Rubber-modified epoxy resins: 1. Equilibrium physical properties

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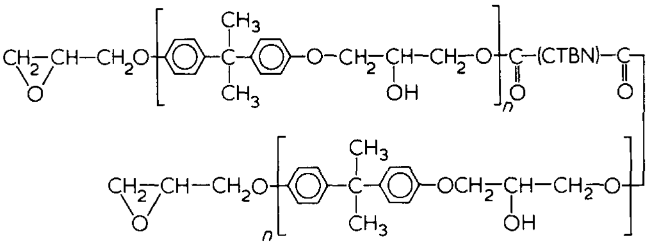
Dilatometry, thermal mechanical analysis, differential scanning calorimetry, electron microscopy and mechanical measurements are reported on a series of rubber-modified epoxy resins. The data obtained is discussed in terms of the interplay of molecular mobility, network and domain structure of the resins. Three transitions were identified; two being assigned respectively to the onset of motion of the acrylonitrile/butadiene units and epoxy units. The higher temperature transition is more difficult to assign, but appears to be associated with specific interactions involving the interface between the epoxy and acrylonitrile/butadiene interfaces or the crosslinked regions of the epoxy resin.

INTRODUCTION

Epoxy resins have found wide application as adhesives, potting and coating compounds[1]. However, the 'pure' epoxy resin suffers from poor fracture properties, lacks flexibility, and exhibits reduced shear and peel strength when cured with conventional 'small' molecule reagents. Certain of these problems can be alleviated by the incorporation of a rubbery component, leading to an increase in the lap and peel strengths of the resin[2-5]. Ideally, the second component should be homogeneously dispersed through the resin. However, a marked tendency towards phase separation has been reported for certain additives[6], such as butadiene. Incorporation of acrylonitrile reduces this tendency of the mixture to separate into two phases. Termination of the acrylonitrile butadiene by a carboxyl group provides an easily-cured system and should assist in increasing the compatbility and produce a stable adhesive. The adhesive properties of a range of such materials have been reported[2-5]. In this study three of these materials will be subjected to a more extensive investigation of their physical properties. This paper deals with the equilibrium physical properties of a series of rubber-modified epoxy resins; dynamic studies will be reported in a subsequent paper.

STRUCTURE AND PREPARATION OF RESINS

The synthesis of the rubber-modified epoxy resins used in this study has been described in detail elsewhere[3,4,7,8]. The materials listed were commercial samples and were used without further purification: diglycidyl ether of bisphenol A, DGEBA (B & K Resins), epoxide value 52 equiv. kg^{-1}; acrylonitrile butadiene rubber CTBN (Hycar 1300X8, B. F. Goodrich carboxyl value 0.53 equiv. kg^{-1}; triethylenetetramine (TETA) and diethylene glycol bispropylamine (DGBP). The epoxy resin and rubber components were mixed thoroughly and heated to the required temperature (423K) for precure to occur. In practice, preheating of the mixture to facilitate mixing was found to have little effect on the properties of the final material. The mixture was held at constant temperature for a minimum of 2 h and then allowed to cool. The rate of cooling was not critical. The resultant resin has the structure:



Previous studies of the lap and peel strengths of a variety of resins as a function of the percentage of prepolymer and the type of curing agent have indicated that a maximum in these properties occurs at approximately 0.1 weight fraction of rubber[8]. The resin was cured in the form of discs, approximately 3 cm in diameter. The mould was constructed from a nylon-lined aluminium block, with a base formed from a Melinex sheet. The DGEBA/acrylonitrile–butadiene resin was preheated to 333K to facilitate thorough mixing and either TETA or DGBP added; the resin was then allowed to cure at ambient temperature for 12 h. In the case of two of the high rubber content resins, cure was achieved by maintaining the sample at 373K for 12 h. The characteristics of the resins and details of their thermal histories are summarized in *Table 1*. The amount of curing agent used was determined by the epoxide value, which involves reaction of the epoxide group with a quaternary salt to

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form the halohydrin ion which is in turn titrated with perchloric acid.

