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Processing–structure relationships for multiphase epoxy matrix systems

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A styrene-modified diglycidyl ether of bisphenol-A (DGEBA) epoxy system cured with trimellitic anhydride (TMA) has been investigated to explore processing and structure relationships. During cure, the reactive styrene precipitated with polymerization into phase domains separate from the epoxy phase. Dynamic mechanical analysis and microscopy studies were performed to gain insight to matrix structure. The DMA studies showed that the styrene-modified epoxy system after cure exhibited two partially overlapped but distinct relaxation peaks, which are associated with the T_gs of the polystyrene and epoxy phases. The glass transition of the polystyrene phase was shown to be broadened and the T_g to depend strongly on processing temperature profiles. While the T_g of the epoxy phase increases with curing agent concentrations, the T_g of the polystyrene phase does not. Microscopic studies showed that the styrene-modified system exhibited a rougher fracture surface but did not reveal well defined phase domains in which the precipitated polystyrene component was aggregated. Overall, the study has demonstrated correlations of the kinetic factors in controlling the morphology in reactive modifier–epoxy systems.

1. Introduction

Styrene incorporation in epoxy resins as a reactive diluent provides one way to reduce the viscosity of epoxy formulations for applications where low viscosities are generally preferred for high-speed continuous composite processing, such as the pulforming process. During cure, the reactive styrene monomer polymerizes and precipitates in distinct phase domains. Processing variables can directly or indirectly affect the structure and properties of these multiphase matrix composites. The kinetics of curing reactions of this resin formulation have been investigated and summarized in a separate paper [1]. In this work the factors controlling phase separation and morphological structure and their effects on the properties of the styrene-modified epoxy networks were investigated.

Toughness improvement of epoxy-based systems can usually be achieved by incorporation of rubbers, elastomers or thermoplastics modifiers. These modifiers can be oligomers [2, 3], thermoplastics such as polysulphone or polyethersulphone [4–7], or reactive rubbers [9–10], such as carboxyl- or amine-terminated butadiene acrylonitrile rubbers (CTBN or ATBN). It is recognized that morphology and phase separation are important and are influenced strongly by such thermodynamic factors as molecular weight of the modifiers, cross-linking density of the epoxy matrix and solubility parameters. The way kinetic factors of the curing process dictate phase separation and morphology is not, however, fully understood. Accordingly, this work focused on kinetic effects as they dictate processing conditions that result into distinct morphology.

2. Experimental procedure

2.1. Materials

The unmodified resin system was Shell EPON Resin 828 based on diglycidyl ether of bisphenol-A (DGEBA). The styrene-modified epoxy system was EPON Resin 9102, which is a homogeneous liquid mixture of DGEBA with 25 p.h.r. (parts per hundred) by weight of styrene monomer per hundred parts of epoxy and minor accelerators and initiators [1]. The resins were cured with EPON Curing Agent 9150 based on trimellitic anhydride (TMA). The recommended concentrations of EPON Curing Agent 9150 for EPON Resin 9102 were 35–41 phr. Samples prepared with a quaternary ammonium salt as the catalyst were also examined in order to investigate the effect of catalysts on matrix structure. The materials were supplied by Shell Development Co. and were used without further purification.

2.2. Resin mixing and sample preparation

Mixing was done using a mechanical stirrer at high rotation speeds for about 5 min until the solid lumps of TMA disappeared. Due to its relatively high melting point, trimellitic anhydride (TMA) was not fully

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compatible with the epoxy at either ambient or the mixing temperature of 60 to 70 °C. For this formulation, however, incompatibility between the epoxy resin and the curing agent was not a problem since the curing agent TMA was quickly dispersed and reacted with the epoxy at curing temperatures between 150 and 177 °C.

Neat resin plaques were prepared by casting the mixture into a glass or aluminium mould coated with a spray of release agent. A standard cure profile was used in preparing most of the DGEBA–TMA (with or without styrene modifier) samples, which were cured at 177 °C (heating rate approximately 5 °C min^{-1}) for two hours. Postcure, if needed, was done at a temperature of 200 °C for 4 h. Additionally, three other processing routes were used to prepare styrene-modified DGEBA–TMA samples for further characterization and are summarized in Table I. Also, a series of samples were prepared having stoichiometric ratios of curing agent to epoxy from 0.25 (10 p.h.r. TMA) to 2.0 (80 p.h.r.), and are also summarized in Table I.

2.3. Apparatus and procedures

2.3.1. Thermal analysis

Differential scanning calorimetry (Dupont 910 DSC) was used to measure residual heats of reaction and to determine the glass transition temperatures. The thermal stability of modified and unmodified cured matrix systems was characterized using a thermogravimetric analyser (Dupont TGA 951). The standard heating rate used was 5 °C min^{-1} unless otherwise indicated.

