Structural and materials properties of a polysulphide-modified epoxide resin

Terence J. Kemp, Andrea Wilford and Oliver W. Howarth
Department of Chemistry, University of Warwick, Coventry CV4 7AL, UK

and Timothy C. P. Lee
Morton International plc, University of Warwick Science Park, Sir William Lyons Road, Coventry CV4 7EZ, UK

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The nature of epoxy resins of the diglycidyl ether of bisphenol A modified by incorporation of 10 to 20 g phr of various linear polysulphides has been examined by ^{13}C n.m.r. spectroscopy (conventional and cross-polarization/magic angle spinning), transmission electron microscopy, scanning transmission electron microscopy and dynamic mechanical thermal analysis. Most, but not all, cured materials feature disperse rubber particles with diameters of <1 μm. The materials properties of the modified resins have been measured by tensile and impact testing: modification entails improvement but not necessarily either in proportion to the linear polysulphide content or dependent on the demonstrable presence of disperse particles.

(Keywords: epoxy resins; structural properties; modification; polysulphide)

INTRODUCTION

The introduction of rubbers as toughening agents into plastics is well-established and has been the subject of a number of reviews[1] and monographs[2–7]. The variety of host materials is considerable, including polystyrene[1,3,5–7], acrylonitrile–butadiene–styrene copolymer[1,3,4,6,7], poly(vinyl chloride)[1,3–6], polyethylene and polypropylene[3,4,6], poly(methyl methacrylate)[1,3], nylon 6,6[1,8] and polyoxymethylene[8]. This approach became extended to thermosetting resins, with carboxyl-terminated butadiene–acrylonitrile rubber being applied to the toughening of epoxy resins[2,9,10], while in later studies alternative end groups were explored such as mercaptan[2,11], amine[12], hydroxyl[2], epoxy[2] and phenol[2]. Attention then focused on alternative rubbers such as carboxyl-terminated polyisobutylene[13], polysiloxanes[14] and n-butyl acrylate rubbers[15]. Later studies utilized n-butyl acrylate–acrylic acid copolymer blends[16,17] and fluoroelastomers[18]. In the present study we report on the application of several types of linear polysulphide rubber as potential toughening agents, all of the general formula:

$$HS\text{-}(C_2H_4OCH_2OC_2H_4SS)_nC_2H_4OCH_2OC_2H_4SH$$

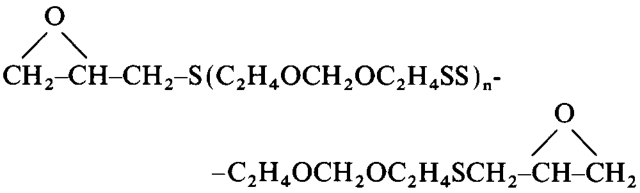
The epoxy resin used was the diglycidyl ether of bisphenol A (DGEBA). The study covered the physical microstructure of the toughened epoxide and its mechanical and dynamic-mechanical properties.

EXPERIMENTAL

Materials

DGEBA was supplied by Shell Chemicals as Epikote 828. The polysulphide polymers, some of which contain branching introduced through the use of the trifunctional monomer 1,2,3-trichloropropane, were supplied by Morton International. Details are given in *Table 1*.

Epoxy-terminated polysulphides were also supplied by Morton International (see *Table 2*):



$$\overbrace{CH_2\text{-}CH}^{O}\text{-}CH_2\text{-}S(C_2H_4OCH_2OC_2H_4SS)_n\text{-}C_2H_4OCH_2OC_2H_4SCH_2\text{-}\overbrace{CH\text{-}CH_2}^{O}$$

The curatives used were as follows: 1,2-diaminoethane (BDH Ltd), 1-(2-aminoethyl)piperazine (AEP, Aldrich Ltd) and triethylene tetramine (BDH Ltd).

Dynamic mechanical thermal analysis (d.m.t.a.)

D.m.t.a. was carried out on a Polymer Laboratories DMTA model Mk II operated in single cantilever mode while data were computer analysed using d.m.t.a. control software (version 1.2). Samples for d.m.t.a. were prepared by casting the mixed system in steel moulds coated with a polytetrafluoroethylene-based release agent, Rocol MRS (Rocol Ltd). Samples were then cut to size using a small circular saw. The normal sample size was ~40 mm × 12 mm × 3 mm. These samples were analysed in the bending mode at a frequency of 1 Hz with a nominal peak-to-peak displacement of 64 μm. A temperature range of 300°C was used in all cases with a ramp rate of 3°C min^{-1}. The relative heights of peaks were measured from the abscissa, whereas the width was recorded at the base of the peak, making due allowance for the background.

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Table 1 Polysulphide polymers

Trade name	RMM	SH content (%)	Branching agent (%)	*n*
LP2C	4000	1.5–2.0	2	23
LP541	4000	1.5–2.0	0	23
LP255	4000	1.5–2.0	4	23
LP70	1000	13–16	40	6

Table 2 Epoxy-terminated polysulphides

Trade name	RMM	Epoxide equivalent ($g\,mol^{-1}$)	Branching agent (%)	*n*
ELP3	1000	700–800	2	6
ELP2	4000	900	2	23

^{13}C n.m.r. spectroscopy

A Bruker 400 MHz n.m.r. spectrometer (WH400) was used for most experiments. The samples were run without the use of an internal standard. Samples were shimmed on a D_2O sample of length equal to the polymer system. A sample of Epikote 828 of the same length was then used for re-tuning. For the initial runs on fully cured systems, the samples were mixed, degassed under vacuum, placed in the n.m.r. tube, degassed again and then allowed to cure in an oil bath at room temperature (nominally 23°C). For the *in situ* cure experiments, spectra were collected at 303 K, from 5 min after the sample was mixed.

A Bruker model MSL 360 n.m.r. spectrometer equipped with cross-polarization/magic angle spinning (CP/MAS) was used to study the degree of phase separation in the cured systems. The sample was presented in a fine powder form which was produced using a fine metal file (previously cleaned in methylene chloride) by rubbing the cured sample against the file. A magnet was then passed through the powder to remove any metallic fragments emanating from the file. Tetramethylsilane was used as the reference in these experiments.

Transmission electron microscopy (TEM)

The initial samples for TEM were prepared by mixing the systems and degassing in a vacuum oven at 40°C for 6 min before pouring into a capsule. The samples were allowed to cure at 23°C for several days before being removed from the capsules and postcured, at 120°C for 15 min. The samples were then cut using a diamond knife microtome and TEM was used to examine thin films of the samples. Photographs were taken to measure the size and distribution of the discrete rubber particles. A group of 20 particles lying within a grid were taken for measurement. Certain samples were analysed by Loughborough Consultants; these were prepared as before but cast as 3 mm thick sheets in steel moulds sprayed with Rocol MRS, rather than using capsules. Some of the samples were cured at 70°C, being placed in an oven at 70°C as soon as the liquid had been poured into the mould. These samples were cut using the macro-mode of the microtome giving sections 0.5 μm thick. The micrographs were taken using a JEOL JEM 100 CX microscope. As the samples were found to be very beam-sensitive, the microscope was used in scanning transmission electron microscopy (STEM) mode which subjects the sample to less irradiation than normal TEM.

