Fracture of polymer networks based on diethylene glycol bis(allyl carbonate)*

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Double torsion tests were used to evaluate the fracture toughness of a brittle organic network, poly[diethylene glycol bis(allyl carbonate)] commonly known as CR-39 resin, and to evaluate the enhancement in fracture toughness due to the incorporation of various additives. These additives were either polymerized to form a second network, an interpenetrating polymer network, or added as a second monomer which was copolymerized with the diethylene glycol bis(allyl carbonate) to form a random copolymer. The additives, which comprised two urethane acrylates, an allyl urethane and an epoxy acrylate, were found to have little effect on toughness at levels of around 2 wt% and 10 wt%. However, the stiffness of the polymer network was reduced by all four additives. Dynamic mechanical analysis revealed that all the additive agents had two competing influences on toughness. Toughening due to the lowering of an upper glass transition was counteracted by an antiplasticization effect, whereby the presence of the second network reduced the available free volume for segmental motion which caused an inherent decrease in toughness. Scanning electron microscopy revealed little evidence to support crazing as being an important mechanism in the deformation of CR-39 resins.

(Keywords: fracture toughness; polymer networks; additives)

INTRODUCTION

Diethylene glycol bis(allyl carbonate), when polymerized, is a highly successful commercial resin (CR-39) used in applications where high optical transparency coupled with low density and acceptable surface hardness and fracture toughness are important. Although CR-39 resin has satisfactory impact strength for many practical applications, it is notch sensitive, and some applications would be enhanced if the impact strength could be improved.

The fracture behaviour of CR-39 was first examined by Shinkai and Sakata[1], who concluded that in their three-point bending test, crack propagation occurred by an arrest-initiation mechanism attributable to plastic yielding at the crack tip.

Realizing the importance of increased impact strength of allyl carbonates, Stevens *et al.*[2] developed a procedure for producing a copolymer of CR-39 and various urethane acrylates. Whilst the results indicated that the impact strength of the materials was increased as the amount of the urethane acrylate increased, the authors did not comment on the concomitant effect on elongation, Young's modulus etc., which must of necessity remain high for the material's usefulness to be retained.

Donatelli *et al.*[3] reported that the impact resistance of high impact polystyrene, a graft copolymer of styrene and butadiene, can be increased by almost 300% if the same constituents are incorporated as an interpenetrating polymer network (IPN). This is despite the observation that the domain size of the polybutadiene phase has decreased from an optimum of 1.0 μm down to about 0.01 μm. It has been postulated that this improvement in impact properties results from homogeneous dispersion of the polybutadiene phase in an IPN, a property that is inherent in the mechanism of formation of the IPN itself.

Although it is relatively easy to increase the fracture toughness of a material at the expense of the material's stiffness, incorporation of relatively low levels (5–10%) of a second phase can improve impact strength with only a slight effect on the material's stiffness. Pottick[4] reported a 20% increase in the fracture toughness of an epoxy resin/rubber blend coupled with only a 3% decrease in the flexural modulus. It may be postulated that greater improvements could have been achieved in an IPN of the same components.

Although there has been a significant increase in the study of IPN systems, very few studies have concentrated on the impact strength improvements noted above.

The study reported in this paper examines the fracture behaviour of CR-39 homopolymer and sequential IPNs and copolymers based on CR-39.

EXPERIMENTAL

CR-39 homopolymerization

CR-39 was polymerized as flat sheets 3 mm thick. The monomer, after oxygen removal and the addition of 3% (w/w) anhydrous benzoyl peroxide, was added to a flat sheet mould. This was placed in an oven and the

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temperature was increased slowly from 50 to 100°C over a period of 21 h. The CR-39 sample was then removed from the mould and annealed at 110°C for 2 h. This procedure ensured a monomer conversion as close as possible to 100%, as determined by density measurements and the absorption of the allyl groups overtone band at 6130 cm^{-1}.

IPN formation

CR-39/IPNs were prepared in a similar way. The CR-39 monomer was premixed with the 'second' monomer and a u.v. polymerization initiator, Irgacure 651 (Ciba-Geigy) was added at a level of 0.4 wt% of the acrylate monomer weight. The acrylate network was formed first by passage of the mould beneath a high intensity u.v. source (Fusion System Ltd) with a rated output of 80 W cm^{-1}. Two passes at this intensity at a belt speed of 30 cm min^{-1} were sufficient for complete conversion of the acrylate network. The CR-39 network was then formed in the same way as the homopolymer network.

