Phase separation of polysulphide polymers in epoxy adhesives

A. Wilford*, T.C.P. Lee* and T.J. Kemp[†]

(*Morton International/[†]University of Warwick, UK)

Modification of an epoxy system with a conventional polysulphide polymer, while resulting in increased adhesion to difficult-to-bond substrates and improved durability, flexibility and impact resistance, also leads to a reduction in the epoxy glass transition temperature (T_g), thereby lowering the upper service temperature, and low peel strength, limiting the material's application. The reduction in T_g is due to reaction of the flexible, rubbery polysulphide into the epoxy/amine system, decreasing the overall rigidity of the matrix. However, if the polysulphide can be made to phase separate then these limitations may potentially be overcome.

In this work, the type of epoxy resin was kept constant and the effect of modifying the polysulphide polymer (rubber molecular weight, degree of branching, rubber end-group and level of rubber used) was investigated for systems cured with liquid amine or dicyandiamide curative. The new systems are shown to exhibit only a small reduction in the epoxy T_g while having improved peel strength and maintaining the greater lap shear strength expected of a polysulphide-modified material.

Key words: adhesives; epoxy; polysulphide; phase separation; polysulphide backbone; curing agent; glass transition temperature; adhesive properties

Polysulphide polymers are very flexible materials with low glass transition temperature (T_g) and of general formula

$$RS-\!\!\left(C_2H_4OCH_2OC_2H_4S_x\right)_{\!n}\, C_2H_4OCH_2OC_2H_4SR$$

where $x = 2$ and $n = 6$–42 for the liquid polymers depending on molecular weight. For many years only polymers where R = H were available and typical examples of these polymers are shown in Table 1. The polymers are available with molecular weights ranging from 1000–8000 and with different levels of branching imparted by the addition of a trifunctional monomer during manufacture. Typical application areas for the different polymers are given in Table 2.

The interest in the modification of epoxy resins with polysulphide polymers has increased in recent years. This has led to the introduction of two new polysulphide polymers where

$$R = -CH_2\overset{O}{CH-CH_2}$$

or where R = an epoxy resin. These new polymers behave similarly to the conventional -SH terminal polymers but with the added benefit of low odour and the ability to be formulated into one-component epoxy systems.

Polysulphide polymers are used to modify epoxy resins because of the benefits they can bring to the epoxy systems[1,2]. One of the most important benefits is improved adhesion, particularly to difficult substrates such as oily, wet or rusty steels. This improved adhesion is illustrated in Fig. 1 which shows lap shear values for a polysulphide–epoxy adhesive on various steel substrates. In all cases the polysulphide–epoxy gives higher values than the unmodified epoxy adhesive. This excellent adhesion leads to the use of these materials in surface-tolerant adhesives and coatings. Associated with the improved initial adhesion is improved long-term adhesion — i.e., durability — even in difficult environments such as those encountered in marine applications.

As the LP polysulphide is a very flexible polymer, improvements in the flexibility of the epoxy systems can also be obtained. This is illustrated in Fig. 2 which

Table 1. Some of the range of mercaptan-terminated polysulphide polymers available

	Average molecular mass	Repeat unit 'n' value	% Trifunctional monomer (mol%)	Average mercaptan content (mol kg^{-1})
LP31	8000	42	0.5	0.38
LP2C	4000	23	2	0.60
LP32C	4000	23	0.5	0.53
LP977	2600	15	2	0.91
LP980	2600	15	0.5	0.91
LP3	1000	6	2	2.06
LP33	1000	6	0.5	1.75

Table 2. Typical application areas for polysulphide polymers

Molecular weight	Application
8000	Printing blankets, aircraft sealants
4000	Construction sealants
2600	Insulated glazing sealants, elastomeric coatings
1000	Epoxy modification

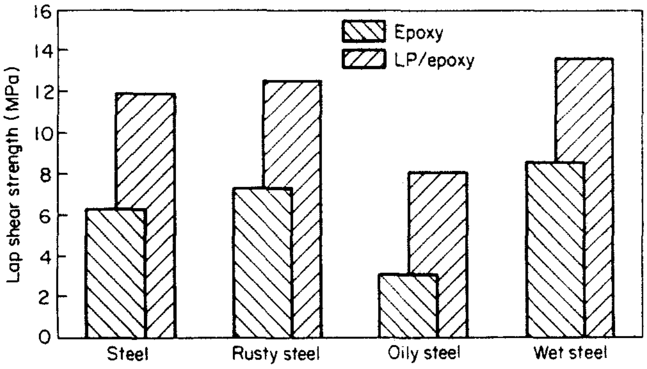

Fig. 1 Adhesion to difficult substrates (overlap 15 × 25 mm, glueline thickness = 0.2 mm)