2.3.2. Dynamic mechanical analysis

Dynamic mechanical properties were measured using the Dupont DMA 982 or 983 modules coupled to the Dupont 9900 Thermal Analysis System for data acquisition and analysis. The dimensions of the specimens used for DMA measurements were approximately 40 × 5–10 × 3 mm. The heating rates for the DMA experiments were 1 and 5 °C min^{-1} from ambient to 300 °C. A sinusoidal oscillation of resonant frequency (DMA 982) or of fixed frequency of 1 Hz (DMA 983) and 0.2 to 0.4 mm in the oscillation amplitude was imposed on the samples in the flexural bending mode. The storage and loss moduli measured by the DMA were the flexural moduli, E' and E'', respectively.

TABLE I Sample designations and processing conditions

Sample Designation	Description
Unmodified Epoxy Formulations	
Uncatalysed DGEBA–TMA	DGEBA, 100 parts TMA, 35 phr
DGEBA–TMA	DGEBA, 100 parts TMA 35 phr 1 phr TBAB
Styrene-modified epoxy formulations	
Styrene–DGEBA–TMA	DGEBA (100 parts), styrene (25 phr), TMA (35 phr), and TBAB (1 phr)
Cure Profiles	
Standard – Normal cure profile. (Cured at 177 °C for 2 h with a 5 °C min^{-1} heating rate)	
L – Low temperature vitrification before final curing. (Ramp at 5 °C min^{-1} to 90 °C, held for 5 h, then ramp 5 °C min^{-1} to 177 °C, held for 2 h)	
S – Slow heating rate. (Ramp at less than 1 °C min^{-1} to 177 °C held for 2 h)	
F – Fast heating rate. (Resin was cast into a mould that was pre-heated to 177 °C, and held at that temperature for 2 h)	

2.3.3. Scanning electron microscopy

An ISI scanning electron microscope (SEM) was used for examining the fracture surfaces of cured samples of bulk resins at 5000 × magnification. To prepare samples, the cured resin plaques were fractured at ambient temperature. Sub-ambient fracture was not employed since there was no concern of plastic deformation during fracture due to the fact that both the epoxy and the polystyrene components have T_gs well above ambient temperature. The fracture surfaces were coated with gold by vapour deposition using a vacuum sputterer for SEM examinations.

3. Results and discussions

3.1. Thermal stability

Fig. 1 shows the thermal degradation behaviour of the polystyrene, the unmodified epoxy, and styrene-modified epoxy which were both cured with 35 phr TMA. This demonstrates that the thermal stability of the styrene-modified DGEBA–TMA epoxy is quite comparable to the unmodified epoxy cured with the same stoichiometry of TMA. The incorporation of polystyrene at 25 phr level into the epoxy formulation did not significantly affect the thermal stability.

3.2. Glass transition temperatures

The effect of the styrene modifier on the glass transition temperature of the cured epoxy system was examined by DSC. Fig. 2 shows that the T_gs of the neat polystyrene and the DGEBA–TMA epoxy are 91

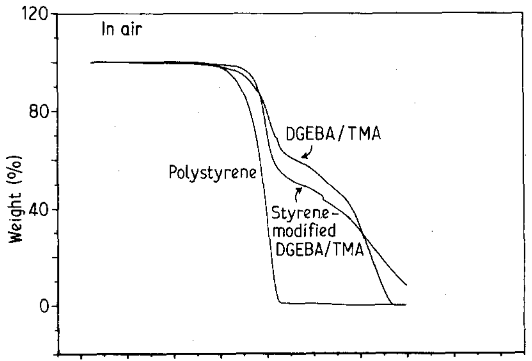


Figure 1 TGA thermograms of reacted and cured polystyrene, unmodified DGEBA–TMA, and styrene–DGEBA–TMA formulations in air.

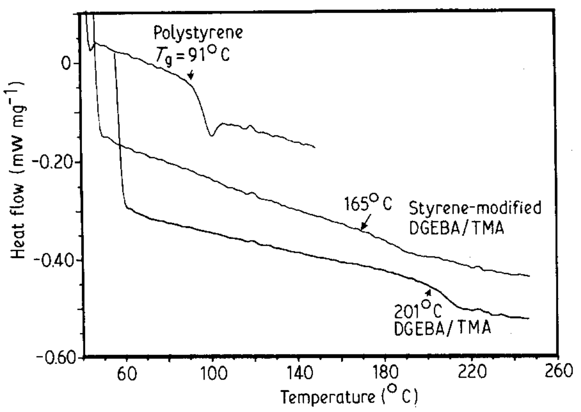


Figure 2 DSC thermograms of reacted and cured polystyrene, DGEBA–TMA, and styrene–DGEBA–TMA formulations.