Tensile testing

Tensile dumb-bells were prepared according to BS 2782 (part 3: method 320A: 1976). The systems were mixed, degassed for 6 min in a vacuum oven at 40°C and then poured into a steel impression mould sprayed with Rocol MRS. The samples were then allowed to cure either at 70°C for 30 min or at room temperature followed by a 15 min postcure at 120°C. The dumb-bells were then left for a further day before being tested on a J. J. Lloyd model M30K tensile testing machine using a 30 kN load cell. The speed of test used was 5 mm min^{-1} and the gauge length used was 25 mm. Elongation was measured using a non-contact i.r. extensometer. Results are expressed in MPa, this being calculated by dividing the load (in N), at break or yield, by the cross-sectional area of the dumb-bell centrepiece. The quoted result is the average of the results from six dumb-bells.

Impact testing

A mould for the impact specimens was made from Silastic J (Dow Corning) silicone rubber using highly polished brass templates. Samples were then mixed, degassed for 6 min in a vacuum oven at 40°C, poured into a mould and allowed to cure; the cure conditions refer to the two regimes given for tensile testing. These were then tested on a bench-top Hounsfield plastic impact machine (model H.20). The quoted result is the average of determinations on 10 samples which are not notched.

RESULTS

^{13}C n.m.r. spectra

Line positions. To create a data base to work from in the n.m.r. study, the spectra listed in *Table 3* were obtained initially. The *in situ* cure studies were carried out on systems 5 and 6. System 6 was chosen as it was a two-phase system according to analysis of d.m.t.a. traces of the fully cured system, while system 5 represents a suitable comparison. In the initial stages of cure, most of the resonances of the constituents are visible (*Figure 1*). The ^{13}C chemical shift (δ) values in ppm of DGEBA were found to be as follows: 156, 143, 127, 113 (aromatic); 68 ($-O-\underline{C}H_2-\overset{/}{C}H-$); 49 ($-CH_2-\overset{\overset{O}{\wedge}}{\underline{C}H}-CH_2$); 44 ($-\overset{\overset{O}{\wedge}}{CH-\underline{C}H_2}$), 41 (quaternary C) in agreement with reference 19. Assignments of the major resonances of LP2C are as follows (in ppm): 95 ($-O-\underline{C}H_2-O-$); 66 ($-O-\underline{C}H_2-CH_2-$); 39 ($-S-\underline{C}H_2-CH_2-$); 25

Table 3 Spectra obtained to build up a data base

System	Formulation (g)	State
1 Epikote 828	–	Liquid
2 LP2C	–	Liquid
3 ELP2	–	Liquid
4 EDA	–	Liquid
5 Epikote 828/EDA	100:8	Cured
6 Epikote 828/LP2C/EDA	100:20:8	Cured
7 Epikote 828/ELP2/EDA	100:20:8	Cured
8 LP2C/CaO_2/H_2O	100:9:5	Cured
9 Epikote 828/LP2C/AEP	100:20:22	Cured
10 Epikote 828/LP2C/TETA	100:20:10	Cured

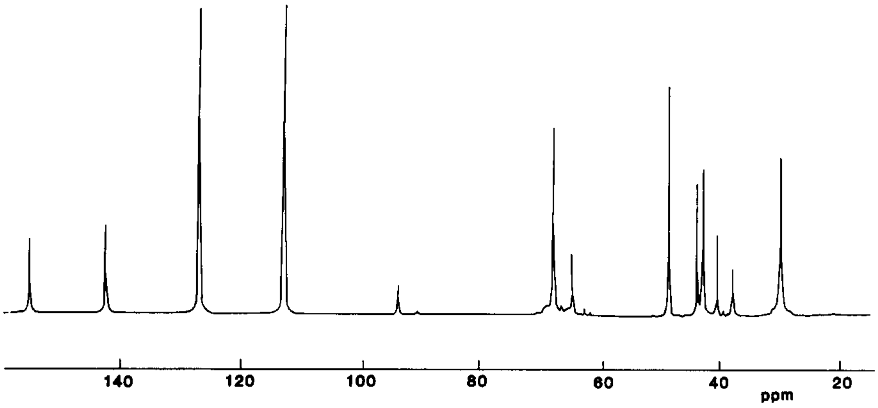

Figure 1 ^{13}C n.m.r. spectrum of a DGEBA/LP2C/EDA mixture showing characteristic resonances of all components

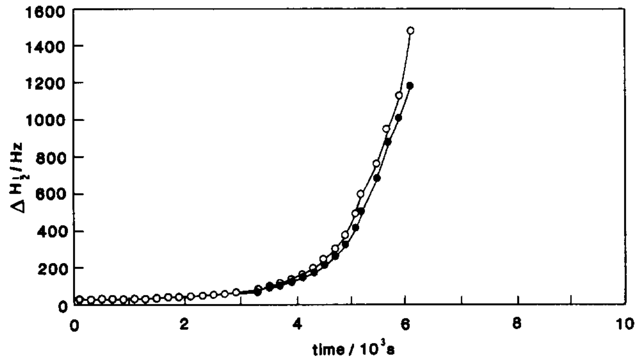

Figure 2 ^{13}C n.m.r. spectral linewidths at 113 (●) and 127 (○) ppm during EDA cure of unmodified epoxy (DGEBA) resin

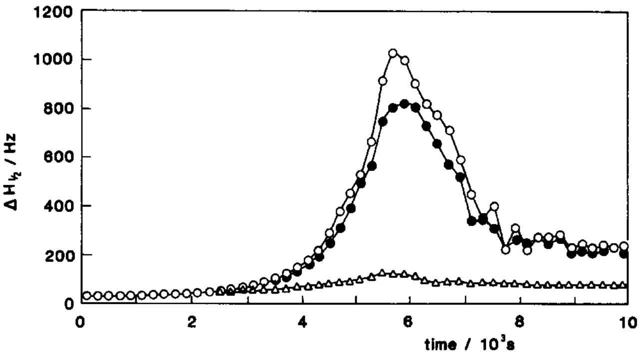

Figure 3 ^{13}C n.m.r. linewidth variations at 94 ppm (△) due to LP and 113 (●) and 127 (○) ppm due to DGEBA during EDA cure of a polysulphide-modified epoxy resin

$(-CH_2-\underline{C}H_2-SH)$. EDA is a simple symmetrical molecule with a single resonance at 45 ppm.

Linewidths. The widths at half height ($\Delta H_{\frac{1}{2}}$) were measured for selected characteristic lines in the spectra, which were determined as the cure progressed. For the unmodified epoxy system these lines were at 113 and 127 ppm. For the epoxy/linear polysulphide (LP) system the lines chosen were at 94, 113 and 127 ppm. EDA was used as curative in all these experiments.

The $\Delta H_{\frac{1}{2}}$ values were plotted against time for both systems. The unmodified epoxy systems gave a graph (*Figure 2*) where $\Delta H_{\frac{1}{2}}$ simply increased until it was no longer possible to measure it accurately due to severe broadening. The epoxy/LP system, however, gave very different behaviour (*Figure 3*): thus $\Delta H_{\frac{1}{2}}$ increased up to ~6000 s and then decreased to a plateau value. This final decrease in $\Delta H_{\frac{1}{2}}$ was accompanied by a change in the line shape, as can be seen from *Figure 4* ($t = 100$, 5122, 5925 and 9139 s, respectively). (The later spectra show lines of a more composite nature, particularly in the case of the epoxy resin. The most likely explanation for this behaviour is the presence of nuclei in two different environments.) The maximum of the peak in the epoxy/LP system occurs at ~6000 s. In the unmodified epoxy system the point at which the epoxy lines become too broad to measure is also at $t =$ ~6000 s. This suggests that up to this point the same process is being monitored in both systems, that is the polymerization of the bulk of the epoxy. After this point the lines due to the nuclei in the bulk epoxy broaden out and eventually merge into the background. In the epoxy/LP system this allows the less intense narrower lines to be seen. These lines are thought to be associated with the small fraction of epoxy resin trapped in the rubbery phase of the system, which has greater mobility and hence produces narrower lines. These narrow lines, although of much lower intensity, can also be seen in the EDA-cured system containing only 10 g phr of LP2C (*Figure 5*) and again in materials containing 20 g phr of LP2C but cured with AEP or TETA (*Figure 6*).