DETERMINATION OF TRANSITION TEMPERATURES

Experimental and results

Dilatometry. The measurements were performed using a dilatometer constructed from a glass U-shaped sealed tube closed at one end with a precision narrow-bore glass tube fitted with an expansion reservoir. For temperatures above ambient mercury (m.pt., 234K) was used to fill the dilatometer; below 298K ethanol (m. pt. 129K) was employed. The height of the liquid column was measured to a precision of ±0.1 mm using a 2 m cathetometer, and the temperature recorded using an electronic thermometer with a precision of ±0.1K.

All the samples were studied over the temperature range 190 to 383K. Within this temperature range three distinct changes in slope were detected. The linear expansion coefficients between the transition temperatures were determined by comparison of the gradient with that for the corresponding pure reference liquids. A typical plot for a resin is shown in *Figure 1*. The data derived from these plots are summarized in *Table 2*. The lowest temperature transition (T_1) was not observed in all the samples studied. Likewise the higher temperature transition was not detected in certain of the high rubber content samples.

Table 1 Composition of resins

Curing agent (pph)	Code	Composition DGEBA (phr)	Composition CTBN (phr)	Weight fraction of rubber	Cure cycle
TETA–8	10%	100	10	0.0909	I
TETA–8	12½%	100	12½	0.1111	I
TETA–8	15%	100	15	0.1304	I
TETA–8	47%	100	47	0.3197	I
TETA–1.5	100/51%	51.7	100	0.6592	II
DGBP–19	10%	100	10	0.0909	I
DGBP–19	12½%	100	12	0.1111	I
DGBP–19	15%	100	15	0.1304	I
DGBP–19	51.4%	100	51.4	0.3397	I
DGBP–3.5	100/45%	45	100	0.6896	II

Cure cycle. I(a) Preheat the polymer to 333K;
(b) add curing agent;
(c) finish cure overnight at ambient.
II(a) and (b) the same as I;
(c) finish overnight at 373K

Differential scanning calorimetry. The heat capacities of the resins were investigated over the temperature range 173 to 473K using a Perkin–Elmer DSC-1 and a Dupont 900 DSC. The heating rate was adjusted to 8K min^{-1}. The instruments were calibrated using naphthalene (m.pt.

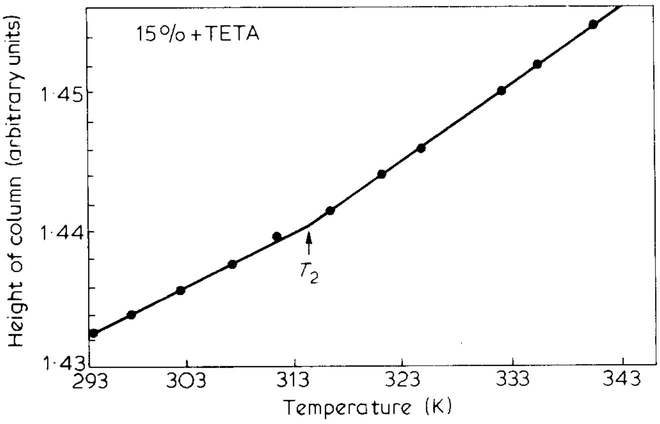

Figure 1 Typical dilatometric plot for a 15% of + TETA-cured material in the temperature range 293–343K

Table 2 Dilatometric and thermal mechanical determinations of the glass transition temperatures and expansion coefficients of rubber-modified epoxy resins

Curing agent	Code	Dilatometric glass transition T_1	Dilatometric glass transition T_2	Dilatometric glass transition T_3	Thermal mechanical temperatures T_1	Thermal mechanical temperatures T_2	Thermal mechanical temperatures T_3	Expansion coefficient x 10^4 Dilatometric	Expansion coefficient x 10^4 TMA
TETA	10%	188	311	359.5	213	300	351	4.0	(i) 2.0 (ii) 3.6 (iii) 7.1
TETA	12½%	183	309	361	–	300	351	4.6	(i) 1.9 (ii) 4.2 (iii) 6.1
TETA	15%	–	315	360	203	298	358	3.0	(i) 2.3 (ii) 4.1 (iii) 5.8
TETA	47%	–	–	–	–	–	–	3.6	–
TETA	100/51%	183	–	–	–	–	–	5.1	–
DGBP	10%	–	314	366	–	309	361	(i) 3.9 (ii) 4.6	(i) 2.0 (ii) 3.9 (iii) 6.1
DGBP	12½%	194	309	362	223	301	342	(i) 2.1 (ii) 5.7	(i) 2.3 (ii) 4.0 (iii) 6.1
DGBP	15%	198	313	368	217	301	349	(i) 2.4 (ii) 4.6	(i) 2.5 (ii) 3.7 (iii) 5.8