CR-39 copolymer

In the sample prepared from CR-39 and the allyl urethane, the two components were copolymerized using the same conditions as for the CR-39 homopolymer.

Materials

Diethylene glycol bis(allyl carbonate) was kindly donated by Sola Optical (Adelaide, Australia) and used without further purification.

An aliphatic urethane diacrylate (CN-9505, Sartomer) an aromatic epoxy diacrylate (CN-104, Sartomer), an aliphatic urethane diacrylate (AB-2260, American Biltrite) and allyl urethane (Dajac Laboratories), a diallyl aliphatic urethane, were all used without further purification.

Six samples were prepared; the components and preparation aspects are shown in *Table 1*.

Mechanical properties

The mechanical and fracture properties of CR-39 homopolymer were determined according to standard testing regimes including double torsion and single-edge notch tensile and bend procedures.

Dynamic mechanical analysis (d.m.a.) was performed using a Du Pont Instruments 983 Dynamic Mechanical Analyser. The d.m.a. samples were cut as rectangles measuring 30 mm × 10 mm and the dynamic mechanical analyser was run in resonant mode from −140 to 150°C at a rate of 10°C min^{-1}.

The fracture properties of samples no. 1 to no. 6 were all determined using double torsion specimens and a 1 mm min^{-1} cross-head speed. The values reported for the critical stress intensity factor, K_c, represent that for crack initiation.

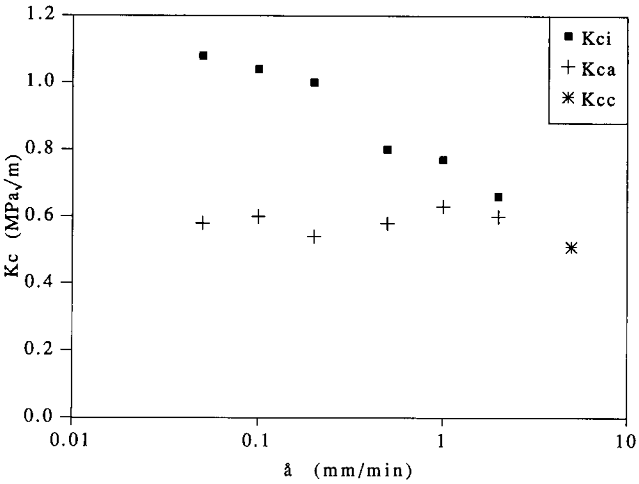

Figure 1 Plot of the critical stress intensity factor for crack initiation, K_{ci}, crack arrest, K_{ca}, and continuous propagation, K_{cc}, for CR-39 as a function of cross-head speed; determined using double torsion fracture method

Table 1 Sample composition and preparation details

Sample no.	Composition (wt%)	Preparation
1	CR-39/CN-9505 97.5/2.5	CN-9505 network formed initially by u.v. polymerization
2	CR-39/CN-9505 90/10	Preparation same as no. 1
3	CR-39/AB-2260 90/10	AB-2660 network formed initially by u.v. polymerization
4	CR-39/CN-104 90/10	CN-104 network formed initially by u.v. polymerization
5	CR-39/allyl urethane 97.5/2.5	Components mixed and copolymerized
6	CR-39/allyl urethane 90/10	Preparation same as no. 5

RESULTS AND DISCUSSION

CR-39 homopolymer

In the determination of fracture toughness of CR-39 by the double torsion method, two types of crack propagation were observed: a stable or continuous crack propagation at high propagation rates, and 'stick–slip' type crack propagation, with a characteristic saw-tooth shaped load *versus* displacement curve, at lower propagation rate. In order to examine the transition between the two modes, K_c was determined as a function of cross-head speed. The results are shown in *Figure 1*. For unstable crack propagation K_{ci} corresponds to the crack initiation load and K_{ca} to the crack arresting load. It can be observed from *Figure 1* that as the crack propagation rate increased, K_{ca} remained essentially constant, whereas K_{ci} decreased until the transition point was reached, where continuous propagation was observed. This occurred at a cross-head speed of around 2 mm min^{-1} for this geometry at 20°C. In single-edge notch bend and tensile fracture tests, K_c decreased with cross-head speed in a similar manner to the K_{ci} values in the double torsion experiment. The results for K_c and the critical energy release rate, G_c, for CR-39 at 20°C and a cross-head speed of 1 mm min^{-1} are tabulated in *Table 2*. The low G_c values indicate that only slight plastic deformation occurs at the crack tip, a result that is confirmed by the electron micrographs of the fracture surface in which there is no evidence of crazing (*Figure 2*). A detailed analysis of the fracture behaviour of CR-39 homopolymer will be published shortly[5].