CP/MAS ^{13}C n.m.r. spectra

Samples of the unmodified epoxy resin and the LP2C/epoxy resin systems were studied using CP/MAS n.m.r. The ^{13}C spectra for both samples contained the same number of resonances, as can be seen by comparing *Figures 7* and *8*. The major resonances all correspond to those for the epoxy resin except for four resonances above 170 ppm. However, the latter shift as the spinning speed is increased, and are considered due to spinning side bands. No resonances corresponding to the LP2C could be seen in the LP2C/epoxy resin spectrum, suggesting that all the rubber had phase-separated and none had entered into the epoxy matrix. The rubber resonances would, however, occur between 0 ppm and 100 ppm where there is a broad and complex epoxy resin resonance. This broad band would probably obscure any rubber resonances present unless they were of considerable intensity: accordingly these measurements meant that no definitive conclusion could be drawn except that any levels of LP2C in the rigid epoxy phase are certainly low.

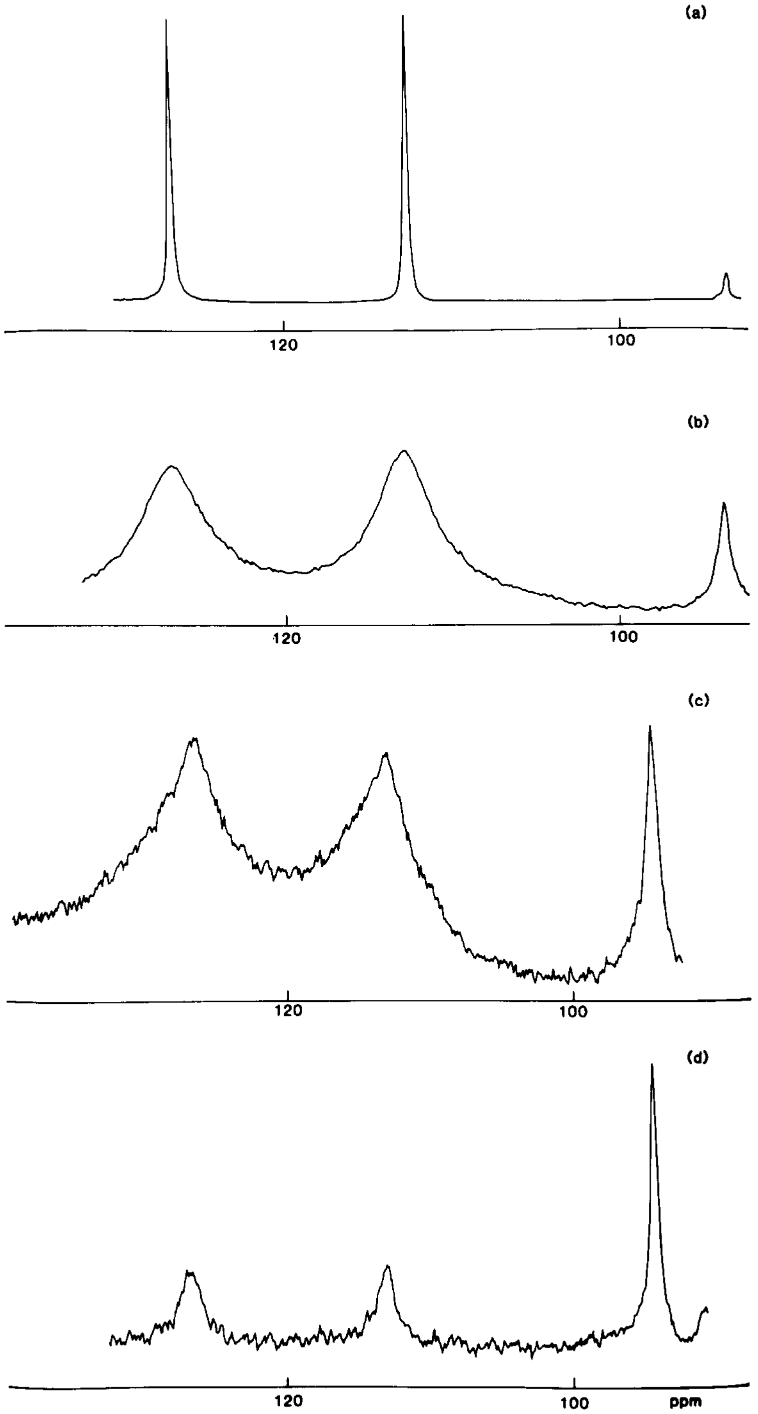

Figure 4 ^{13}C n.m.r. part-spectra during cure of a DGEBA/LP2C/EDA system: (a) $t = 100$ s; (b) $t = 5122$ s; (c) $t = 5925$ s; (d) $t = 9139$ s

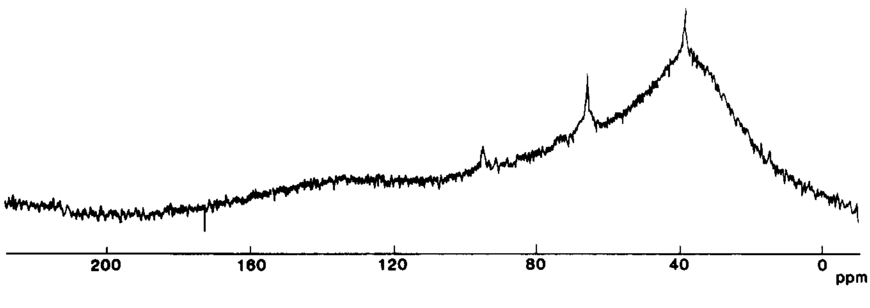

Figure 5 ^{13}C n.m.r. spectrum of a cured sample of DGEBA/LP2C/EDA containing 10 g phr of LP2C