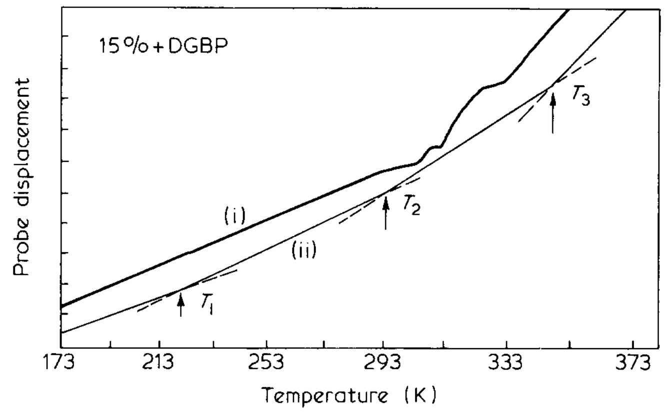

Figure 2 Typical set of thermal mechanical traces obtained for 15% + DGBP-cured material: (i) original trace for the material; (ii) trace after thermal annealing of sample; note the development of three distinct glass transitions

353K) as standard. Despite an extensive investigation of the resins it was not possible precisely to identify the position of the transitions. A general change in slope consistent with changes in the total heat capacity was observed throughout the whole temperature range.

Thermal mechanical analysis. The thermal expansion of the resins was investigated over the temperature range 173 to 383K using a Dupont 941 TMA. A heating rate of 10K min^{-1} and a load of 1 g were used. The instrument was calibrated using an aluminium block.

Changes in the rate of expansion were observed to occur in the range 173 to 383K (*Figure 2*). The expansion coefficients were calculated by comparison of the slopes with those obtained from the standard aluminium block. Thermal cycling of the sample leads to distinct changes in the shape of trace obtained. The initial trace was usually observed to exhibit an oscillatory form which on further cycling was modified to a well-defined trace with three distinct changes in slope. These observations may be attributed to a release of internal stress and the development of a more well-defined morphology as a consequence of heating the sample above its curing temperature. The expansion coefficients and glass transitions temperatures are summarized in *Table 2*.

DISCUSSION

From the results summarized in *Table 2* it is clear that there are three distinct transitions in these resins. Assignment of these transitions to specific molecular relaxation processes is possible by comparison of the data with the literature values for the glass transitions in the component phases (*Table 3*)[1,9–12]. The lowest transition temperature (approximately 190–220K) is consistent with the onset of motion of an acrylonitrile–butadiene copolymer of the type used as a chain-extender. The position of the epoxy glass transition is a function of the curing agent and also of the presence of any dispersed phases. Assignment of the second transition to the onset of motion of the epoxy groupings would appear consistent with the existing literature, but the higher temperature transition is somewhat more difficult to assign. Multiple transitions have been observed in acrylonitrile–butadiene copolymers[9–12], usually observed in the temperature range 320 to 345K. The higher temperature transition may tentatively be attributed either to the occurrence of less mobile regions within the acrylonitrile or epoxy phases associated with crosslinking or to the mixed phase which might be expected to occur if the polymer is phase separated.

Further evidence for the existence of a higher temperature transition has recently been obtained from positron annihiliation studies of these epoxy resins[13]. In these measurements the positron lifetime is directly dependent on the distribution of free volume in the polymer and this is observed to exhibit a distinct discontinuity at approximately 363K. The dilatometry and thermal mechanical data presented in this paper is consistent with these observations and provides further support for the observation of three distinct transitions in these materials.

