Toughening epoxy resins with poly(methyl methacrylate)-*grafted*-natural rubber, and its use in adhesive formulations

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*Poly(methyl methacrylate)-*grafted*-natural rubber (Heveaplus MG) has been studied as a novel toughening agent for epoxy resin systems based on diglycidyl ether of bisphenol A (Shell Epikote 828), both in bulk and as an adhesive. Secondary and tertiary phase distributions were shown to be a function of the solubility parameter of the epoxy, and optimum bulk fracture toughness and adhesive joint failure strengths were thus achieved by controlling the resin solubility parameter. Adhesive joint strengths were measured at −35, 20 and 50°C for formulations containing up to 7 parts per hundred of resin (pph) of MG rubber and 15 pph of carboxyl-terminated butadiene–acrylonitrile rubber, and were compared with that of a proprietary epoxy-based structural adhesive film under the same conditions.*

Key words: epoxy resin; adhesives; toughening agent; natural rubber; strength

Epoxy resins are one of the most widely used structural polymers employed as adhesives and composite matrices. They can be used with a variety of curing agents to produce a comprehensive range of useful mechanical and thermal properties[1]. Unmodified epoxies are brittle, glassy polymers that have fracture energies some two orders of magnitude lower than modern comparable thermoplastics. However, epoxies benefit from easier processing and cost advantages and must therefore be formulated for improved fracture toughness in order to retain their position as materials of choice.

The toughness of epoxy resins may be increased through plasticization[2], by adding fortifiers[3], or by blending with a rubber or tough thermoplastic[4–7]. The latter technique is the most successful commercially used method and involves addition of an elastomer so that phases separate during cure. The epoxy and the dispersed phase must be closely matched and controlled so that the final material is a continuous phase of epoxy with discrete particles dispersed and well bonded to the matrix[7]. The two-phase nature of the elastomer-modified system enhances energy dissipative failure mechanisms that hardly exist in the single-phase material[6, 8–10]. These mechanisms can greatly increase the materials's resistance to crack propagation and, since the matrix itself contains very little elastomer, the bulk properties such as modulus and glass transition temperature (T_g) are close to those of the unmodified epoxy.

The most common version of these elastomers is marketed by B.F. Goodrich Chemicals as Hycar® carboxyl-terminated butadiene–acrylonitrile (CTBN) and some 10 to 15% of the copolymer rubber is generally used to achieve optimum improvements in bulk or adhesive[11,12]. CTBN systems suffer from a number of shortcomings such as inability to toughen the more highly crosslinked species of epoxy which are proportionally more brittle[5,13] and limitations of use at sub-zero temperatures due to a relatively high T_g (proportionally higher with increased content of acrylonitrile). They are also pose secondary problems with high cost and handling of hazardous chemicals.

In this paper, the use of a modified form of natural rubber (Heveaplus MG) to toughen the diglycidyl ether of bisphenol (DGEBA) resin in bulk and as adhesive is reported. Heveaplus MG (MG) is a commercially available graft copolymer of poly(methyl methacrylate) (PMMA) and natural rubber (NR). Natural rubber has a number of attractive properties from a toughening viewpoint which include a low T_g (−68°C) and, in its high molecular weight form, high tear and tensile strengths.

Experimental

Materials and fabrication

DGEBA epoxy resin (Shell, Epikote 828) was modified with either CTBN rubber (B.F. Goodrich, Hycar 1300 × 13 or 1300 × 8) or poly(methyl methacrylate)-*grafted*-natural rubber (PMMA-*g*-NR) obtained from the Malaysian Rubber Producers Research Association (MRPRA) as Heveaplus MG30 and MG50 (Table 1). The digits in the MG designations refer to the weight percentage of PMMA, of which at least half is chemically bound to the rubber.

Prior to inclusion in the epoxy resin system, the MG rubbers were masticated on a cold two-roll mill for 5 min to break down their gel content and facilitate dissolution. Some formulations of the MG rubber were modified by Soxhlet extraction of either or both of the homopolymers of poly(methyl methacrylate) and poly(*cis*-1,4-isoprene) using appropriate solvents: acetone for PMMA and n-hexane for NR. Homogeneous distribution of the MG rubber was obtained by diluting a 'premix concentrate' of MG in epoxy with epoxy resin to the desired concentration. The premix was prepared by dissolving 10 g of masticated MG in methyl ethyl ketone or dichloromethane, adding 100 g of epoxy resin to the solution and removing the solvent *in vacuo*. Epoxy formulations containing CTBN were prepared by admixture of epoxy and rubber in ratio appropriate to the desired concentration.