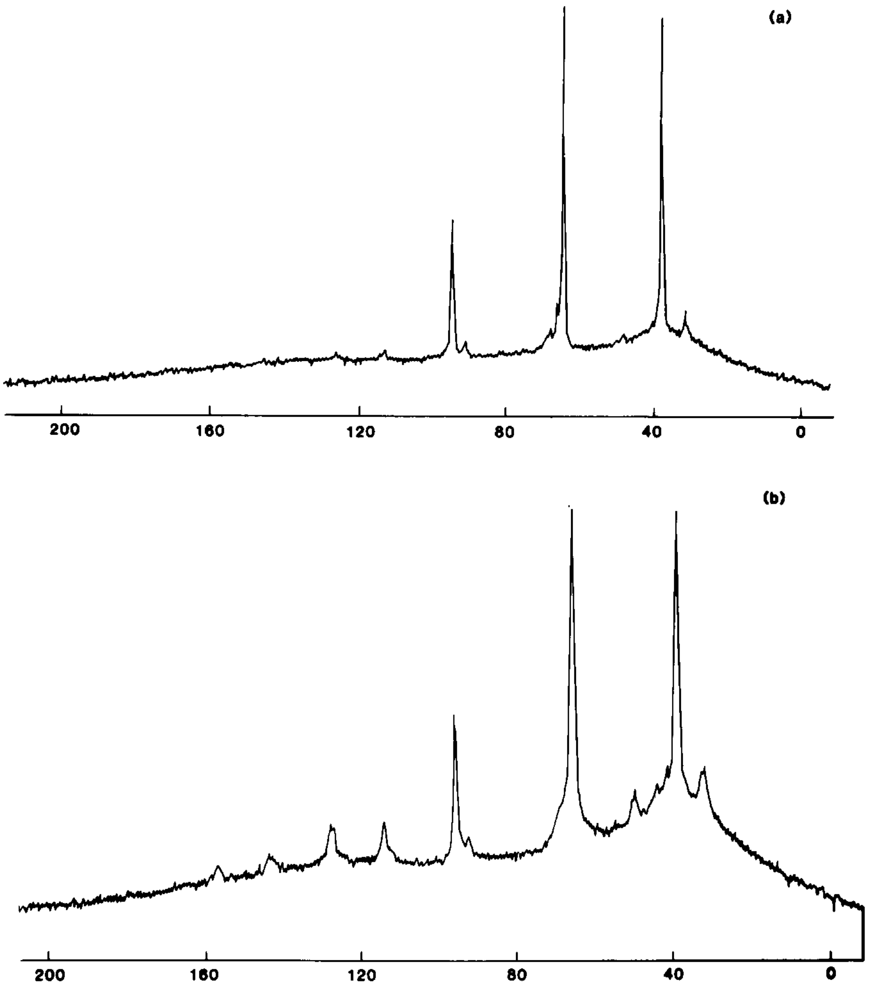

Figure 6 ^{13}C n.m.r. spectra of cured DGEBA/LP2C systems: (a) curative AEP; (b) curative TETA

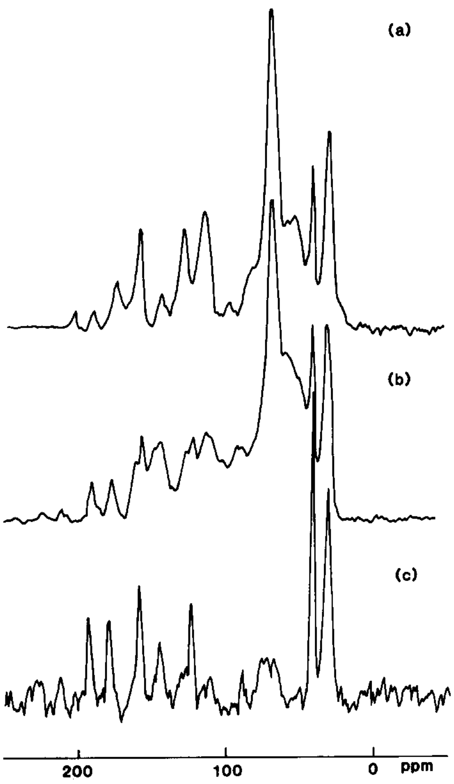

Figure 7 ^{13}C CP/MAS spectrum of cured, powdered DGEBA (EDA curative): (a) spinning speed = 4.05 kHz; (b) spinning speed = 3.05 kHz; (c) spinning speed = 3.05 kHz NQS

D.m.t.a. studies

This technique has been widely used in investigations of toughened polymers[20–22]. The d.m.t.a. results for cures carried out at room temperature are summarized in *Table 4*. These data are determined from the tan δ trace and are for systems cured for 14 days at room temperature (23°C/50% relative humidity). In this work the tan δ peak (α peak) maximum temperature is taken as the glass transition temperature (T_g).

The unmodified epoxy system shows two high temperature peaks (*Figure 9a*). One of these peaks is the α' peak associated with unreacted epoxy groups. This was confirmed by postcuring the system and then repeating the d.m.t.a. analysis as summarized in the data given in *Table 5*. Postcuring removed the second peak as can be seen from *Figure 9b*. The minor transition visible at ~ -50°C in *Figure 9a* is the epoxy β transition[21]. The peak at ~ 50°C in *Figure 9b* is regarded as a residue of the strong, corresponding transition in *Figure 9a*.

The polysulphide rubbers listed in *Tables 1* and *2* were added at two concentrations, namely 10 g and 20 g per 100 g of epoxy resin (phr). At the 10 g phr level no second phase was apparent in any of the systems. (A shoulder was present on the epoxy α peak, again associated with unreacted epoxy groups. This was confirmed by postcuring as a result of which the shoulder vanished.) At the 20 g phr level all the systems, except those containing LP70 and ELP3, showed a second phase (*Figure 10a*). These systems also exhibited a shoulder on the epoxy α

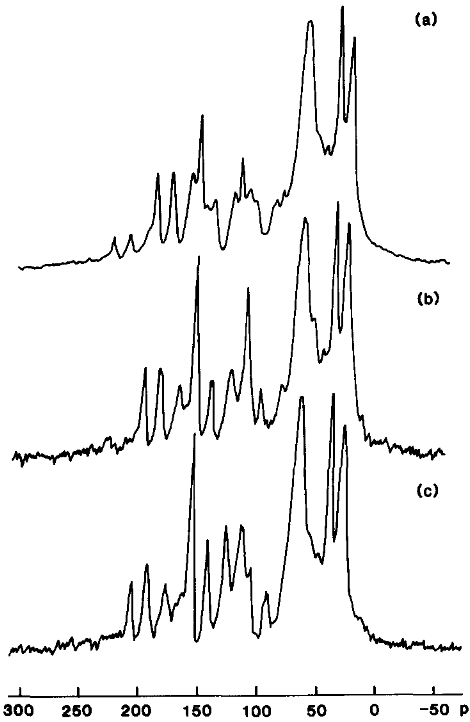

Figure 8 ^{13}C CP/MAS spectrum of cured, powdered LP2C-modified DGEBA (EDA curative): (a) spinning speed = 3.2 kHz; (b) spinning speed = 3.8 kHz; (c) spinning speed = 4.5 kHz

Table 4 D.m.t.a. results (room temperature cure)

System	Tan δ peak temp. (°C) Epoxy	Tan δ peak temp. (°C) Rubber	Relative height of epoxy α peak	Width of epoxy α peak (°C)
DGEBA/EDA (100 g: 8 g)	68; 125	–	0.4	–[a]
DGEBA/rubber/EDA (100 g: 10 g: 8 g)				
LP2C	70.5	–	1.17	87
LP541	69.5		1.25	89
LP255	67	–	1.3	86
LP70	66	–	1.39	83
ELP2	69	–	1.38	97
ELP3	68	–	1.35	87
DGEBA/rubber/EDA (100 g: 20 g: 8 g)				
LP2C	67.5	−39	1.32	84
LP541	66.5	−41	1.83	89
LP255	64.5	–	1.15	73
LP70	61.5	–	1.34	65
ELP2	66	−44	1.58	90
ELP3	66.5	–	1.27	77

[a] Peaks merged

peak. On postcuring the systems (*Table 5*) the shoulder was removed and the position of the α peak moved to higher temperature (*Figure 10b*); the height and width of the α peak were also reduced. All these various factors indicate a more tightly bound matrix and thus a higher degree of cure. As a result of postcuring, the rubber α peak remained virtually unaffected by the postcure, indicating no further epoxy–polysulphide interaction.

The system modified with 20 g phr of LP70 shows neither a rubber α peak nor a shoulder on the epoxy α peak. LP70 is a highly functionalized rubber with 40% branching agent added during manufacture. This high functionality makes the rubber too compatible to phase separate[23].

Although ELP3 has an RMM of only ~1000 which would not normally favour phase separation, it has a very low reactivity towards amine curatives. This latter factor would be expected to favour phase separation; however, with this level of rubber and for this particular curative, no phase separation is apparent.

