Polymer Vol. 37 No. 10, pp. 1897–1905, 1996
Copyright © 1996 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0032-3861/96/$15.00 + 0.00

Ternary blends of epoxy, rubber and polycarbonate: phase behaviour, mechanical properties and chemical interactions

Laurent Jayle, Clive B. Bucknall and Ivana K. Partridge*
Advanced Materials Group, Cranfield University, Cranfield, Bedford, MK43 0AL, UK

and John N. Hay* and Alan Fernyhough
Kobe Steel Europe Ltd, 10 Nugent Road, Guildford, Surrey, GU2 5AF, UK

and Ikuo Nozue
Kobe Steel Ltd, 5-5 Takatsukadai 1-chome, Nishi-ku, Kobe, Hyogo 651-22, Japan
(Received 22 August 1995)

A ductile thermoplastic, polycarbonate, has been blended with the diglycidyl ether of bisphenol A (DGEBA) epoxy resin to increase the 'toughenability' of the resin. Cured epoxy–polycarbonate systems showed no increase in fracture toughness relative to the neat epoxy resin. The binary blends were miscible, single-phase systems. Addition of rubber to both the epoxy and the epoxy–polycarbonate blends leads to significant improvements in the critical strain energy release rate, G_{IC}, of the cured resin. The presence of the polycarbonate produced no additional improvement in G_{IC} relative to rubber toughening alone. This is ascribed to a degradation reaction of the polycarbonate occurring during blending. The chemical nature of this reaction is discussed. Copyright © 1996 Elsevier Science Ltd.

(Keywords: epoxy–rubber–PC blends; fracture toughness; morphology)

INTRODUCTION

Epoxy resins are well established in a variety of applications, ranging from moulding compounds for integrated circuit encapsulation to carbon fibre reinforced composites for structural aerospace applications. The ability to toughen these resins and to translate this toughness into improvements in the impact resistance of their fibre reinforced composites is an important factor in their continued expansion into new applications.

Two main approaches have been taken to increasing the fracture toughness of epoxy resins, namely rubber toughening[1] and thermoplastic toughening[2]. In rubber toughening, the rubber particles are normally present as a separate second phase within the epoxy matrix. Large increases in fracture toughness can be observed at relatively low rubber addition levels[3], but usually with a sacrifice in resin modulus and end-use temperature. To overcome these drawbacks, other approaches have been adopted, including toughening by thermoplastics[2] and addition of inorganic fillers such as ceramic whiskers[4]. In thermoplastic toughening, the thermoplastic is usually dissolved in the liquid epoxy precursor(s), with phase separation occurring during subsequent cure[2,5,6].

For highly crosslinked thermosets, the intrinsic ability of the resin to be toughened (the 'toughenability') is often too low for rubber toughening to be effective. A number of studies have demonstrated the importance of matrix ductility in promoting effective toughening in epoxy resins[7–11]. One route to increasing the ductility of the matrix is by reducing the crosslink density[9,11]. The approach adopted in this present study was to increase the epoxy resin ductility by the addition of a miscible, ductile thermoplastic which should then allow the matrix to be toughened effectively by the addition of rubber. The ductile thermoplastic selected was polycarbonate (PC). Subsequent to our initial communication on this subject[12], other workers independently have reported studies of the toughening of epoxy resins by the addition of polycarbonate alone[13–15]. Ohsako *et al.*[16] have also reported the effect of added polycarbonate on the elongation properties of rubber-modified epoxies.

EXPERIMENTAL

Materials

The diglycidyl ether of bisphenol A (DGEBA) (Araldite MY750; M_n ca. 380 g mol^{-1}), triglycidyl-*p*-aminophenol (Araldite MY0510; M_n ca. 300 g mol^{-1}) and curing agent, 4,4′-diaminodiphenylmethane (DDM) (HT972), were all obtained from Ciba-Geigy. The amorphous polycarbonate Lexan L141 (M_n ca. 28 700 g mol^{-1}) was supplied by General Electric, and was abbreviated as PC.H. Hydroxyl-terminated polycarbonates were prepared by the Manchester Materials Science Centre; these functionalized polymers had molecular weights (M_n) of 7100 (fPC.L), 9200 (fPC.M),

---

*To whom correspondence should be addressed. Present address: Department of Chemistry, University of Surrey, Guildford, Surrey, GU2 5XH, UK and 26000 (fPC.H) g mol^{-1}, respectively. The rubber used was HYCAR CTBN 1300X8 from BFGoodrich and had a molecular weight, M_n of 3600 g mol^{-1}. The rubber was prereacted with epoxy resin prior to use, following the procedure of Verchere *et al.*[17], to give an epoxy-terminated rubber, ETBN.

Blending and curing procedures

In the blending procedure used to prepare the epoxy–PC blends, a 15 wt% solution of the PC in dichloromethane was added to hot epoxy resin at 120°C, such that the final concentration of PC in the epoxy was 10 parts per hundred parts of epoxy (phr). The mixture was degassed *in vacuo* at 100–110°C for 1 h. Resin plaques were moulded in upright glass-faced moulds pretreated with Frekote 44 release agent. For neat epoxy resin and PC-modified resin, the stoichiometric amount of molten DDM (26 phr) was added to the hot resin at 80°C and, when homogeneous, the mix was poured into the preheated mould at 60°C. After degassing, the resins were cured at 80°C for 6 h, followed by 3 h at 150°C. For resins containing rubber, the ETBN adduct was added to the hot epoxy or epoxy–PC blend at 60°C. After degassing, molten DDM was added to the resin at 80°C and the resin was then cured as above.

A shorthand nomenclature is used to describe the different cured resin systems. For example, 750-fPC.M7.4 means the MY750 epoxy modified by 7.4 wt% of fPC.M polycarbonate, while 750–PC.H5–R15 is the abbreviation for MY750 epoxy which has been modified by 5 wt% of L141 polycarbonate and 15 wt% of CTBN rubber.

Characterization methods

The phase separation of epoxy–PC blends was examined in transmitted light using an Olympus microscope. Scanning electron microscopy (SEM) was carried out on fracture surfaces and etched samples using an ISI/ABT 55 instrument with an accelerating voltage of 15 kV. Etched samples were prepared by immersing the fractured samples in dichloromethane for 1 or 3 h.

Differential scanning calorimetry (d.s.c.) was conducted on a Perkin-Elmer Series 4 system, at a heating rate of 10°C min^{-1}. The glass transition temperature (T_g) was taken as the temperature of onset of the transition.