Some epoxy formulations were modified by addition of bisphenol A (BPA), in which case the resin and BPA were reacted in appropriate ratio at 130°C for 30 min before addition of rubber[14]. This reaction leads to chain extension of the epoxy molecule and increased solubility parameter[10].

Piperidine (pip) was used as curing agent in the bulk samples of epoxy, which were cast between glass plates at 120°C for 16 h. More detailed description of the materials, processing and characterizations pertinent to the bulk resin samples can be found elsewhere[10,15,16].

One-part adhesive formulations were cured with dicyandiamide (dicy). This is a micronized white powder of reagent grade, supplied by Anchor Chemicals, UK. Phenyl dimethylurea (Aldrich Chemical Co) was used to catalyse the reaction of dicy and epoxy[17]. The cure schedule was 1 h at 120°C followed by slow cooling in the oven.

Aluminium butt joints 25 mm in diameter and 20 mm wide aluminium lap-shear joints were used to evaluate the adhesive formulations. The adherend surfaces were initially sand-blasted with alumina grit to a homogeneous finish. The substrates were then washed in a container of acetone and rinsed. The next step involved chemical cleaning by immersing the contact surfaces into a 1 M aqueous solution of sodium hydroxide. They were then rinsed with ample distilled water and tested with the water break technique for cleanliness. Finally, the contact surfaces were subjected to a thorough rinse with acetone prior to use. The substrates were pre-heated at the cure temperature prior to assembly. The joint thicknesses were controlled to 0.2 mm following an evaluation study for optimum glue-line thickness.

Results and discussion

MG rubbers are prepared by free-radical grafting of methyl methacrylate to natural rubber in its latex state using hydroperoxide–polyamine initiator[18]. The resulting graft copolymer comprises[19] an NR main chain with a molecular weight of about 200 000 and an average of one or two grafted PMMA side chains with molecular weights in excess of 100 000. As shown in Table 1, both types of MG rubber contain unbonded PMMA and NR constituents. By extraction of these homopolymers three new types of MG rubber were thus produced (Table 2): one with no PMMA homopolymer, one with no NR homopolymer and one without both homopolymer varieties.

Table 1. Characteristics of the various toughening agents

Elastomer	Source	Molecular weight*	Properties or comments
Hycar CTBN 1300 × 8	B.F. Goodrich	3500^w	Contains 17 wt% acrylonitrile
Hycar CTBN 1300 × 13	B.F. Goodrich	3500^w	Contains 27 wt% acrylonitrile
MG30	MRPRA	$34\,000–39\,000^v$	Contains 35% ungrafted natural rubber, 12% unbound PMMA
MG50	MRPRA	$850\,000–900\,000^v$	Contains 24% ungrafted natural rubber, 25% unbound PMMA

*Weight-average molecular weights are signified by w superscript; viscosity-average molecular weights are signified by v superscript

Table 2. Compositional changes in MG30 and MG50 after extraction of homopolymers of PMMA and/or NR

Original graft rubber	PMMA homopolymer extracted* (%)	NR homopolymer extracted* (%)	Both homopolymers extracted* (%)
MG30	19 (MG30A)	28 (MG30B)	47 (MG30C)
MG50	28 (MG50A)	23 (MG50B)	51 (MG50C)

*New code names are given in parentheses

Table 3. Measured values of compact tension fracture toughness for various MG- and CTBN-toughened formulations

Rubber type*	Rubber content (pph)	BPA content (pph)	K_{Ic} (MPa m$^{1/2}$)	G_{Ic} (J m^{-2})
None	0.0	0.0	1.34	602
MG30	2.0	0.0	2.0	1389
MG50	2.0	0.0	1.81	1130
MG30	5.0	0.0	2.77	2720
MG50	5.0	0.0	2.20	1640
MG30	10.0	0.0	2.88	3005
CTBN 1300 × 8	10.0	0.0	2.28	2014
None	0.0	24.0	1.42	752
MG30	2.0	24.0	2.25	1936
MG50	2.0	24.0	2.27	1990
MG30	5.0	24.0	3.13	4015
MG50	5.0	24.0	3.35	4471
MG30A	5.0	24.0	3.34	4535
MG50A	5.0	24.0	3.58	5385
MG30B	5.0	24.0	2.95	3547
MG50B	5.0	24.0	2.73	2906
MG30C	5.0	24.0	3.10	4089
MG50C	5.0	24.0	3.25	4419
MG30	10.0	24.0	3.75	6114
MG50	10.0	24.0	3.85	6389
CTBN 1300 × 8	10.0	24.0	2.81	3249