Our results show that it is essential to postcure the EDA systems to achieve a fully cured product. EDA is

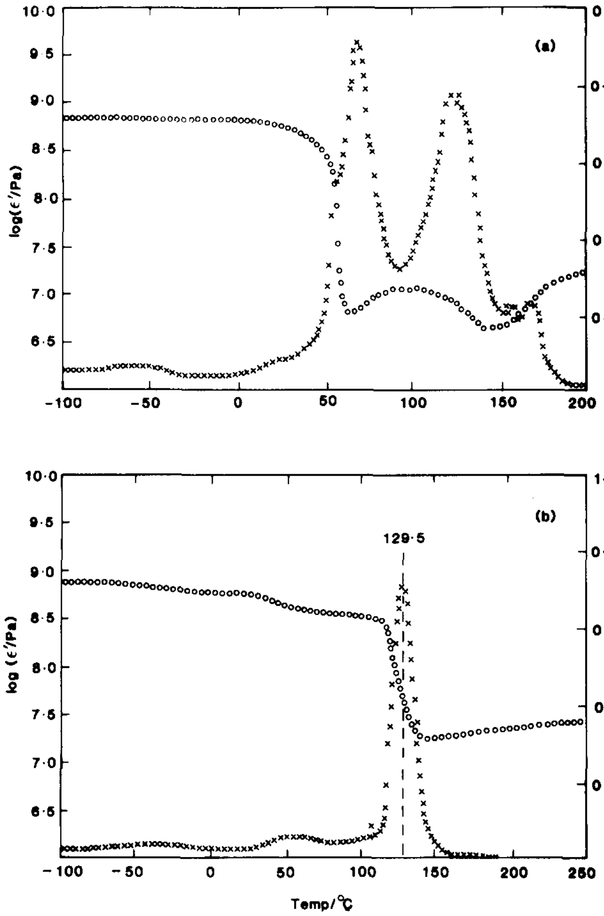

Figure 9 (a) D.m.t.a. trace of a DGEBA/EDA system cured at room temperature and (b) followed by postcuring at 120°C

Table 5 D.m.t.a. results (postcured systems)

System	Tan δ peak temp. (°C) Epoxy	Tan δ peak temp. (°C) Rubber	Relative height of epoxy α peak	Width of epoxy α peak (°C)
DGEBA/EDA (100 g: 8 g)	129.5	–	0.71	43
DGEBA/rubber/EDA (100 g: 20 g: 8 g)				
LP2C	116.5	−39.5	0.59	69
LP541	117	−38.5	0.66	61
LP255	114.5	−36.5	0.61	72
LP70	96	–	0.81	58
ELP2	116.5	−43	0.65	69
ELP3	95	–	0.73	70

All samples were allowed to cure at 23°C and 50% relative humidity for at least 24 h before postcuring for 15 min at 120°C

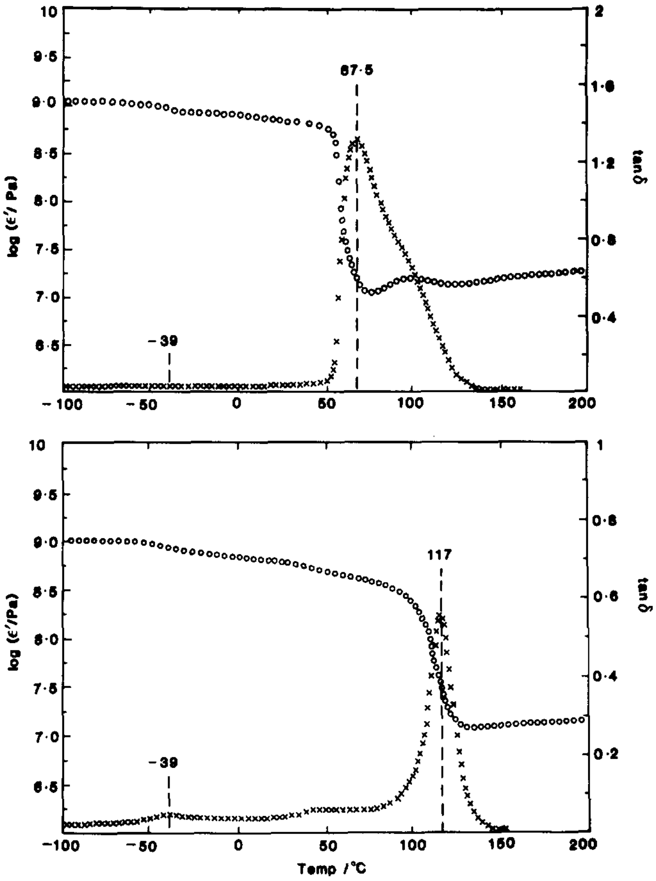

Figure 10 (a) D.m.t.a. trace of an LP2C-modified DGEBA (EDA curative) cured at room temperature and (b) followed by postcuring at 120°C

Table 6 D.m.t.a. results (effect of different curative and cure schedules)

System	Tan δ peak temp. (°C) Epoxy	Tan δ peak temp. (°C) Rubber	Relative height of epoxy α peak	Width of epoxy α peak (°C)
DGEBA/EDA (100 g: 8 g)				
Room temp.	68; 125	–	0.4	–[a]
Room temp. + 15 min at 120°C	129.5	–	0.71	43
30 min at 70°C	112	–	0.9	69
DGEBA/LP2C/EDA (100 g: 20 g: 8 g)				
Room temp.	67.5	−39	1.32	84
Room temp. + 15 min at 120°C	117	−37	0.59	61
30 min at 70°C	100.5	−41.5	0.81	75
DGEBA/AEP (100 g: 22 g)				
Room temp.	–[b]	–[b]		
Room temp. + 15 min at 120°C	116.5	–	1.06	54
30 min at 70°C	107	–	1.38	62
DGEBA/LP2C/AEP (100 g: 20 g: 22 g)				
Room temp.	66	−47	1.84	75
Room temp. + 15 min at 120°C	98.5	−47	1.06	61
30 min at 70°C	91.5	−47	1.19	70
DGEBA/LP2C/TETA (100 g: 20 g: 10 g)				
Room temp.	65.5	−35.5	1.28	69

[a] Peaks merged
[b] Too brittle to measure

a primary amine, where the first hydrogen of each amine group reacts quickly, but the second hydrogen can take much longer to react due to steric hindrance[24]. The postcuring temperature chosen is close to the T_g of the materials. At this temperature there should be sufficient mobility within the matrix for the curing reaction to go to completion. AEP and TETA were also used as curatives. In the room temperature cured systems modified with 20 g phr of LP2C, both curatives produced similar results to EDA (*Table 6*), a rubber α peak being clearly visible.

AEP and EDA were also used in a brief study of the effect of the cure schedule on phase separation. The unmodified epoxy resin and the system modified with 20 g phr of LP2C were assessed. The three cure schedules used were room temperature, room temperature + 15 min at 120°C, and 30 min at 70°C. A rubber α peak was found in the LP2C-modified system for each of these cure schedules. However, the degree of cure could be seen to vary with the different cure schedules, as judged from position, height and width of the epoxy α peak.

The highest degree of cure was seen in the systems postcured at 120°C, followed by the systems cured at 70°C, with the room temperature cured systems showing the lowest degree of cure.