VISUALIZATION OF THE PHASE STRUCTURE IN THE RESINS

Experimental results and discussion

Using a Philips scanning electron microscope, micrographs of fracture surfaces were obtained after subjecting a resin sample cooled to 173K to a sudden impact. The surfaces were coated with gold before examination. Thin films of the resin were obtained by curing the premixed resin on the surface of a water trough, the sample being lifted from the surface using graphite-coated copper grids, dried and then examined using a Jeol transmission electron microscope (*TEM*). The films were typically 0.1 μm or less in thickness. Direct observation of thin films was possible without significant charging effects, although in certain areas the effects of electron beam damage were detected. The use of ultrasonic cleaning of the fracture surfaces did not appear to have any effect on the morphology observed; However, it did remove surface dust and other foreign particles.

The specimens used for scanning electron microscopy were prepared by subjecting nitrogen-cooled pieces

Table 3 Glass transitions of component phases and composites

System	Glass transition (K)	Reference
TETA—cured diglycidyl Ether of bisphenol	328	I
Butadiene	188	9
Acrylonitrile	360	10–12
Acrylonitrile butadiene	212	9
Copolymer cured with TETA		
10% + TETA	311 (dilatometry 300 (t.m.a.) 312 (see below*)	This work
12½% + TETA	309 (dilatometry) 300 (t.m.a.) 309 (see below*)	This work
15% + TETA	315 (dilatometry) 298 (t.m.a.) 306 (see below*)	This work

* Calculated on the basis of a simple composite equation of the form:

$$\frac{1}{T_g^{AB}} = \frac{\phi_A}{T_g^A} + \frac{\phi_B}{T_g^B}$$

where T_g^{AB} is the glass transition of the composite with T_g^A and T_g^B being the glass transitions of the respective component phases present in weight fractions of ϕ_A and ϕ_B. Other more complex equations have been proposed but we have no prior reason for assuming that they should be more applicable than the one used

