Polymers from renewable sources:
5. Myrcene-based polyols as rubber-toughening agents in glassy polyurethanes

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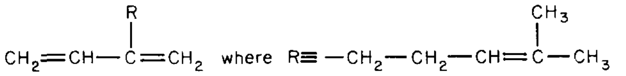
A reactive liquid rubber based on hydroxy-functionalized polymyrcene was used to modify a highly-crosslinked, glassy polyurethane network. During the polymerization, the products formed from the reacting liquid rubber and the polyurethane matrix components become incompatible leading to precipitation of the rubber as a discrete particulate phase. Phase-separation in the resultant rubber-modified polyurethanes is essentially complete, and the materials possess improved stress–strain and impact properties relative to the unmodified network, without reduction of the glass transition temperature (155°C) of the network. Impact data have been analysed using linear elastic fracture mechanics to give G_{IC}, the critical strain-energy release rate. On incorporating low levels of polymyrcene liquid rubber ($<10\%$ w/w) in the polyurethane matrix, G_{IC} increased and passed through a maximum value. The mechanisms of energy dissipation accounting for the toughness changes are reviewed and compared with those observed in epoxy resins modified by polybutadiene-based liquid rubbers.

(Keywords: polyurethane networks; polymyrcene liquid rubber; morphology; toughening mechanisms)

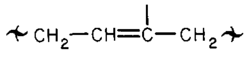
INTRODUCTION

Previous papers in this series have described the synthesis of hydroxy-functionalized liquid rubbers from myrcene[1] and the use of these polyols for the preparation of polyurethane elastomers[2]. The interest in myrcene stemmed from the desire to produce polyols from renewable non-oil based sources. Myrcene (shown below) is a readily available terpene derived from the major constituent of turpentine, a by-product resulting from the sulphite wood-pulping processes.



$CH_2{=}CH{-}\overset{R}{C}{=}CH_2$ where $R \equiv -CH_2-CH_2-CH{=}\overset{CH_3}{C}-CH_3$

When polymerized using hydrogen peroxide as catalyst, myrcene yields hydroxy-functionalized pre-polymers of mixed composition in which the principal moiety is the 1,4-propagated unit[1].



$\sim CH_2-CH{=}\overset{R}{C}-CH_2\sim$

These hydroxy functionalized polymyrcenes have similar structures and polyurethane-forming capabilities to the commercially available (but oil-based) polybutadiene liquid rubbers. By analogy with polybutadiene liquid rubbers, a further potential area for the use of polymyrcene liquid rubbers is in the toughening of thermosets, and this forms the subject of the present paper.

The introduction of reactive liquid rubbers into thermosets, especially epoxy resins, is a well established method for improving the tensile and impact properties[3–5]. In epoxy resin-forming systems, a carboxyl terminated, copoly(butadiene-acrylonitrile) liquid rubber (CTBN) is mixed with epoxy components and hardener. As the curing process progresses, competitive reactions occur, resulting in high molar mass rubber being formed together with the epoxy resin matrix. Since the two polymeric phases are incompatible they separate to produce a heterogeneous material in which discrete particles of rubber are intimately dispersed, within the highly crosslinked matrix. Further phase separation of rubber is not possible after the gel point[6] and gelation of the matrix 'locks' the morphology.

The degree of phase separation achieved in these materials largely determines their properties. For example if there is a significant amount of dissolved rubber, toughening can result from matrix plasticization[7], whereas if most of the rubber exists as a dispersed phase the particles can act as stress concentrators leading to crack diversion and consequent increase in fracture energy[8]. Although rubber toughening of epoxy resins has been extensively studied, the development of rubber-modified highly crosslinked polyurethanes as high temperature thermosets has received little attention. However, previous work in this Department has shown the feasibility of using hydroxy-terminated polybutadienes for toughening highly-crosslinked polyurethanes[9] in a fashion analogous to epoxy systems.

The current paper describes the use of a polymyrcene polyol as a rubber-modifier for a high T_g, polyurethane matrix.

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EXPERIMENTAL

Materials

Polyol blend. Two polyols were used to form the polyurethane matrix.