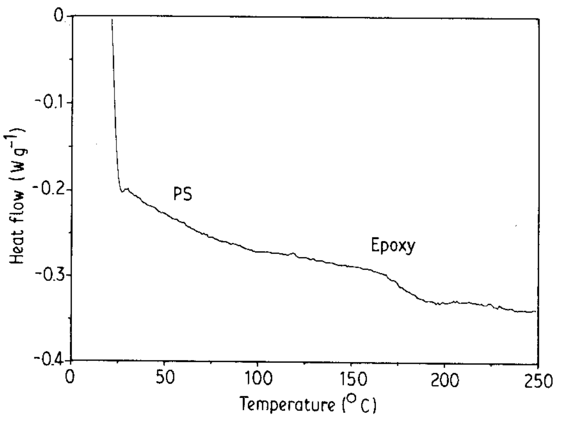


Figure 3 DSC curve of cured styrene–DGEBA–TMA sample showing two broadened T_gs.

and 201 °C, respectively. The cured styrene-modified DGEBA–TMA appeared visually cloudy, indicating multiphase structure. DSC results, however, revealed only one glass transition at 175 °C, apparently related to the epoxy-rich phase, while the glass transition related to the polystyrene-rich phase was not detected by DSC. Higher heating rates of 20 and 30 °C min^{-1} were then used to increase DSC sensitivity. Still, no T_g of the polystyrene (PS) phase domain was detected. A distinct T_g at 90 °C was, however, observed in the styrene-modified DGEBA–TMA if the styrene concentration was increased from 25 to 40 phr. As shown in the DSC traces, the T_g's of both phases appeared more significantly broadened than the T_g's of the individual neat components. The observation suggests that while excess polystyrene did precipitate out, partial plasticization in the phase domain also took place.

A sample was prepared by having styrene polymerized and precipitated from a styrene–DGEBA resin mixture where no curing agent was added until complete polymerization of styrene. Fig. 3 shows the DSC trace of this sample. An extremely broadened glass transition, ranging from 30 to 90 °C, of the polystyrene phase indicates extensive dissolution of the unreacted liquid epoxy component that accompanied the precipitated polystyrene component. Since polystyrene was precipitated from an originally homogeneous mixture of styrene with the epoxy resin, the polystyrene phase could also be plasticized by unreacted epoxy resin. As can be seen from the figure, the T_g of the polystyrene phase was lower and the transition more broadened than the T_g of the neat polystyrene. Further evidence of dissolution of the liquid epoxy to the precipitated polystyrene was provided by the observation that the resin, upon subsequent curing by TMA, yielded a sample plaque with high porosity (voids). This might be caused by dissolved liquid DGEBA in the polystyrene phase domain that evaporated.

The anhydride cured epoxy systems are usually formulated with a catalyst. In this case, cure reactions were catalysed with a quaternary ammonium salt, tetra-n-butylammonium bromide (TBAB). Its effect on kinetics of cure has been discussed in a related paper [1]. In this study, its effect on matrix T_g was also investigated using DSC. Fig. 4 shows T_g as a function of isothermal cure temperature (T_c) for DGEBA–TMA (40 p.h.r.) epoxy systems with and without 1 p.h.r. of TBAB (accelerator). The sample T_g was measured using DSC at a heating rate of 5° C min^{-1} after the sample had been cured for 2 h at each isothermal temperature. The results showed that the accelerator enhanced the glass transition temperature of the epoxy matrices by as much as 20 °C. In the presence of the accelerator, the onium ion species are responsible for opening more anhydride rings in TMA at the same temperatures; and the increase in T_g and cross-linking densities is a result of increased functionality of the TMA curing agent.

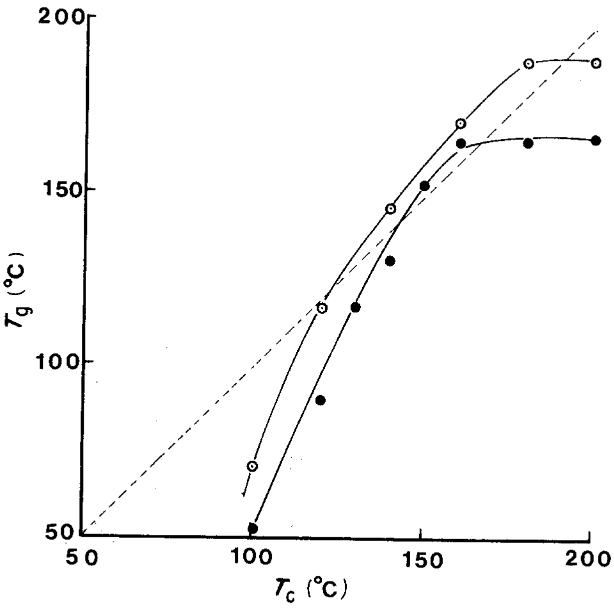


Figure 4 DSC determination (5 °C min^{-1}) of T_gs of the DGEBA–TMA systems (with and without the catalyst) as a function of cure temperature. (○ 1 phr onium salt, ● no onium salt, --- $T_g = T_c$).

3.3. Epoxy matrix structure

The DSC technique usually has less sensitivity on detecting phase and structure of multiphase systems. To investigate the multiphase matrices further, DMA was utilized to elucidate the structure as related to phase behaviour and molecular relaxations.