The major energy absorbing process would appear to be highly localized shear yielding in the vicinity of the crack tip, leading to the stick–slip mechanism observed

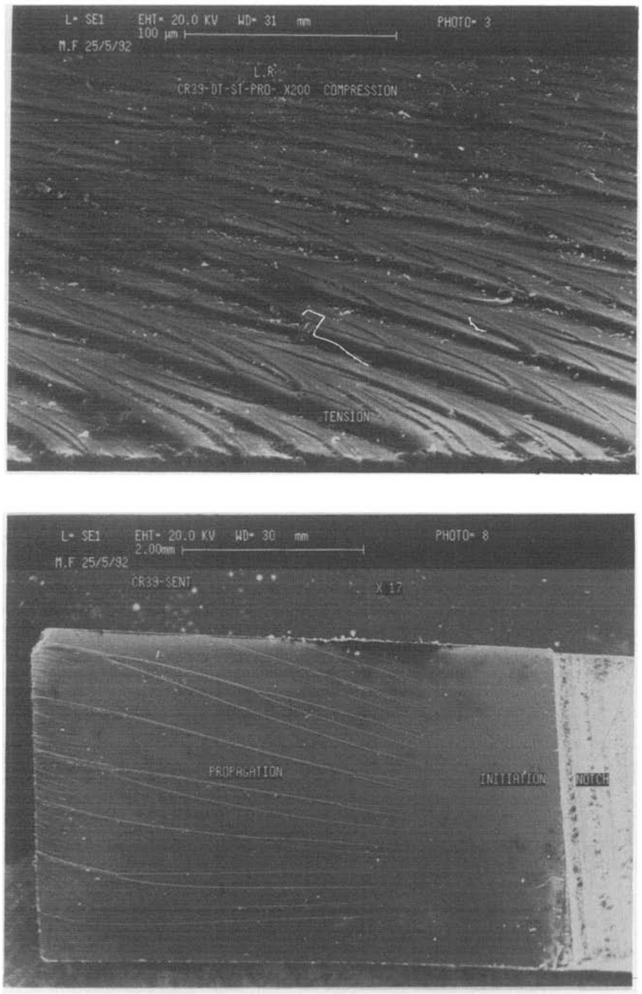

Figure 2 Scanning electron micrographs of CR-39 fracture surface

Table 2 K_c and G_c values at 20°C for CR-39 resin at a cross-head speed of 1 mm min^{-1}

Testing method	K (MPa m$^{1/2}$)	$G_c{}^a$ (J m^{-2})
Double torsion K_{ci}	0.77	347
Double torsion K_{ca}	0.63	231
Double torsion $K_c{}^b$	0.51	151
Single-edge notch bend	0.68	270
Single-edge notch tensile	0.60	211

[a] $G_c = [(1-\gamma^2)K_c^2]/E$, where γ = Poissons ratio (0.35) and E = Young's modulus (determined in a separate experiment)
[b] The value extrapolated from the data in *Figure 1*

at low propagation rates. This is confirmed in the electron micrographs, which show identical fracture surface morphology independent of the mode of fracture. This mechanism was tested by plotting K_{ci} *versus* compressive yield stress determined on each specimen at varying crack propagation rates, as shown in *Figure 3*. As compressive yield stress increases with cross-head speed, localized shear yielding processes give way to a continuous crack propagation process. This occurs at a compression yield stress of around 56 MPa at 20°C for the CR-39 resin.

CR-39 IPNs and copolymer

Most of the samples were optically clear, with optical transparencies greater than 85%. The exception was the 10% allyl urethane/CR-39 copolymer, which exhibited some degree of haze.

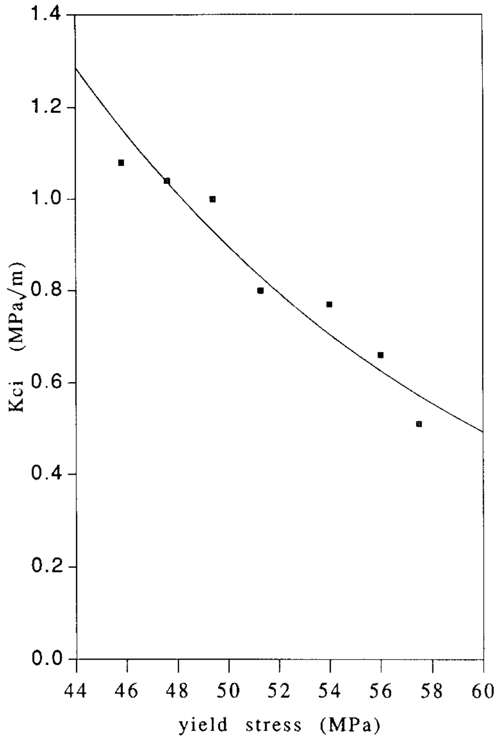

Figure 3 Plot of the critical stress intensity factor for crack initiation, K_{ci}, as a function of compressive yield stress for CR-39