(i) LHT240 (Union Carbide Corporation), a liquid oxypropylated 1,2,6-hexanetriol, of equivalent weight* of 227.6 ± 1.0 (end group acetylation) was dried by vacuum rotary film evaporation at 100°C/0.1 mm.

(ii) Trimethylol propane, TMP (BDH) was used as received.

Liquid rubber. The hydroxy functionalized polymyrcene, prepared as described previously[1], was a colourless, faintly cloudy liquid which was protected from atmospheric oxidation by the addition of a trace of benzoquinone. The pre-polymer had a $\bar{M}_n$ of 2810* and polydispersity of 1.37 (gel chromatography) and an equivalent weight of 1410 (acetylation) from which the number average functionality was calculated to be 1.99. The microstructure of this polyol has been reported previously[1].

Diisocyanate. The aromatic 4,4′-methylenediphenylene diisocyanate, MDI (Bayer), in flake form, was melted and filtered through a grade 3 sinter at 50°C before use. It had an equivalent weight of 127 (NCO titration).

Polymer preparation

The polyol blend, TMP and LHT240, which on reaction with MDI forms the glassy polyurethane matrix, together with liquid rubber (when used) were mixed under vacuum (~0.5 mm Hg) for 20 to 30 min in a 3-necked flask immersed in a water bath at 50°C. The vacuum was broken and the required amount of molten MDI, also at 50°C, was added. The flask was re-evacuated with continued rapid stirring (250 rpm) to ensure thorough mixing of the initially incompatible components. The mixture changed in appearance from milky (initially) to clear over a three minute period and then rapidly became milky again as rubber particles began to precipitate. At this stage (i.e. within 30 s of the onset of phase separation) the mixture was poured into a rectangular mould (150 × 150 × 3 mm) and subsequently cured for 90 min at 160°C.

In each polymer, the ratio of TMP:LHT240 was held constant at 9:1 by equivalents and the stoichiometric ratio of isocyanate to total hydroxyl groups was 1.00 ± 0.01. This produced an unmodified polyurethane matrix which was a clear, colourless glass whereas the rubber-modified materials were opaque, milky-white rigid glasses. Polymers were stored over silica gel until required for testing.

Polymer characterization

Stress–strain. Dumb-bell shaped specimens were machined from the moulded plaques and tested on an Instron model 1122 at 23°C, using a strain gauge extensometer. The specimen gauge length was 75 mm and the strain rate $4.5 \times 10^{-4}\,\mathrm{s}^{-1}$.

Impact tests. Data were obtained by testing razor-notched beams using a Hounsfield pendulum tester in the Charpy three-point bending mode. Impact specimens were machined accurately from 3 mm sheets to give notched beams, 50 mm long and 10 mm deep, with notch depths in the range 0.5 to 4.0 mm. The span length was 40 mm, impact velocity $2\,\mathrm{m\,s}^{-1}$ and the tests were carried out at 20°C. Precise notch depths were measured after fracture using a travelling microscope. The data were analysed according to the linear elastic fracture mechanics (LEFM) approach described by Williams *et al.*[10], without corrections for kinetic energy effects[11].

Scanning electron microscopy (SEM). The fracture surfaces of samples from tensile and impact tests were sputter-coated with gold and examined on an ISI instrument (Model 100A).

Differential scanning calorimetry (DSC). The specimens all possessed a clear, elevated temperature glass transition associated with the matrix, and these upper transition temperatures were determined by DSC on samples of 13 to 15 mg (sealed in aluminium pans) using a Perkin Elmer DSC2. Samples were heated from ambient to 180°C then quenched in liquid nitrogen and reheated at $20°\mathrm{C\,min}^{-1}$, and the T_g was determined (as the intercept of tangents at the step-change in the baseline) from the latter run.

