Rubber-toughened polyurethane network and composite materials

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(Received 21 April 1986; revised 21 July 1986; accepted 13 October 1986)

Highly-crosslinked polyurethane networks ($T_g > 150°C$) have been modified by incorporating up to 10% w/w of an hydroxy-functionalized, polybutadiene liquid rubber. Composite materials comprising polyurethane networks and up to 30% w/w of hammer-milled glass have also been investigated. The effects of polyurethane network structure, processing conditions and rubber content on the morphology of the dispersed rubber phase and thence on tensile stress–strain, dynamic mechanical and impact properties are described. Essentially, the brittle unmodified polyurethanes are transformed into semi-ductile materials with maximum toughening enhancement occurring at 4% w/w of added rubber. In terms of G_{IC}, the critical strain-energy release rate, the unmodified polyurethane ($G_{IC} \approx 2.0\,kJ\,m^{-2}$) is relatively tough compared with unmodified epoxy resins ($G_{IC} \approx 0.2\,kJ\,m^{-2}$). Comparison of fracture energies from blunt-notch and sharp-notch impact data shows the various polyurethanes to be very notch-insensitive materials but not to be affected by the addition of rubber. The feasibility of producing rubber-modified, highly-crosslinked polyurethanes from fast reacting systems in the context of reaction injection moulding is discussed.

(Keywords: polyurethane networks; composites; liquid rubbers; toughening; impact; fracture energy)

INTRODUCTION

Highly crosslinked (network) polymers, generally referred to as thermosetting resins, exhibit high strength and stiffness with good retention of physical properties at elevated temperatures (>150°C), but as materials they are intrinsically brittle. However, significant improvements in fracture toughness can be achieved by the incorporation of small amounts of elastomer in the form of well-bonded and dispersed second-phase particles. Although rubber-toughening of glassy polymers originated with the development of high performance thermoplastics[1] such as high impact polystyrene and rubber-modified poly(vinyl chloride), the same concepts have also been established for thermosetting resins such as epoxy resins[2–4]. In the latter case, rubber-toughened epoxies have been performed by incorporating up to 20% by weight of reactive liquid rubber into the epoxide resin formulation. The resulting epoxy resins are more accurately described as grafted copolymers in which the grafted rubber phase is generated *in situ* by reaction of a functional liquid polybutadiene with the epoxide prepolymer: simultaneous reaction between epoxide prepolymer and curing or crosslinking agent generates the epoxy network polymer. At some stage during the overall polymerization but prior to gelation of the epoxy network, the rubbery polybutadiene-epoxy oligomers become incompatible with the network-forming epoxy, and phase separation occurs. Rubber-rich domains then precipitate as the *discontinuous* phase in a *continuous* matrix of epoxide-rich network polymer (resin). The nature of the phase separation determines the morphology and thence the physical properties of the finally-formed material. In particular, the low strain-rate toughness and impact behaviour[5] of these cured epoxy resins are significantly improved by the presence of a dispersed rubber phase. The rubber-rich domains (typically 0.1 to 5.0 μm in diameter) can promote toughening by various energy-absorbing mechanisms during deformation[6–8].

One objective of the present work was to extend the concept of rubber-modified thermosets to highly-crosslinked polyurethane materials formed from polymerization systems which are relatively fast (<5 min) at low temperatures (<50°C). Polyurethanes provide a versatile class of polymeric materials primarily because of the extensive range of physical properties attainable through the controlled variation of chemical reactants and polymer-forming conditions, and also because of their ease of fabrication by a variety of processing methods. One such method, reaction injection moulding (RIM), exploits the intrinsically high reactivity of low viscosity polyols towards liquid polyisocyanates at ambient temperatures in a one-stage, *in situ* moulding process. RIM-polyurethanes are segmented block copolymers which, due to segment incompatibility under the conditions used during processing, undergo microphase separation resulting in the formation of soft and hard segment domains. The gross morphological structure may be described as being two-phase in which the *discontinuous* phase, comprising hard crystalline domains of high density, extensively hydrogen bonded urethane groups, acts both as a reinforcing filler and physical crosslinks for the *continuous* phase formed by the soft, elastomeric network matrix. The physical properties depend strongly on the phase structure and the proportions of soft and hard segments which in turn depend on the chemical structure, molar mass and

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0032-3861/87/030356-12$03.00

functionality of the reactants used during polyurethane formation. In addition, the degrees of phase separation and crystallinity, and the size of domains determine the morphological structure of RIM-polyurethanes, which consequently affect the overall properties of the moulded materials[9,10]. Generally, RIM-polyurethanes are linear or lightly crosslinked, semi-rigid materials with wide application in the automotive industry for which the principal requirements are for materials with high strength and stiffness, good thermal and dimensional stability at elevated temperatures (> 150°C), and high impact resistance.

Another objective of the present work was to develop highly-crosslinked, rigid polyurethanes with potential for RIM. Such glassy materials are characterized by high values of T_g, strength and stiffness, and due to their well-developed network structure are capable of retaining physical properties up to at least 150°C[11]. However, their ultimate elongation and fracture toughness are low and these polyurethane networks are obvious candidates for rubber toughening.

Another approach to enhancing stiffness and temperature resistance is to incorporate mineral fibrous fillers and in this context, reinforced-RIM has focussed most attention on polyurethanes containing glass in the form of chopped-strand or hammer-milled fibre[9]. Also included in this paper, therefore, is the development of composite materials based on one of the rubber-modified polyurethane networks containing various loadings of hammer-milled glass fibres.

EXPERIMENTAL

Materials

Hydroxy-functionalized polybutadiene, ARCO R45-HT (ex. Cornelius Chemical Company.) Polybutadiene (PB) liquid reactive rubber was characterized by independent determinations of equivalent weight* (end-group acetylation) and number-average molar mass (vapour pressure osmometry) to give values of 1088 and 2343, respectively.

Niax triol LHT240 (ex. Union Carbide Corporation.) This polyol was a polyoxpropylene adduct of 1,2,6-hexane triol and its equivalent weight (end-group acetylation) was determined to be 228.

Trimethylol propane, TMP (ex. British Drug Houses.) This hydroxy compound was re-crystallized from ethyl acetate prior to use.

4,4′-Methylenediphenylene diisocyanate, MDI. This was used in one of three forms whose equivalent weights were assessed by NCO titration: (i) powder form (ex. British Drug Houses), which after purification by distillation had an equivalent weight of 125; (ii) flake form (ex. Bayer), which was partially purified by melting and hot-sintering through a no. 3 sinter, and had an equivalent weight of 127; (iii) liquid form, Isocon-M, (ex. Lankro Chemicals) was used as received and had an equivalent weight of 137.

Hammer-milled glass (HMG) fibres, XG 1629 (ex. Turner Brothers.) This filler comprises $12\,\mu$m diameter fibres with a distribution of fibre-lengths having a mean value of $110\,\mu$m and was supplied without any surface treatment. The filler was oven-dried (120°C/1 hour) before use.

Polymerization processes

All polymerizations were carried out with stoichiometric equivalence of NCO and OH groups. Generally, initial mixing of reactants was carried out under anhydrous conditions at 46°C without added catalysts. Two different processes were used which are designated 'one-shot' and 'pre-polymer'.

'One-shot' process. In this process the various polyol components were mixed under vacuum in a sealed, 2-neck flask maintained at the required temperature. Molten MDI (46°C) was then added, the vacuum re-applied and stirring resumed until all reactants were thoroughly mixed and the reaction mixture, initially cloudy, became clear. (When HMG filler was used, it was completely dispersed in the polyol blend prior to the addition of MDI.) A schematic representation of the polymerization process is given in *Figure 1*. Generally, after the addition of molten MDI, the initially immiscible reactants became clear within 3 min and vitrification occurred after a further 5 min. In the presence of the reactive rubber PB component, precipitation of the rubber polyurethane phase led to a milky appearance about 15 to 30 s after the initial clarification. All of the polyurethane-forming reactions were exothermic, even without added catalysts, and temperature rises in excess of 140°C were observed during the vitrification stage. In all cases, casting had to be completed within 40 s from the time at which the mixture became clear.