*Refer to Table 2 for name codes

Table 3 highlights the levels of toughness that were achieved by incorporation of the various MG rubbers into the 828 and BPA-modified 828 resins[10,16]. These results show that superior fracture toughness values are achieved with 5 parts per hundred of resin (pph) of the MG systems compared with 10 parts of the conventional CTBN systems, while the addition of BPA produces a marked improvement with all the rubber-toughened systems and in particular the MG systems. Extraction of the PMMA homopolymer also has beneficial effects while the opposite effect is derived by extraction of the NR homopolymer. Fig. 1 is a micrograph obtained by transmission electron microscopy (TEM) of a 5 MG50/828 system which shows PMMA precipitation as a tertiary phase on the outside of the rubber phase at its interface with the continuous epoxy phase. The rubber particles have been stained with osmium tetroxide and hence appear black; the PMMA phase has a greater electron transparency and is also subject to chain scission due to electron beam damage and hence appears as a bright halo. Fig. 2 shows the same formulation when applied to a BPA-modified matrix. The rubber particles are more evenly dispersed and exhibit a binodal size distribution. It is also clear that the PMMA phase is no longer visible. Similar morphological changes have been observed with the BPA modification of the MG30 systems, where the PMMA phase is less concentrated.

The observed toughness phenomena may be explained in terms of the ability of the rubber phase to trigger energy dissipative processes. The key to successful toughening lies in a finely and discretely dispersed rubbery phase with a good interfacial bond. In the MG systems the solubility of the PMMA in the epoxy matrix is the controlling parameter. When the solubility parameter of the epoxy matrix is increased by chain extension with the BPA molecules, compatibility

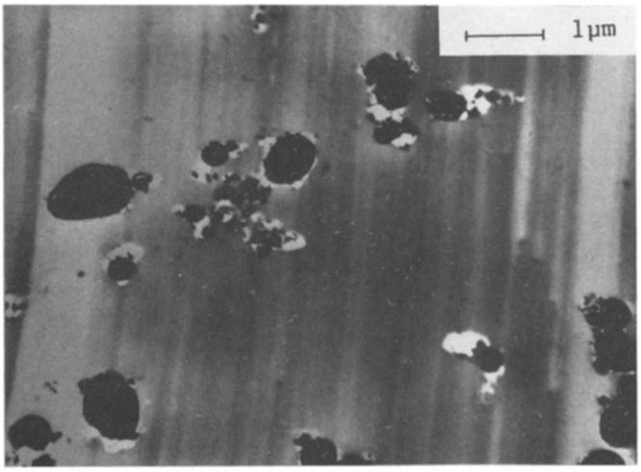

Fig. 1 TEM micrograph of 5 pph MG50/828/pip system. The rubber phase morphology is distinguished by staining with osmium tetroxide

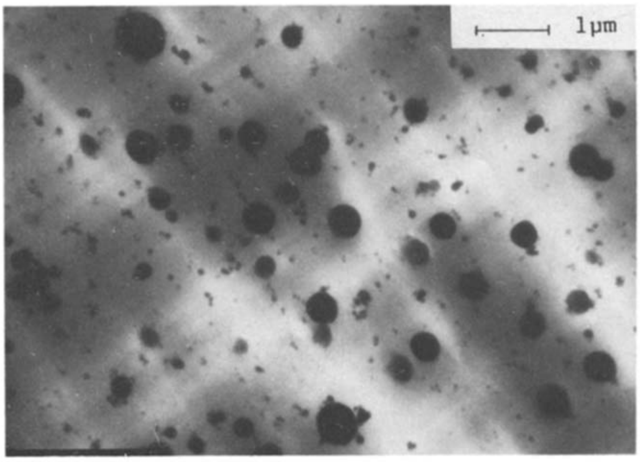

Fig. 2 TEM micrograph of 5 pph MG50/828/24 BPA/pip

between the epoxy and the PMMA is improved such that the PMMA does not phase separate and is thus randomly dispersed in the matrix. The rubber phase, however, is completely incompatible with the epoxy due to differing solubility parameters and hence phase separates during the solvent evaporation stage. However, the polyisoprene is chemically linked to the PMMA and thus its dispersion is dependent on the dispersion of the same. The PMMA also behaves as a coupling agent between the elastomeric and continuous phases, improving the interfacial bond.