TEM studies

Using TEM and STEM, clear evidence for rubber particles was obtained in a number of the materials (*Figures 11–13*). In each case the rubber was present as a uniform dispersion of submicrometre particles, with the smallest being found in the materials cured initially at room temperature followed by postcure at 120°C. In these systems the particle size ranged from 0.06 to 0.14 μm in diameter (*Table 7*). Particles were also found in both the EDA- and AEP-cured systems modified with 10 and 20 g phr of ELP2, the largest particles being present in the system containing 20 g phr of ELP2. With the LP2C-modified systems, particles were found in both the EDA- and AEP-cured systems containing 20 g phr of LP2C. The equivalent EDA system could not be analysed as it was impossible to cut a suitable section for TEM examination.

When the materials were cured at 70°C, the particle

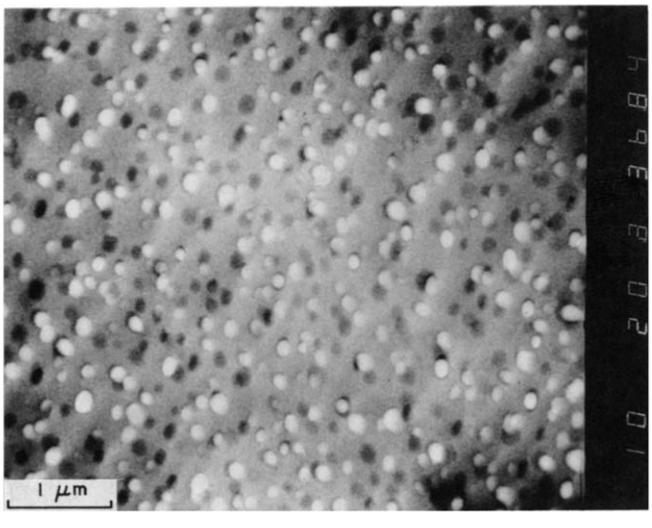

Figure 11 STEM micrograph of an LP2C-modified DGEBA system cured with AEP at 70°C

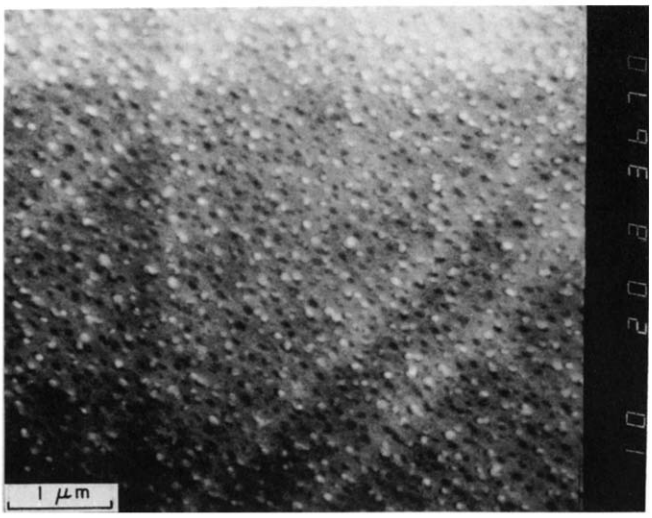

Figure 12 STEM micrograph of an ELP2-modified DGEBA system cured with EDA initially at room temperature and then postcured at 120°C

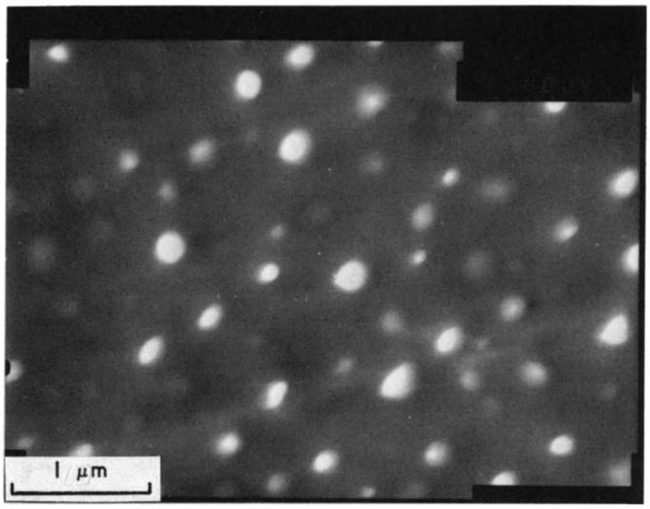

Figure 13 TEM micrograph of an LP2C-modified DGEBA system cured with EDA at room temperature

sizes ranged from 0.13 to 0.33 μm in diameter (*Table 8*). Again the larger particles were found in the system modified with 20 g phr of ELP2. All the systems containing 20 g phr of rubber have particles present. Only one of the systems modified with 10 g phr of rubber, i.e. the EDA-cured system with 10 g phr of ELP2, contained discernible particles. The formation of these rubber particles appears to be analogous to crystal growth in semicrystalline polymers[22]. Thus, initial nucleation is followed by the growth of the particles by mass transfer of the rubber through the fluid phase. This process is controlled by a number of competing factors[25,26]. Lower temperatures produce a more incompatible mixture and a higher nucleation rate. However, the fluid phase is more viscous and thus mass transfer is hindered, leading to smaller particles. At higher temperatures the rubber and resin are more compatible but[22,27] the fluid phase is also less viscous. This allows mass transfer to occur more readily, producing larger particles, thus explaining why larger particles are found in those systems cured at a higher temperature[28,29]. Even so, all the particles found under all conditions are very small, for which the most probable explanation is the high compatibility between the polysulphide rubber and the epoxy resin in the systems under investigation[2,30].

Physical testing

Tensile strength. The unmodified epoxy resin and systems modified with 10 g and 20 g phr of LP2C or ELP2 were evaluated. Both EDA and AEP were used as curatives and two cure schedules were employed: room temperature (23°C) + 15 min postcure at 120°C; and 30 min at 70°C. The tensile strength results are shown in *Tables 9* and *10*.

The unmodified epoxy systems cured at room temperature with a 120°C postcure both failed in a brittle manner, showing no yield point and low elongations to break. The four EDA-cured polysulphide-modified materials produced by this cure schedule all showed improved properties in comparison to the unmodified epoxy control. These materials failed in a ductile manner,

Table 7 Average rubber particle size as determined by TEM and STEM (cure = room temperature + 15 min at 120°C)

System	Particle size (μm)
DGEBA/EDA (100 g: 8 g)	No particles apparent[a]
DGEBA/LP2C/EDA	
(100 g: 10 g: 8 g)	Could not be analysed[b]
(100 g: 20 g: 8 g)	0.062 ± 0.004[a]
DGEBA/ELP2/EDA	
(100 g: 10 g: 8 g)	0.060 ± 0.005[b]
(100 g: 20 g: 8 g)	0.17 ± 0.02[a]
DGEBA/AEP (100 g: 22 g)	No particles apparent[b]
DGEBA/LP2C/AEP	
(100 g: 10 g: 22 g)	No particles apparent[b]
(100 g: 20 g: 22 g)	0.060 ± 0.007[b]
DGEBA/ELP2/AEP	
(100 g: 10 g: 22 g)	0.07 ± 0.01[b]
(100 g: 20 g: 22 g)	0.14 ± 0.02[b]

[a] As determined by TEM
[b] As determined by STEM

Table 8 Average rubber particle size as determined by STEM (cure = 30 min at 70°C)