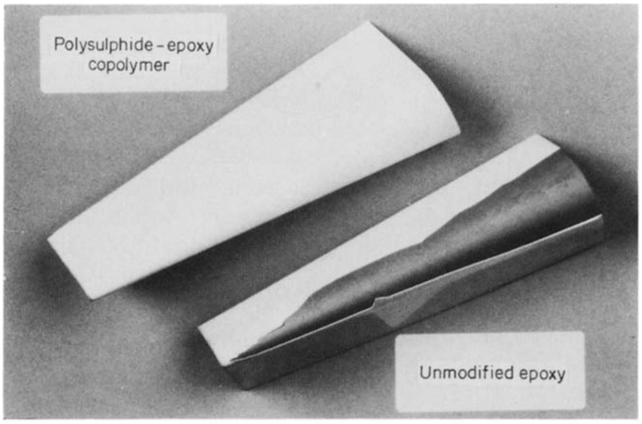

Fig. 2 Comparison of a polysulphide-modified and an unmodified epoxy coating after conical mandrel testing

shows two panels that have been tested using a conical mandrel. The polysulphide-epoxy coating has remained intact, whereas the unmodified epoxy coating has debonded along the entire length of the panel. In addition to this improved flexibility is improved impact resistance, particularly at lower temperatures.

However, there are limitations to the use of polysulphide-modified epoxy materials. These are:

- reduction in the epoxy T_g, leading to a reduction in the upper service temperature; and
- low peel strength, limiting the application areas in which the materials can be used.

The reduction in the epoxy T_g is due to the polysulphide polymers being reactive modifiers. Both the mercaptan and epoxy end-groups are capable of reacting in a normal epoxy/amine system. As the polysulphide polymers are flexible, rubbery polymers, the overall rigidity of the matrix is reduced, hence producing a lower T_g. This is illustrated in Fig. 3 which shows the tan δ traces at 1 Hz of an epoxy/amine system modified with different levels of a polysulphide polymer.

If polysulphide polymers could be made to phase separate rather than react into the matrix, then there is a potential route to overcoming these limitations. The studies in this area fell into two parts: (1) systems using liquid amine as curative; and (2) systems using dicyandiamide as curative.

Materials and methods

Liquid-amine-cured systems

A liquid diglycidyl ether of bisphenol A with an epoxy equivalent weight of approx. 190 g mol^{-1} was used for all formulations. A range of polysulphide polymers

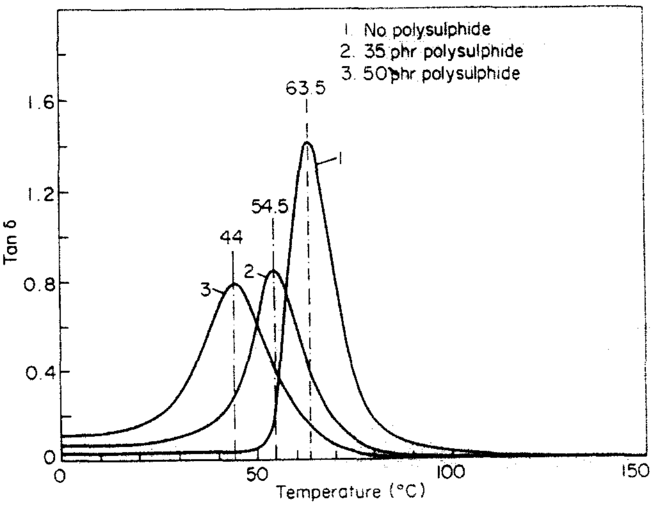

Fig. 3 DMTA 1 Hz tan δ curves for an epoxy/amine system modified with different levels of a polysulphide polymer

Table 3. Polysulphide polymers evaluated in liquid-amine-cured systems

	Molecular weight	% Trifunction monomer added	End-group
LP541	4000	0	-SH
LP2C	4000	2	-SH
ZL255	4000	4	-SH
ELP2	4000	2	Epoxy
ELP3	1000	2	Epoxy

(shown in Table 3) were evaluated at levels of up to 20 g of rubber per 100 g of epoxy resin. The curatives evaluated were ethylene diamine, aminoethyl piperazine and triethylene tetramine, all used at stoichiometric levels calculated according to the hydrogen equivalent weight of the curative. Two cure schedules were employed: (1) 24 h at 23°C + 20 min at 120°C; and (2) 30 min at 70°C.