Fig. 3 shows a scanning electron micrograph of a typical MG-toughened epoxy compact tension fracture surface, showing cavitated rubber particles with associated matrix deformation and a generally topographic failure. Evidence from an extensive study into the failure mechanism of the MG rubbers[10,16] suggests four energy dispersive mechanisms are responsible for the observed improvements in fracture energy:

1) local cavitation in the *in situ* rubber particles and immediate surrounding matrix, caused by dilational triaxial stress in and around each elastomeric particle[6,11];
2) plastic shear yielding in the resin matrix, enhanced by stress concentrations associated with the embedded soft particles[6,11,12,20];
3) stretching and tearing of embedded rubber particles in the wake of a moving crack[8]; and
4) induction of multilevel fracture paths, leading to enlargement of the fracture surface area[9,21].

Evidence for each of the four mechanisms has been observed and it has been shown that in all cases the distinct properties of the MG rubbers, such as evenly distributed multimodal particle size, high tear energy and strong nature of their interfacial bond, are complementary to these mechanisms. Further in-depth discussions are outside the scope of this paper and can be found elsewhere[10,15,16].

Evaluation of toughening agents in an adhesive

Figs 4 and 5 show the mean measured butt joint strength of toughened adhesives as a function of rubber content for the systems 828/dicy and 828/BPA/dicy, respectively. The figures show that addition of the MG and CTBN rubbers has beneficial effects upon the joint strength, while the MG systems are seen to be more effective at much lower levels of rubber. This is particularly noted in the formulations modified with 24 parts BPA, where the particle size and spatial distributions are more widely dispersed. The BPA-modified formulations also suggest that there is a plateau effect at MG additions of around 5 to 7 pph. This is in agreement with the bulk sample observations (Table 3), which showed diminishing toughness gains with additions above 5 pph.

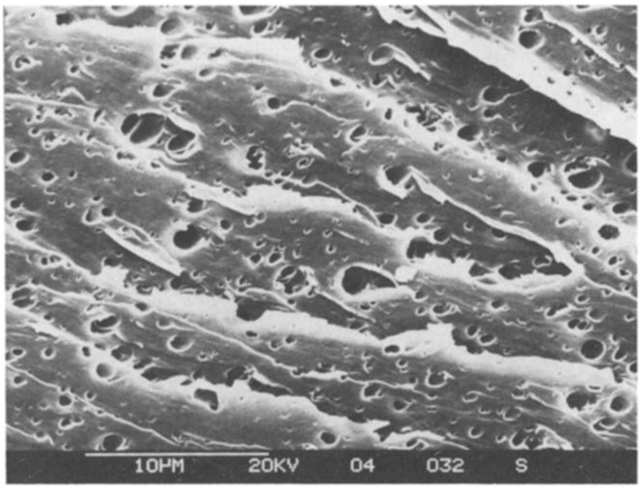

Fig. 3 SEM micrograph of a typical compact tension fracture surface for 5 pph MG50/828/24 BPA/pip

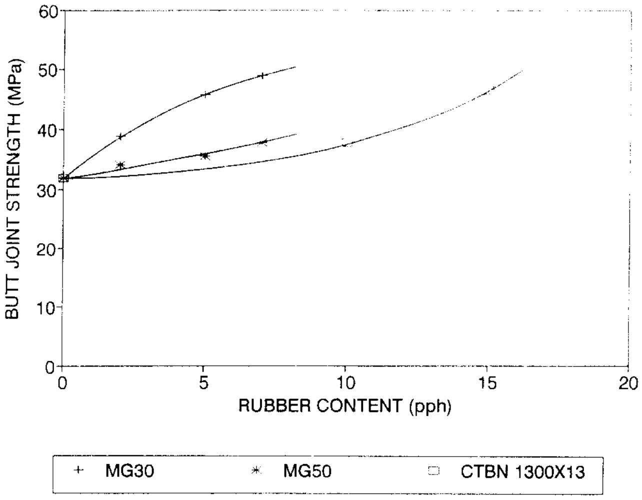

Fig. 4 Mean aluminium butt joint strength data for various levels of rubber in a 828/dicy system