System	Particle size (μm)
DGEBA/EDA (100 g: 8 g)	No particles apparent
DGEBA/LP2C/EDA	
(100 g: 10 g: 8 g)	No particles apparent
(100 g: 20 g: 8 g)	0.17 ± 0.02
DGEBA/ELP2/EDA	
(100 g: 10 g: 8 g)	0.13 ± 0.01
(100 g: 20 g: 8 g)	0.33 ± 0.05
DGEBA/AEP (100 g: 22 g)	No particles apparent
DGEBA/LP2C/AEP	
(100 g: 10 g: 22 g)	No particles apparent
(100 g: 20 g: 22 g)	0.16 ± 0.03
DGEBA/ELP2/AEP	
(100 g: 10 g: 22 g)	No particles apparent
(100 g: 20 g: 22 g)	0.28 ± 0.03

Table 9 Tensile testing results (cure = room temperature + 15 min at 120°C)

System	Tensile strength (MPa)		Elongation (mm)
	at yield stress	at break point	
DGEBA/EDA			
(100 g: 8 g)	–[a]	35.6 ± 3.1	0.1 ± 0.1
DGEBA/LP2C/EDA			
(100 g: 10 g: 8 g)	72.5 ± 1.3	63.4 ± 0.7	1.2 ± 0.5
(100 g: 20 g: 8 g)	57.6 ± 2.2	45.9 ± 2.1	3.3 ± 0.3
DGEBA/ELP2/EDA			
(100 g: 10 g: 8 g)	66.8 ± 1.4	52.9 ± 9.1	1.1 ± 0.4
(100 g: 20 g: 8 g)	58.1 ± 0.8	52.3 ± 3.7	1.5 ± 0.4
DGEBA/AEP			
(100 g: 22 g)	–[a]	59.1 ± 8	0.9 ± 0.2
DGEBA/LP2C/AEP			
(100 g: 10 g: 22 g)	63.3 ± 8.7	51.2 ± 7.7	1.6 ± 0.1
(100 g: 20 g: 22 g)	–[a]	45.7 ± 6.0	0.6 ± 0.1
DGEBA/ELP2/AEP			
(100 g: 10 g: 22 g)	65.3 ± 2.6	45.9 ± 2.1	0.7 ± 0.1

[a] No yield

Table 10 Tensile testing results (cure = 30 min at 70°C)

System	Tensile strength (MPa)		Elongation (mm)
	at yield stress	at break point	
DGEBA/EDA			
(100 g: 8 g)	–[a]	37.2 ± 4.1	0.4 ± 0.1
DGEBA/LP2C/EDA			
(100 g: 10 g: 8 g)	70.0 ± 0.4	63.4 ± 4.1	1.1 ± 0.7
(100 g: 20 g: 8 g)	57.4 ± 2.1	48.3 ± 6.2	1.6 ± 0.2
DGEBA/ELP2/EDA			
(100 g: 10 g: 8 g)	–[a]	56.6 ± 6.4	0.8 ± 0.3
(100 g: 20 g: 8 g)	–[b]	–[b]	
DGEBA/AEP			
(100 g: 22 g)	–[a]	51.2 ± 6.4	0.6 ± 0.2
DGEBA/LP2C/AEP			
(100 g: 10 g: 22 g)	68.1 ± 0.9	60.9 ± 2.6	1.2 ± 0.4
(100 g: 20 g: 22 g)	62.4 ± 6.5	46.6 ± 6.6	1.0 ± 0.5
DGEBA/ELP2/AEP			
(100 g: 10 g: 22 g)	–[a]	35.2 ± 6.3	0.6 ± 0.1
(100 g: 20 g: 22 g)	–[a]	55.6 ± 1.2	0.6 ± 0.1

[a] No yield
[b] All samples broke out of gauge

giving a yield point before breaking at a load and elongation greater than that for the epoxy control (*Table 9*).

It is unusual when modifying epoxy systems to observe an increase in both load and elongation at break. Normally an increase in one property would lead to a decrease in the other. This suggests that the unmodified epoxy/EDA system contained significant internal stresses. Such a material would tend to fail at loads and elongations lower than would normally be expected, the internal stresses acting as mechanically weak spots. Addition of the rubber reduces the internal stress with the resulting materials failing at both higher load and greater elongation. If the rubber was acting purely as a flexibilizing agent then the load at break would be expected to decrease slightly, while the elongation would increase.

The polysulphide-modified systems cured with AEP at room temperature with a 120°C postcure gave somewhat different results from their EDA counterparts. The materials containing 10 g phr of polysulphide rubber failed in a ductile manner, showing a yield point, although the load at break for these systems was less than for the epoxy control. However, the materials containing 20 g phr of polysulphide failed, surprisingly, in a brittle manner, breaking at a load and elongation less than the epoxy control.

With the materials cured at 70°C (*Table 10*) both the unmodified epoxy controls failed in a brittle manner. The EDA-cured systems containing LP2C both failed in a ductile manner, giving a yield point, before breaking at a load and elongation greater than that for the epoxy control. Once again this indicates that the epoxy/EDA system contained a significant degree of internal stress. The EDA-cured system containing 10 g phr of ELP2 failed in a brittle manner but with a load greater than the epoxy control.

The AEP system cured at 70°C gave similar results. The LP2C-modified systems failed in a ductile manner, whilst the ELP2-modified systems failed in a brittle manner.

Impact testing. The same systems that were used for the tensile strength determinations were submitted to impact testing. The results are shown in *Tables 11* and *12*. With both cure schedules, the AEP-cured systems had higher fracture energy values than the EDA-cured systems. For the EDA systems, cured by either schedule, the fracture energy for the unmodified epoxy was lower than for the polysulphide-modified materials (with one exception). With the AEP-cured systems the unmodified epoxy resins also had lower fracture energies than the polysulphide-modified materials (again, with one exception). However the fracture energies for the EDA-cured systems were similar for the two cure schedules. The AEP-cured materials gave significantly different values. The fracture energies for the materials produced using the room temperature + 120°C postcure schedules

Table 11 Impact testing results (cure = room temperature + 15 min at 120°C)

System	Impact fracture energy (kJ m^{-2})
DGEBA/EDA	
(100 g: 8 g)	1.59 ± 0.12
DGEBA/LP2C/EDA	
(100 g: 10 g: 8 g)	1.86 ± 0.3
(100 g: 20 g: 8 g)	2.31 ± 0.35
DGEBA/ELP2/EDA	
(100 g: 10 g: 8 g)	1.81 ± 0.32
(100 g: 20 g: 8 g)	2.13 ± 0.3
DGEBA/AEP	
(100 g: 22 g)	22.58 ± 7.69
DGEBA/LP2C/AEP	
(100 g: 10 g: 22 g)	15.14 ± 4.71
(100 g: 20 g: 22 g)	23.82 ± 6.45
DGEBA/ELP2/AEP	
(100 g: 10 g: 22 g)	25.06 ± 8.19
(100 g: 20 g: 22 g)	32.01 ± 5.46

Table 12 Impact testing results (cure = 30 min at 70°C)

System	Impact fracture energy (kJ m^{-2})
DGEBA/EDA	
(100 g: 8 g)	2.21 ± 0.27
DGEBA/LP2C/EDA	
(100 g: 10 g: 8 g)	1.56 ± 0.27
(100 g: 20 g: 8 g)	2.93 ± 0.67
DGEBA/ELP2/EDA	
(100 g: 10 g: 8 g)	1.86 ± 0.27
(100 g: 20 g: 8 g)	2.18 ± 0.25
DGEBA/AEP	
(100 g: 22 g)	6.45 ± 1.74
DGEBA/LP2C/AEP	
(100 g: 10 g: 22 g)	9.18 ± 1.74
(100 g: 20 g: 22 g)	8.19 ± 2.23
DGEBA/ELP2/AEP	
(100 g: 10 g: 22 g)	11.91 ± 1.99
(100 g: 20 g: 22 g)	24.57 ± 7.94

were more than double those obtained for the materials cured at 70°C.