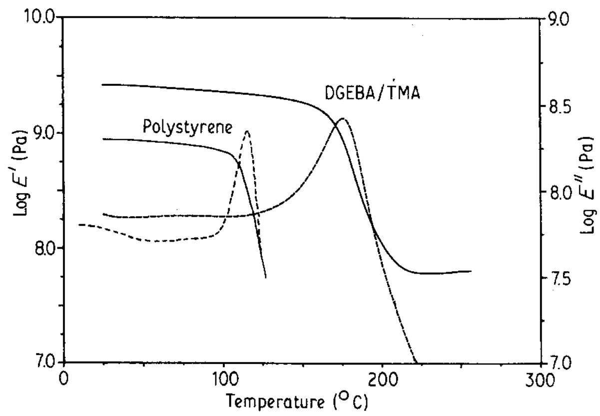


Figure 5 Storage and loss flexural moduli of polystyrene and the cured DGEBA–TMA system. (—— log E', – – – log E'')

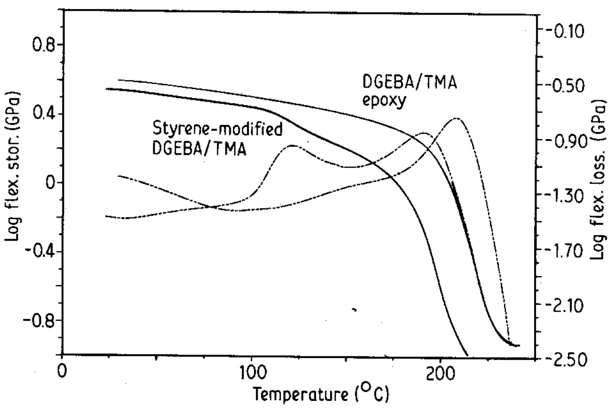


Figure 6 Storage (——) and loss (– – –) flexural moduli of cured DGEBA–TMA and styrene-modified DGEBA–TMA.

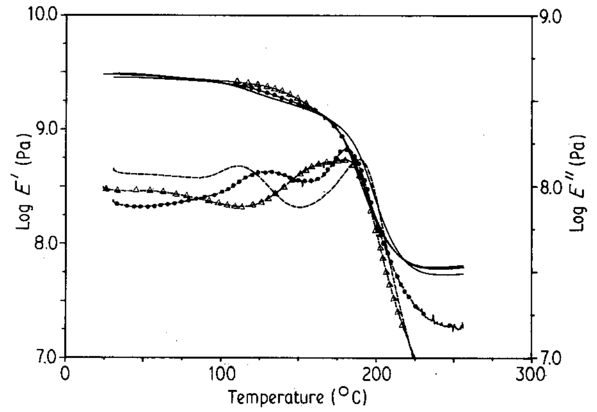


Figure 7 Dynamic mechanical properties of styrene–DGEBA–TMA. L (△), S (●), and F (– – –) samples. (—— log E', – – – log E'').

Fig. 5 shows the storage and loss moduli of the individual components: the polystyrene ($T_g = 105\,°C$) and the unmodified DGEBA–TMA epoxy matrix ($T_g = 180\,°C$). It should be noted that the T_g of the epoxy matrix was not as high as it could have been since no onium salt accelerator was used in the formulation. As can be seen in Fig. 5, the relaxation peak of the polystyrene was quite sharp, while the epoxy relaxation peak was more broadened even though the epoxy matrix is single phase.

When the mixture of the styrene and epoxy resin was cured, the matrix network structure was again examined using the DMA. Fig. 6 shows that two broad molecular relaxations in flexural loss modulus, E'', were observed for the 25 phr styrene-modified DGEBA–TMA sample. The higher-temperature T_g (190 °C) is for the epoxy-rich phase, and the lower-temperature T_g (118 °C) is related to the polystyrene-rich phase. The figure also shows that although the two relaxation peaks are well resolved, they are not completely separated from each other. The overlapping of these peaks indicates that there may be some interaction between the two phases.

An initiator is usually needed to polymerize the styrene monomer. In this study, an aliphatic peroxide (Lupersol 101, Pennwalt), as suggested in the literature [11], was used. In the absence of the peroxide, the styrene–epoxy resin mixture did not result in a two-phase structure upon completion of cure. The cured plaque of the styrene–DGEBA–TMA formulation appeared transparent, indicating lack of phase separation. DMA results revealed that there was only a minor peak between 50 and 100 °C. The DMA results suggested that the styrene did not polymerize and/or precipitate to any significant extent in the absence of the initiator. Although the styrene component in the epoxy formulation is capable of undergoing polymerization at high temperatures in the absence of an initiator, the reaction rate may be too slow to form a distinct phase before gelation of the epoxy network.