Dynamic mechanical thermal analysis (DMTA) was carried out using a Polymer Laboratories DMTA Mk II with version 1.2 IBM software. All the results quoted are for samples run at 1 Hz with a ramp rate of 3°C min^{-1} and relate to peak tan δ temperatures.

The ^{13}C NMR *in situ* cure experiments were carried out using a Bruker 400 MHz spectrometer (model WH-400). Spectra were collected at 30°C starting 5 min after the sample was mixed.

The microscopy studies were carried out using a Jeol JEM 100 CX microscope in the scanning transmission electron microscopy (STEM) mode. Samples of 0.5 μm thickness were analysed.

Dicyandiamide-cured systems

The same liquid epoxy resin was used. A micronized grade of dicyandiamide with 98% of particles of a size less than 10 μm was used in all systems. A number of different cure accelerators based on amine adduct, 2-methylimidazole, urone and tolyl bis(dimethyl urea) structures were evaluated. Precipitated calcium carbonate at 20% by weight level was added to all formulations for ease of handling at elevated temperatures. All the systems were dispersed using a Marchant triple-roll mill. Cure optimization was carried out using differential scanning calorimetry (DSC) on a Polymer Laboratories DSC 700 instrument.

DMTA was carried out as previously described, on samples cured for 30 min at 140°C.

The lap shear testing was carried out using ground mild steel coupons 25 × 100 × 1.6 mm in size. A bondline of 0.2 mm was used with an overlap of 12.5 × 25 mm. The bonds were tested at 1.3 mm min^{-1} on a J.J. Lloyd MK30 tensile testing machine.

T-peel testing was carried out using mild steel strips 300 × 25 × 0.6 mm in size. A bondline of 0.5 mm was used and the samples tested on a J.J. Lloyd MK30 tensile testing machine at 256 mm min^{-1}.

Results and discussion

Liquid-amine-cured systems

There are a number of factors known to affect phase separation and thus the ultimate properties of a polymer system[3]. These include factors relating to the polymers themselves as well as such considerations as curative type[4, 5] and cure schedule[6–8]. As detailed above, three curatives and two cure schedules were evaluated. The type of epoxy resin was kept constant and the following factors relating to the polysulphide rubbers were evaluated:

- rubber molecular weight[4, 9, 10];
- rubber branching[11];
- rubber end-group[12]; and
- level of rubber used[5, 13].

The polysulphide polymers evaluated are shown in Table 3, which also shows molecular weight, end-group and branching information. As it is known[1, 2] that mercaptan-terminated polymers of molecular weight 1000 are highly compatible with epoxy resins, only the polymers with a molecular weight of 4000 were evaluated. For the epoxy-terminated polymers, both the 1000 and 4000 molecular weight materials were evaluated. All the polysulphide rubbers were added at levels of up to 20 g per 100 g of epoxy resin.

When the cured systems were studied using DMTA, all the polysulphide-modified systems, with the exception of ELP3, gave very similar results. A typical tan δ trace of a polysulphide-modified system is shown in Fig. 4. As can be seen, some degree of phase separation in the polysulphide-modified systems has been obtained, as a low-temperature rubber transition is present. However, reduction in the epoxy T_g temperature is also apparent as can be seen in Table 4. These results are for systems modified with 20 g of polysulphide polymer per 100 g of epoxy resin. This suggests that some of the polysulphide polymer is still reacting into the epoxy matrix rather than phase separating. The ELP3-modified systems showed no phase separation.

The presence of a rubber phase was confirmed by ^{13}C NMR cure studies. Spectra were collected for both unmodified and polysulphide-modified epoxy systems. When graphs of peak width at half height ($\Delta H_{1/2}$) were plotted for backbone carbons rather than for those carbons associated with the cure reaction, some interesting results were observed. Fig. 5 shows the $\Delta H_{1/2}$ vs. time plot for an unmodified epoxy system. As can

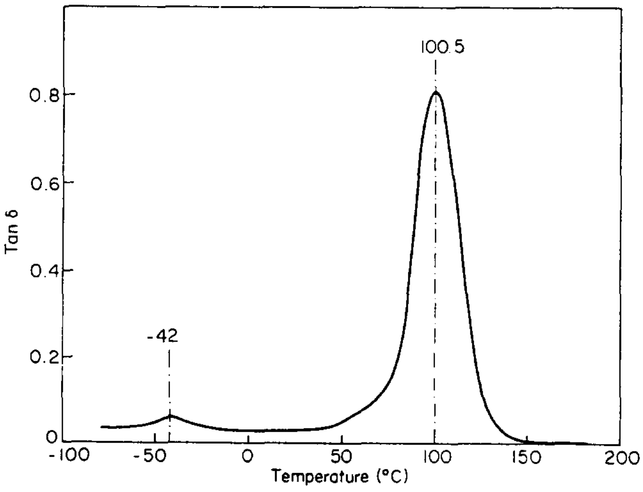

Fig. 4 Typical 1 Hz tan δ trace of a polysulphide-modified system cured with a liquid amine