Table 3 Glass transition temperatures and storage modulus at 25°C

Sample no.	T_g from tan δ (°C)	Storage modulus at 25°C (GPa)
CR-39 Homopolymer	112	3.5
1	99	3.6
2	83	2.9
3	77	3.3
4	80	3.2
5	81	3.2
6	59	1.7

The phase behaviour of the samples was investigated by d.m.a. and comparative plots for CR-39 homopolymer and sample no. 3 are shown in *Figure 4*. From examination of the tan δ *versus* temperature plot it is apparent that there is extensive phase integration in the IPN, with the glass transition temperature, T_g, for CR-39 networks decreasing from 112 to 77°C. This correlates with the absence of separated tan δ maxima. The storage modulus at 25°C has also decreased slightly to 3.29 GPa, indicating the high flexibility of the urethane acrylate network. The comparison between IPN formation and copolymer formation is also evident in the allyl urethane/CR-39 copolymers, where the sample T_g has been reduced to 59°C and the storage modulus to 1.7 GPa in the 10% allyl urethane sample. These data are summarized in *Table 3*. The fracture mechanics data of the samples are summarized in *Table 4*.

It can be concluded from *Table 3* that as the level of CN-9505 is increased (samples no. 1 and no. 2), the high temperature transition decreases from about 112°C for the homopolymer to 99°C for 2.5% CN-9505 and 83°C for the 10% CN-9505. The drop in transition temperature

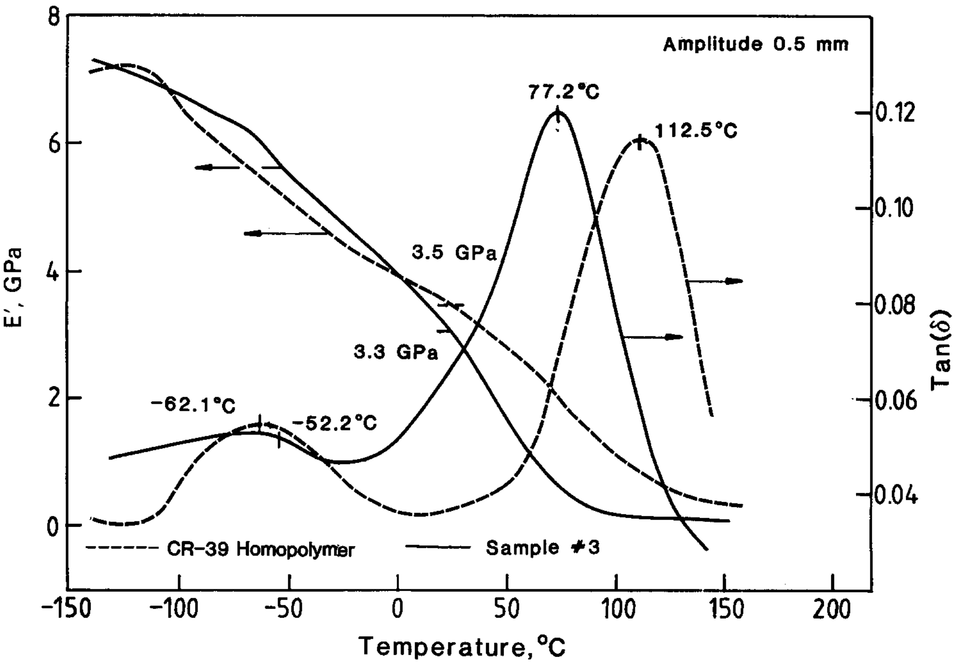

Figure 4 Storage modulus, E', and tan δ plots for CR-39 homopolymer, and the CR-39/AB-2260 IPN as a function of temperature, as determined by dynamic mechanical analysis

Table 4 K_c, E' and G_c for CR-39, IPNs and copolymers, determined from fracture data using double torsion method