Fig. 7 shows the dynamic mechanical properties of the cured styrene-modified DGEBA–TMA samples, cured using the three different cure temperature profiles, L, S, and F as shown in Table I. The structures as revealed by the DMA results were drastically different. Sample L (cured using the cure profile L) exhibited near miscibility between the polystyrene and the epoxy components, while sample F exhibited extensive phase separation, as the two relaxation peaks in the loss modulus curves were well separated. By comparison, the extent of phase separation of sample S was intermediate between those of samples L and F. The explanations of correlations between structure and processing are as follows. Sample F was produced by a fast-heating temperature profile, where styrene polymerized and aggregated more freely into spherical agglomerates just before gelation of the epoxy. Precipitation of the polystyrene component was unhindered and, therefore, more pronounced. Sample L was vitrified at 90 °C before it was subsequently cured at the normal cure temperature. It has been shown that styrene polymerization in the styrene–DGEBA–TMA formulation does not take place significantly until 175 °C [1]. At 90 °C, the epoxy cure reaction could, however, advance enough to the vitrification point. Therefore, the styrene component was dispersed in a fine domain and was confined in the vitrified epoxy matrix. During subsequent cure, large-scale aggregation of the polystyrene component might be hindered. This cure profile therefore produced a matrix exhibiting borderline two-phase morphology with near miscibility, thus the phase behaviour of sample L might be at a quasi-equilibrium or meta-stable state, which could be brought to a more stable equilibrium upon postcuring at above the epoxy T_g.

Fig. 8 shows a comparison of the DMA flexural loss moduli curves of sample L (Curve a) and the same sample subjected to two postcuring lengths of time: 10 and 15 h (curves b and c, respectively). These results demonstrate that postcuring at 180 to 200 °C tends to facilitate precipitation of the polystyrene phase since postcuring at above the T_g of the epoxy phase brings the structure toward an equilibrium state, i.e., a structure with two stable, separated phases.

During cure, the styrene polymerized to a high-molecular-weight polymer, which precipitated out in the epoxy network and formed a distinct phase domain. Without the kinetic factor of gelation of the epoxy component, phase separation is determined by the thermodynamic parameters such as temperature, solubility parameters (enthalpy), and molecular weights (entropy). In general, phase separation behaviour may be described by the Gibbs free energy of mixing [12]

$$\begin{aligned}\Delta G_{\text{mix}} &= \Delta H_{\text{mix}} - T\Delta S_{\text{mix}} \\ &= V(\delta_1 - \delta_2)^2\Phi_1\Phi_2 \\ &\quad + RT(N_1 \ln \Phi_1 + N_2 \ln \Phi_2) \qquad (1)\end{aligned}$$

where V is the total molar volume, δ_1 and δ_2 the solubility parameters, Φ_1 and Φ_2 the volume fractions, and N_1 and N_2 the number of molecules of components 1 and 2, respectively.

Before curing, the styrene monomer and the epoxy resin form a homogeneous mixture, indicating a negative Gibbs free energy of mixing. During cure, phase separation occurs because the Gibbs free energy of mixing, ΔG_{mix}, becomes unfavourable (positive). The Gibbs free energy of mixing can change from negative to positive because the molecular weights rise due to polymerization of the styrene monomers and cross-linking reaction of the epoxy resin. The contribution from the entropic term, ΔS_{mix}, becomes progressively smaller when the components to be mixed are both high molecular weight species, thus the entropic term, $T\Delta S$, is greater for the monomeric styrene–epoxy system than for that of the cured matrix of polystyrene–epoxy. On the other hand, the enthalpic contribution can also change during cure. Before cure, the styrene monomer is soluble in the epoxy resin, indicating a good match of solubility parameters of these two components. Polymerization of the styrene component and the cross-linking reaction of the epoxy component can, however, change the solubility parameters.

Temperature also affected the phase behaviour. The Gibbs free energy of mixing, ΔG_{mix}, might become more favourable for mixing since the $T\Delta S$ term was greater at higher temperatures. As a result, the phase domain of the polystyrene component became less visible. Therefore, upon postcuring at higher temperatures, the plaques turned from cloudy to between translucent and quite transparent in appearance.

Fig. 9 is a plot of the glass transition temperature (measured by DMA) as a function of composition of the curing agent, TMA, employed in the formulation. At the concentrations where the TMA curing agent was higher than 20 phr, two relaxation peaks were observed for each sample. While the T_g of the polystyrene-rich phase remained relatively constant between 100 and 120 °C, depending on the processing route used, the T_g of the epoxy-rich phase increased almost linearly with the TMA concentration. The TMA concentration did not seem to significantly affect the glass transition of the polystyrene-rich phase.

At low concentrations of the curing agent, i.e. between 0 and 20 p.h.r., there is only one relaxation peak observed in the DMA spectrum, as shown in Fig. 10.