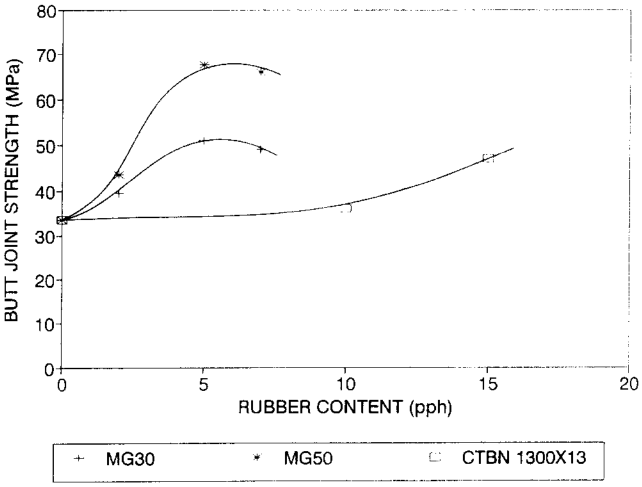

Fig. 5 Mean aluminium butt joint strength data for various levels of rubber in a 828/24 BPA/dicy system

Figs 6 and 7 illustrate the results of the butt tensile tests at −35, 20 and 50°C (typical service temperature range of a motor vehicle) for a series of neat and rubber-modified formulations; Fig. 7 referring to formulations modified with 24 pph BPA. All the adhesives considered show improved performance at the sub-zero temperature, even though the fracture toughness of the epoxy reduces at such temperatures[6,16]. Conversely, the fracture toughness of the bulk formulations is known to increase with temperatures above room temperature. However, only the neat formulations display the same trend. The highest recorded strengths are 52.9 and 50.7 MPa for

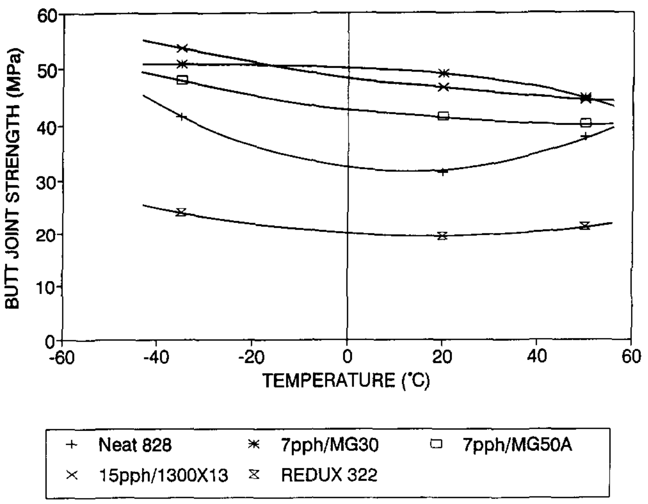

Fig. 6 Mean adhesive butt joint strength data as a function of test temperature for non-BPA modified formulations

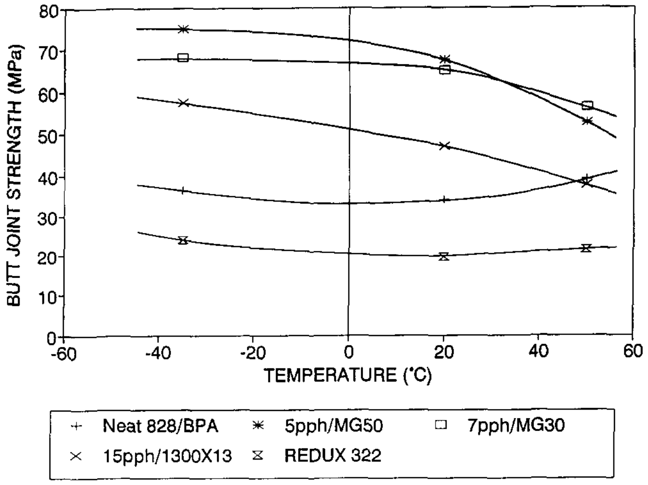

Fig. 7 Mean adhesive butt joint strength data as a function of test temperature for BPA-modified formulations

the formulations with, respectively, 15 parts of 1300 × 13 and 7 parts of MG30 in 828, while for the BPA-modified adhesives the highest recorded values are for systems containing 5 parts of MG50 and 7 parts of MG50 at 74.6 and 68.2 MPa, respectively. Redux 322, a commercial one-part structural film adhesive (Ciba-Geigy Plastics), was used to contrast the results but only exhibited failure stresses of the order of 20 MPa, in spite of failing cohesively.