'Pre-polymer' process. The MDI and PB reactants were pre-reacted under vacuum for 1 h at 50°C in a sealed, stirred reaction flask to yield a completely miscible, liquid product comprising an isocyanate-tipped, polybutadiene pre-polymer and excess, unreacted MDI. The remaining polyol reactants (TMP and LHT240) were then added and the vacuum re-applied. The resulting reactant mixture was cast into moulds as described for the 'one-shot' process.

Characterization techniques

Thermal properties. These were determined from differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). For DSC, a Perkin–Elmer DSC2 machine was used and samples (≈ 10 mg) were encapsulated in aluminium pans and subjected to temperature scans at a heating rate of 20°C min^{-1} in the

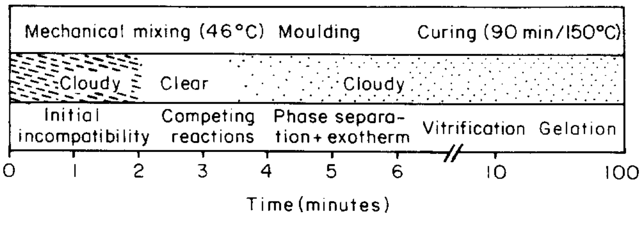

Figure 1 Processing stages and associated reaction profile involved in the preparation of phase-separated, rubber-modified polyurethane networks by a 'one-shot' process

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* Equivalent weight is defined as the molar mass per OH or NCO functional group. All values of equivalent weight and molar mass are expressed in g mol^{-1}.

temperature range −100°C to 250°C. DMA was conducted on a torsion pendulum operating in a free-vibration mode at approximately 1 Hz. Beam specimens, $100 \times 10 \times 3$ mm were used to obtain shear storage modulus (G') and mechanical damping ($\tan \delta$) data over the temperature range −200°C to 200°C at a heating rate of $1°\mathrm{C\,min^{-1}}$.

Stress–strain properties. For each material these were derived from the mean of at least 5 tensile tests carried out at 23°C on an Instron 1122 machine. Dumb-bell shaped specimens with a 70 mm gauge length were tested at an extension rate of $2\,\mathrm{mm\,min^{-1}}$, corresponding to a strain rate of $4.8 \times 10^{-4}\,\mathrm{s^{-1}}$.

Impact properties. These were determined from Charpy impact tests conducted at 23°C on a Hounsfield pendulum apparatus according to British Standard BS2782 (306A). Additional Charpy impact tests were conducted using specimens containing razor-sharp notches of various depths to yield data amenable to analysis by linear elastic fracture mechanics.

RESULTS AND DISCUSSION

Development and characterization of a suitable polyurethane network matrix

Previous studies[11,12] on model polyurethane networks have established relationships between reactant structure in terms of molar mass and functionality, conditions of network formation (including gelation) and physical properties. Based on these studies, initial investigations were carried out on a series of polyurethane networks formed from a polyol blend of LHT240 and TMP reacted with MDI. From this series, a suitable high T_g ($\approx 150°$C) network matrix was selected for subsequent rubber modification.

Various proportions of LHT240 and TMP were mixed to give polyol blends of predetermined molar ratios LHT240:TMP in the range 100:0 to 5:95, calculated in terms of hydroxyl group concentrations. Each blend was reacted with pure MDI and the resulting polyurethane-forming systems were cured at a temperature exceeding the T_g of each polyurethane. DSC measurements on each of the completely-reacted polyurethane networks showed that for all compositions, a single major transition was obtained, which was attributed to the T_g. The results in *Table 1* show the expected increase in T_g with increasing crosslink density. Although a high value of T_g was a major factor in the selection of a polyurethane matrix, matrix U5 was selected for further study in preference to matrix U6, despite the higher T_g of the latter, because U6 had a very short gel-time (<2 min) making it difficult to cast and mould. Matrix U5 is a clear, colourless, amorphous glass with the tensile stress–strain and Charpy impact properties (23°C) shown in the first column of *Table 2*. As expected the unmodified matrix U5 possesses good tensile strength and modulus but low ultimate elongation which makes it a suitable candidate for rubber-modification.

Table 1 Molar ratios of LHT240 and TMP used to form polyurethane network matrix materials together with corresponding values of T_g

Polyurethane network unmodified matrix	Molar (OH) ratio LHT240:TMP	T_g value (°C)
U1	100:0	39
U2	50:50	73
U3	25:75	113
U4	15:85	142
U5	10:90	165
U6	5:95	180

Table 2 Tensile stress–strain and impact properties (23°C) of unmodified (U5) and rubber-modified (R-U5/4) materials based on polyurethane network U5 in *Table 1*. Data give a comparison of 'one-shot' and 'pre-polymer' polymerization techniques for R-U5 materials containing 4% w/w of added polybutadiene

Property	U5*	R-U5/4* ('one-shot')	R-U5/4 ('pre-polymer')
Young's modulus, E ($\mathrm{GN\,m^{-2}}$)	2.75	2.58	2.25
Tensile strength, σ_u ($\mathrm{MN\,m^{-2}}$)	78	79	55
Ultimate strain, ε_u (%)	4	8	3
Impact strength[a], I_s ($\mathrm{kJ\,m^{-2}}$)	6.0 ± 2.0	4.1 ± 0.7	1.7 ± 0.2

[a] I_s values obtained from blunt-notch specimens

Rubber-modification of polyurethane network matrix U5

Comparison of 'one-shot' and 'pre-polymer' polymerization processes. Formulations used to prepare rubber-modified epoxy resins involve, typically, carboxyl-terminated, polybutadiene-based (CTBN) liquid rubbers. However, in polyurethane-forming systems, the reaction between CTBN and isocyanates yields an intermediate which rapidly decomposes to produce carbon dioxide. The gaseous product in turn acts as a blowing agent during the overall polyurethane formation so that the final material obtained is a foam. This foaming-reaction is undesirable in the preparation of rigid, bulk materials. An obvious alternative to CTBN is an hydroxy-functionalized liquid rubber which when reacted with isocyanates such as MDI, leads directly to polyurethane elastomer but without undesirable side-reactions. The range of hydroxy-functionalized polybutadienes commercially available is limited, but nevertheless similar criteria to those used in epoxy formulations for the selection of a reactive liquid rubber also apply to polyurethanes. The criteria are summarized as follows:

(a) Reactant compatibility: at some stage during overall polymerization, the liquid rubber and other reactants (polyols/diisocyanate) must be compatible so that homogeneous and simultaneous formation of network matrix and chain extended rubber phases can occur.
(b) Solubility parameters: sufficient difference between the solubility parameters of the essentially linear, polybutadiene–urethane oligomers and the polyurethane network-forming matrix must be achieved so that phase separation occurs *before* gelation of the matrix.
(c) Phase separation: during overall polymerization, however, phase separation must not progress to such an extent that the rubber domains so formed become either too large to provide effective toughening in the fully-cured resin or too discrete so that very weak interphase bonding is developed between rubber particles and network matrix.

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*The sample identification code used throughout this paper is as follows: R≡rubber modified; U5≡unmodified polyurethane network matrix defined in *Table 1*; 4≡weight of added PB liquid rubber expressed as a percentage of the total formulation.

Using the 'one-shot' process, it was possible to prepare rubber-modified polyurethane glasses containing up to 8% by weight of added polybutadiene rubber, ARCO R45-HT. Attempts to incorporate larger amounts (10 to 20% w/w) of liquid rubber resulted in undesirable partial phase-inversion so that the materials obtained were 'cheesy' in nature and possessed properties too inferior to those of the glassy polyurethanes containing less than 8% w/w. At even higher levels (30% w/w) of added rubber, materials with complete phase-inversion were obtained which were elastomeric and were therefore not studied further.