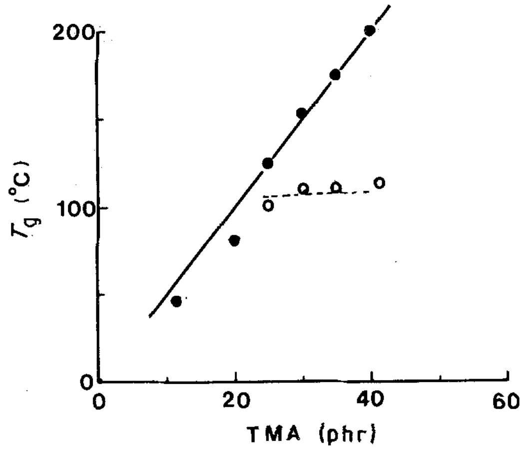


Figure 9 DMA determination of T_gs of the epoxy (●) and polystyrene (○) phases in the cured styrene–DGEBA–TMA as a function of TMA concentration.

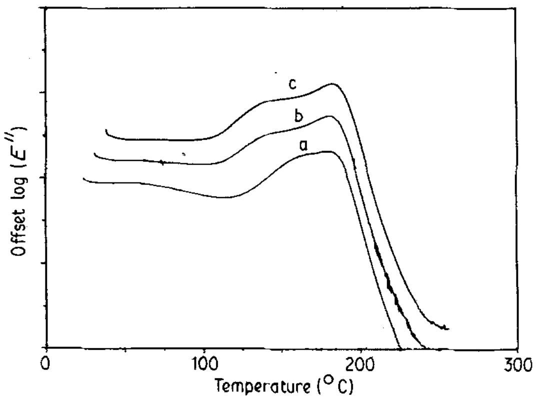


Figure 8 DMA flexural loss moduli showing the styrene–DGEBA–TMA. L sample that has been subjected to postcuring at 177 °C for 2 h.

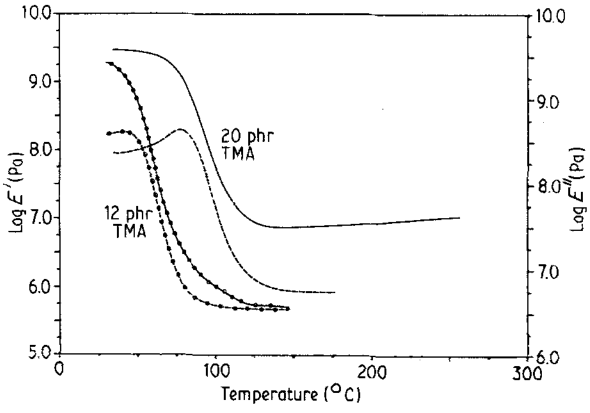


Figure 10 Flexural storage and losses moduli of cured styrene-modified DGEBA–TMA formulations with 12 (——) and 20 phr (—·—) of TMA, respectively.

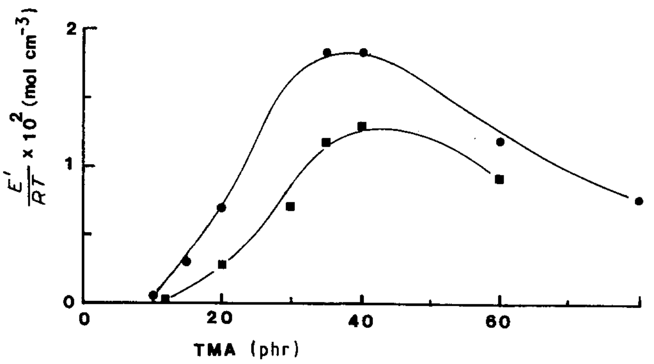


Figure 11 Cross-linking densities of cured unmodified DGEBA–TMA (●) and styrene–DGEBA–TMA (■) as a function of TMA concentration.

The polystyrene did not separate out from the epoxy domain when the styrene–epoxy mixture was cured with 12 and 20 phr of TMA, respectively.

The cross-linking densities may be related to the quantity, E'/RT, according to the rubber-like elasticity theory [13, 14], as follows

$$E'/RT = 3\varphi'\sigma/v = d/M_c \quad (2)$$

where φ' is a constant, σ the cross-linking density, R the gas constant, v the specific volume $= 1/d$ (where d is the density) and M_c the average molecular weight between cross-links.

Fig. 11 provides a comparison of the cross-linking density of the styrene-modified and unmodified epoxy systems calculated according to Equation 2. The cross-linking density, which is related to E'/RT, of the modified epoxy system was apparently lower than the unmodified epoxy system cured with the same concentration of TMA. This might be attributed to the linear polystyrene component which decreased the cross-linking density of the cured epoxy network.

3.4. Morphology

Fig. 12 shows the SEM micrographs of the fracture surfaces of three epoxy samples examined to demonstrate the effect of processing on morphology. A rough fracture surface of the cured styrene–DGEBA–TMA sample was observed but the polystyrene component did not seem to aggregate in domains with a distinct boundary. Fig. 12b shows a typical fracture surface of the unmodified DGEBA–TMA sample. The fracture surface at 5000 × was observed free of any heterogeneous structure. However, Fig. 12c demonstrates that the polystyrene separated and aggregated in regular spherical phase domains for the cured styrene–DGEBA–TMA resin whose styrene component had been pre-polymerized before cure. This result demonstrates that the styrene polymerized and precipitated freely in the absence of gelation of the epoxy network.