DISCUSSION

Existence of a discrete rubber phase

The ^{13}C n.m.r. spectra of fully cured epoxy samples containing polysulphide polymers and prepared using a variety of curatives (*Figures 5–7*) indicate the presence of a mobile (i.e. liquid or rubber) phase, as indicated by narrowing of the resonances due to LP2C carbon atoms, against a background of a broad resonance due to the carbon atoms of DGEBA. Assignments are given in the Results section. Minor, narrow line resonances due to DGEBA were apparent in all spectra, suggesting some entrainment of the epoxy into the rubber-like regions associated with LP2C.

The time dependence of the spectra during curing featured in *Figure 4* clearly illustrate the selective broadening of the epoxy resonances as cure proceeds, together with the development of some asymmetry, most clearly visible in the high-field epoxy resonance in *Figure 4c*. Measurements of the linewidth parameter $\Delta H_{\frac{1}{2}}$ of the LP2C-modified system summarized in *Figure 3* exhibit several features, namely:

1. a monotonic increase in $\Delta H_{\frac{1}{2}}$ for the epoxy resonances from ~200 Hz to 1 kHz over 4000–6000 s, closely in parallel with the behaviour of the unmodified epoxy (*Figure 2*);
2. a much smaller increase in $\Delta H_{\frac{1}{2}}$ for the LP2C resonance over the same time-scale, to a maximum of ~100 Hz;
3. as the bulk of the epoxy resonance broadened to become immeasurable, a residual weak resonance remained which gradually *narrowed* as cure continued until a final plateau figure of ~200 Hz was reached, which refers to motion of epoxy entrained within the rubber phase of LP2C.

The rigid character of the bulk epoxy is apparent from the CP/MAS results shown in *Figure 7* which agree well with the spectra recorded in the literature[19,31]. The amounts of LP2C which have entered the rigid phase according to CP/MAS are undetectably low; however, the shift in T_g for the modified system as compared to the control indicate some incorporation of LP2C.

D.m.t.a. data (*Figures 9* and *10*) show the presence of a second, necessarily minor, phase in fully cured polysulphide-modified product provided polysulphide levels exceed 10 g phr and that neither very highly epoxy-reactive polysulphides, such as LP70, nor low mass epoxy compatible polysulphides, such as ELP3, are used.

The most direct evidence for phase separation (rather than the existence of interpenetrating networks) comes from TEM and STEM measurements. The dispersed particles are submicrometre in diameter in contrast to those produced in an earlier study using Ancamide 501, where the diameter was >100 μm.

The results of the materials testing experiments (given in *Tables 13* and *14* compiled with the results on rubber particle sizing) show that addition of relatively low levels of LP2C or ELP2 can lead to improvements in the materials properties of epoxy systems. However, it is not clear whether these improvements are necessarily due to the presence of the rubber as a discrete phase. For example, the values of the tensile strength for all the rubber-modified systems (with one exception) are greater than for the unmodified controls, regardless of whether rubber particles are present or not.

If the impact fracture energy results are considered as a group, it appears that this property is directly related to the level of rubber present in the system. In all cases (except one) the impact fracture energies for the systems containing 20 g phr of rubber are greater than those for systems containing only 10 g phr of rubber, irrespective of whether rubber particles are present or not.

With the AEP-cured materials and those EDA systems cured at room temperature followed by a 120°C postcure, all the rubber-modified systems (with one exception) give higher impact fracture energies than the unmodified controls. This again does not depend on the presence of rubber particles.

The EDA systems cured at 70°C give different results. Only the 20 g phr LP2C-containing system shows a fracture energy greater than the unmodified control. This system features rubber particles, but this is also true for the other rubber-modified systems in this series.

Thus, in summary, it would appear that although additions of LP2C or ELP2 does, in most cases, improve materials properties, these improvements are not necessarily due to the presence of the rubber in the form of a disperse phase of particles.

CONCLUSIONS

The results of this investigation can be summarized as follows.

^{13}C n.m.r., d.m.t.a. and, especially, TEM demonstrate the existence of a discrete rubber phase of submicrometre dimensions in epoxy resins cured in the presence of linear polysulphide rubbers. The ^{13}C n.m.r. linewidth results indicate the presence of a mobile region in all cured products: this is, however, much more apparent at the 20 g phr level than at 10 g phr, although there was clear evidence from the n.m.r. spectrum of a rubber region, albeit at a significantly reduced level. This points to the presence of rubber regions of dimensions below the scope of the TEM apparatus used (i.e. <0.01 μm).

Addition of polysulphide rubbers to the epoxy nearly always leads to improvements in materials properties,

Table 13 Compiled materials results (cure = room temperature + 15 min at 120°C)

System	Particle size (μm)	Tensile strength (MPa)		Elongation at break (mm)	Impact fracture energy (kJ m^{-2})
		at yield stress	at break point		
DGEBA/EDA					
(100 g : 8 g)	–	–	35.6	0.1	1.59
DGEBA/LP2C/EDA					
(100 g : 10 g : 8 g)	–[a]	72.5	63.4	1.2	1.86
(100 g : 20 g : 8 g)	0.06	57.6	45.9	3.3	2.31
DGEBA/ELP2/EDA					
(100 g : 10 g : 8 g)	0.06	66.8	52.9	1.1	1.81
(100 g : 20 g : 8 g)	0.17	58.1	52.3	1.3	2.13
DGEBA/AEP					
(100 g : 22 g)	–	–	59.1	0.9	22.50
DGEBA/LP2C/AEP					
(100 g : 10 g : 22 g)	–	63.3	51.2	1.6	15.41
(100 g : 20 g : 22 g)	0.06	–	45.7	0.6	23.82
DGEBA/ELP2/AEP					
(100 g : 10 g : 22 g)	0.07	65.3	49.2	1.0	25.06
(100 g : 20 g : 22 g)	0.14	–	45.9	0.7	32.01

[a] Sample not mechanically amenable to analysis

Table 14 Compiled materials results (cure = 30 min at 70°C)

System	Particle size (μm)	Tensile strength (MPa)		Elongation at break (mm)	Impact fracture energy (kJ m^{-2})
		at yield stress	at break point		
DGEBA/EDA					
(100 g : 8 g)	–	–	37.2	0.4	2.21
DGEBA/LP2C/EDA					
(100 g : 10 g : 8 g)	–	70	63.4	1.1	1.56
(100 g : 20 g : 8 g)	0.17	57.4	48.3	1.6	2.93
DGEBA/ELP2/EDA					
(100 g : 10 g : 8 g)	0.13	–	56.5	0.8	1.86
(100 g : 20 g : 8 g)	0.33	–[a]	–[a]		2.18
DGEBA/AEP					
(100 g : 22 g)	–	–	51.2	0.6	6.45
DGEBA/LP2C/AEP					
(100 g : 10 g : 22 g)	–	68.1	60.1	1.2	9.18
(100 g : 20 g : 22 g)	0.16	62.4	46.6	1.0	8.19
DGEBA/ELP2/AEP					
(100 g : 10 g : 22 g)	–	–	35.2	0.6	11.91
(100 g : 20 g : 22 g)	0.28	–	55.6	0.6	24.57

[a] All samples broke out of gauge

particularly the development of ductility. However, the improvements also occur in systems not exhibiting disperse particles, that is where the rubber is present either as a solution or as aggregates of submicroscopic dimensions.

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