Table 4. DMTA results for liquid-amine-cured materials

	Tan δ peak temperature (°C)	
Rubber	Epoxy	Rubber
None	129	None
LP541	117	−38
LP2C	116	−39
ZL255	114	−36
ELP2	116	−43
ELP3	95	None

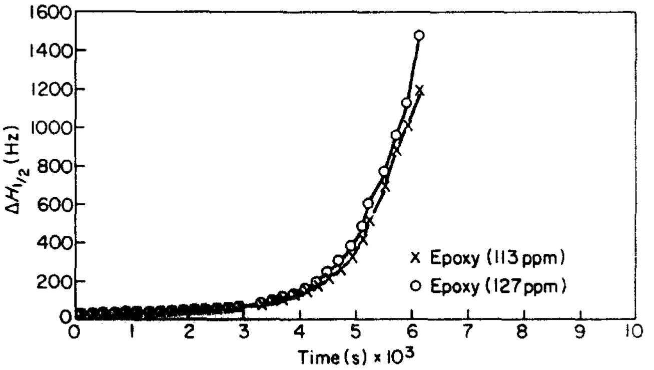

Fig. 5 ^{13}C NMR line width variation during cure of an unmodified epoxy system

be seen, up to ~4000 s there is little change in the $\Delta H_{1/2}$ values but after this time the $\Delta H_{1/2}$ values rise rapidly until at ~6000 s the lines have broadened to such an extent that they are lost in the background and cannot be measured with any accuracy. The shape of this graph is as would be expected from a polymer cure reaction monitored using ^{13}C NMR. However, when the polysulphide-modified systems were evaluated somewhat different behaviour was seen. Fig. 6 shows the $\Delta H_{1/2}$ vs. time graph for a polysulphide-modifed epoxy system. Up to 6000 s the graph is very similar to the graph in Fig. 5 for an unmodified epoxy resin. However, instead of losing all signals into the background at this point, a reduction in $\Delta H_{1/2}$ value is seen, dropping to a plateau at ~8000 s. This reduction in $\Delta H_{1/2}$ is also accompanied by a change in line shape as shown in Fig. 7. This figure shows three ^{13}C NMR part spectra taken at different times (t) during the cure reaction of a polysulphide-modified epoxy system. Initially all the lines are quite narrow as shown in the spectrum for t = 100 s. As the cure approaches 6000 s the lines become much broader as shown in the spectrum for t = 5122 s. However, after 6000 s the lines can be seen to have narrowed considerably and show a more composite shape, suggesting we are observing a line made up of two slightly different signals; this can be seen in the spectrum for t = 9139 s. The most likely explanation for this unusual behaviour after 6000 s is the presence of nuclei in two different environments. Up to 6000 s the similarity between Figs 5 and 6 suggests that, up to this point, the same process — i.e., the polymerization of the bulk epoxy resin — is being monitored. When the lines due to these nuclei broaden into the background, the narrower lines in the polysulphide-modified systems become evident. The narrowness of these lines indicate that they are due to the presence of epoxy nuclei in a mobile environment. Thus they could be associated with epoxy resin trapped in a rubbery phase.

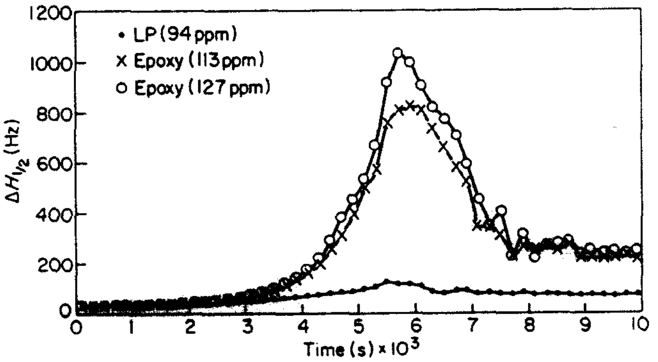

Fig. 6 ^{13}C NMR line width variation during cure of a polysulphide-modified epoxy system