RESULTS AND DISCUSSION

In stress–strain experiments, all the materials showed behaviour typical of amorphous, glassy polymers as shown in *Figure 1*, with the 'matrix' polymer failing in a brittle manner at ~5% strain with no visible yield point. One effect of incorporating rubber into the glassy 'matrix' polymer, is to reduce the modulus in a manner described by the modified Kerner equation[12]:

$$\frac{E_c}{E_m} = \frac{1 + AB\,V_r}{1 - B\psi\,V_r} \qquad (1)$$

where

$$A = \frac{7 - 5\nu}{8 - 10\nu} \qquad (2)$$

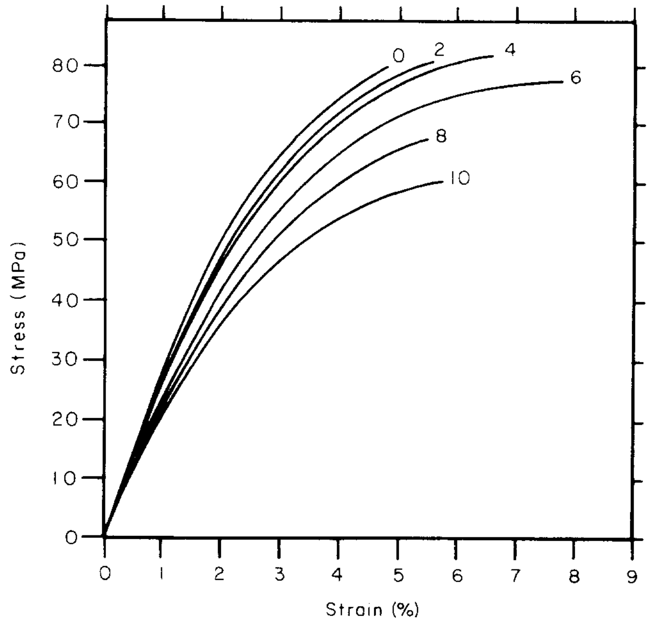

Figure 1 Tensile stress–strain curves (23°C) of unmodified and polymyrcene-modified polyurethane networks. Figures on curves denote the weight percentage of added polymyrcene polyol in the polyurethanes

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* Equivalent weight is defined as the molar mass per hydroxyl functional group: all values of molar mass are expressed in $\mathrm{g\,mol}^{-1}$.

Table 1 Composition, tensile and thermal properties of polyurethane materials

Rubber content (%)							
Weight^a	Volume^b	ε_u (%)	σ_u (MPa)	E (GPa)	T (kJ m^{-3})	T_g (°C)	d (μm)
0	0	4.8	79.4	3.00	192	155	0
2	2.8	5.6	79.1	2.71	222	155	3.9
4	5.6	7.1	81.4	2.76	308	153	3.2
6	8.3	7.8	77.5	2.53	339	154	5.2
8	11.0	5.6	67.0	2.34	190	153	5.8
10	13.6	5.7	57.1	1.90	180	156	8.1

^{a}Weight of rubber as a % of total reactant weight
^{b}Calculated, assuming 1 mol rubber = 1 mol MDI and using density of rubber = 950 kg m^{-3} and density of matrix = 1230 kg m^{-3}
ε_u = ultimate strain, σ_u = ultimate stress, E = Young's modulus, T = toughness (area under stress–strain curve); d = mean particle diameter

and

$$B=\frac{(E_r/E_m)-1}{(E_r/E_m)+A} \tag{3}$$

with

$$\psi=1+[(1-\theta)/\theta^2]V_r \tag{4}$$

In these equations, V_r is the volume fraction of the rubber phase and θ is the maximum packing fraction taken as 0.64 assuming the rubber particles to be spherical. The moduli E_c, E_m and E_r refer to the rubber-modified composite, the matrix (unmodified) polyurethane and the rubber particles respectively, and v is the Poisson's ratio of the matrix (assumed to have a value of 0.35[12]). Values of V_r in *Table 1* have been calculated from corresponding weight fractions of added rubber, and predicted values of E_c/E_m according to equation (1) are shown as the solid line in *Figure 2* together with the experimental data points. Agreement between theory and experiment is good particularly at lower volume fractions of rubber (< 0.10) which indicates that the actual volumes of phase separated rubber are close to the calculated values. This in turn implies that minimal mutual dissolution of the phases has occurred, an observation substantiated by the almost constant value of 155°C for the matrix T_g (see *Table 1*) over the entire composition range. The effects of added rubber on this T_g value are discussed in greater detail later.