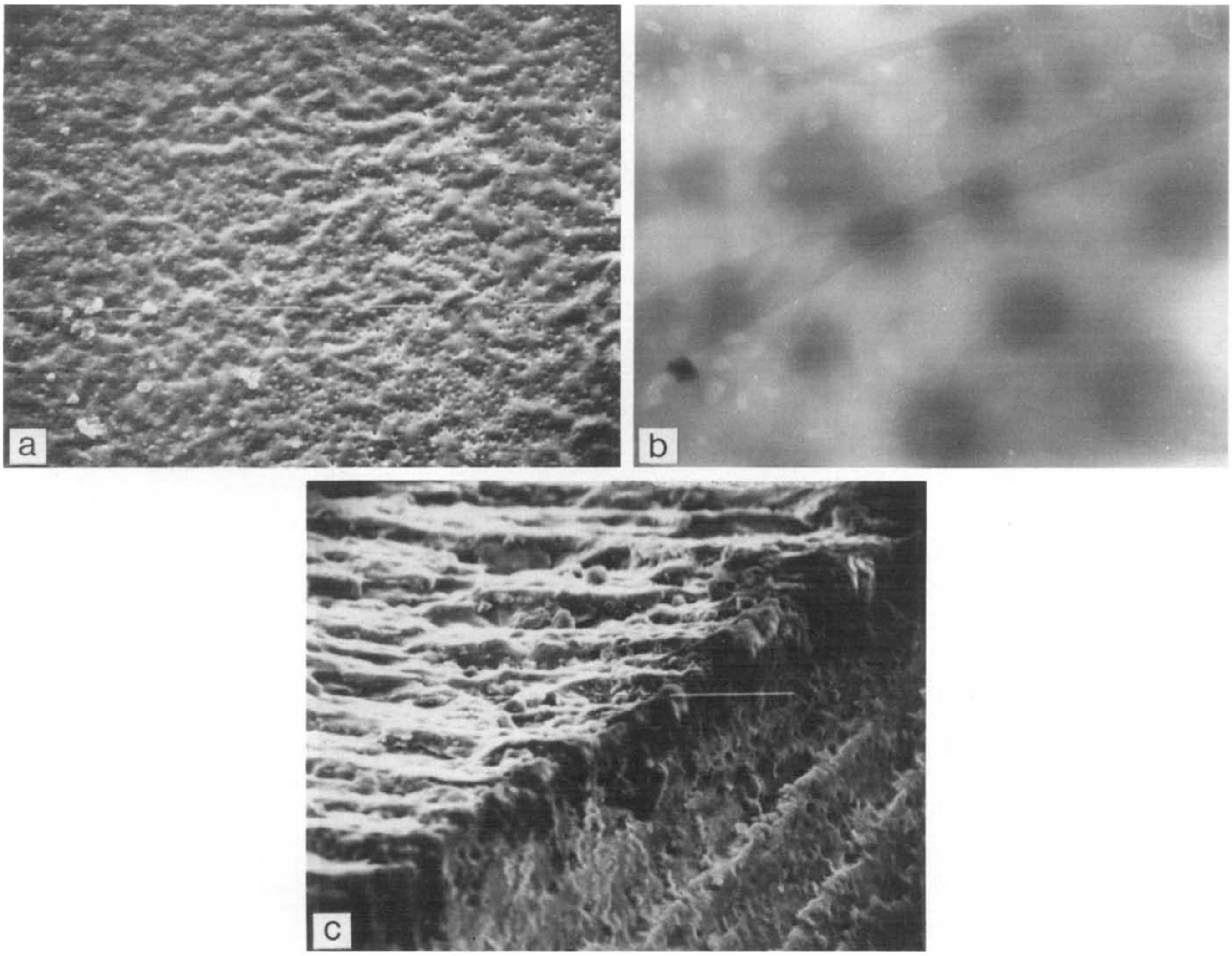

Figure 3 Electron micrographs of TETA- and DGBP-cured rubber modified epoxy resins. (a) 15% + DGBP cured material; surface showing the typical holes and ductile surface; markers, 10 μm; (b) transmission micrographs of 12½% + DGBP cured materials; rubbery phases appear black and are typically between 0.5 and 1.5 μm in diameter; (c) an edge showing the highly-reflective fracture surface and layered structures; dimpled structure is evident throughout the bulk of the material possibly arising from the removal of the rubbery occlusions on fracture; markers, 10 μm

of resin (1 cm^3) taken from the centre of the disc, to sudden impact. The most striking feature observed in these materials (*Figure 3a*) is the presence of 'holes'. Similar structures were observed in TETA-cured resins and have been reported previously in piperidine-cured materials[14-16] where they have been attributed to the presence of rubber occlusions. If this were so, then it would be expected that there would be a replication of the holes in terms of nodules on the companion surface. A careful examination of the surfaces failed to reveal any such features.

Transmission electron micrographs of thin films of the resin, (*Figure 3b*) indicates that phase separation occurs. The occlusions have dimensions between 0.5 and 1.5 μm in diameter, consistent with observations of similar features in other epoxy resins. A careful examination of the fracture surfaces indicated that in certain cases failure appears to follow well-defined layers, (*Figure 3c*). This layer structure appears to exist throughout the bulk of the resin and possibly arises as a consequence of the inefficient mixing of the resin and the curing agent. As the resin cures, so the viscosity rises and further restricts diffusion into the bulk. The high concentration of curing agent leads to a highly crosslinked region which is more susceptible to failure than the ductile bulk material. The layers appear brighter in the electron micrograph due to the higher electron capture cross-section of the nitrogen-containing material.

MECHANICAL STUDIES

Experimental, results and discussion

Specimens of gauge length 78.75 mm and cross-section 52.82 mm^2 were fractured in tension in a standard Instron machine at a constant crosshead speed of 5.25 mm min^{-1}. The measurements were performed over a temperature range 293 to 328K in an environmental chamber fitted on the Instron which maintained the sample temperature to within ±1K.

Table 4 compares the values of fracture stress of the specimens measured as a function of temperature. The modulus values (*Figure 4*) were computed from the initial part of the load–extension curves. The fracture toughness values in *Figure 4* were estimated from the area under the entire load–extension curve obtained during the fracture

Table 4 Typical values of fracture stress of rubber-modified epoxy resins

Curing agent	Code	Temperature (K)	Fracture stress (MN m^{-2})
TETA	10%	293	12
		308	28
		328	0.2
TETA	12½%	293	12
		308	43
		328	0.2
TETA	15%	293	18
		308	31
		328	14
DGBP	10%	293	46
		308	22
		328	0.2
DGBP	12%	293	47
		308	14
		328	0.2
DGBP	15%	293	41
		308	15
		328	0.2

of an unnotched specimen in tension and, as such, are not directly comparable with conventional toughness data.