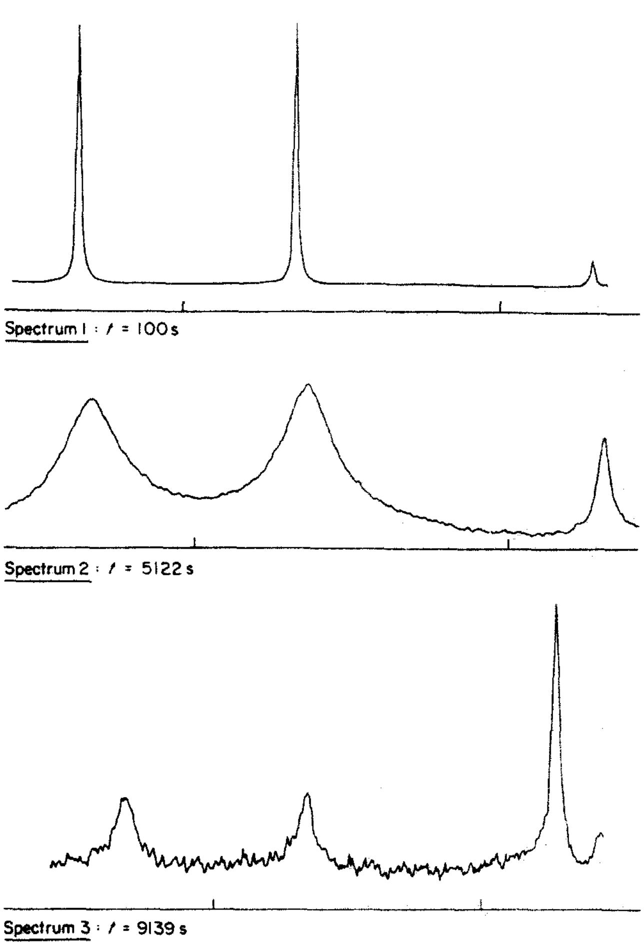

Fig. 7 Part ^{13}C NMR spectra taken during cure of a polysulphide-modified epoxy system

Having confirmed the presence of the polysulphide rubber in a discrete phase, samples were analysed using TEM to assess the size of the rubber particles. Table 5 shows some of the results from this analysis. As can be seen, overall the rubber particles are very small, the largest being only 0.33 μm in diameter. However, despite this some trends can be seen. The ELP2 appears to have a greater tendency to phase separate than the LP2C, giving particles at both 10 g and 20 g addition levels. The particles are also larger in

Table 5. Results of TEM analysis for liquid-amine-cured materials

System	Rubber particle size (μm)	
	RT cure	70°C cure
No rubber	None	None
10 phr LP2C	None	None
20 phr LP2C	0.06	0.17
10 phr ELP2	0.06	0.13
20 phr ELP2	0.17	0.33

the ELP2-modified systems. The results also show that, as would be expected, the cure schedule plays an important role in determining the size of the rubber particles produced. The rubber particles found in the systems cured at 70°C are larger than those found in the room-temperature (RT) cured materials.

Finally, the above systems were tested for tensile strength and impact properties. Although most of the polysulphide-modified systems gave improved properties compared with the unmodified epoxy systems, these improvements could not be related to the presence of the polysulphide polymer as a discrete phase.

Dicyandiamide-cured systems

In this study a slightly different range of polysulphide polymers were evaluated, as shown in Table 6. Polymers of molecular weight 8000 were included as well as the polymers of molecular weight 4000 previously evaluated. In addition, epoxy-polysulphide copolymers were also evaluated. The polysulphide polymers were again added at levels to give systems containing up to 20 g rubber per 100 g of epoxy resin.

Initially dicyandiamide was used as the sole curative and the materials were cured for 30 min at 190°C. When these materials were analysed using DMTA some degree of phase separation was observed but it was not of the form that had been expected. Fig. 8 shows a typical tan δ trace for a polysulphide-modified material. As can be seen there is no low-temperature transition indicating the presence of a rubber phase. However, there is a high-temperature shoulder present on the epoxy tan δ peak. Initially, this was thought to be due to undercure but extensive post-curing failed to eliminate the shoulder. As this shoulder was not seen in the unmodified epoxy resin and increased in magnitude with increasing rubber content, the shoulder was attributed to the presence of the polysulphide rubber. The temperature of the epoxy T_g peak was also reduced by the addition of the polysulphide polymers, as can be seen in Table 7. This reduction in T_g is similar for all the polysulphide rubbers evaluated. Also the reduction becomes greater as the level of polysulphide rubber is increased.