Another effect of adding polymyrcene liquid rubber is to increase ultimate strain and tensile strength to maximum values at rubber contents between 4 and 6% w/w (see *Figure 1* and ε_u and σ_u values in *Table 1*). Visual observations of tensile specimens showed that yielding had occurred in some cases but only for materials containing 4 and 6% w/w of added rubber. The formation of a dispersed particulate rubber phase therefore causes these highly-crosslinked polyurethanes to exhibit a change from brittle to semi-ductile behaviour when subjected to tensile deformation. The combined effect of increasing ε_u and σ_u to produce maximum values (which override the decrease in tensile modulus) is to produce a maximum in material toughness as shown in *Table 1* by the value of T, viz. 339 kJ m^{-3} at 6% w/w of added rubber. At higher rubber contents, the properties begin to decline in a manner similar to that observed for a liquid polybutadiene rubber modified material involving the same polyurethane matrix[9].

To obtain an overall evaluation of ultimate properties the tensile data discussed above should be considered in conjunction with those obtained from impact tests. Thus, the critical strain-energy release rate G_{IC}, obtained from notched, 3-point bending impact tests is a measure of the material's resistance to crack propagation. G_{IC} is obtained from equation (5) which relates the energy, W, absorbed during impact to specimen geometry, $BD\phi$

$$W=G_{IC}.BD\phi \tag{5}$$

In this expression, B and D are the width and depth of the beam specimen containing a notch of depth a, and ϕ is a calibration factor which is a function of a/D, the notch-to-depth ratio and may be calculated by the method of Plati and Williams[11]. Fracture energy, W, is found directly from the dial reading of the impact-testing instrument. Values of G_{IC} were obtained for each material from the slopes of plots of W against $BD\phi$, and representative plots are shown in *Figure 3*.

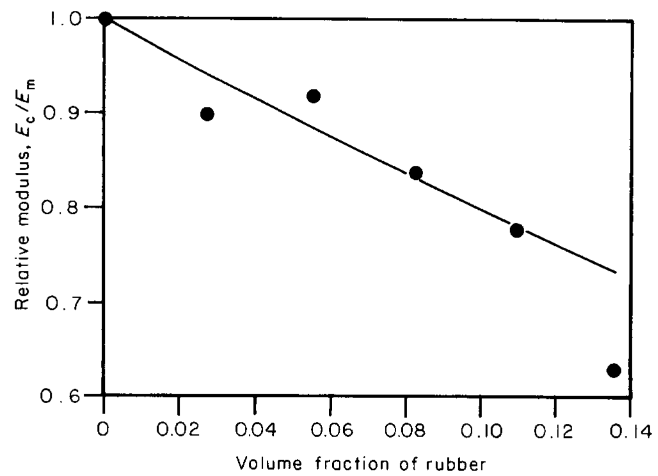

Figure 2 Application of modified Kerner equation to dependence of relative modulus on volume fraction of rubber: (———) modified Kerner equation with $v = 0.35$; (●) experimental data

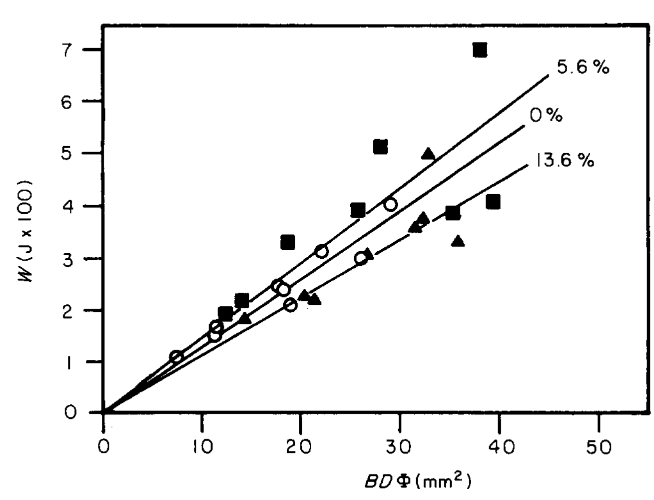

Figure 3 Charpy impact data plotted according to LEFM approach given by equation (5). Representative data are shown for three of the rubber-modified composites containing 0, 5.6 and 13.6% by volume of rubber phase. Lines are least squares plots through the origin: (○), 0%; (■), 5.6%; (▲), 13.6%