In order to compare polymerization processes, materials based on matrix U5 (see *Table 1*) containing 4% w/w of added rubber were prepared by 'one-shot' and 'pre-polymer' methods. These two rubber-modified materials, after post-curing at 150°C for 90 min, exhibited significantly different tensile and impact properties as shown by the last two columns in *Table 2*. The ultimate properties of the 'pre-polymer' material R-U5/4 are markedly inferior to those of the 'one-shot' material and the reason for this becomes clear when the morphology of the materials is examined. *Figures 2a* and *b* are scanning electron micrographs (SEM) of tensile fracture surfaces which show that although both materials contain discrete rubber particles in the size range 1 to 100 μm, those in the 'one-shot' material are much better bonded to the matrix as there is some evidence of rubber particle tearing which has occurred during fracture. Conversely, in the 'pre-polymer' material, considerable debonding has occurred resulting in crater formation indicating an excessive degree of incompatibility between rubber and matrix phases. Consequently the poorly-bonded rubber particles behave more as voids during fracture which is the major reason accounting for the relatively poor ultimate properties shown in *Table 2*. The 'pre-polymer' process clearly results in essentially linear rubber molecules of high molar mass which precipitate too rapidly on addition of the other polyols. Consequently there is reduced grafting between the rubber domains and the final polyurethane network matrix. The 'pre-polymer' process was therefore abandoned in favour of the 'one-shot' process in further studies.

Effects of stirring rate on properties. Unlike the rubber-modified epoxy systems, the polyurethane networks studied here undergo phase separation and vitrification within minutes (rather than hours) of the initial mixing of reactants. The stirring rate used during polyurethane formation was therefore expected to influence particle size and size distribution particularly once phase separation commenced. These stirring rate effects are in addition to those on particle size caused by the relative compatibilities and molar masses of the rubber and network matrix phases. However, rapid stirring is not *essential* for the generation of discrete rubber particles in these polyurethane materials in the way that high shear rates are essential for the generation of dispersed rubber particles in high impact polystyrene[1], since the latter is only formed by a phase inversion process. In the polyurethanes, the rubber never constitutes the major, continuous phase, even recognizing that inclusions of glassy matrix material within the rubber particles must occur. The effect of stirring rate may well be to vary the number and thus the size of particles at a constant volume fraction, and this number might well remain constant after the gel-point.

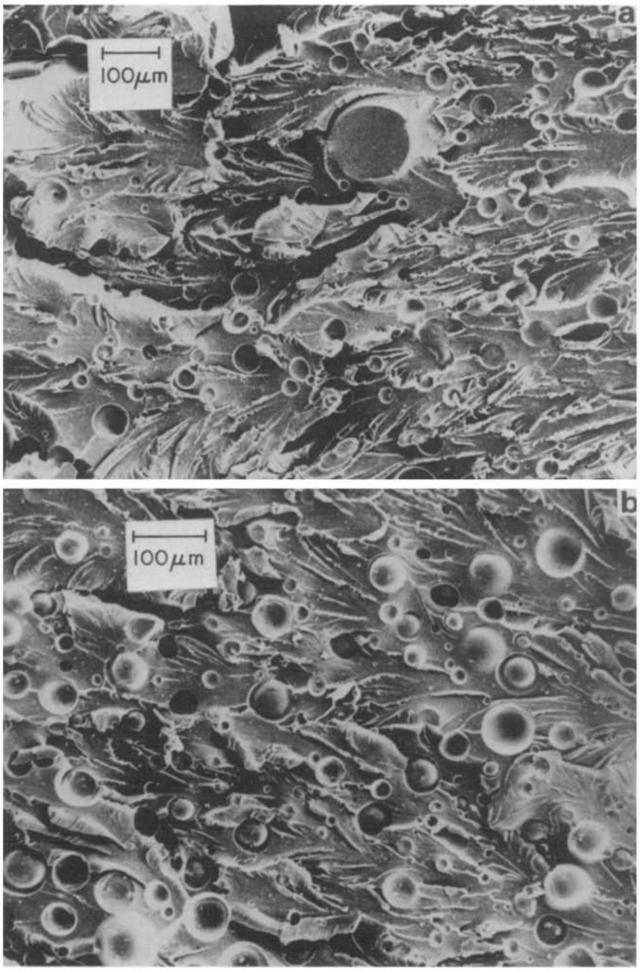

Figure 2 Comparative scanning electron micrographs of typical fracture surfaces of rubber-modified polyurethanes R-U5/4, containing 4% w/w of added polybutadiene, illustrating the effects of processing technique on dispersed rubber phase. (a) 'One-shot' process showing well-bonded and torn rubber particles. (b) 'Pre-polymer' process showing debonded rubber particles and craters

In these studies, the stirrer used was of a simple paddle design and during the initial stages of polymerization a constant stirring rate of 140 rpm was used for all systems up to the onset of phase separation (0 to 4 min, see *Figure 1*). Stirring was continued using different stirring rates in the range 0 to 200 rpm, for a further 30 s into the phase-separation period (4 to 6 min), after which time the mixture was cast into moulds. The stirring conditions, the numbers and sizes of particles and materials properties are summarized in *Table 3*. All of the R-U5/4 materials were similar in appearance, being cream or white coloured, but clearly optimum tensile properties are observed at intermediate stirring rates. In particular, specimens of the material formed using 100 rpm stirring rate all exhibited distinct yield behaviour at 8% strain in tensile tests. Examination of typical SEM fractographs in *Figures 3a* and *b* shows that a greater number of smaller particles with a narrower particle size distribution is formed at the highest stirring rate (200 rpm). However, the material formed using 200 rpm stirring rate possessed inferior properties to the slower stirring rate (100 rpm) material which also had a broader distribution of rubber particle sizes. The stirring rate of 100 rpm was therefore used in subsequent materials formation.

Table 3 Relationships between stirring rate, rubber particle size and tensile properties (23°C) for 4% w/w rubber-modified materials R-U5/4. All materials were formed at a reaction temperature of 46°C and cured at 150°C for 90 min

Stirring rate (rpm)	Particle density (m^{-2})[a]	Particle mean size (μm)	Tensile modulus, E ($GN\ m^{-2}$)	Tensile strength, σ_u ($MN\ m^{-2}$)	Ultimate elongation, ε_u (%)
0	–	–	2.61	76.9	6.7
100	12.3×10^8	11.8	2.75	80.6	8.2
140	–	–	2.63	78.4	5.8
200	45.8×10^8	5.8	2.68	74.7	5.2

[a] Particle density expressed as number per unit fracture surface area

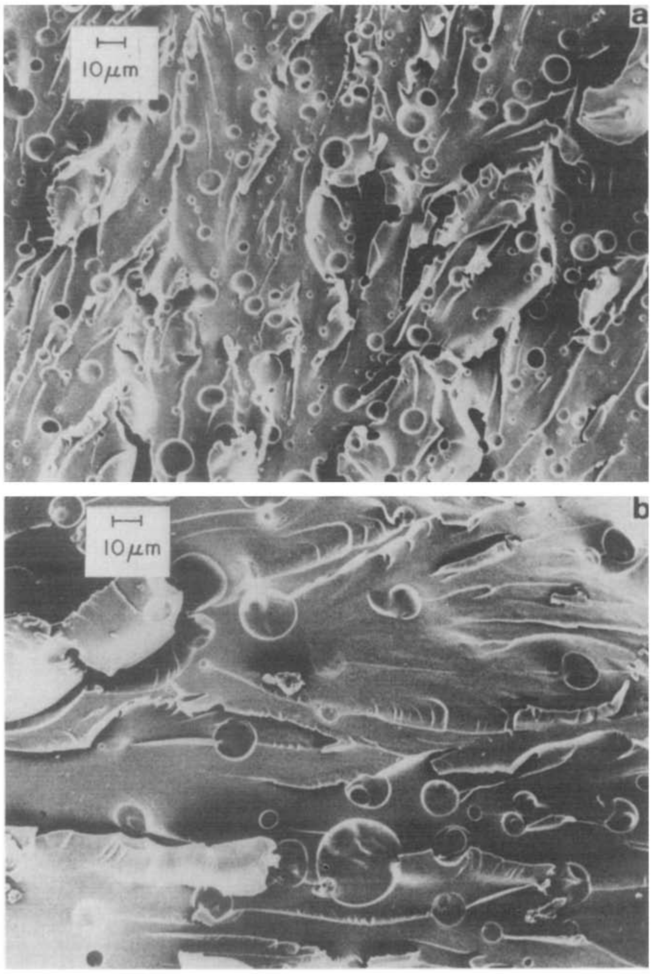

Figure 3 Comparative scanning electron micrographs of typical fracture surfaces of rubber-modified polyurethanes R-U5/4, illustrating the effects of stirring-rate on the size and size-distribution of rubber particles formed in materials prepared by the 'one-shot' process. (a) High stirring rate (200 rpm) showing small rubber particles (mean diameter, 5.8 μm) with narrow size distribution. (b) Low stirring rate (100 rpm) showing large rubber particles (mean diameter, 11.8 μm) with broad size distribution

Effects of reaction temperature and cure time on properties. The three polyols TMP, LHT240 and R45-HT, used in admixture in these studies contain hydroxyl groups with different intrinsic reactivities toward MDI. Furthermore, the different temperature-dependence of the various OH/NCO reactions occurring simultaneously during polymer formation may very well affect (i) the rates of molar mass development of rubber and network phases; (ii) the phase separation process itself and its proximity to the gel-point; and (iii) the amounts and size of rubber particles ultimately formed.