Table 6. Polysulphide polymers evaluated in dicyandiamide-cured systems

Mercaptan-terminated
— LP2C, LP32C, LP31

Epoxy-terminated
— ELP2, ELP32, ELP31

Epoxy-polysulphide copolymers of
— LP2C, LP32C, LP31

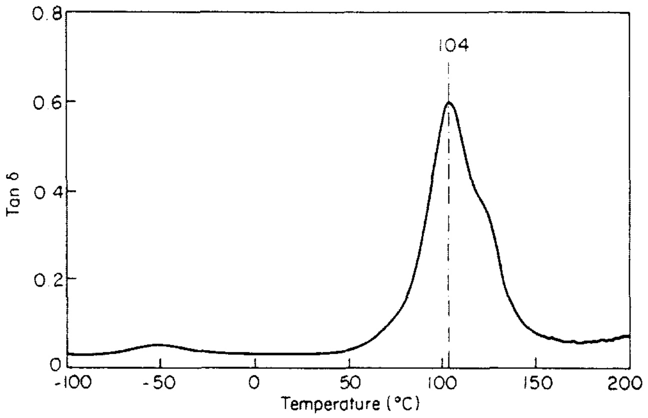

Fig. 8 Typical 1 Hz tan δ trace for a dicyandiamide-cured system modified with a conventional polysulphide polymer

To try to stimulate more conventional phase separation, a number of catalysts were evaluated to allow cures to be carried out at lower temperatures. However, when these catalysed systems were evaluated using DMTA the tan δ traces produced were of the same shape as those found for the uncatalysed materials.

Some of these dicyandiamide-cured materials, both with and without catalyst, were evaluated using lap shear and T-peel tests. Compared with the unmodified epoxy systems, there was little improvement in either lap shear or T-peel strength for these polysulphide-modified systems.

Thus, using standard polysulphide polymers, the effects of rubber molecular weight, branching, end-group, addition level, different cure schedules and curatives were evaluated with only limited success. As the type of epoxy resin had to be kept constant, the only other variable factor was the structure of the polysulphide backbone.

As epoxy resins are very polar, it was thought that the compatibility of the polysulphide polymers with the

Table 7. DMTA results at 1 Hz for dicyandiamide-cured systems

System	Epoxy tan δ peak temperature (°C)
No rubber	141
LP2C	
10 phr	115
20 phr	107
ELP2	
10 phr	120
20 phr	105
LP2C copolymer (equivalent LP content)	
10 phr	116
20 phr	105

epoxy resin could be reduced if non-polar segments were introduced into the backbone. Thus polymers were synthesized using a hydrocarbon monomer as well as the usual formal monomer. These new polymers can be produced in the usual range of molecular weights, but for this study work was concentrated on polymers of molecular weight 4000. The mole ratio of the monomers was varied between 20:80 and 40:60 hydrocarbon:formal monomers. All the polymers were initially mercaptan-terminated but were copolymerized with epoxy resin before use. The copolymers were added to the epoxy/dicyandiamide/catalyst systems to give levels of rubber of up to 20 g per 100 g of epoxy resin.

The cure schedules for the different dicyandiamide/catalyst systems were first optimized using DSC. A cure schedule of 30 min at 140°C was found to be suitable for all of the systems. Using this cure schedule materials were cured and then assessed, using DMTA, for their degree of phase separation. This assessment was based on the position of the epoxy T_g compared with an unmodified epoxy system, and whether a rubber T_g was present. The T_g is taken as the peak tan δ temperature. The determination of the presence of a rubber T_g was complicated by the presence of the epoxy β-transition at approximately the same temperature. From the DMTA analysis it could be seen that the degree of phase separation became more marked with the increasing hydrocarbon content of the polysulphide rubber. This was indicated by a lesser reduction in the epoxy T_g, as illustrated in Fig. 9, and an increase in the magnitude of the rubber tan δ peak.

Fig. 10 shows the DMTA plot for an unmodified epoxy system, while Fig. 11 shows a similar plot for the same system modified with 20 g of the 40:60 hydrocarbon:formal mole ratio polysulphide polymer per 100 g epoxy resin. The addition of the polysulphide polymer reduced the epoxy T_g by only about 8°C. A rubber phase is indicated at −45°C by both the greater inflection in the modulus in Fig. 11, and the larger tan δ peak at this temperature compared with the unmodified epoxy system.