At first sight the above results pose some anomalies for direct correlation of bulk toughness and joint strength. However, close examination of the data indicates that the failure stresses may be approaching the materials' ultimate tensile strengths (UTS)[17]. Chen and Cheng[22] have considered the stress distribution of the adhesive layer in a butt joint using two-dimensional elasticity theory. They showed that, unlike in the lap-shear test, the stress distribution in a butt joint may be regarded as largely uniform. The test configuration induces very little edge effects and in fact the stress at the outer edges is at about 80% of the applied stress level (σ). This rises to about 105% of σ at around 1.4 mm inside the edge (for a 28 mm diameter substrate) but reverts back to a plateau at around 3.4 mm inside the edge. Therefore it may be concluded that, as the failures are cohesive, the joint strengths may be related to UTS of the bulk adhesive material. A brittle epoxy tested under tension tends to suffer brittle failure at a stress level below its inherent tensile strength or yield point, due to the presence of embedded or surface flaws. Rubber modification is known to have two distinct and competing effects upon this behaviour. First, the yield stress is reduced so that the brittle failure may be suppressed or delayed by localized plastic deformation at a sub-critical crack tip. Second, both the material's Young's modulus and UTS are reduced so that ultimately, with extensive modification, the resulting stress versus strain characteristic would approach that of the elastomer. Furthermore, direct comparison with the bulk tensile properties may be limited by considerations of size effect and also the configuration of the joint, or other stress-field constraints that a thin glue-line may experience. Hence, the phenomena of increased joint strength at reduced temperatures and relatively reduced strengths of the rubber-modified formulations at 50°C may be elucidated by these competing mechanisms.

In terms of TEM observations, the adoption of the dicy curing agent had no notable effects on the morphology or distribution of the MG rubber phase in the adhesive, and appear similar to those of Figs 1 and 2. The MG rubber morphology is largely insensitive to such processing variables as curing agent, cure time and gel time, as the elastomeric phase has already precipitated at the start of the cure schedule. The rubber phase morphology of the CTBN 1300 × 13 is shown in Fig. 8.

Figs 9 and 10 are scanning electron micrographs of 7 pph MG50/BPA/828 and 15 pph 1300 × 13/BPA/828, respectively, at two magnifications. Although the failures can be classified as cohesive in both cases, in the latter the fracture path is always very close to one of the interfaces but alternates between the two surfaces during the fracture process with a few random steps into and out of the adhesive layer. The fracture surface of the non-rubberized epoxy formulations also exhibited similar features, but with characteristically smoother brittle fractures. The higher magnification micrograph shows a large number of partially cavitated rubber domains with evidence of some localized plastic