For reactive blends, the heat of reaction, ΔH (J g^{-1}), was measured and normalized for the blends MY750/polycarbonate/DDM (100/PC phr/26) according to the following expression:

$$\Delta H_{100\%} = \Delta H \times \frac{126 + \text{PCphr}}{126} \qquad (1)$$

where ΔH is the measured heat of reaction (J g^{-1}) and $\Delta H_{100\%}$ is the normalized heat of reaction (J g^{-1}). Each result is the average of two measurements.

Dynamic mechanical thermal analysis (d.m.t.a.) was performed on a Polymer Laboratories instrument, using the single cantilever bending mode. A heating rate of 3°C min^{-1} was used, with T_g being taken as the maximum in the $\tan\delta$ curve. Image analysis was carried out on SEM photographs by using a Joyce Loebl image analyser with Genias 2.5 software. The volume fraction of the dispersed phase, V_D, was taken as the surface fraction observed on the micrographs[18]. Particle size and particle size distribution were analysed statistically. Infra-red (i.r.) spectroscopy was performed on a Perkin-Elmer 1420 spectrophotometer, using a heated KBr cell to follow the cure reactions. Gel permeation chromatography (g.p.c.) was carried out on a Perkin-Elmer Series 250 + LC135 system, using 0.2 wt% solutions in dichloromethane. A guard column and two polystyrene columns of porosity 500 and 10^4 Å were used.

Mechanical testing

The compressive yield stress was obtained by uniaxial compression testing on a Nene mechanical testing machine with a crosshead speed of 0.5 mm min^{-1}. Samples of dimensions $10 \times 10 \times 4$ mm^3 were used. The compressive yield stress, σ_y, is the average of five measurements. The Young's moduli of the materials were determined by using a Darlington-Saunders creep machine fitted with an extensometer. The 100 s isochronous modulus at small strains, E_{100}, is calculated from the slope of the stress–strain curve; the E_{100} values are the average of two measurements. Fracture testing was carried out on an Instron test machine, using single-edge-notched, three-point-bend specimens, according to the protocol of the European Structural Integrity Society (ESIS), formerly the European Group on Fracture (EGF)[19]. The critical stress intensity factor, K_{IC}, and the critical strain energy release rate, G_{IC}, were determined according to the protocol; the K_{IC} and G_{IC} values were taken as the average of eight valid tests.

RESULTS AND DISCUSSION

The overall aim of this work was to enhance the ductility and therefore the toughenability of an epoxy matrix. A prerequisite for this was anticipated to be complete dissolution of the ductile thermoplastic in the cured epoxy resin. Addition of a rubber which phase-separates as discrete particles during the cure process should consequently result in an increase in toughness of the thermoplastic-modified matrix[11].

Miscibility prior to cure

The phase separation of the system prior to cure was studied first. Solubility parameter calculations were carried out according to the method of Fedors[20], with the results shown in *Table 1*. These suggest that the polycarbonate should be more soluble in trifunctional (MY0510) than in difunctional (MY750) uncured epoxy resin. This theoretical conclusion was supported experimentally. Whereas neat PC could be dissolved in MY0510 at elevated temperatures, dissolution in MY750 was much more difficult. Solution blending of the functionalized polycarbonates in dichloromethane with MY750 epoxy resin invariably gave turbid blends above

Table 1 Solubility parameter values at 25°C for different materials

Material	Solubility parameter, δ ((cal cm^{-3})$^{0.5}$)
Difunctional epoxy (MY750)	9.2
Trifunctional epoxy (MY0510)	10.0
Polycarbonate	10.3
CTBN rubber	8.8[a]

[a] From ref. 21

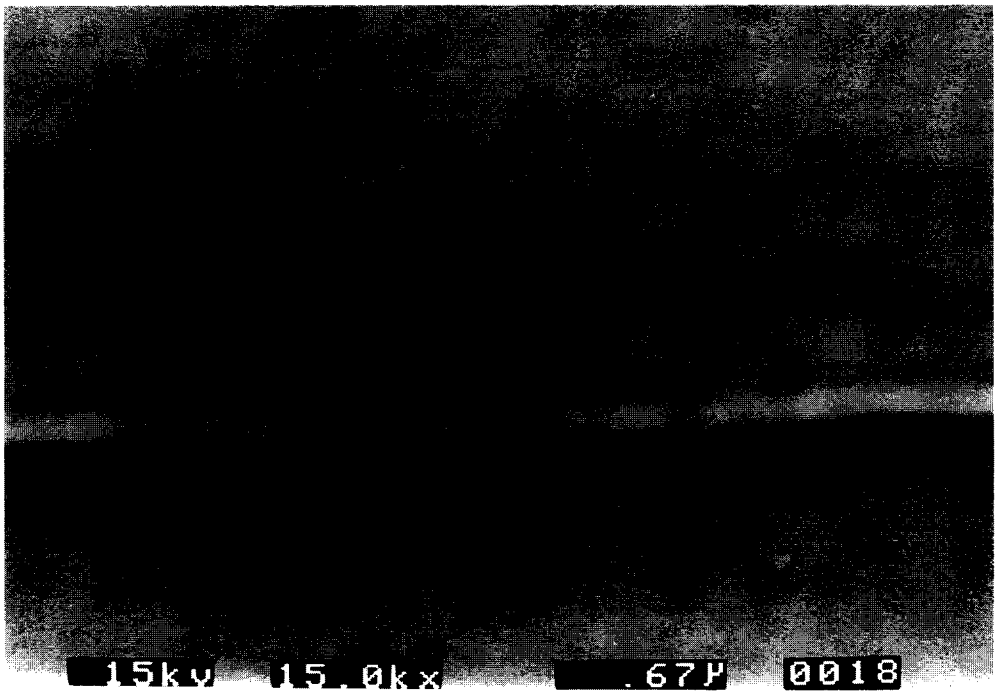


Figure 1 Scanning electron micrograph of the fracture surface of a cured epoxy–PC blend