Table 4 Effect of initial reaction temperature on tensile properties (23°C) of rubber-modified polyurethanes R-U5/2 and R-U5/5 containing two different amounts of added rubber. All materials were cured for 90 minutes at 150°C

Temperature (°C)	Rubber w/w (%)	Modulus, E ($GN\ m^{-2}$)	Tensile strength, σ_u ($MN\ m^{-2}$)	Ultimate elongation ε_u (%)
42	2	3.03	82.4	5.9
46	2	2.75	83.2	4.8
50	2	2.70	78.6	5.5
42	5	2.50	71.5	5.5
46	5	2.50	74.4	6.5
50	5	2.34	72.0	6.2

The range of reaction temperatures used for initial mixing and polymerization in the present studies was considerably limited, since MDI solidifies below 40°C, and above 50°C, reaction rates are too fast to allow efficient mixing and moulding. Thus, only three different temperatures (42°C, 46°C and 50°C) were used to assess the effects of initial reaction temperature on the tensile properties of rubber-modified materials. *Table 4* summarizes the results obtained for two series of materials containing respectively 2% and 5% w/w of added rubber. Overall the differences in properties within each series are small so that reaction temperature therefore does not appear to be an important variable in these systems. However, the temperature range studied is probably too small to show any significant effects on structure–property relations and is almost certainly of secondary importance when compared with the temperatures generated subsequently by the highly exothermic polymerization. Nevertheless, at lower rubber content (2% w/w), there is a small trend in modulus and the highest modulus obtained for R-U5/2 formed using the lowest reaction temperature of 42°C is attributed to the formation of a smaller amount of phase-separated rubber as observed from SEM studies on fracture surfaces.

Although all reaction mixtures in these studies were observed to vitrify within approximately 7 min at (nominally) room temperature, polymerization is of course incomplete at this stage, even allowing for the exotherm generated. Thus to effect gelation and thence complete reaction, the temperature of the material during the subsequent cure stage must be raised to the vicinity of the T_g expected for the fully-reacted polyurethane network. Clearly the cure stage will determine the degrees of phase separation and ultimate interphase bonding. Furthermore, incomplete cure will result in unreacted functional groups which would plasticize the otherwise glassy network material.

The effects on physical properties of varying cure time at a constant cure temperature (150°C) were studied for the rubber-modified material R-U5/4 containing 4% w/w of added rubber. The results are summarized in *Table 5* which shows T_g-values and tensile properties for materials cured for times ranging from 15 to 120 min. It is apparent from the data in *Table 5* that the minimum time necessary for complete cure at 150°C is between 60 and 120 min, after which time the T_g of the material reaches a limiting value of 150°C. Tensile strength and elongation also reach limiting values of approximately 83 MN m^{-2} and 8.5% respectively after this cure time. The results show that reaction of functional groups has been maximized, certainly within the matrix, and that optimum development of phase morphology has been achieved. Evidence for matrix plasticization, arising from unreacted molecular species present in the material cured for the shortest time (15 min), was obtained during tensile testing of all specimens in the form of pronounced yielding and stress whitening at approximately 5% strain. This phenomenon is in addition to the reduced value of T_g (135°C) observed for this material. Stress-whitening was not observed during tensile testing of specimens from materials cured for the longer times. On the basis of the results shown in *Tables 4* and *5*, all materials subsequently studied were formed using an initial reaction temperature of 46°C and a curing time of 90 min at 150°C.

Effects of added rubber content on properties. With optimum preparative and curing conditions established for these rubber-modified polyurethanes, the effects on physical properties of varying the amount of added polybutadiene liquid rubber were then studied. The objective was to maximize material ductility and toughness whilst at the same time retaining high values of T_g, strength and modulus. Since added rubber contents in excess of 8% w/w produced inferior materials, the composition range of interest in this section was limited to between 2 and 8% w/w of added rubber based on polyurethane network matrix U5. In addition, a comparison of rubber-modified polyurethanes formed using flake-MDI and liquid-MDI (Isocon M) with identical polyol mixtures and processing/curing conditions was conducted. Studies on materials formed using a liquid-MDI reactant are important in the context of industrial polyurethane production. This is particularly so in the case of RIM for which liquid polyol and polyisocyanate reactants are essential. The use of Isocon M compared with molten flake-MDI however did make the 'one-shot' process more demanding in terms of the various mixing and moulding stages shown schematically in *Figure 1*. Isocon M is dark brown in colour which made the observation of phase-separation during the mixing stage more difficult, and its greater rate of reaction made the time available for the moulding stage much shorter (5 compared with 7 min). Nevertheless, it was possible to prepare a range of Isocon M-based materials containing 0 to 8% w/w of added rubber, corresponding to those based on flake-MDI.

Table 5 Effect of cure time on T_g and tensile properties (23°C) of rubber modified polyurethane R-U5/4. All materials were formed at an initial reaction temperature of 46°C and cured at 150°C

Cure time (min)	Rubber w/w (%)	T_g (°C)	Modulus, E (GN m^{-2})	Tensile strength, σ_u (MN m^{-2})	Ultimate elongation ε_u (%)
15	4	135	2.75	75.3	5.3
30	4	143	2.79	77.2	6.7
60	4	148	2.68	79.0	7.7
90	4	150	2.73	82.2	8.3
120	4	150	2.76	82.6	8.5

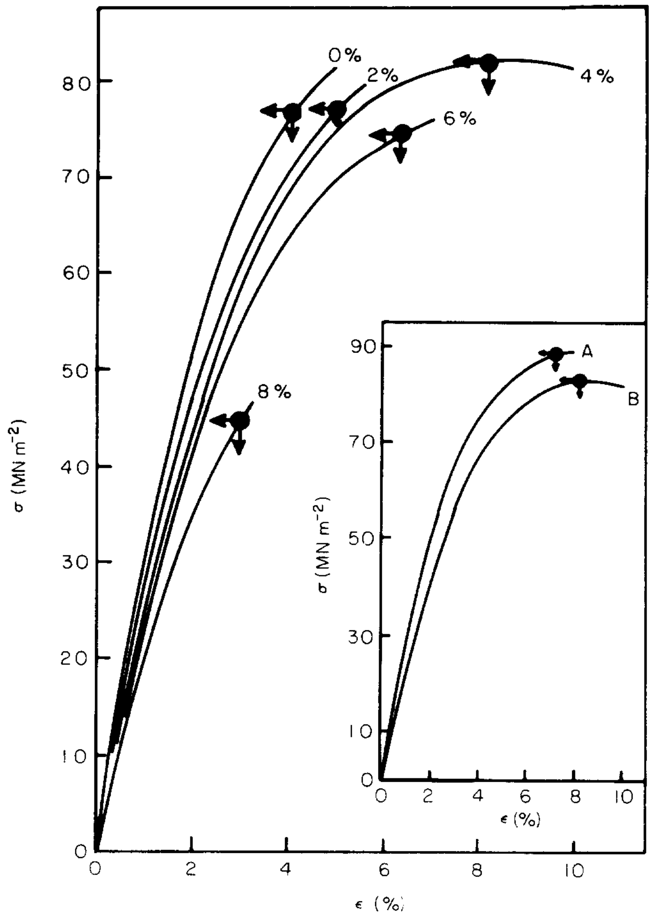

Figure 4 Tensile stress–strain curves (23°C) of unmodified (U5) and rubber-modified (R-U5) polyurethane networks containing 2 to 8% w/w of added polybutadiene rubber. [Inset: comparative tensile stress–strain curves for rubber-modified polyurethanes R-U5/4 based on (A) flake-MDI and (B) liquid-MDI (Isocon M). Both materials contain 4% w/w of added rubber.] Each curve is the average of 5 tests and the circles denote the mean failure points. Tensile properties derived from each mean stress–strain curve are summarized in *Table 6*