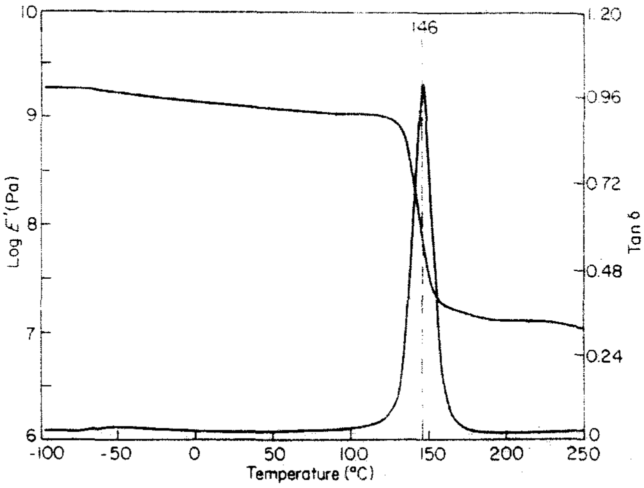

Fig. 10 DMTA trace for an unmodified dicyandiamide-cured epoxy system

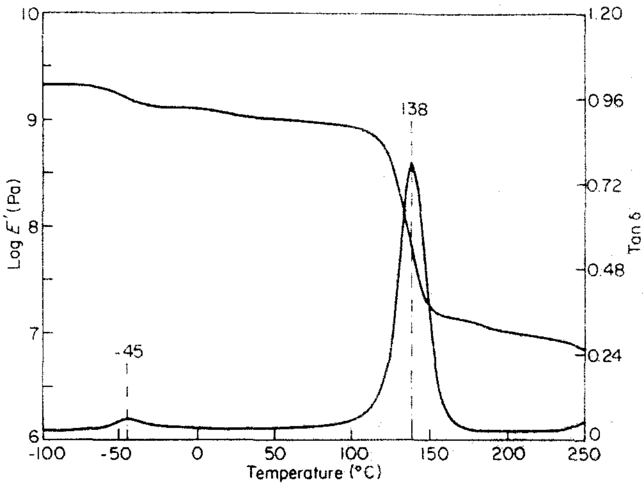

Fig. 11 DMTA trace for a dicyandiamide-cured system modified with 20 g of a 40:60 mole ratio hydrocarbon:formal polysulphide polymer per 100 g of epoxy resin

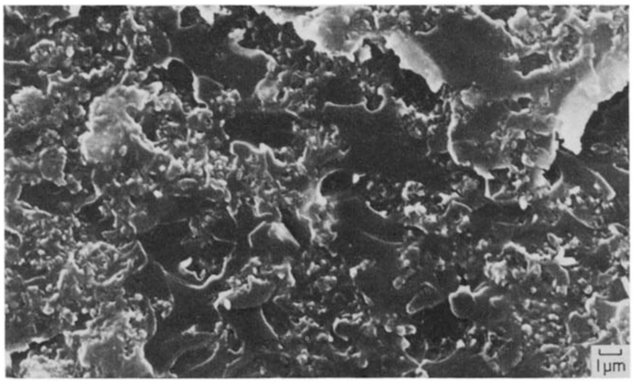

Fig. 12 Micrograph of an unmodified dicyandiamide-cured epoxy system

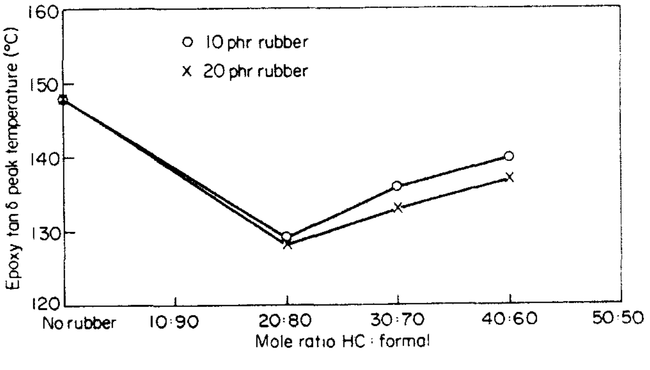

Fig. 9 DMTA results at 1 Hz for dicyandiamide-cured systems modified with hydrocarbon:formal polysulphide polymers

To confirm the presence of the polysulphide rubber as a discrete phase of particles, scanning electron microscopy (SEM) was undertaken. This proved conclusively the presence of polysulphide rubber particles as can be seen in Figs 12 and 13. Fig. 12 is a micrograph of an unmodified epoxy system and Fig. 13 is a micrograph of the same system modified with 10 g of the 40:60 hydrocarbon:formal polysulphide per 100 g of epoxy resin. The micrographs were both taken using the same magnification. The rubber particles in this particular example are between 1 and 3 µm in diameter.