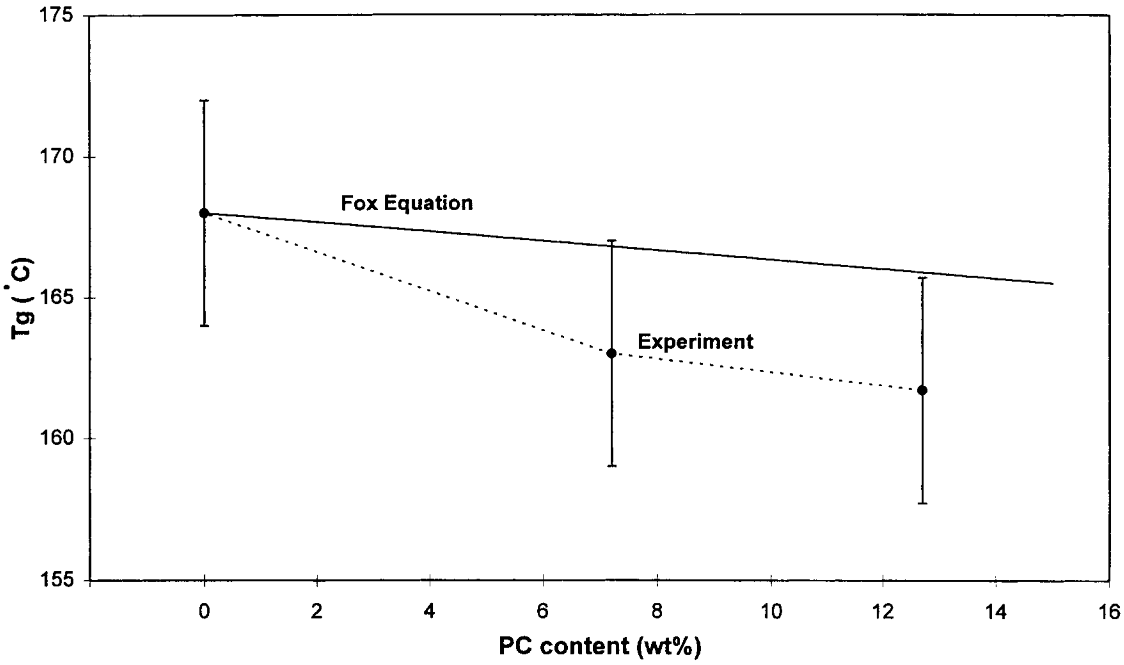


Figure 2 T_g as a function of PC content in cured epoxy–PC blends

5 phr PC content. Phase separation was confirmed by optical microscopy. Lexan L141, however, could be dissolved in MY750 to give a homogeneous mixture at concentrations up to 20 phr by using a modified solution blending procedure. Addition of the DDM hardener was found to have no effect on the miscibility of the above systems prior to cure.

Morphology of cured blends

Cured quasi-binary blends (epoxy + PC + DDM hardener) were studied by using SEM and d.m.t.a. All cured blends containing less than 30 phr PC were transparent. They exhibited brittle, featureless fracture surfaces up to a magnification of 20 000 (*Figure 1*). Etching with dichloromethane had no observable effect on the appearance of the fracture surfaces. The d.m.t.a. traces were in agreement with the SEM results and showed no evidence for phase separation in these systems. The results indicate that the epoxy and the PC are fully miscible in the cured blends.

The glass transition temperatures (T_g's) of the cured blends were determined by d.m.t.a. As expected, the T_g

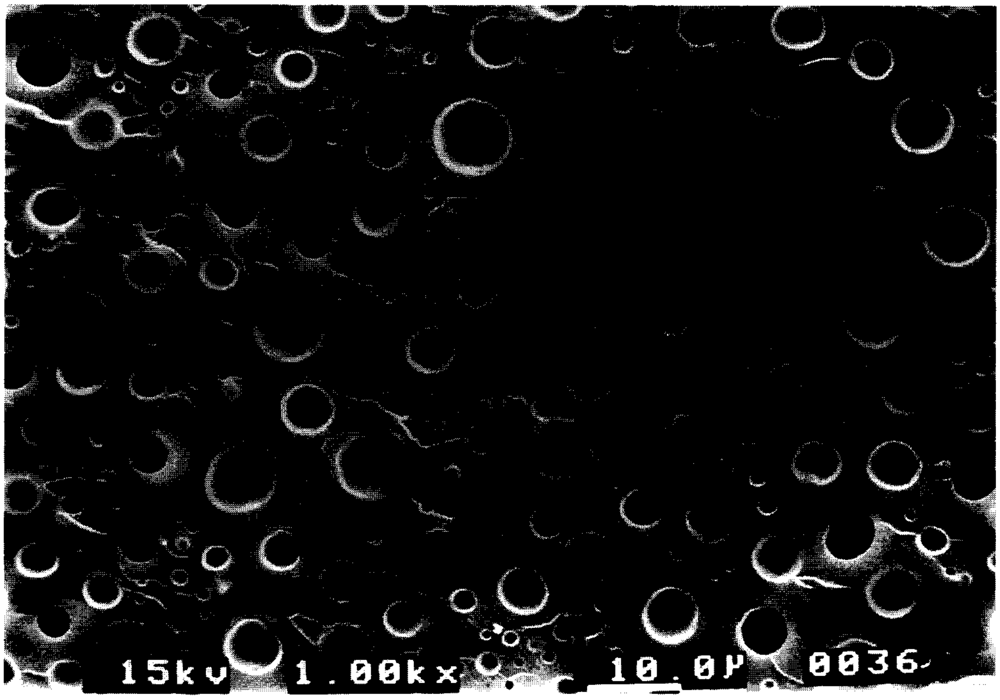


Figure 3 Scanning electron micrograph of the fracture surface of a cured epoxy–PC–rubber blend (CH_2Cl_2 etch)

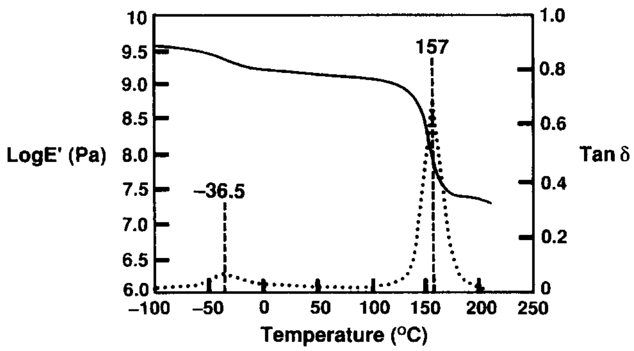


Figure 4 D.m.t.a. of a cured epoxy–PC–rubber blend

decreases as a function of increasing PC content (*Figure 2*), but to a greater extent than that predicted by the Fox equation[22]:

$$\frac{1}{T_g} = \frac{m_1}{T_{g1}} + \frac{m_2}{T_{g2}} \qquad (2)$$

where m_1, m_2 and T_{g1}, T_{g2} are, respectively, the mass fractions and T_g values of components 1 and 2 in the blend. Assuming this deviation from the expected graph is not simply a result of experimental error, the data suggest that the interaction between the epoxy resin and the polycarbonate is more than just a simple dissolution. This conclusion is supported by other evidence (see later).