Mean stress–strain curves (the average of at least 4 specimens) for unmodified U5 and rubber-modified materials R-U5/2 to R-U5/8 based on flake MDI are shown in *Figure 4*. The derived tensile properties together with Charpy impact data are given in *Table 6*. The general effect on properties of increasing rubber content up to an optimum level of 4% w/w is to maximize tensile strength and, in particular, ultimate elongation values. Above 4% w/w of added rubber, materials properties decrease relatively dramatically and are significantly inferior to those of the unmodified polyurethane network U5. Overall, the brittle matrix U5 is thus transformed by the added rubber into a semi-ductile material which, as can be seen in *Figure 4*, shows a small but nonetheless distinct yield point. As a direct consequence, the fracture toughness of U5 as determined by the value of U_y is more than doubled for material R-U5/4 whilst the modulus and tensile strength are essentially unaltered. Clearly optimum tensile properties are obtained at the 4% w/w

Table 6 Effects of added rubber content on T_g, tensile and impact properties (23°C) of modified polyurethane network U5. Comparative data are shown for two series based on either flake-MDI or liquid-MDI. Identical polyol mixtures and processing conditions were used in each series. Symbols E, σ_u, ε_u and I_s are defined in *Table 2*

		Flake-MDI						Liquid-MDI			
Material code	Rubber w/w (%)	T_g (°C)	E (GN m^{-2})	σ_u (MN m^{-2})	ε_u (%)	U_y[a] (MJ m^{-3})	I_s[b] (kJ m^{-2})	T_g (°C)	E (GN m^{-2})	σ_u (MN m^{-2})	ε_u (%)
U5	0	147	2.75	76.5	4.2	2.0	6.1±2.0	175	3.10	85.6	4.2
R-U5/2	2	153	2.70	76.5	5.0	1.7	4.7±0.7	–	–	–	–
R-U5/4	4	149	2.73	82.2	8.3	4.9	4.5±0.7	177	2.85	88.8	7.3
R-U5/6	6	148	2.38	74.3	6.4	3.2	4.1±0.7	169	2.72	82.4	7.3
R-U5/8	8	153	2.10	46.4	3.1	0.8	2.5±0.8	174	–	–	–

[a] U_y is defined as the tensile work of fracture as determined from the area under the mean stress–strain curve

[b] Blunt-notch Charpy data. Comparable values determined for poly(methylmethacrylate) and polypropylene are 1.1±0.1 and 3.3±0.4 kJ m^{-2} respectively

level of added rubber for this particular polyurethane network material.

For both series of flake-MDI and liquid-MDI based materials, a high degree of phase separation is evident as shown by the essentially constant T_g-values of approximately 150°C and 174°C, respectively. The higher value in the latter case is undoubtedly due to the mixed chemical composition of Isocon M which contains predominantly difunctional ($f=2$) MDI, and a significant proportion of oligomeric MDI units of higher NCO functionality ($f>2$). The increased functionality and intrinsic rigidity of polyurethane networks derived from the liquid-MDI compared with flake-MDI therefore accounts for the higher T_g of the former*. Further comparison of the tensile data shows that the materials based on liquid-MDI are generally stiffer and stronger as shown by the values of E and σ_u in *Table 6*. In the specific case of materials containing 4% w/w of added rubber, the inset in *Figure 4* shows the effect of MDI structure on stress–strain behaviour, and despite the higher E and σ_u values of the liquid-MDI product (curve A), the higher ε_u-value for the flake-MDI material (curve B) is more significant in terms of material toughness as measured in terms of the respective values of U_y, namely, 4.9 and 4.0 MJ m^{-3}. Overall both series of materials show similar improvements in tensile and toughness properties at an optimum level of 4% w/w of added rubber.

Surprisingly, the improvements in tensile fracture toughness are not observed for materials containing added rubber when tested under impact conditions. Consideration of the values for impact strength (I_s) given in *Table 6* shows two important features for these polyurethane materials. Firstly, the unmodified network U5 is relatively tough, with a mean value of 6.1 kJ m^{-2}, when compared with other ductile polymers such as polypropylene (3.3 kJ m^{-2}) tested under identical conditions. Secondly, the value of I_s is reduced on the addition of rubber and then decreases slightly from 4.7 to 4.1 kJ m^{-2} as rubber content increases from 2 to 6% w/w before the sudden reduction to 2.5 kJ m^{-2} at 8% w/w. Also significant is the reduction by more than a half of the experimental scatter associated with the mean values of I_s on addition of rubber. The reduced scatter is presumably due to the localization of stresses in the vicinity of the crack-tip during fracture, by the dispersed rubber particles.

The dynamic mechanical properties obtained from torsion pendulum data at 1 Hz for unmodified U5 and rubber-modified R-U5/4 polyurethanes are shown in *Figure 5a* and *b* as plots of G' and $\tan\delta$, respectively, *versus* temperature. The highly crosslinked, amorphous nature of these materials is illustrated in *Figure 5a* by the high, glassy values of G' which are retained up to temperatures approaching 140°C. Also, the addition of 4% w/w of rubber has very little effect on the values of G' over the entire temperature range studied. Moreover, the damping behaviour of *Figure 5b* gives further evidence of the almost complete phase separation achieved in the rubber-modified materials. For the unmodified polyurethane network U5, α- and β-relaxations are observed at approximately 160°C and −90°C, respectively. The α-transition, α_n corresponding to T_g of the network, is virtually unaffected by the addition of rubber whereas the β-relaxation, designated β_n, appears to be intensified and shifted 10°C to the higher temperature of −80°C. However, the α-transition or T_g, designated α_r, of the poly(butadiene–urethane) rubber is known[13] to occur at −60°C so that the apparent β-relaxation in the rubber-modified material R-U5/4 is in fact a merged peak comprising the network β- and rubber α-relaxations. Similar low-temperature relaxational behaviour was also observed by Kinloch *et al.*[7] in epoxy resins modified with a liquid rubber based on a carboxyl-terminated, random copolymer of butadiene and acrylonitrile (CTBN). That is, the β-relaxation of unmodified epoxy resin (−74°C) was observed to shift and merge with the higher temperature, α-relaxation of the rubber copolymer (−55°C).

Also shown in *Figures 5a* and *b* are G' and $\tan\delta$ *versus* temperature curves for the unmodified polyurethane network corresponding to U5, but which was formed using liquid-MDI (Isocon M). The data again illustrate the effects of higher functionality and mixed chemical composition of the liquid-MDI referred to previously, since the α-relaxation for this network compared with that based on powder MDI is both broadened and shifted to a higher temperature (T_g) around 200°C.

Clearly, the results demonstrate that a discrete rubber phase is obtained in these highly-crosslinked polyurethanes which does improve the materials ultimate tensile properties. The mechanisms of fracture operative within these and similar rubber-modified polyurethanes are discussed in a subsequent paper[14]. In the case of

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* Comparison of T_g values for U5 materials derived from powder-MDI ($T_g=165$°C, *Table 1*) and flake-MDI ($T_g=147$°C, *Table 5*) also demonstrates the effect of MDI structure and purity. Powder-MDI is distilled whereas flake-MDI is only hot-filtered so that the latter is less free of impurity.