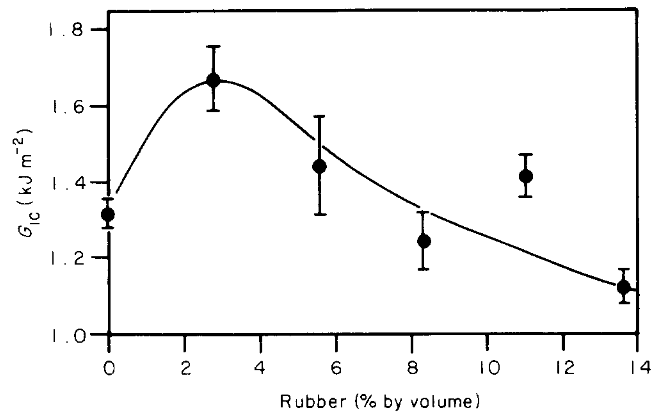

Figure 4 Variation of fracture energy, G_{IC}, with the volume fraction of rubber phase

Figure 4 summarizes the effect of volume fraction of rubber on G_{IC} and shows that G_{IC} increases by about 25% at about 2% w/w of added rubber, and then decreases to a value below that of the matrix at 10% w/w of added rubber. The maximum in G_{IC} therefore occurs at lower rubber contents than the maxima in ε_u, σ_u and T as shown in *Table 1*. A similar trend in fracture energy as a function of rubber content has been observed in low strain rate studies on rubber-toughened epoxies[13].

In this work, all the *W versus BDϕ* plots are linear through the origin ($W=0$, $BD\phi=0$), justifying the LEFM approach and showing that the region around the notch is not subject to localized yielding. If yielding occurred, the *W versus BDϕ* plots would exhibit curvature towards the *BDϕ*-axis. Interestingly, no improvement in G_{IC} was observed when the identical matrix was modified with a liquid polybutadiene rubber[9]. Since impact tests are effectively high-strain rate flexural tests, the values of G_{IC} measured might be expected to vary as a consequence of strain rate effects[5]. This might explain differences between the toughening ability of various rubber-modifiers having different chemical structures. Materials containing rubber-modifiers of different chemical structure and hence T_g, will display differing responses when deformed at high strain rates. This arises because at room temperature the dispersed rubber may be shifted into its brittle–ductile transition region. However, since the T_g of the polymyrcene rubber (−57°C) is already higher than that of the polybutadiene (−81°C), it is unlikely that strain-rate effects could explain the observed difference in relative toughening efficiency. In order to facilitate further analysis of these results, some knowledge of the degree of phase separation and the nature of the rubber particles in these systems is required and DSC and SEM can be used to obtain this information. Thus, studies by DSC on these rubber modified materials showed them to have a glass transition at a similar temperature to that of the unmodified matrix with no obvious trend (*Table 1*). If significant phase mixing had occurred the T_g would have been reduced because of the plasticizing effect of the rubber dissolved within the matrix. T_g data have not always been reported in the literature for rubber-modified epoxies but the T_g values of such materials usually show a decrease when compared to the unmodified resin[13]. For example, Manzione *et al.*[7] reported a decrease of the order of 10°C to 25°C when 15% w/w of CTBN liquid rubber was incorporated into an unmodified epoxy resin matrix which had a T_g of 102°C. For epoxy resins, some of the improvement in low strain-rate toughness has therefore been attributed to matrix plasticization[7], but DSC results suggest that this cannot be a significant effect in these polyurethane-based systems.

The scanning electron micrographs of fracture surfaces resulting from tensile and impact-tested specimens for a particular material were very similar and in the case of the rubber-modified polyurethanes, fracture has occurred in such a way as to expose the rubber particles. The unmodified polyurethane network has a fracture surface (*Figure 5(a)*) which is relatively smooth and featureless apart from a few river markings which are fairly uniformly distributed across the surface and appear to radiate from the point at which the crack initiated. The addition of polymyrcene liquid rubber clearly results in the formation of phase-separated rubber particles as seen in *Figures 5(b)* to *(d)*. Moreover, the expected trends in the number and size of rubber particles with increasing concentration of added rubber are well illustrated. Comparison of *Figure 5(b)* and *(c)* shows that as the concentration of added rubber increases from 2 to 8%, the number of particles per unit surface area increases markedly and there is a small but noticeable increase from 3.9 to 5.8 μm in the mean particle diameter as shown by the values of *d* in *Table 1*. Further increase (to 10% w/w) in added rubber, however, results in a significant decrease in the number of rubber particles as shown in *Figure 5(d)* whilst the mean particle size increases yet again to 8.1 μm. These trends in particle density and size, and their effects on properties, are discussed later in more detail with particular reference to energy-absorbing mechanisms during fracture of these rubber-modified materials.