Despite this possible complication, the miscibility of epoxy and PC, which was believed to be a prerequisite for increasing the epoxy resin toughenability, was obtained in these systems. Cured rubber-toughened blends (epoxy/rubber/DDM or epoxy/PC/rubber/DDM) were studied in the same way as the quasi-binary epoxy–PC blends. All of the cured blends were opaque. SEM of the fracture surfaces shows spherical particles dispersed uniformly in a continuous matrix. These particles are largely removed by etching with dichloromethane (*Figure 3*). These particles clearly represent a rubber-rich phase. It is assumed that the PC remains dissolved in the epoxy resin, although this was not demonstrated unequivocally: some dissolution or phase-separation of PC within the rubber particles is not ruled out. The system is therefore believed to consist of a polycarbonate-modified epoxy-resin continuous phase containing a dispersed rubber-rich phase.

D.m.t.a. confirmed the presence of a phase-separated rubber-rich phase (*Figure 4*). For all of the blends, a broad tan δ peak appears at around −35°C, corresponding to the T_g of the rubber-rich phase. The T_g is higher than expected, presumably due to incorporation of some epoxy or PC in the rubber-rich phase. The T_g of the epoxy-rich phase is up to 10°C lower than that of the neat MY750-DDM resin, due to dissolution of PC or rubber in the epoxy matrix. The nature of the PC used has little effect on these observations.

Image analysis has been used to analyse the electron micrographs of the fracture surfaces (see Appendix). In some cases, a bimodal distribution of particle sizes was observed. The volume fractions of the second phases are much higher (*Table 2*) than would be expected for phase separation of all of the rubber or rubber plus polycarbonate. This suggests that some epoxy resin is also included in the rubber-rich particles. Estimates based on the Fox equation suggest that at least 30% (by volume) of neat or PC-modified epoxy is contained within the rubber particles (perhaps as sub-inclusions). Very little rubber is dissolved in the neat or PC-modified epoxy resin.

Mechanical properties of cured epoxy resins

Mechanical testing of the cured epoxy resin systems was mostly restricted to those modified by the commercial polycarbonate PC L141, since insufficient quantities of the functionalized PCs were available. The mechanical

Table 2 Image analysis results and phase composition of epoxy systems modified by rubber and polycarbonate

System	Φ_R[a] (%)	V_D[b] (%)	d[c] (μm)	$d\sigma n$[d] (μm)	T_g (°C)	Φ_E^{C}[e] (%)	Φ_E^{D}[f] (%)	ϕ_R^{C}[g] (%)	Φ_R^{D}[h] (%)
750–R15	17.9	28.9	3.3	2.0	165	99.2	38.5	0.8	61.5
750–fPC.L5–R15	17.9	25.7	3.4	2.8	157.5	97.2	38.8	2.8	61.8
750–PC.H5–R15	17.9	24.1	4.1	2.6	159	97.6	33.3	2.4	66.7

[a] Volume fraction of rubber

[b] Volume fraction of the dispersed phase

[c] Average particle diameter

[d] Population standard deviation

[e] Volume fraction of epoxy in the continuous phase (estimated)

[f] Volume fraction of epoxy in the dispersed phase (estimated)

[g] Volume fraction of rubber dissolved in the continuous phase (estimated)

[h] Volume fraction of rubber in the dispersed phase (estimated)

Table 3 Mechanical properties of neat epoxy, polycarbonate, polycarbonate-modified epoxy, rubber-modified epoxy, and rubber and polycarbonate-modified epoxy systems

System	E_{100} (GPa)	σ_y[a] (MPa)	K_{IC} (MPa m$^{0.5}$)	G_{IC} (kJ m^{-2})	G_{IC}[b] (kJ m^{-2})
750 (neat)	2.70 ± 01	99 ± 2	0.81 ± 0.02	0.19 ± 0.01	0.26
PC.H (neat)	2.21 ± 0.05	66 ± 3	2.80 ± 0.15	3.50 ± 0.43	3.11
750–PC.H7.4	2.80 ± 0.1	95 ± 1	0.71 ± 0.05	0.10 ± 0.01	0.17
750–PC.H13.7	2.70 ± 0.1	89 ± 2	0.66 ± 0.02	0.12 ± 0.01	0.14
750–R15	1.81 ± 0.01	65 ± 2	0.84 ± 0.02	0.31 ± 0.02	0.34
750–FPC.L5–R15	1.83 ± 0.01	64 ± 1	0.84 ± 0.02	0.30 ± 0.03	0.34
750–PC.H5–R15	1.86 ± 0.02	65 ± 1	0.87 ± 0.02	0.31 ± 0.01	0.36

[a] *Compressive* yield stress

[b] Calculated using equation (3)

properties measured were 100 s isochronous modulus (E_{100}), compressive yield stress (σ_y), critical stress intensity factor (K_{IC}) and critical strain energy release rate (G_{IC}). The mechanical test results obtained are summarized in *Table 3*. All of the resin plaques tested exhibited brittle fracture.

In the PC-modified epoxy resins, E_{100} did not change significantly with varying PC content; K_{IC}, G_{IC} and σ_y were all found to decrease slightly with increasing PC content. This simultaneous decrease in fracture toughness and compressive yield stress is unexpected, since a decrease in σ_y usually leads to an increase in the ability of the matrix to deform plastically, assuming no change in network structure[9,15,23–25]. The lack of toughness enhancement in the PC-modified epoxy does not necessarily mean that the ability to be toughened by rubber particles is not improved[9]. The slight decrease in σ_y and T_g in the PC-modified epoxies might suggest that shear band formation could be promoted in the rubber-containing systems.