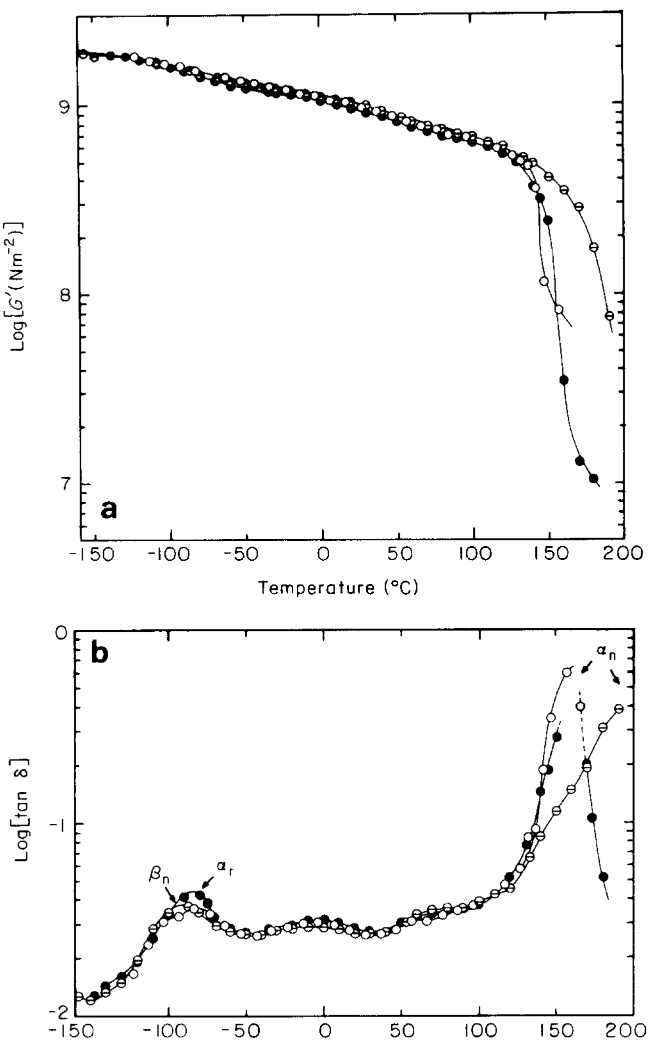

Figure 5 Dynamic mechanical properties of polyurethane networks in terms of (a) storage moduli, G', and (b) mechanical damping, tan δ, as functions of temperature at 1 Hz. (-○-) and (-⊖-), unmodified polyurethanes U5 formed using, respectively, flake-MDI and liquid-MDI (Isocon M). (-●-) rubber-modified polyurethane R-U5/4 containing 4% w/w of added rubber

rubber-modified epoxies, various mechanisms such as yielding and plastic shear flow of the matrix, and dilatation and void formation within the rubber particles or at the particle/matrix interfaces have been suggested but are still the subject of some controversy[7]. Nevertheless, despite the controversy surrounding the exact nature of the energy-dissipative deformations occurring in the vicinity of the crack-tip during fracture, the results in these studies are in accord with the widely accepted view[1] that the existence of an α-transition at about -50°C for the rubbery phase is one of the essential features for effective rubber toughening.

Composite materials comprising glass-fibres and a rubber-modified polyurethane

The incorporation of rigid fillers into polymers to form composite materials is a well established practice for improving certain physical and mechanical properties. Generally, the filler phase may be described as reinforcing fibres or as filler particles, both of which modify polymer properties but in quite different ways. All rigid fillers will increase stiffness and dimensional stability (particularly at elevated temperatures), but will reduce viscoelastic properties such as creep. In addition, reinforcing fibres of sufficient aspect ratio will improve fracture strength and toughness provided adequate bonding exists between fibres and polymeric matrix. However, particulate fillers can have opposing effects on ultimate properties depending largely on the polymer type, and it is impossible to generalize with particulate composites. There has been little work reported on the use of rubber-modified polymers as matrix materials for composites although some claims for the improvement of impact properties of carbon fibre/epoxy resin composites have been made[15] in which up to 25% w/w of CTBN liquid rubber was incorporated in the epoxy resin formulation. In the case of RIM-polyurethanes, the requirements for materials with improved stiffness, dimensional stability and fracture toughness are usually achieved by incorporating hammer milled glass (HMG) fibres into the polyol reactant prior to processing[9], although other fillers are used. The present study was therefore extended to compare unmodified and rubber-modified polyurethanes described in previous sections, as matrix materials in composites containing HMG-fibres.

Two series of polyurethane composites based on U5 and R-U5/4 were prepared by incorporating various amounts of HMG-fibres into the polyurethane-forming mixtures. The composites formed contained weight fractions (W_f) of fibres in the range $0 < W_f < 0.30$. The tensile properties of the composites, derived from mean tensile stress–strain curves, are shown as functions of W_f in *Figure 6a, b* and *c*. As expected, improvements in modulus (2.7 to 5.8 GN m^{-2}) and tensile strength σ_u (77 to 92 MN m^{-2}) with concomitant reductions in ultimate elongation ε_u as W_f increases were observed for both series of composites.

Comparison of the increasing trends in E and σ_u for U5 and R-U5/4-based materials shows that the incorporation of a rubber phase in the latter case serves only to diminish slightly the reinforcing effects of the HMG-fibres. On the other hand, the presence of rubber does improve ε_u-values for composites with low filler contents ($W_f < 0.20$) although at higher W_f, values of ε_u for both U5 and R-U5/4 composites are reduced to similar values of about 5%.

Interestingly for both series of composites, similar monotonic increases in the value of T_g (148°C to 161°C) with increasing W_f were observed, as shown in *Figure 6d*. The similarity between the data for U5 and R-U5/4 composites, irrespective of the presence of filler, again indicates that the phase-separated rubber has an insignificant effect on the T_g of the polyurethane network. The increase in T_g with W_f in these composites must be attributed to restricted segmental mobility within the network matrix of polyurethane chains which have been chemically bonded to the surface of the filler. Clearly there is a possibility of chemical reaction between isocyanate groups and free silanol groups on the surfaces of HMG-fibres during the overall formation of the polyurethane composites. The amount of such interfacial reactions and the value of T_g of the final composite will therefore both increase with increasing fibre content. Further evidence of strong interfacial bonding in these composites is provided by the SEM fractograph in *Figure 7* which shows the occurrence of both fibre pull-out and fibre fracture processes in different regions of the fracture surface. Thus, although the HMG-filler contains a

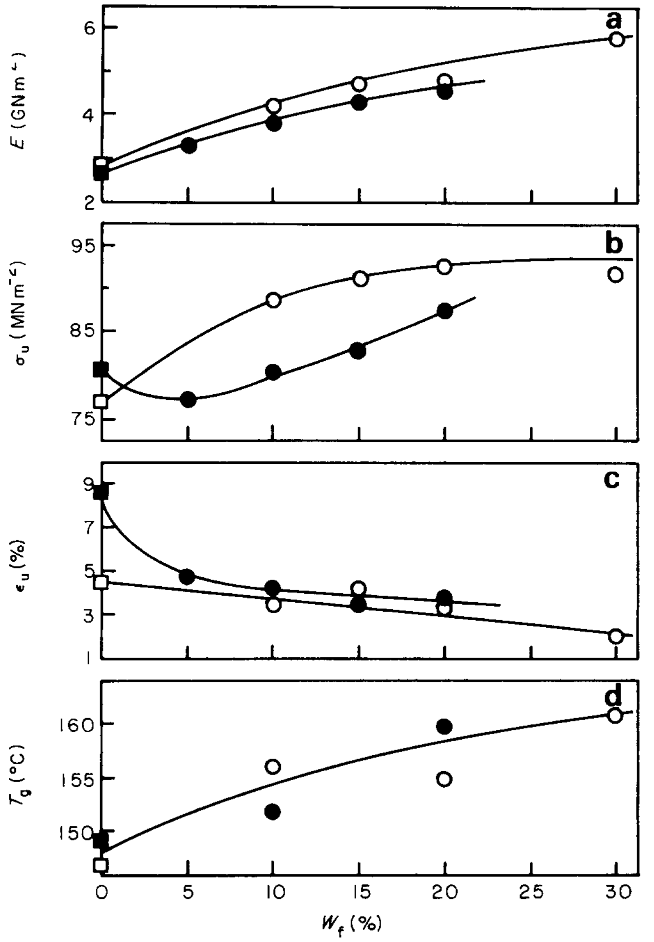

Figure 6 Effects of HMG-fibre content (W_f) on (a) modulus, E; (b) tensile strength, σ_u; (c) ultimate elongation, ε_u; and (d) glass transition temperature, T_g, for composite materials based on unmodified and rubber-modified polyurethane networks. (-□-) unmodified matrix U5 (unfilled); (-■-) 4% w/w rubber-modified matrix R-U5/4 (unfilled); (-○-) HMG-composites based on U5; (-●-) HMG-composites based on R-U5/4