A previous study[17] of a series of carboxyl-terminated butadiene/acrylonitrile/epoxy systems cured with piperidine has shown that strength and modulus decrease with increasing rubber content. A similar trend was identified both in TETA- and DGBP-cured resins. The largest change observed between the polymers studied is between the TETA- and DGBP-cured materials. For the same rubber concentration the former exhibited a fracture stress (*Table 4*) a factor of 4 less than the glycol-cured materials at room temperature. For DGBP-cured material, the value of the fracture toughness decreased with an increase in temperature (*Figure 4*). In contrast, the TETA-cured materials exhibited the lowest fracture toughness value 0.1–0.3 kJ m^{-2} at room temperature, where they all failed without much plastic deformation. The fracture toughness values of these materials showed an initial increase, followed by a decrease with increasing temperature, except for the case of the 15% materials where the value increased right up to 328K.

These changes in modulus and fracture toughness, may in part be attributed to differences in the effective functionality of the curing agent. The TETA-cure is tetrafunctional (2 NH_2 and 2 NH groups per unit) whereas the DGBP is bifunctional (2 NH_2 groups per unit) with respect to its reactivity towards the epoxy grouping of the bisphenol A unit. Statistically the effective functionality of the curing agent will be lower than the value indicated above. However, it is not unreasonable to expect that the probability of formation of a three-dimensional network will be higher in the TETA-cured system than in the DGBP.

For both the TETA- and DGBP-cured materials there is a marked decrease in the tensile modulus between 308 and 328K. Clearly this decrease can be associated with an increase in mobility on passing through the glass transition of the epoxy phase. A further consequence of the three-dimensional network formation in the TETA-cured system is the retention of a high modulus value above T_g.

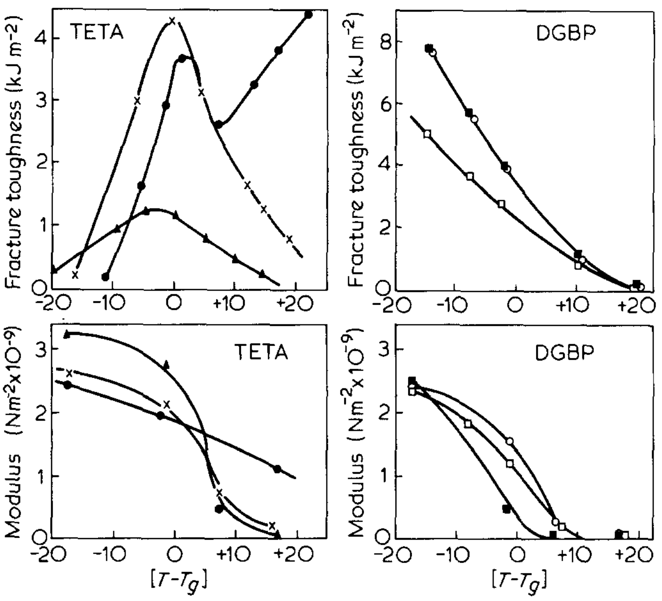

Figure 4 Variation of the fracture toughness and modulus with temperature for TETA- and DGBP-cured materials. The reduced temperature axis used is obtained by subtracting the glass transition temperature from the actual temperature of measurement. TETA: ▲, 10%; X, 12½%; ●, 15% DGBP: ■, 10%; ○, 12½%; □, 15%

CONCLUSIONS

From this study it has been shown that the rubber-modified epoxy resins are, at certain concentrations, multiphase systems. The equilibrium physical properties are consistent with the rubbery phase occurring as occlusions within the bulk epoxy phase. The change of functionality of the curing agent has a marked effect on the mechanical properties of the resin and this is reflected in the fracture strength, toughness and tensile modulus.

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