These results contrast with some recent reports of epoxy resins toughened by polycarbonates. Hourston and coworkers[13] showed that the addition of a PC to a DGEBA resin cured with diethylenetriamine (DETA) led to a small increase in K_{IC} and G_{IC}. The PC used had an M_n value of 34 000, close to that of the L141 which was used in this present study. The resultant blends were also miscible. A more recent paper[26] reported the effect of PC on a DGEBA epoxy cured by DDM, as investigated in this present work. In this case, the epoxy and the PC were prereacted by a thermal transesterification reaction. A two-phase morphology was obtained by controlling the degree of co-reaction. An increase in the Izod impact strength was reported for the PC-modified epoxy. Di Liello *et al.*[15] studied a PC-modified epoxy cured with an anhydride curing agent. No phase separation was observed from d.m.t.a. or SEM measurements. Significant increases in both K_{IC} and G_{IC} were found on increasing the PC content. These increases in fracture toughness were ascribed to an enhanced capacity for plastic deformation of the matrix due to formation of an epoxy–PC network[14,15]. A shear yielding mechanism was proposed. Yield stress was found to decrease with increasing PC content, in agreement with our results; however, the expected correlation between reduced yield stress and increasing fracture toughness due to enhanced plastic deformation was observed in the study by Di Liello *et al.*[15].

For the epoxy and PC-modified epoxy systems containing rubber, the results shown in *Table 3* may be summarized as follows. As expected, the presence of rubber particles led to a large decrease in modulus and yield stress, independent of the type of PC being used. In contrast to the slight decrease in G_{IC} on adding PC to the epoxy resin, the addition of rubber only to the epoxy increased G_{IC} by a factor of two. The combination of PC and rubber produced no *additional* increase in G_{IC} relative to rubber toughening alone. Thus the addition of PC to the epoxy resin does not improve its ability to be toughened by rubber particles, despite the slight decrease in σ_y observed in the PC-modified epoxies. Any potential improvements in fracture toughness may have been

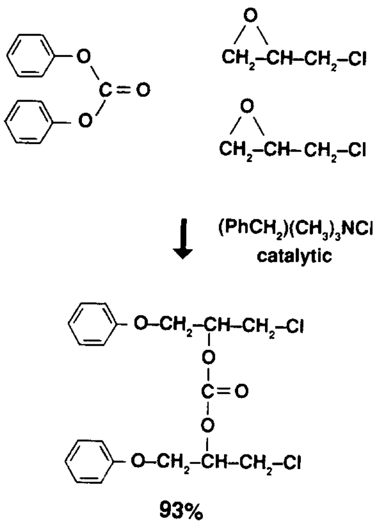


Figure 5 Catalysed epoxy–PC reaction

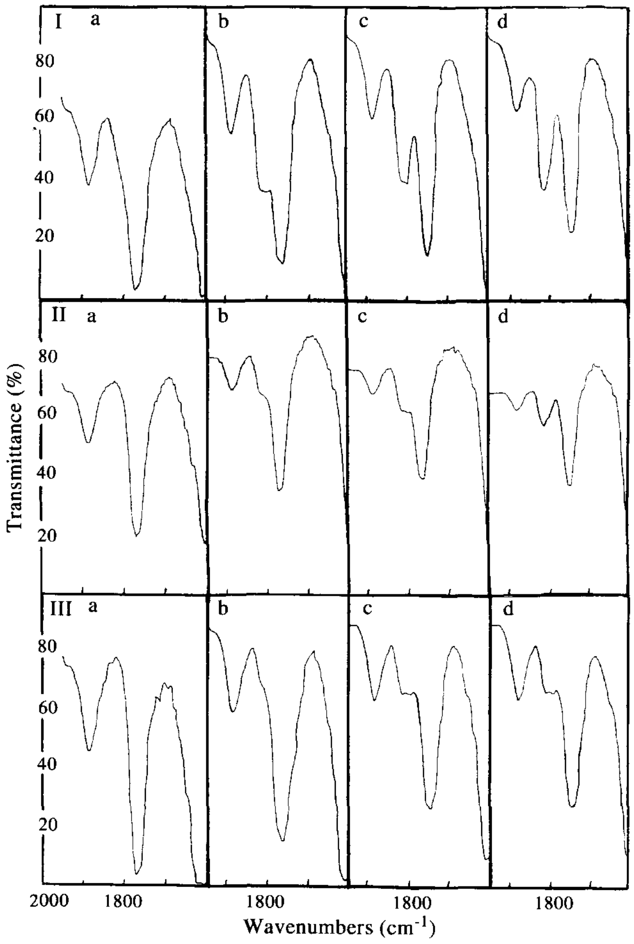


Figure 6 I.r. spectra of MY750–fPC.M blends. I MY750–fPC.M–BTMAC (100 : 10 : 0.2): (a) 23°C; (b) 35 min, 80°C; (c) 3 h 32 min, 80°C; (d) 4 h 10 min, 80°C + 20 min, 150°C. II MY750–fPC.M (100 : 10): (a) 23°C; (b) 31 min, 80°C; (c) 3 h 07 min, 80°C; (d) 3 h 07 min, 80°C + 1 h 04 min, 150°C. III MY750–fPC.M–DDM (100 : 10 : 26): (a) 23°C; (b) 3 h 32 min, 80°C; (c) 7 h 16 min, 80°C + 1 h 14 min, 150°C; (d) 7 h 16 min, 80°C + 3 h 31 min, 150°C

counterbalanced by the reduction in the G_{IC} of the epoxy on adding PC. Although the presence of rubber led to large increases in G_{IC}, the change in K_{IC} was insignificant, due to the large reduction in modulus:

$$G_{IC} = \frac{K_{IC}^2(1-\nu^2)}{E_{100}} \tag{3}$$

where ν is the Poisson ratio. Assuming a constant Poisson ratio of 0.35 for all of the blends, *Table 3* shows that the experimental values for G_{IC} are in good agreement with the values calculated by using equation (3).

The use of combinations of polysulfone thermoplastic and rubber to toughen epoxy resins has been reported recently[27]. The combination of the two toughening agents produced a much larger increase in epoxy fracture toughness than the addition of either alone. Morphological examination of these systems showed that the rubber was acting as a 'coupling agent', thus improving the interfacial bonding between the epoxy resin and the phase-separated polysulfone domains. Other work in our laboratories[28] has shown that significant increases in the fracture toughness of a DGEBA epoxy can be obtained by blending this with a brominated bisphenol A carbonate oligomer and CTBN rubber. The increased fracture toughness is ascribed to the production of a bimodal particle size distribution of the rubber particles.