distribution of fibre lengths, there is a proportion of them with sufficient aspect ratio for fibre fracture to occur during composite failure. These observations are consistent with the small but steady increase in composite tensile strengths with W_f obtained for these materials. Overall, the results show that the rigid filler dominates the physical properties of these polyurethane composites, irrespective of the presence of a dispersed rubber phase. Furthermore, as explained by Bucknall[16], the mechanism of deformation and failure of the polymer composites is undoubtedly changed by the rigid filler which completely masks the relatively subtle modifications to the glassy polyurethane network matrix brought about by the inclusion of dispersed rubber particles.

Fracture mechanics analysis of impact behaviour

The values of impact strength, I_s, presented in previous sections were obtained from Charpy specimens in which blunt notches of constant length, a, were used in accordance with impact testing standards BS 2782(306A) or ASTM-D 256-73. As noted, however, the results are subject to significant experimental scatter since I_s is influenced by the energy required for both crack initiation and subsequent propagation. Thus, to improve reproducibility, it is often better to use sharp-notched specimens. Furthermore, the presence of sharp notches during impact loading simulates the most severe conditions to which a material may be subjected and determines the notch-sensitivity of the material, as well as rendering the impact data obtained amenable to analysis using linear elastic fracture mechanics (LEFM). It is well known[6,17,18] that changes in the geometry of test specimens, by varying notch-tip radius, ρ_c, notch-to-depth ratio, a/D, specimen thickness, B, and length, $2L$, have profound effects on the impact behaviour and values of I_s for glassy polymers. Sharp and deep notches reduce I_s due to the combined effects of creating plane strain[19] conditions with high triaxial stress concentrations[17,20,21] and increasing strain rate[6] in the locality of the crack tip. Increasing specimen thickness, B, also induces plane strain conditions[6] and reduces I_s, whilst increasing specimen length, $2L$, tends to increase I_s by decreasing the strain rate during the impact loading Charpy specimens.

In general, specimen geometry not only influences I_s but also alters the apparent ranking order of different polymers, so that a more fundamental and systematic approach in terms of LEFM was used in the present study to analyse the impact behaviour of unmodified and rubber-modified polyurethane networks and composites. Following the analysis of Plati and Williams[22], the impact energies, W, of Charpy specimens containing razor-sharp notches of varying lengths, giving a/D values in the range 0.05 to 0.22, were determined as functions of reduced specimen cross-sectional area, $BD\phi$. The parameter ϕ is a geometrical factor, approximate values of which are given by the equation

$$\phi = \frac{(a/D)}{2} + \frac{2L}{18\pi D} \cdot \frac{1}{(a/D)}$$

The LEFM analysis relates impact energy, W, to $BD\phi$ by the equation

$$W = G_{IC} \cdot BD\phi$$

where G_{IC} is known as the critical strain energy release rate and is a measure of a materials resistance to crack propagation during fracture. Thus, on the basis of LEFM, G_{IC} is a true materials constant whose magnitude is independent of specimen geometry (and test method).

Figure 7 Scanning electron micrograph of the impact fracture surface of a polyurethane composite comprising an unmodified matrix based on polyurethane network U5 and 15% W_f of HMG-fibres

The impact behaviour of the various polyurethane materials described in previous sections was determined using the LEFM approach and the effects on the value of G_{IC} of varying processing conditions such as (a) stirring rate and (b) curing time, (c) added rubber and (d) HMG-fibre contents were investigated. Thus, for each material studied, experimental W and $BD\phi$ data were obtained and, in all cases, plots of W *versus* $BD\phi$ were completely linear through the origin ($W=0$, $BD\phi=0$) and values of G_{IC} were evaluated from least squares analysis of the data points. The results are shown in *Figure 8a–d* as plots of G_{IC} *versus* stirring rate, cure time, added rubber and HMG-fibre contents, respectively.

Overall the values of G_{IC} obtained from the various polyurethane network materials (1.0 to 2.0 kJ m^{-2}) indicate that these materials are relatively tough when compared with other highly crosslinked polymers such as epoxy and polyester resins[6] (0.05 to 0.60 kJ m^{-2}) or polyimides[23] (0.01 to 0.07 kJ m^{-2}). Moreover, the polyurethane materials are quite notch-insensitive since the range of G_{IC} values is only a factor of about 3 less than the fracture energy values (2.5 to 6.1 kJ m^{-2}) obtained from blunt-notch impact data. In contrast, the epoxy resins are extremely notch-sensitive since on the same basis, fracture energy values are reduced by factors of the order of 100*.

The trends in G_{IC} values with processing conditions shown in *Figure 8a* and *b* reflect to a large extent the tensile data discussed previously for polyurethanes containing 4% w/w of added rubber (see *Tables 3* and *5*). A small but detectable maximum in G_{IC} (1.8 kJ m^{-2}) is observed at the intermediate stirring rate (100 rpm) used, which again illustrates with reference to SEM *Figures 3a* and *b*, the effects of particle size and size distribution on ultimate properties. The effect of cure time at 150°C is to decrease G_{IC} from about 2.1 kJ m^{-2} after 15 min to a limiting value of about 1.6 kJ m^{-2} after 90 min which reflects exactly the increases in tensile strength and ultimate elongation to the limiting values shown in *Table 5*. As before, the changes in ultimate properties correlate with the observed increase in material T_g with cure time and in the case of G_{IC}, the apparent toughness of the partially-cured material is decreased as expected since optimization of phase morphology and maximized reaction of functional groups eliminate plasticization effects within the material. Similar effects of cure conditions on the trend of G_{IC} with matrix T_g have also been observed[24] for rubber-modified epoxy resins.

Considering the top curve in *Figure 8c*, the effect of increasing rubber content in polyurethanes formed using flake-MDI is to produce a small, gradual decrease in G_{IC} from 1.8 kJ m^{-2} for unmodified U5, to 1.6 kJ m^{-2} for R-U5/8 containing 8% w/w of added rubber. However, this reduction of about 10% in the value of G_{IC} is much smaller than for the corresponding series of fracture energies obtained from blunt-notch impact data (see the I_s data in *Table 6*) and further illustrates the notch-insensitivity of these polyurethane materials. The unexpected decrease in G_{IC} on adding rubber may be attributable to an insufficient number of rubber particles which are too large to adequately initiate or control the energy dissipative mechanisms[6] required for enhanced fracture resistance. It is more likely, however, that the reduction in G_{IC} is a consequence of the intrinsic toughness (or relatively high G_{IC} value) of the unmodified polyurethane network. This factor seems to be borne out by the data shown by the lower curve in *Figure 8c* for polyurethanes formed using liquid-MDI (Isocon M). As discussed previously, the liquid-MDI has a higher isocyanate functionality than flake-MDI and its use results in more highly-crosslinked and therefore more brittle polyurethane materials. This is clearly illustrated by the value of G_{IC} (0.9 kJ m^{-2}) for the unmodified polyurethane based on liquid-MDI which is half of that for the corresponding material (U5) based on flake-MDI. Moreover, the addition of rubber to the former material produces a steady increase in G_{IC} which reaches a value of 1.5 kJ m^{-2} at 8% w/w of added rubber.