Overall for materials containing up to 8% w/w added rubber, the rubber particles are well bonded to the matrix and this is borne out by the small number of completely empty cavities on the fracture surfaces. Good adhesion between the phases is to be expected given the chemical reactivity of the various components forming the polyurethane. This adhesion between the rubber particles and the matrix in the vicinity of the fracture is clearly demonstrated by the plastically deformed material which is particularly pronounced along the ridges and comprises almost linear sequences of rubber particles (*Figures 5(b)* and *(c)*). It appears therefore that these rubber particles interacted in a concerted fashion with the advancing crack-front during fracture. Only when the rubber content reaches 10% w/w is there evidence of poor rubber–matrix adhesion which would result in interfacial debonding during fracture as seen in the central region of *Figure 5(d)*, further illustrated by the higher magnification micrograph of a debonded particle from the same specimen shown in *Figure 5(e)*. However, even in this case it is difficult to distinguish between true debonding with pull-out of particles, and tearing along a curved path close to the interfacial region[14]. Debonding would lead to the absorption of some of the energy involved in fracture but because of the apparent absence of debonding on any large scale in these polyurethanes, other processes must be responsible for the observed toughening effects. Also apparent on the micrographs of the fracture surfaces are many failed or torn rubber particles which appear mainly as particles containing holes. Since there are differences in the coefficients of expansion of polymyrcene-based rubber and the highly-crosslinked polyurethane matrix