Chemical interactions

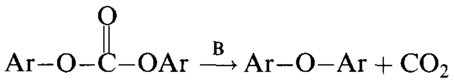
The simultaneous decrease in both fracture toughness and compressive yield stress on modifying the epoxy with PC suggests that the epoxy network structure has changed. This may also explain the observed T_g effects. Recent reports[14–16,26] provide a precedent for chemical interactions occurring in the epoxy–PC systems. I.r. spectroscopy, g.p.c. and d.s.c. were used to study the chemical changes occurring during cure of the resins. Earlier work by Yu and Bell had demonstrated the existence of a reaction between epoxy and PC when catalysed by an ammonium salt (*Figure 5*)[29]. The reaction effectively produces a modified epoxy resin crosslinked by carbonate groups. The reaction was not observed, however, in the absence of a catalyst.

Using the resins described in our study, comparative studies were carried out on epoxy–PC blends, both uncatalysed and catalysed by benzyltrimethylammonium chloride (BTMAC), to determine whether the same reaction occurs in our system. The standard blending procedure was used, with catalyst (0.2 phr if required) added immediately before beginning cure and analysis. D.s.c. experiments showed an exotherm peak in the catalysed systems, but none in the uncatalysed blends. Thus if the reaction occurs at all in uncatalysed epoxy–PC blends, it is either very slow or occurs to a very small extent. I.r. spectroscopy was used to probe the interactions further (*Figure 6*). It was first demonstrated by d.s.c. that potassium bromide also catalyses an epoxy–PC reaction, but at a much higher temperature than BTMAC (peak exotherm at 220°C *versus* 154°C). This effect was therefore borne in mind when interpreting the i.r. spectra produced using KBr discs. Heating the epoxy–PC blend in the presence of BTMAC produced a distinct shoulder and eventually a peak at 1810 cm⁻¹ on a carbonate peak originally centred at around

$1770\,cm^{-1}$[26]. This is thought to be due to the reaction proposed by Yu and Bell[29], although an epoxy peak at $915\,cm^{-1}$ did not change significantly. A similar phenomenon is observed in the uncatalysed blends (perhaps due to KBr catalysis?), but to a much lesser extent. In the presence of DDM hardener, development of the shoulder at $1810\,cm^{-1}$ is much reduced due to preferential reaction of the epoxy rings with the primary amine groups. The mixing and degassing steps prior to addition of the hardener were studied in more detail. At the mixing temperature of 120°C, a very distinct shoulder appears on the higher-wavenumber side of the carbonate peak at $1770\,cm^{-1}$. Some splitting of the peak centred on $1770\,cm^{-1}$ may also occur. Broadly similar effects are observed after degassing. The differences between these observations and the i.r. spectra obtained in the case of the catalysed epoxy–PC reaction provide no clear evidence for this reaction occurring during the mixing and degassing procedures; however, some kind of interaction is clearly promoted by mixing and degassing.

Further evidence was obtained from g.p.c. The effect of the degassing procedure is shown in the chromatogram of the epoxy–PC blend in comparison with the starting epoxy and PC (*Figure 7*). It can be seen clearly that there is no peak at an elution time corresponding to the original PC, while a broad hump appears at a longer elution time, i.e. lower molecular weight. Heating the epoxy resin alone under the same conditions does not lead to formation of this peak, which is therefore not accounted for by homopolymerization of the epoxy. The peak is believed to correspond to a degraded PC of lower molecular weight than the original PC (PC.H). Thus the PC chains are cleaved in the presence of epoxy resin at elevated temperature, and this degradation was found to increase with heating time. Clearly, any reaction between the epoxy and PC, analogous to that of Yu and Bell[29], does not occur to any significant extent since that would have the effect of producing high-molecular-weight species. Incorporation of the BTMAC catalyst into the blends produced a complex, widely spread peak after degassing, with elution times varying between those of the original PC and epoxy. This peak is believed to result from competition between the PC degradation and reaction between the epoxy and degraded PC fragments. The nature of this degradation is discussed below.

The experiments described above consider only those interactions which occur in the absence of the DDM hardener. Further experiments were carried out in the heated KBr i.r. cell using epoxy–PC–DDM mixtures. An absorption not observed in the case of epoxy–DDM and epoxy–PC blends appeared at $2330\,cm^{-1}$ when the cure temperature reached 150 °C. This absorption was thought to be due to carbon dioxide produced by base-catalysed decomposition of the PC[30]:



$$Ar{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OAr \xrightarrow{B} Ar{-}O{-}Ar + CO_2$$

Attempts to substantiate this by studying the reaction of PC–DDM blends were inconclusive. No CO_2 absorption could be observed, perhaps as a result of the very low viscosity of these blends at elevated temperatures allowing the gas to escape readily—the epoxy–PC–DDM blends in contrast are very viscous. The PC–DDM samples do show a steady reduction in the intensity of the carbonate absorption with increasing time and temperature. Initially a new absorption appears at $1735\,cm^{-1}$, but both the new absorption and the carbonate absorption have virtually disappeared by the time the temperature reaches 150°C. The disappearance of the carbonate band is consistent with the mechanism outlined above. The appearance of the absorption at $1735\,cm^{-1}$, however, might be indicative of the formation of urethane groups by reaction of the carbonate with the amine. In the epoxy–PC–DDM mixtures, the intensity of the carbonate band was unchanged during the course of the reaction, suggesting that in the real resin system, preferential reaction of the DDM with the epoxy limits the amount of PC degradation caused by the hardener. Hydrolysis and subsequent decarboxylation has also been proposed in similar blends, leading to evolution of carbon dioxide[14]. This alternative mechanism can neither be proved nor disproved by the above observations.

The effect of the PC and its degradation products on the epoxy–DDM cure reaction was studied by d.s.c. A slightly modified blending procedure (B) (c.f. the normal blending procedure (A)) was used for most of these experiments. This involved adding the PC solution to the epoxy resin at 80°C instead of 120°C, prior to degassing. The results of the measurements of the peak exotherm temperature (T_{min}), the heat of reaction (ΔH) and the calculated $\Delta H_{100\%}$ are listed in *Table 4*. A number of trends are evident, e.g. T_{min} decreases and hence the rate of the epoxy cure reaction increases on addition of PC to MY750–DDM. As the polycarbonate molecular weight increases there is a small increase in the rate of the cure reaction. It is also apparent that degassing produces an increase in the cure rate. Combining all these observations, it is not unreasonable to conclude that the epoxy cure reaction is being catalysed by species arising from the PC, in particular by the degradation products produced during the degassing procedure. One of the present authors has observed a similar accelerating effect in the cure of epoxy–CTBN blends cured by a cycloaliphatic diamine when a brominated bisphenol A carbonate oligomer is added[28]: dynamic dielectric analysis was used to compare reaction rates, but the reasons for the cure acceleration were not elucidated.