The DSC results did not reveal a T_g associated with the precipitated polystyrene phase, but the DMA results suggested clearly the presence of the polystyrene phase. Accordingly, the sizes of the phase domain might be between the heterogeneity levels detectable by the DSC and DMA techniques, respectively. In a review paper by Kaplan [15], it was concluded that two T_gs will be apparent only when the level of heterogeneity is greater than 100 nm (0.1 µm), while for less than 15 nm, the blends will exhibit only one T_g. Based on this, the sizes of the precipitated polystyrene

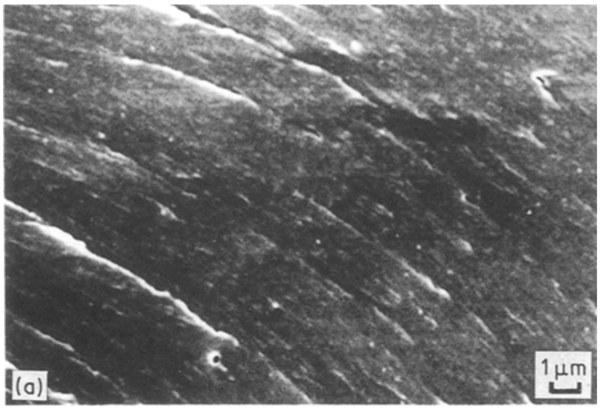
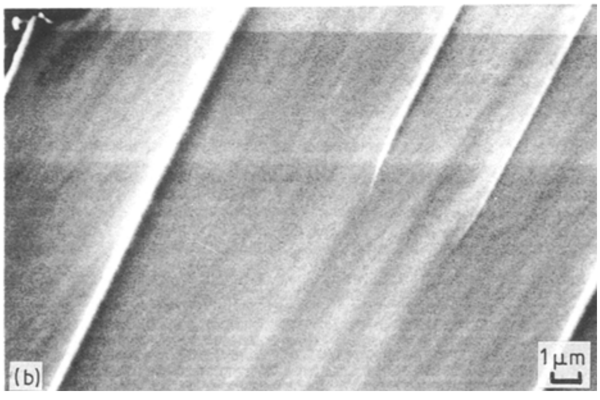
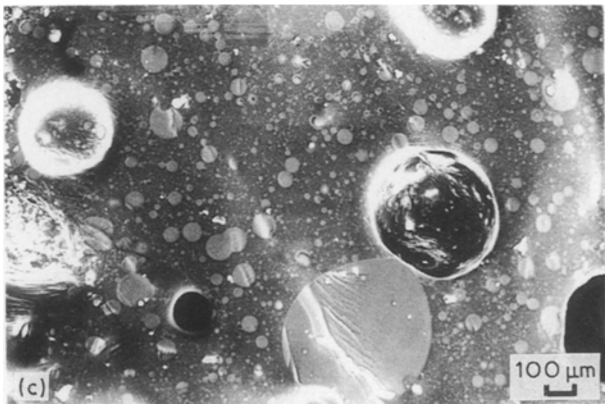


Figure 12 SEM of fracture surfaces: (a) styrene–DGEBA–TMA; (b) unmodified DGEBA–TMA (no styrene); (c) DGEBA–TMA styrene pre-polymerized.





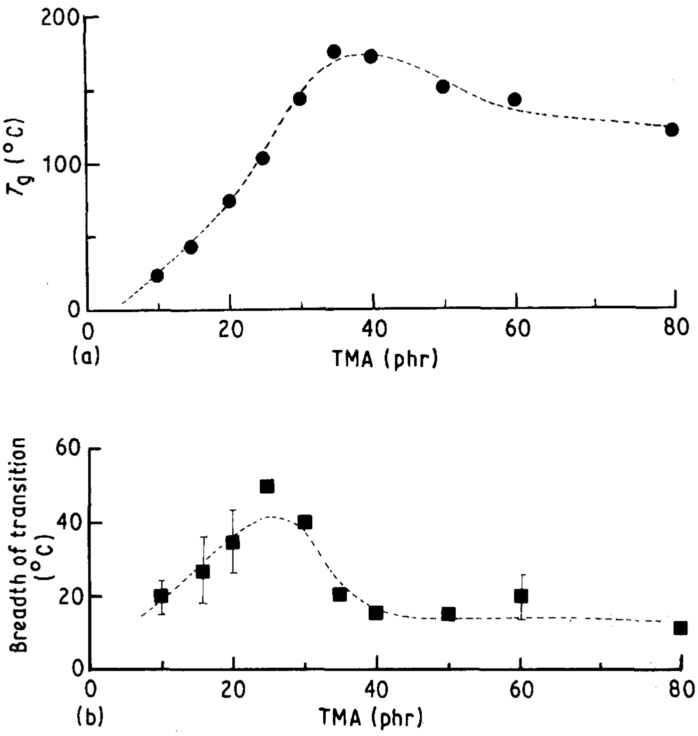


Figure 13 DSC determination of (a) T_g; (b) breadths of transitions for cured unmodified DGEBA–TMA.

phase domain were estimated to be between 15 to 100 nm (0.015 to 0.1 µm). Therefore, the sizes of the precipitated phase domains were probably much too small and their shapes too irregular to be easily observed using SEM. As a result, although the matrices might be heterogeneous as revealed by DMA, the phase domain sizes were not optimal (too small) to have an effect on fracture properties of the matrices. By comparison, most rubber-modified epoxy matrices contain a rubber phase with a domain size of about 0.1 to 5 µm [10].