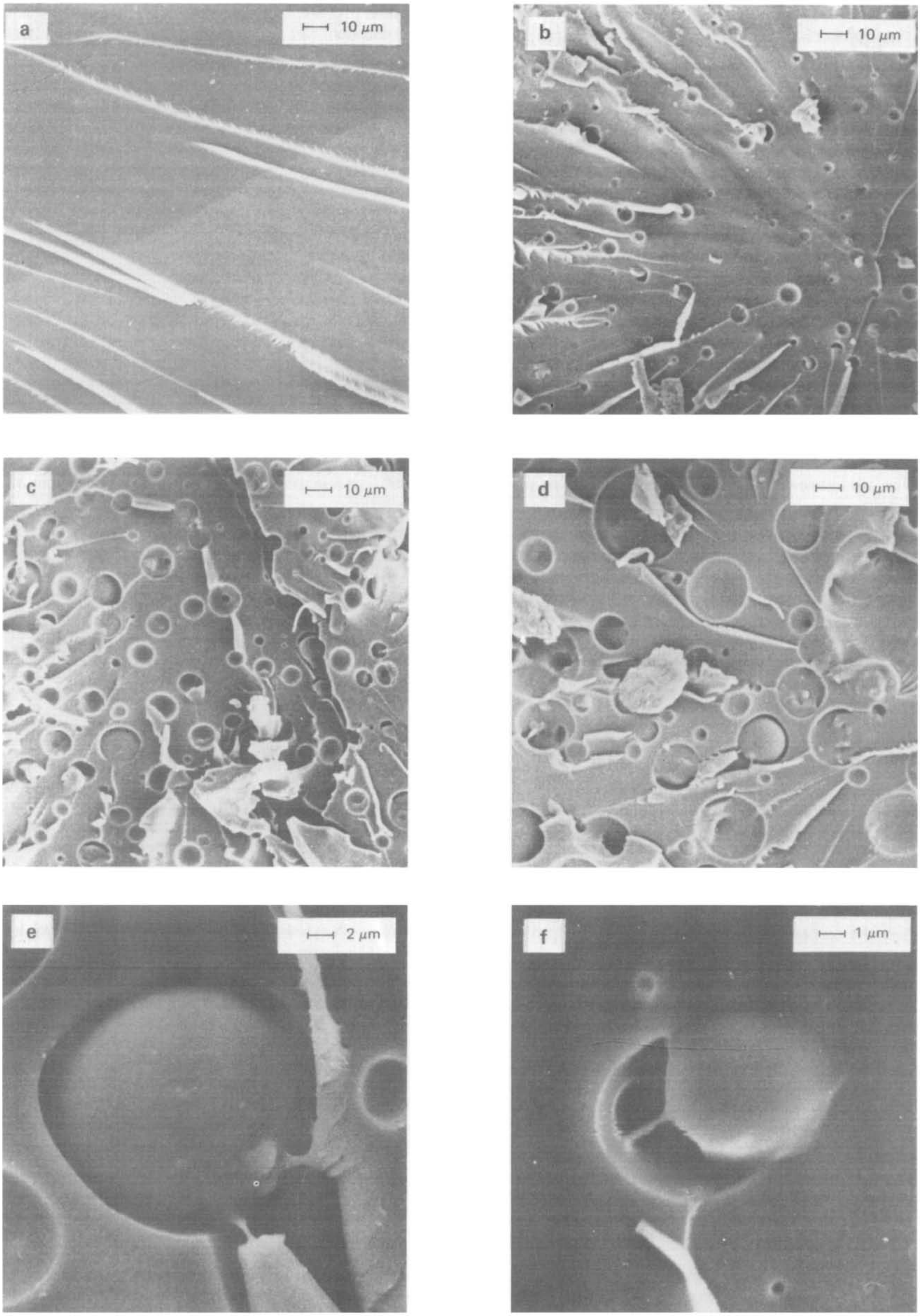

Figure 5 Scanning electron micrographs of representative fracture surfaces of (a) unmodified polyurethane network and rubber-modified polyurethanes containing (b) 2% w/w, (c) 8% w/w and (d) 10% w/w of added polymyrcene liquid rubber. Micrograph (e) shows a debonded rubber particle in a polyurethane containing 10% w/w of added rubber. Micrograph (f) is from a 4% w/w rubber-modified polyurethane showing a partially-debonded and torn rubber particle with characteristic cavity and inner hole

the rubber particles are in hydrostatic tension on cooling after cure[15]. During fracture the triaxial stress associated with the initial hydrostatic tension that exists in a particle causes the rubber to contract. In addition the size of a cavity containing a contracted rubber particle is itself increased because of the gross deformation of the matrix. Both factors result in the following features seen in the micrographs (*Figures 5*(*b–e*)), namely, (i) a small number of cavities; (ii) torn rubber particles containing holes; (iii) apparently undeformed rubber particles which are completely debonded from the matrix and reside within a cavity (*Figure 5*(*e*)).

Tearing of the rubber particles during gross fracture must also be an important energy-absorbing mechanism in these materials. Extension of rubber particles in the vicinity of the propagating crack front, followed by tearing would also produce small domes on the fracture surface (as well as the interior holes just referred to), as shown in the higher magnification micrograph in *Figure 5*(*f*) in which partial-particle debonding is evident before tearing was complete. Although this fracture process was one of the earlier mechanisms proposed for toughening in rubber-modified thermoplastics, it appears unable to account solely for the increase in fracture energy[8]. However, it has been shown to be an important mechanism for energy dissipation in rubber-modified epoxy resins. Kunz-Douglass *et al.*[14] found that the increase in fracture energy, G_{IC}, obtained from double torsion tests, varied directly with increased rubber content as a result of the strain-energy of the rubber particles being dissipated (as heat) when the particles tore. It was predicted that for particle sizes greater than 20 μm, the toughening effect would decrease as a result of the lower tear strain which obtains for larger particle diameters. This may partly explain the decrease in G_{IC} observed in the present work at the higher rubber contents as shown in *Figure 4*.