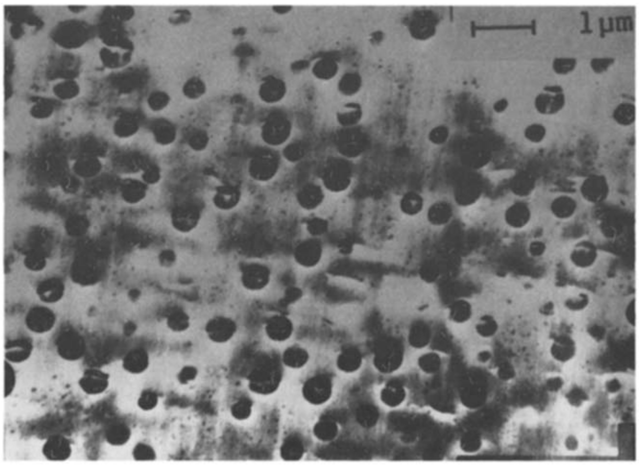

Fig. 8 TEM micrograph of 15 pph 1300 × 13/828/24 BPA/dicy adhesive

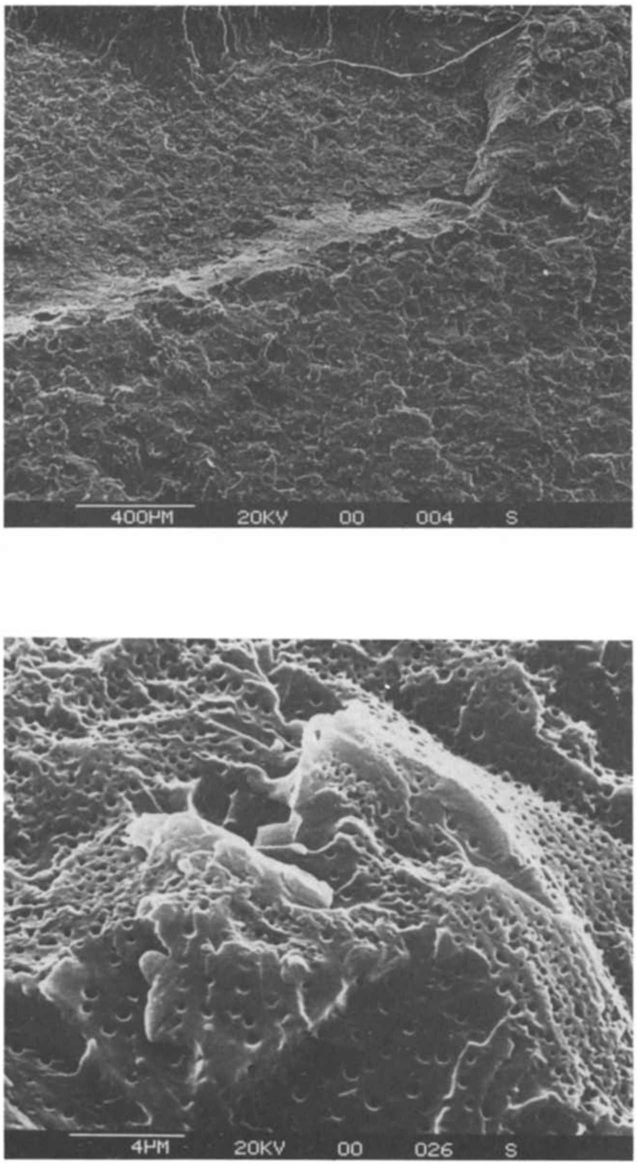

Fig. 9 SEM micrographs of typical fracture surface for butt joint bonded with 15 pph 1300 × 13/24 BPA/828/dicy. Magnification: top, 40×; bottom, 4000×

deformation. By comparison, the MG-toughened variety clearly exhibited a more topographic fracture surface which tends to be contained within the adhesive layer, away from the interface with the substrate. The higher magnification micrograph displays an even distribution of cavitated rubber particles, indicating localized plastic deformation. In a previous study, the three distinct mechanisms of crack-tip blunting — rubber stretching and tearing and multilevel fracture paths — were used to elucidate the increased bulk fracture toughness[10, 16]. The latter mechanism appears particularly relevant to the observations of toughness in adhesive joints. The original advocates of this theory[9, 21] suggested that there is a preferential crack front trajectory which coincides with the equatorial plane of the rubbery particles (i.e., the location of maximum triaxial stress concentration[23]), and explained that this localized variation in crack path would lead to an increase in the fracture energy of the material due to the increased cumulative area of fracture surface. This mechanism may be justified here in the light of the more topographic fracture in MG-modified systems, where a wider distribution of particle sizes in close vicinity can promote an enhanced multilevel fracture.