In summary, these studies of the chemical interactions provide no evidence for a reaction between the epoxy and the PC, even in the case of the hydroxyl-functionalized PCs. Some degradation of the PC by DDM may occur, but preferential reaction of DDM with the epoxy limits

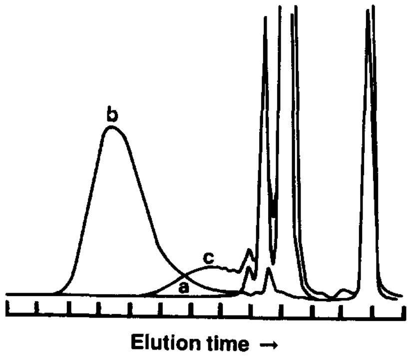


Figure 7 Results of g.p.c. studies: (a) epoxy resin; (b) PC; (c) degassed epoxy–PC blend

Table 4 D.s.c. results obtained for the polycarbonate-modified epoxy blends (composition in parts by weight)

MY750	fPC.L	fPC.M	fPC.H	PC.H	DDM	Procedure[a]	ΔH (J g^{-1})	$\Delta H_{100\%}$ (J g^{-1})	T_{min} (°C)
100	0	0	0	0	26	MY750, degassed[b]	425 ± 18	424 ± 18	163.8 ± 1
100	5	0	0	0	26	B	359 ± 4	388 ± 4	155.5 ± 1
100	10	0	0	0	26	B	425 ± 7	443 ± 7	157.1 ± 1
100	0	5	0	0	26	B	392 ± 4	408 ± 4	159.7 ± 1
100	0	10	0	0	26	B	386 ± 11	417 ± 11	155.3 ± 1
100	0	10	0	0	26	B, without degassing	383 ± 13	413 ± 13	162.8 ± 1
100	0	0	10	0	26	B	375 ± 7	404 ± 5	153.3 ± 1
100	0	0	0	10	26	A	415 ± 6	448 ± 6	154.7 ± 1
100	0	0	0	10	26	A, without degassing	424 ± 10	458 ± 10	165.2 ± 1

[a] A, normal blending procedure; B, modified blending procedure
[b] MY750 degassed for 1 h at 100–110°C before adding DDM

the effect of the degradation. The dominant effect appears to be degradation of the PC during the blending procedure. These degradation products seem to act as catalysts for the epoxy–DDM cure reaction.

The precise nature of these degradation products has not been established. Some clues are provided by the observed reduction in molecular weight and by other studies reported in the literature. The occurrence of both transesterification and transamidation during the cure of an epoxy–PC–diamine system has been reported[26]. Transesterification does not necessarily lead to a reduction in the PC molecular weight, although transamidation will cleave the PC to produce a phenol-terminated fragment and a urethane (carbamate)-containing fragment. Evidence was found for the presence of a urethane in the i.r. spectra of PC–DDM systems, but such a mechanism cannot explain degradation during degassing and prior to the addition of DDM.

In a detailed study of anhydride-cured novolac epoxy–PC blends, Martuscelli's group also observed a reduction in the PC molecular weight following high-temperature mixing of the epoxy and PC components[14]. This was attributed to hydrolysis and decarboxylation of the PC giving phenol-terminated PC fragments. They also produced evidence for reaction of these PC fragments with the novolac epoxy to form epoxy-terminated PC chains. The resultant network structure is important in determining the properties of the cured resins[15]. Kinetic analysis of these systems demonstrated that both the initial curing rate and the final reactant conversion were reduced by the presence of PC[14]. The effect on the cure rate was ascribed to the increased viscosity of the PC-containing system as well as the participation of the PC in the crosslinking processes. Ohsako *et al.* also reported PC degradation in blends similar to those reported here[16]. An increase in the concentration of phenolic OH groups was also observed on heating the epoxy with PC, consistent with a mechanism such as PC hydrolysis.

In conclusion, hydrolysis of the PC by water present in the epoxy resin may be the cause of the PC degradation during blending. The data, however, do not provide unequivocal evidence for this mechanism. This mechanism would, however, explain the origin of the catalytic effect on the cure reaction, since the resultant increase in the concentration of phenolic groups would lead to an acceleration of the epoxy-amine reaction[31].

CONCLUSIONS

DGEBA epoxy resin and polycarbonate have been found to form miscible blends following cure by DDM hardener. The mechanical properties of the cured resins suggested that the matrix might be capable of promoting shear band formation in rubber-toughened systems. Epoxy–PC–rubber systems, however, showed no improvement in fracture toughness compared to the corresponding epoxy–rubber systems. It was also found that while addition of rubber to the epoxy or epoxy–PC systems produced a large increase in G_{IC}, little improvement in K_{IC} was observed owing to a large reduction in resin modulus. Evidence was obtained for degradation of the PC during the blending procedure and this is probably the dominant effect in determining the mechanical properties of these systems.

In summary, while it may be possible to improve matrix ductility by adding a ductile thermoplastic, it is necessary to ensure stability of the thermoplastic under the cure conditions to avoid undesirable chain scission. Use of alternative engineering thermoplastics miscible with epoxy resin might provide improvements in the performance of the PC system.

ACKNOWLEDGEMENTS

The authors thank the Manchester Materials Science Centre for supplying the functionalized polycarbonates and Kobe Steel for permission to publish this paper.