A similar trend in fracture energy with rubber content has been observed[16] although for a totally different chemical system in which a 6% w/w polybutadiene solution in styrene was used to form a series of rubber-modified polystyrenes. Different volume fractions were achieved by varying the rate of agitation since for this system the lower the rate, the higher the resulting rubber volume fraction. Both impact fracture energy and ultimate tensile strain passed through maximum values at a volume fraction of about 0.2. It was further observed in these materials that as the volume fraction increased so did the average size of rubber particles formed. It is generally accepted[17] that if rubbery particles are too large then the total number that may initiate localized fracture sites is not maximized, and that if particles are too small they act as poor localized crack initiators. Maximum toughness enhancement will consequently occur at intermediate rubber phase volume fraction.

Other possible fracture mechanisms accounting for toughening effects include shear yielding and craze formation, although the latter is normally observed in the fracture of linear polymers and there is not evidence for either mechanism in the micrographs obtained for these highly-crosslinked polyurethanes. Generally, these two mechanisms are found in association and are usually accompanied by a third mechanism, namely, stress whitening. Wu[18] observed all three mechanisms occurring in the fracture of rubber-toughened nylons containing rubber particles less than 1 μm in size, although the principal mechanism was that involving matrix yielding. The energy dissipation was shown to be almost exclusively within the stress-whitened zone, 1 to 2 mm below the notch. Since stress-whitening is not observed in polyurethane specimens subjected to impact loading in the present study, and is rarely observed for rubber-modified epoxy resins[5], the combined phenomena of crazing and yielding appear to be of minor importance in the fracture behaviour of these highly crosslinked polymers.

It is clear that the correlation of fracture behaviour with rubber concentration is complex because various morphological features such as rubber particle volume fraction, particle size and size distribution, and particle structure (and occlusions) are all interrelated making it virtually impossible to change one feature independently of the others. For these reasons, there is much controversy[19] as to the precise mechanisms responsible for the enhanced toughening observed in rubber-modified thermosets. Certainly there is conflicting experimental evidence[13,20,21] even on similar epoxy resin systems. Earlier work by Bucknall and Yoshi[20] on epoxy resins, all containing 8.7% w/w of CTBN but with various volume fractions of rubbery phase (achieved by varying the curing conditions employed), showed G_{IC} to increase linearly by a factor of about 10 over the volume fraction range 0 to 20%. This linear relation appears to be in agreement with a simple rubber particle-deformation model proposed by Beaumont and co-workers[14,21]. However, Bascom *et al.*[13] have reported that for epoxy resins containing a wide range of CTBN contents, G_{IC} passes through a maximum at 20% w/w which was attributed to the phase mixing and matrix plasticization effects referred to previously. Considering, therefore, the obviously different chemistry of the present polyurethane systems, and the complex relationships between morphology and toughness described above, a simple direct relation between toughness and composition would be extremely difficult to establish for these materials.

CONCLUSIONS

Hydroxy-functionalized, polymyrcene liquid rubber produces useful toughening effects when incorporated into a highly crosslinked polyurethane. During reaction, the rubber rapidly reached a stage where it is incompatible with the matrix reactants, so phase separation is virtually complete before the gel point. Nonetheless a strong interfacial bond is achieved by way of urethane links from matrix to rubber generated during the cure stage. The particle size distribution produced by the mechanical mixing method used in this work falls into the range required for useful toughening effects. It is possible that if smaller particles were generated the toughening mechanisms might change as found in some thermoplastics, but it seems that in the present systems the toughening can be explained in terms of the strain-energy and tearing energy of the rubber particles. In previous work[9] on highly crosslinked polyurethanes modified by hydroxy-functionalized polybutadienes, the added rubber led to improved stress–strain behaviour but there was no change in G_{IC}. Although the polybutadiene rubber is similar in some respects to the reactive polymyrcene rubber, there are differences in T_g, functionality and solubility characteristics as discussed in the previous papers[1,2], but the main source of the improved G_{IC} behaviour with the polymyrcene rubber may be due to its higher extensibility (200% compared with 100% for the polybutadiene) which enables dissipation of further energy in straining the rubber particles. Despite its higher T_g, the polymyrcene rubber remains elastomeric at the strain rates encountered in the impact test and is still able to dissipate energy in these tests. This liquid rubber is therefore capable of improving stress–strain and impact properties, with no decrease in the T_g of the matrix and only small decreases in modulus, when added to an otherwise brittle matrix.

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