When these systems were tested as lap shear and T-peel samples, the polysulphide-modified materials showed improvements in both cases, when compared with an equivalent unmodified epoxy system. However, the degree of improvement for a given polysulphide polymer was found to be dependent on the accelerator

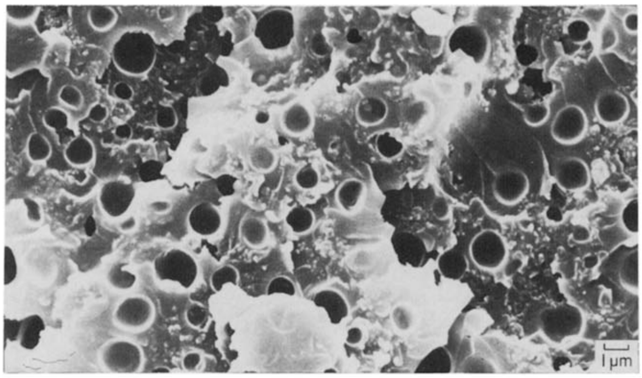

Fig. 13 Micrograph of a dicyandiamide-cured epoxy system modified with 10 g per 100 g of epoxy resin of a 40:60 mole ratio hydrocarbon:formal polysulphide polymer

Table 8. Lap shear and T-peel results for systems cured at 140°C

Accelerator*/polysulphide type and level	Lap shear strength (MPa)	Peel load (N)
Accelerator 1		
No polysulphide	25.4	12.5
30:70 mole ratio polysulphide		
10 g	31	16.9
20 g	26.6	15
40:60 mole ratio polysulphide		
10 g	29.5	16.3
20 g	28.2	16.7
Accelerator 2		
No polysulphide	23.9	10.6
30:70 mole ratio polysulphide		
10 g	29.3	17.1
20 g	27.9	26
40:60 mole ratio polysulphide		
10 g	29.7	14.8
20 g	26.6	27

*Both accelerators are urea-based

system used at a given temperature. This is illustrated in Table 8 which shows lap shear and T-peel results for two different accelerator systems.

Conclusions

By modifying the backbone of the polysulphide polymer it has been possible to overcome, to some extent, the limitations of the conventional polysulphide-modified epoxy systems. The new systems show only a small reduction in the position of the epoxy T_g. They have improved peel strength while maintaining the greater lap shear strength expected of a polysulphide-modifed epoxy material.

Acknowledgements

The authors would like to thank Dr Oliver Howarth of Warwick University for his guidance and advice concerning ^{13}C NMR studies; Dr John Bates of Loughborough University for undertaking the TEM analysis; and the technicians at Morton International, Saika Ismail, Julie Hingley, Emma Griffiths and Catherine Lilly.

Work in the latter part of the programme was carried out by Bernard Kaesmacher under the auspices of the European Community COMETT programme, arranged by Professor J.M. Liegeois of the Laboratoire Materiaux Polymers et Composite, University of Liège, Belgium.

References

1 **Rees, T.M., Thompson, N. and Wilford, A.** *JOCCA* **71** (1988) p 39
2 **Rees, T.M. and Wilford, A.** *JOCCA* **72** (1989) p 72
3 **Bucknall, C.B. and Yoshii, T.** *Brit Polym J* **10** (1978) p 53
4 **Sultan, J.N. and McGarry, F.J.** *Polym Engng Sci* **13** (1973) p 29
5 **Meeks, A.C.** *Polymer* **15** (1974) p 675
6 **Gillham, J.K., Chan, L.C., Kinloch, A.J. and Shaw, S.J.** 'Rubber modified epoxies: cure transitions, morphology and mechanical properties' *Toughening of Plastics II, PRI Conference, London, UK* (1985)
7 **Nae, H.N.** *ACS Polymeric Mater Sci Engng* **51** (1984) p 426
8 *'Rubber Toughened Plastics'* edited by C.K. Riew *ACS Adv Chem Ser* **222** (1989) chapter 8
9 **Noshay, A. and Robeson, L.H.** *J Polym Sci Chem Ed* **12** (1974) p 689
10 **Dusek, K.** *et al.* *ACS Adv Chem Ser* **208** (1984) p 27
11 **Bell, S.P. and Ochi, M.** *ACS Polymeric Mater Sci Engng, 186th National Meeting* (1983) p 393
12 **Riew, C.K., Rowe, E.H. and Siebert, A.R.** 'Rubber toughened thermosets' *Symp on Toughness and Brittleness of Plastics', Div of Org Coatings and Plast Chem, 168th ACS National Meeting* (1974)
13 **Soldatos, A.C. and Burhans, A.S.** *ACS Adv Chem Ser* **99** (1971) p 531

Authors

A. Wilford, formerly at Morton International, has now moved to SATRA Footwear Technology Centre, Kettering, UK. T.C.P. Lee is with Morton International, Coventry CV4 7EZ, UK. T.J. Kemp, to whom correspondence should be addressed, is with the Department of Chemistry, University of Warwick, Coventry CV4 7AL, UK.