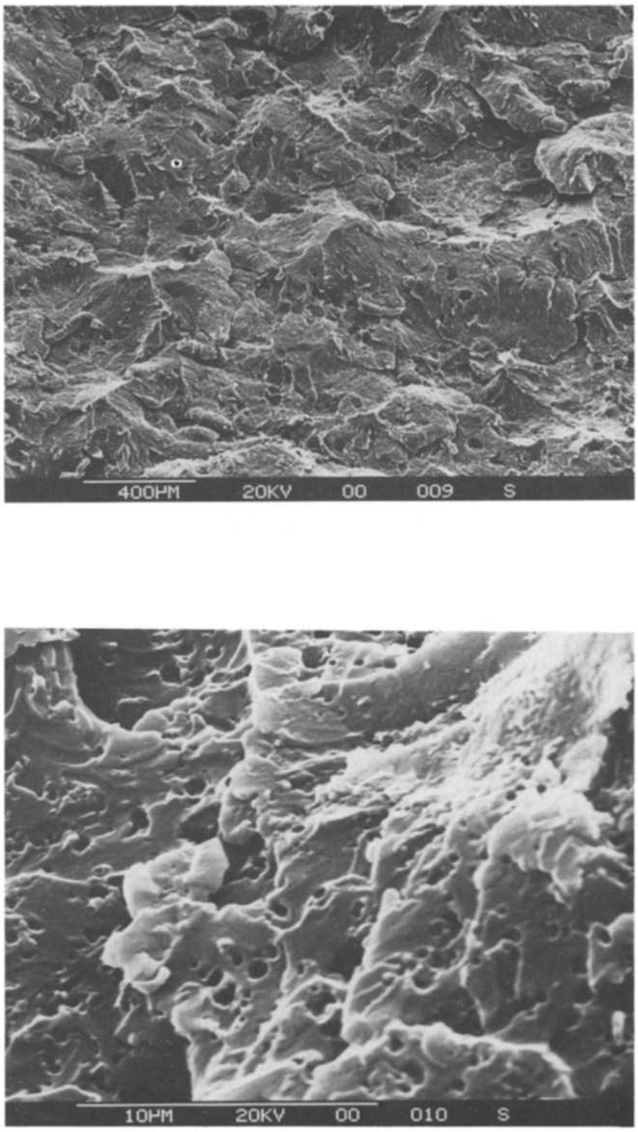

Fig. 10 SEM micrographs of typical fracture surface for butt joint bonded with 5 pph MG50/24 BPA/828/dicy. Magnification: top, 40×; bottom, 4000×

As discussed earlier, the butt joint configuration used in this study provides values which are related to the material's UTS which in turn may not be solely related to toughness. In order to provide further assessment of toughness effects on adhesive performance, some lap-shear tensile tests were also conducted. Fig. 11 compares the mean results of a set of aluminium lap-shear joints prepared with a glue-line of 0.25 mm. The 828/BPA/dicy adhesive formulation was modified with 5 pph of MG50 and 10 pph of 1300 × 13 CTBN for direct comparison. The outcome confirms the superior effectiveness of the MG system.

Conclusions

The MG rubbers have been shown to impart a greater toughness to epoxy resin both in bulk and adhesive forms, compared with the conventional CTBN rubbers. Furthermore, the resulting improvements are obtained with relatively smaller quantities of rubber which register insignificant losses in terms of the epoxy's T_g.

MG30 is a more effective toughening agent than

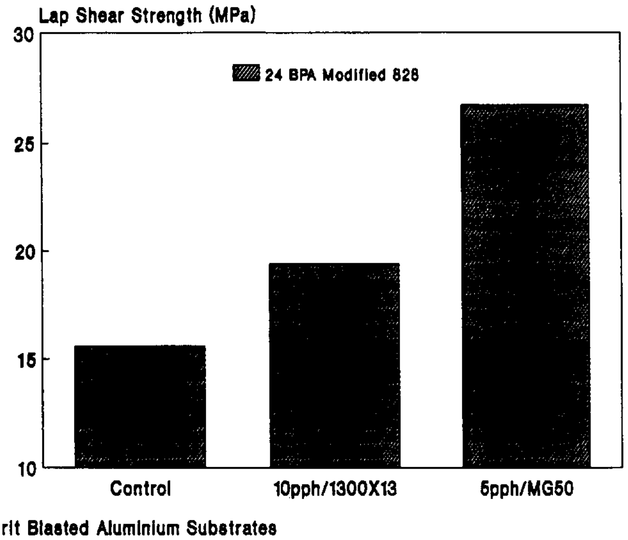

Fig. 11 Comparison of tensile lap-shear failure strength for 24 BPA/828/dicy system modified with 10 pph 1300 × 13 and 5 pph MG50 rubbers

MG50 when applied to the 828/dicy adhesive system, but the latter displays greater toughening in conjunction with a 24 pph BPA-modified epoxy.

The MG-toughened adhesives result in a more topographic fracture surface, which may be attributed to their ability to promote a more enhanced multilevel fracture path.

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