3.5. Micro inhomogeneity in unmodified networks

Thermosetting epoxy matrices are inherently inhomogeneous [16, 17]. The level of this heterogeneity is small, typically in the range of 10 to 20 nm, and is usually caused by uneven cross-linking densities in the networks [18]. This is called "micro-inhomogeneity", so as to distinguish it from the heterogeneity discussed earlier in this paper. Therefore, while the styrene-modified epoxy matrices show structural inhomogeneity of a greater level caused by phase separation of the polystyrene phase from the epoxy domains, the unmodified epoxy matrices can be considered as networks of inhomogeneity of a smaller level caused by uneven distribution of cross-links.

Fig. 13 shows T_gs measured by DSC (Fig. 13a) and the breadth of the glass transitions (Fig. 13b), as a function of TMA concentration employed in the formulations. As can be seen, the T_g increases as TMA increases, reaching an asymptotic limit at 35 to 40 p.h.r. of TMA. The micro-inhomogeneity of the unmodified epoxy matrices as measured by the glass transition breadth (in °C) shows a maximum at TMA equal to 25 p.h.r.

Fig. 14 shows the DMA results of the same samples of the unmodified DGEBA–TMA system (no styrene), as a function of TMA concentration. Here the width of the peak at half height was taken as a measure of transition breadth, which is related to structural inhomogeneity. As can be seen, the T_gs as observed by DMA correlate well with the earlier T_gs determined by DSC.

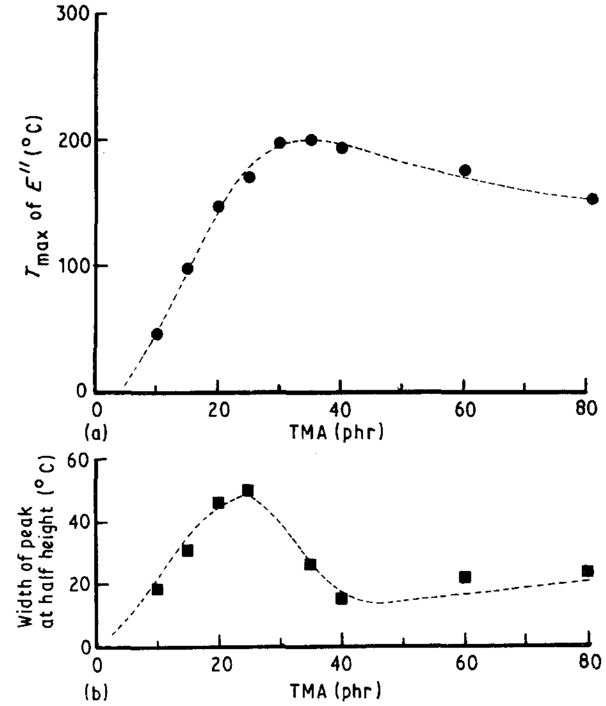


Figure 14 DMA determination of (a) T_g; (b) breadths of transitions for cured unmodified DGEBA–TMA.

4. Conclusion

Using as a model system, a styrene-modified DGEBA epoxy formulation cured with trimellitic anhydride, this study investigated epoxy network structure in relation to processing. During cure, a distinct polystyrene-rich phase was precipitated within the epoxy matrix, and its phase domain size was estimated to be on the order of 100 nm or less. The precipitated phase could be detected and the structure could be interpreted from the molecular relaxations using DMA. However, the phase domain sizes were too small to be discerned easily by SEM. The morphology was not clearly defined due to the small phase domain size and poorly defined phase boundary. However, this study has shown that the phase domain sizes and structure could be changed by employing different processing.

Processing routes were shown to drastically affect the structure of the two-phase matrix. Two extreme cases of phase separation were discussed. In the epoxy matrix vitrified by the curing agent at low temperatures, the styrene component could still polymerize but did not aggregate freely and thus, did not separate completely from the epoxy matrix upon subsequent cure at higher temperatures. The opposite extreme case of phase separation was observed when styrene polymerized at high temperatures in the liquid TMA-free epoxy resin without accompanying gelation of the network. Subsequent cure of the polystyrene–epoxy mixture by TMA produced a distinct two-phase matrix with spherical agglomerates with a well defined phase boundary.

Overall, this study has demonstrated the importance of processing specifications in a reacting matrix system in order to control the resulting morphology in the cured systems.

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