REFERENCES

1 Bucknall, C. B. 'Toughened Plastics', Applied Science, London, 1977
2 Bucknall, C. B. and Partridge, I. K. *Polym. Eng. Sci.* 1986, **26**, 54
3 Bucknall, C. B. and Yoshii, T. *Br. Polym. J.* 1978, **10**, 53
4 Jang, B. Z., Liau, J. Y., Hwang, L. R. and Shih, W. K. *J. Reinforced Plas. Compos.* 1989, **8**, 312
5 Raghava, R. S. *J. Polym. Sci. Polym. Phys. Edn* 1988, **26**, 65
6 Hedricks, J. L., Yilgor, I., Wilkes, G. L. and McGrath, J. E. *Polym. Bull* 1985, **13**, 201
7 Manzione, L. T., Gillham, J. K. and McPherson, C. A. *J. Appl. Polym. Sci.* 1981, **26**, 907
8 Kirschenbaum, S. L. and Bell, J. P. *J. Appl. Polym. Sci.* 1985, **30**, 1875
9 Yee, A. F. and Pearson, R. A. in 'Fractography and Failure

Mechanisms of Polymers and Composites' (Ed. A. C. Roulin-Moloney), Elsevier Applied Science, London, 1989, p. 291

10 Yee, A. F. and Pearson, R. A. NASA Contract Report 3852, 1984

11 Pearson, R. A. and Yee, A. F. *J. Mater. Sci.* 1989, **24**, 2571

12 Bucknall, C. B., Partridge, I. K., Jayle, L., Nozue, I., Fernyhough, A. and Hay, J. N. *Am. Chem. Soc. Div. Polym. Chem. Polym. Prepr.* 1992, **33**, 378

13 Chen, M. C., Hourston, D. J. and Sun, W. B. *Eur. Polym. J.* 1992, **28**, 1471

14 Abbate, M., Martuscelli, E., Musto, P., Ragosta, G. and Scarinzi, G. *J. Polym. Sci. Polym. Phys. Edn* 1994, **32**, 395

15 Di Liello, V., Martuscelli, E., Musto, P., Ragosta, G. and Scarinzi, G. *J. Polym. Sci. Polym. Phys. Edn* 1994, **32**, 409

16 Ohsako, T., Nagura, K. and Nozue, I. *Polymer* 1993, **34**, 5080

17 Verchere, D., Sautereau, H., Pascault, J. P., Moschiar, S. M., Riccardi, C. C. and Williams, R. J. J. *Polymer* 1989, **30**, 107

18 Underwood, E. E. 'Quantitative Stereology', Addison–Wesley, Reading, MA, 1970

19 'A Linear Elastic Fracture Mechanics (LEFM) Standard for Determining K_c and G_c for Plastics', ESIS Testing Protocol, March 1990

20 Fedors, R. F. *Polym. Eng. Sci.* 1974, **14**, 147

21 Manzione, L. T., Gillham, J. K. and McPherson, C. A. *J. Appl. Polym. Sci.* 1981, **26**, 889

22 Fox, T. G. *Bull. Am. Phys. Soc.* 1956, **1**, 123

23 Kinloch, A. J., Shaw, S. J. and Hunston, D. L. *Polymer* 1983, **24**, 1355

24 Pearson, R. A. and Yee, A. F. *J. Mater. Sci.* 1986, **21**, 2475

25 Pearson, R. A. and Yee, A. F. *J. Mater. Sci.* 1986, **21**, 2462

26 Don, T-M., Yu, Y. and Bell, J. P. *Am. Chem. Soc. Polym. Mater. Sci. Eng.* 1994, **70**, 49

27 Woo, E. M., Bravenec, L. D. and Seferis, J. C. *Polym. Eng. Sci.* 1994, **34**, 1664

28 Partridge, I. K. and Maistros, G. *Plast. Rubber Compos. Process Appl.* in press

29 Yu, Y. and Bell, J. P. *J. Polym. Sci. Polym. Chem. Edn* 1988, **26**, 247

30 Jost, P., Forestiere, A., Sillion, B. and Le Perchec, P. *Tetrahedron Lett.* 1982, **23**, 4311

31 Buist, G. J., Barton, J. M., Howlin, B. J., Jones, J. R. and Parker, M. J. *J. Mater. Chem.* submitted

APPENDIX

Composition of the dispersed and continuous domains in the cured epoxy resins

In order to calculate the phase composition in the rubber and rubber–polycarbonate modified systems, it is necessary to assume that there is no polycarbonate in the dispersed rubber particles, but that the polycarbonate is homogeneously blended with the epoxy matrix.

The weight fraction of rubber dissolved in the polycarbonate-modified epoxy matrix, W_R^C can be estimated by using the Fox equation as follows:

$$W_R^C = \left(\frac{T_{g1} \times T_{g2}}{T_g} - T_{g2}\right) \times \frac{1}{(T_{g1} - T_{g2})} \qquad \text{(A1)}$$

where T_{g1} is the T_g of the polycarbonate-modified epoxy matrix, taken as the T_g of the neat epoxy matrix ($T_{g1} = 441\,\text{K}$) (T_g values of polycarbonate-modified epoxy systems are close to the T_g values of neat epoxy systems), T_{g2} is the T_g of the pure rubber ($T_{g2} = 213\,\text{K}$), and T_g is the T_g of the system being investigated.

The corresponding volume fraction can be expressed as follows:

$$\Phi_R^C = \frac{\left(\dfrac{W_R^C}{\rho_R}\right)}{\left(\dfrac{W_R^C}{\rho_R}\right) + \left(\dfrac{1 - W_R^C}{\rho_E}\right)} \qquad \text{(A2)}$$

where ρ_R is the specific gravity of the rubber ($\rho_R = 0.948$), and ρ_E is the specific gravity of the polycarbonate-modified epoxy matrix ($\rho_E = 1.17$), which is calculated from the specific gravity of the pure epoxy resin (1.17) and pure polycarbonate ($\rho_{PC} = 1.20$), respectively.

The volume fraction of rubber in the dispersed phase, Φ_R^D is obtained by the equation expressing the conservation of the initial amount of rubber added into the blend:

$$\Phi_R^0 = (\Phi_R^D \times V_D) + \Phi_R^C(1 - V_D) \qquad \text{(A3)}$$

or

$$\Phi_R^D = \frac{\Phi_R^0 - \Phi_R^C(1 - V_D)}{V_D} \qquad \text{(A4)}$$

where Φ_R^0 is the initial rubber volume fraction, and V_D is the volume fraction of the dispersed phase, which is determined by image analysis.

In the above, Φ_R^0 is given by the following expression:

$$\Phi_R^0 = \frac{\left(\dfrac{W_R^0}{\rho_R}\right)}{\left(\dfrac{W_R^0}{\rho_R} + \dfrac{W_E^0}{\rho_E} + \dfrac{W_{PC}^0}{\rho_{PC}}\right)} \qquad \text{(A5)}$$

where W_R^0 is the initial rubber weight fraction, W_E^0 is the initial epoxy resin weight fraction (including the hardener), W_{PC}^0 is the initial polycarbonate weight fraction, and ρ_R, ρ_E and ρ_{PC} are the respective specific gravities of rubber (0.948), epoxy resin (1.17), and polycarbonate (taken as that of L141 : 1.20).