear elasticity in the stress-strain curve. Free volume effects may also contribute to the decrease of modulus with cure time. Whereas the 2 h samples exhibited normal, linear stress-strain curves, both the 8 and 14 h samples showed nonlinear regions at strains beyond the linear elastic limit. These non-

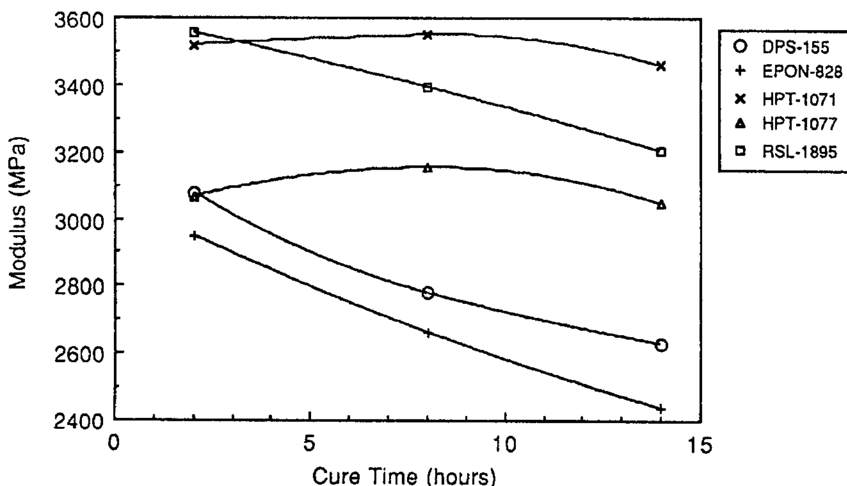

Fig. 9 Modulus for the epoxy systems as a function of cure time

linear regions were made from the elongation of the epoxy's molecular structure, which at longer cure times contained fewer localized weak points in the network. The elimination of these weak points provided the epoxy with a greater strain to failure, and accounts for both the lower observed moduli, and as will be shown later, greater toughness. Another factor that affects the modulus is free volume, which forms in the epoxy network as the material is quenched below its T_g, after processing [6]. Since T_g was observed to increase with cure time, samples cured at 14 h were expected to generate more free volume than the 2 h cured samples when cooled to room temperature. With more space for the polymer chains to move, the material as a whole has a lower room temperature modulus. The moduli of resins HPT-1071 and HPT-1077 did not change much from 2 to 14 h cure. These results occur because no further, significant reaction occurred after 2 h, and thus the cross-link density is expected to be relatively constant for all cure times. Jordan *et al.* also found the similar modulus decrease at a high degree of cure range [13], and they described this decrease by free volume theory.

The last mechanical property measured was toughness, which is plotted against cure time in Fig. 10. Toughness is defined as the area under the stress-strain curve, and was expected to improve with cure time since if both yield stress and yield strain improved. Yield stress improved due to greater cross-linking and the elimination of local molecular defects, as stated earlier. However, as the molecular structure becomes more developed at longer cure times, the epoxy network was able to sustain further elongation beyond the elastic limit, and hence the material has a greater yield strain. Toughness showed significant improvement for HPT-1071, HPT-1077, and RSL-1895 resins at 14 h cure. EPON-828 and DPS-155 showed the largest increases in toughness

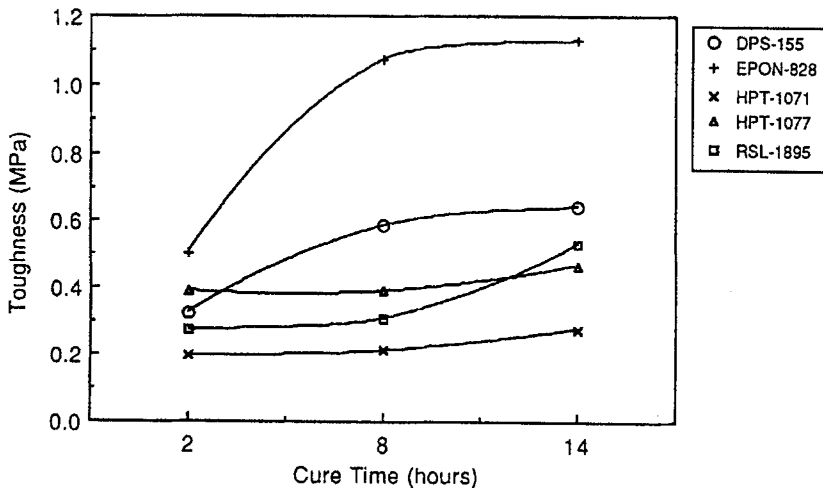

Fig. 10 Toughness for the epoxy systems as a function of cure time

after 8 h cure, but then no longer improved after 14 h. These different behaviors in toughness may be attributed to the molecular chemistry and cure kinetics, and should be further investigated in the future.

Table 3 Densities of epoxy systems, determined by the density gradient column method

Epoxy system	Density/g cm^{-3}		
	2 h cure	8 h cure	14 h cure
EPON-828	1.2400	1.2355	1.2363
DPS-155	1.2786	1.2792	1.2793
HPT-1071	1.2188	1.2158	1.2156
HPT-1077	1.2823	1.2815	1.2820
RSL-1895	1.2759	1.2760	1.2764

Density measurements for all the epoxy systems are summarized in Table 3. The total density of the epoxy is attributed to two competing factors, [1] crosslink density, and [2] free volume effects. Both phenomena become more pronounced as the cure time is increased. However, greater cross-link density leads to higher bulk density at a certain degree of cure, while samples with excessive free volume are expected to be less dense. From Table 3, EPON-828, HPT-1071, and HPT-1077 all had lower densities after 2 h cure, and thus free volume effects may be predominant. The increased densities after 2 h for DPS-155 and RSL-1895 suggest cross-link density as the dominating factor. However, the densities of the epoxies changed very slightly (<1%) between cure times, so conclusively neither cross-link density nor free volume alone can completely explain the property changes.

Overall, both thermal (DSC and TMA) and mechanical (Instron) characterization methods demonstrated that yield stress and fracture toughness improved with longer cure times. The most pronounced increases were seen in the EPON-828 and DPS-155 systems, which were both fully cured after 2 h. However, the extended cure times alone were not sufficient for full reaction among the other systems. The degree of cure for the HPT-1071, HPT-1077, and RSL-1895 resins never exceeded 0.9 even after 14 h with the current cure cycle. This indicates that an increased post cure temperature is required to construct the full molecular structure. Further investigation and a new cure cycle may be required to characterize these systems.

Conclusion

Thermal and mechanical characterization techniques were performed on epoxy resins cured for 2, 8, and 14 h. DSC analysis showed that both EPON-828 and DPS-155 resins exhibited complete cure at all process times. However, HPT-1071, HPT-1077, and RSL-1895 were not cured completely with the

specified, isothermal cure process, even at extended cure times. TMA analysis demonstrated that both T_g and CTE at relaxation increased with cure time. Mechanical properties such as yield stress and toughness generally improved with cure time. Such phenomena are attributed to the greater extent of cross-linking and the development of the resin's molecular structure through molecular rearrangement. Density measurements confirmed that neither factor alone accounted for the property changes at extended cure times. Extended cure times thus provided resin properties superior to those obtained after conventional 2 h cure cycles. However, longer cure times may not be a feasible process consideration since industry requires fast cure cycles. Collectively, both thermal and mechanical analysis methods need to be integrated to fully characterize the cured epoxy systems and to design an appropriate cure cycle for high performance composites processing.

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