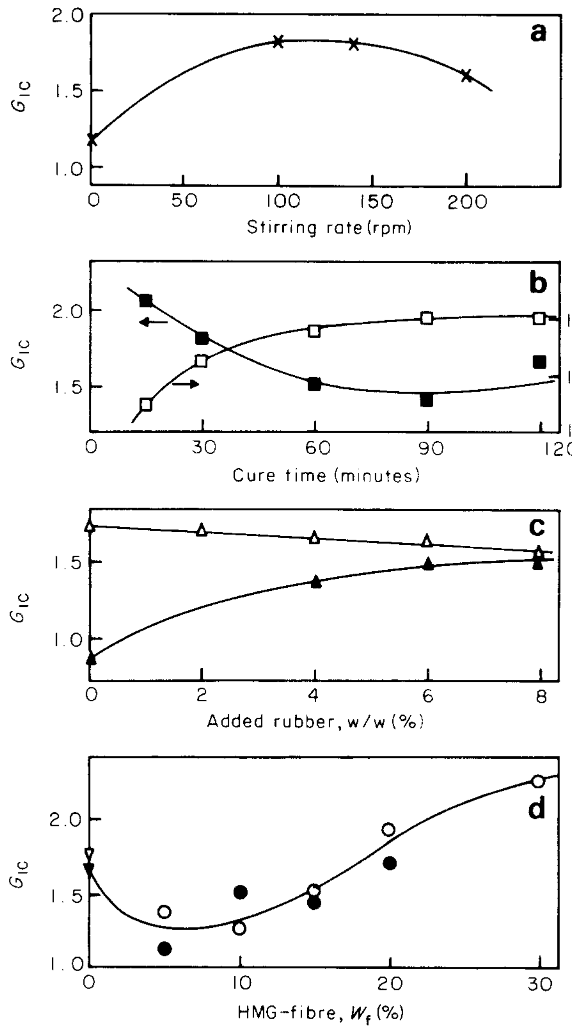

Figure 8 Variation of critical strain energy release rate, G_{IC} (in kJ m^{-2}), with processing conditions and material composition for various polyurethane networks. Individual plots show the effects on G_{IC} of (a) stirring rate (—×—) for R-U5/4; (b) cure time (—■—) compared with T_g (—□—) for R-U5/4; (c) added rubber content for U5 networks formed using flake-MDI (—△—); (d) HMG-fibre content for composites based on unmodified U5 (unfilled —▽—, filled —○—) and rubber-modified R-U5/4 (unfilled —▼—, filled —●—) as matrix materials

The incorporation of a rigid filler into these polyurethanes causes variations in G_{IC} with filler content which are complex and difficult to interpret. In addition, rubber modification of the polyurethane matrix has little

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* Values of 'apparent' fracture energy, G_{IB}, for blunt-notch ($\rho_c = 0.25$ mm) samples can be calculated using the approximate expression derived by Williams[22], namely, $G_{IB} = G_{IC}\,(0.5 + \rho_c/8c)$ assuming typical values of G_{IC} and critical distance, c, reported for various epoxy materials[6].

effect on G_{IC} due to the overriding effects of the rigid filler on composite properties as discussed previously. *Figure 8d* shows that G_{IC} decreases initially at low HMG content, reaching a minimum value of about 1.3 kJ m^{-2} between 5 and 10% weight fraction, W_f; thereafter G_{IC} increases steadily to its highest value of 2.3 kJ m^{-2} at 30% W_f, well above G_{IC} for the unfilled polyurethane. Other workers have shown that for relatively tough polymers such as poly(phenylene oxide)[25] ($G_{IC} = 4.7$ kJ m^{-2}), G_{IC} decreases with increasing filler content in a manner predicted by the effective area model, which implies little or no energy absorbtion in overcoming filler–matrix interactions. In direct contrast, G_{IC} for brittle thermosets such as epoxy resins[26] ($G_{IC} = 0.2$ kJ m^{-2}) increases with filler content and passes through a maximum at a filler level whose value depends on filler size. It would appear, therefore, that the polyurethane materials in the present study, having intermediate toughness values ($G_{IC} \approx 2.0$ kJ m^{-2}), exhibit both types of behaviour with a change in fracture mode occurring at about 10% W_f of HMG. This change in fracture mode, however, is not sudden and may be attributed to additional energy-absorbing mechanisms due to the presence of imperfectly bonded, low aspect ratio fibres which gradually dominate the overall fracture process(es) at higher filler levels. It is well known[27] that energy absorption due to fibre de-bonding and pull-out can make significant contributions to the total energy during the fracture of fibrous composites. Also at higher W_f, the filler may not be completely dispersed within the composites and weakly bonded aggregates may exist which act as sites of energy absorption during fracture. These additional fracture mechanisms arising from both filler–matrix and filler–filler interactions probably account for the upturn in G_{IC} at higher W_f observed for these polyurethane composites.

CONCLUSIONS

The principle of producing discrete, phase-separated rubber particles within highly-crosslinked, glassy polyurethane networks in a manner analogous to that for rubber-modified epoxy resins has been demonstrated. The results showed that the rubber-modified polyurethanes with high T_g values (>150°C) could be prepared from fast reaction (<7 min) systems by a simple one-stage process. The microstructure, tensile and impact behaviour of modified compared with unmodified polyurethanes have been correlated with processing conditions, rubber content, polyurethane network structure and rigid filler content.

The processing method, either 'one-shot' or 'prepolymer', and the stirring rate used in the preparation of materials have been shown to influence rubber particle size, size distribution and rubber–matrix adhesion, and hence material properties. Maximum improvement in tensile properties and toughness were obtained at 4% w/w of added rubber for which, typically, the distribution of particle sizes ranged from 0 to 30 μm with a mean particle diameter of 11.8 μm. Scanning electron microscopy and dynamic mechanical analysis have shown that negligible dissolution of rubber in the polyurethane network occurred, although the polybutadiene-based rubber particles did contain glassy inclusions. The brittle, tensile behaviour of the unmodified polyurethane was transformed into semi-ductile behaviour by the dispersed rubber phase with values of 8.3%, 82.2 MPa and 4.9 MJ m^{-3} for ε_u, σ_u and U_Y at 4% w/w of added rubber, compared to 4.2%, 76.5 MPa and 2.0 MJ m^{-3} respectively for the unmodified material, but with negligible decrease in E (2.7 GPa). These properties compare very favourably to those reported[26] for epoxy resins.

Fracture energies have been determined from Charpy impact data to give blunt-notch, I_s-values and to give by LEFM analysis, sharp-notch, G_{IC}-values. For 4% w/w rubber-modified materials, $I_s = 4.5$ kJ m^{-2} and $G_{IC} = 1.6$ kJ m^{-2} compared with 6.1 and 1.8 kJ m^{-2}, respectively, for the unmodified polyurethane. These values showed that the unmodified polyurethane, despite its highly-crosslinked nature, was relatively tough compared with other thermosets, that all the polyurethane materials studied were very notch-insensitive and that incorporating rubber increased further this notch-insensitivity. However, the dramatic increases in fracture energy on addition of rubber, typical of the epoxy resin systems, were not observed. Only when a more brittle polyurethane network (formed using a higher-functionality isocyanate reactant) was used as matrix were improvements in G_{IC} obtained by rubber modification.

The incorporation of up to 30% w/w of HMG into polyurethanes gave composite materials with improved stiffness, strength and noticeable increases in T_g, which indicated strong glass-polyurethane adhesion in these composites. Fracture energy (G_{IC}) was reduced initially then increased to exceed G_{IC} for the unfilled polyurethanes, suggesting a change in fracture mechanism with increasing fibre content. The effects on composite properties of added rubber were completely masked by the presence of the rigid filler.

Clearly further work on these polyurethanes is required to optimize microstructural features such as volume fraction of dispersed rubber, particle size and size distribution in order to maximize the toughness enhancement, particularly in terms of G_{IC}. This study, however, has illustrated the feasibility of producing rubber-modified, highly crosslinked polyurethanes from liquid reactant mixtures and rigid fillers commonly utilized in reaction injection moulding. In this way, materials with properties comparable to other, more established rubber-modified thermosets are achievable but more importantly, are capable of being produced as large complex mouldings in a one-stage process with cycle times of less than a minute.

ACKNOWLEDGEMENTS

The authors wish to thank the Polymer Engineering Directorate, SERC, for support of this research.

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