Sample no.	K_c (MPa m$^{1/2}$)	E' (GPa)	G_c (J m^{-2})
CR-39 Homopolymer	0.77	3.6	347
1	0.69	3.6	278
2	0.61	2.9	270
3	0.71	3.3	321
4	0.59	3.2	229
5	0.58	3.2	221
6	Sample too flexible to measure K_c data		

was accompanied by an increase in peak height and a broadening of the peak to give an increase in area under the tan δ curve. This trend indicates a softening mechanism occurring as the urethane acrylate content is increased. This is not unexpected as the flexibility of the urethane backbone acts as a softener through the ease of rotation (or segmental motion). It would be expected that the toughness would increase correspondingly. However, it is seen from *Table 4* that there was no significant change in the value of K_c for urethane acrylate contents of 2.5% or 10% compared with that of the CR-39 homopolymer. This unexpected result of the fracture toughness can be explained by the behaviour of the lower tan δ peak in *Figure 4*. One would expect that as the urethane content is increased, more flexible segments are available to undergo segmental motion. Hence, the magnitude of the damping peak at -62°C, often called the β transition, would be expected to increase. However, it is observed that there is a reduction in size of the β peak as the urethane acrylate content is increased. This is attributable to antiplasticization[6], where a second component (in this case a urethane acrylate network) reduces the available free volume in the system[7]. Since segmental motion relies to some extent on the available free volume, the amount of segmental motion that is possible will be reduced. In other words, segmental motion is less likely when there is no free volume available for molecular segments to rotate through. This can be viewed as a raising of the energy barrier for segmental motion and explains the decreasing magnitude of the lower damping peak[8]. As segmental motion acts as a toughening mechanism, antiplasticization reduces the effect of such a toughening mechanism.

Owing to the fact that urethane acrylate contents of 2.5% and 10% had no effect on K_c, we conclude that the toughening effect demonstrated by the high temperature peak behaviour is counteracted by the anti-plasticization effect demonstrated by the low temperature peak. Therefore, as previously mentioned, additions of urethane acrylate CN-9505 at levels of 2.5% and 10% result in no significant enhancement in toughness.

Changes in storage modulus at 25°C are also given in *Table 4*. Although there was no significant difference at 25°C between pure CR-39 and the 2.5% CN-9505 sample, at the 10% level of the CN-9505 additive the storage modulus decreased by 20%. Similar results are observed for the CR-39/epoxy acrylate IPN, the aromatic groups having little effect on the overall properties of the IPN samples. Similar trends were noticed for allyl urethane addition, but here the changes were more dramatic, probably as a consequence of the sample being a copolymer.

The transition temperature decreased to 59°C for the 10% allyl urethane copolymer compared to the value of 83°C exhibited by sample no. 2, the 10% CN-9595 IPN. This peak is also significantly broader in the copolymer sample, with the beginning of the transition occurring around -25°C, well below room temperature. The storage modulus at room temperature has also dropped considerably from the value obtained for the CR-39 homopolymer, and is also considerably lower than the modulus value found for 10% urethane acrylate CN-9505 sample.

Antiplasticization effects were also evident for the allyl urethane compositions as for the CN-9505, as discussed in the previous section. As the allyl urethane content was increased to 2% and 10% respectively, the β transition peak area decreased in magnitude in a similar fashion as for CN-9505 modifications. From the magnitude of the peaks it appears that antiplasticization could be more pronounced than for the CN-9505. The values of G_c calculated for 2% allyl urethane and the 2.5% and 10% acrylated urethane confirm this, with toughness values being essentially the same. Therefore, the extra toughening exhibited by the allyl urethane upper transition is probably being compensated for by the extra antiplasticization effect exhibited by the allyl urethane lower transition.

CONCLUSIONS

This study has confirmed that the CR-39 polymer is a brittle material. The critical stress intensity factor, K_c, and the critical energy release rate, G_c, had very low values (0.6 MPa m$^{1/2}$ and 230 J m^{-2}, respectively) when determined using the double torsion technique.

No enhancement in toughness was observed through the incorporation of the four modifying polymers as interpenetrating networks. This was attributed to two conflicting mechanisms that had opposite effects on toughness. The addition of a flexible modifying network demonstrated a toughening effect by lowering the glass transition temperature and also broadening and increasing the magnitude of the corresponding tan δ peak. However, this was offset by antiplasticization whereby the flexible network filled the voids around the network, hence decreasing the level of segmental motion possible.

Owing to the antiplasticization effect and the loss in stiffness of the IPNs compared to pure CR-39, it appears that these modifying polymers do not offer potential as toughening agents for CR-39.

Dynamic mechanical analysis also revealed a high level of miscibility for each system studied.

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