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The effect of stoichiometry on the fracture toughness of a polyurethane-urea elastomer

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Abstract

The fracture toughness of a series of polyurethane elastomers based on polytetramethylene glycol (PTMEG) soft segment, a toluene di-isocyanate (TDI) and a dimethyl-thio-toluenediamine (Ethacure E300) curative with different ratios of isocyanate to amine groups has been studied. The fracture toughness required to initiate crack growth was found to be invariant with stoichiometry but the degree of stable crack growth was found to vary with stoichiometry. This behaviour has been discussed in terms of the molecular and physical structure of the polymers, particularly the extent of cross-linking which varied with the isocyanate/amine ratio. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Polyurethanes; Fracture toughness; Crack growth

1. Introduction

This work was undertaken as part of a study on the wear behaviour of polyurethane elastomers where it was found that subtle differences in the molecular structure caused by changes in the curative and the stoichiometry of the polyurethane had significant effects on the wear resistance. Since the wear mechanisms in elastomers often involve crack growth, the effect of molecular variables caused by changes in curative and stoichiometry on the fracture toughness have been studied. In a previous paper [1], the effect of curative on the fracture toughness of a polyurethane-urea was presented. This work was based on a series of polyurethanes using a polytetraethylene glycol (PTMEG) soft segment, a toluene di-isocyanate (TDI) and two curatives, methylene-bis-orthochloro-annaline (MBOCA) and a dimethyl-thio-toluenediamine (Ethacure E300). Materials with two different hardness resulting from two different soft segment molecular weights were tested. In the softer 83 Shore A material which is relevant to the work of this paper, it was found that the elastomer made with the MBOCA curative required higher strain energy densities to initiate crack growth than its Ethacure counterpart and that both materials exhibited a degree of stable crack growth before catastrophic failure of the sample. It was suggested that the higher strain energy density required for crack growth in the MBOCA material could result from either a higher intrinsic fracture toughness or greater energy dissipation due to viscoelastic processes. The intrinsic fracture toughness has been related to the cross-link density [2,3] in rubbers. However, in polyurethane-ureas, the effective cross-links for the elastomer are the hard domains and consequently the intrinsic fracture toughness should be related to the microstructure of the material.

This work has now been extended to a study of the effect of stoichiometry on one of these systems, namely, those cured with the Ethacure E300 curative. It is known that changing the ratio of the isocyanate to curative can alter the amount of hydrogen bonding and chemical cross-linking in polyurethane-ureas [4]. By making materials with different stoichiometries, an independent assessment of these two variables on the fracture toughness can be made.

Measurement of the fracture toughness or tear resistance of rubbers was developed by Rivlin and Thomas [5] based on simple energy balance concepts. A cut or tear in a rubber will propagate if the change in the stored elastic energy in the sample as the tear advances is greater than the energy required to produce the new crack area. This may be written as

$$-dU/dA = \Im \tag{1}$$

where dU/dA is the change in stored energy density per unit area of new crack and $\Im$ is the characteristic energy required

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to produce a crack. The theory was developed to give solutions for a number of specimen types. Of interest here is the solution for a side edge notch in a strip of rubber which gives the fracture toughness in terms of the strain energy density, W, and the crack length, a, as

$$\Im = k\,a\,W \qquad (2)$$

where k is a factor which depends on the crack length and the extension ratio [6,7].

dU/da is the stored elastic energy released by propagation of the crack. Many highly extensible rubbers show significant hysteresis when loaded and unloaded. To account for this, Ahagon et al. [8] and Thomas and Kadir [9] used the recoverable strain energy density defined as the area under the load/extension curve on unloading to study the fracture behaviour of rubbers that showed significant internal energy dissipation away from the immediate crack tip region. This approach was found to give sensible fracture toughness measurements for polyurethane materials in previous work [1].

2. Materials

The polyurethane polymers used in this study were based on poly tetramethylene ether glycol (PTMEG) soft segments and a di-isocyanate containing a 80:20 ratio of 2,4 and 2,6 isomers of toluene di-isocyanate (TDI). The chain extender used was a mononuclear aromatic diamine based on isomeric 3,5 dimethyl thio (80%2,4;20%2,6) toluene diamine (Ethacure E300). Materials with a hardness of 83 Shore A were made with different % stoichiometries of 95, 97, 100 and 105%. The stoichiometry was defined as the ratio of the number of amine reactive groups to the isocyanate groups. The molecular weight of the PTMEG segments was approximately 2000 g mol^{-1}. The materials were cured at 100°C for 1–2 h followed by postcuring at 100°C for a period of 16 h.

2.1. Characterisation

All of the materials were analysed for carbon, hydrogen and nitrogen content from which the hard segment contents of the materials could be calculated. The calculations revealed that all materials had approximately the same hard segment content of 19–20%.

To assess the degree of cross-linking in the materials, 0.2–0.3 g of each of the polyurethanes were placed in glass vials and swollen in a solution of Dimethyl Formamide (DMF). The samples were left for a period of 24 h at room temperature. The materials with 100% and 105% stoichiometry dissolved completely after several hours in the DMF, indicating that these materials were not cross-linked. The 95% and 97% materials did not dissolve but were merely swollen, indicating the presence of cross-links. These swollen materials were removed from the vial and weighed after excess DMF had been removed with a soft cloth. They were then dried in a vacuum oven for 48 h at a temperature of 50°C and again weighed. The swell ratio, Q, was calculated as:

$$Q = \frac{W_s}{W_{ds}} - 1 \qquad (3)$$

where W_s is the mass of the swollen material, and W_{ds}, the mass of the deswollen material. Results for the different materials are shown in Table 1. These results indicate that the amount of cross-linking increased with decreasing stoichiometry as expected.

Table 1
Swell ratio for the polyurethane-ureas with different stoichiometries used in this work.

Sample	Q
95% etha	4.95
97% etha	5.93
100%, 105%	—

Dynamic Mechanical Thermal Analysis (DMTA) was conducted on all samples using a Perkin Elmer DMA 7 with 5 mm parallel plates under a dynamic stress of 1000 mN and a static stress of 1200 mN at a frequency of 10 Hz. Samples were cut from the sheets into small squares, slightly bigger than the size of the parallel plates. All samples were run over a temperature range of −100°C to 200°C at a rate of 5°C min^{-1}. The DMTA was cooled with liquid nitrogen and the samples purged with helium gas. Storage modulus results for all the materials are shown in Fig. 1. The materials displayed soft segment T_g's (defined as the inflection point of the curves) at approximately − 50°C with the T_g of the 100% stoichiometry materials being 2°C to 3°C higher than the other materials. The lower stoichiometry materials showed a slightly lower slope in the modulus temperature curve through the soft segment T_g. All materials displayed a second transition attributed to soft segment melting at approximately −20°C.

Hard segment softening occurred at −145°C to 165°C with the 95% and 97% (cross-linked) materials showing a higher softening temperature than the non-cross-linked material. Similar relaxations were observed using Differential Scanning Calorimetry.

3. Mechanical testing methods

Tests were conducted at room temperature on an Instron tensile tester at a cross head speed of 50 mm min^{-1}. The specimens were dumbbell shaped similar to those used previously [1] with a gauge length of 50 mm and a gauge width of 10 mm. Thickness varied slightly between sheets but was approximately 2 mm. Stress strain curves were obtained for all the polyurethanes by taking the strain to 50%, unloading and then reloading to a strain of 100%. Loading and unloading

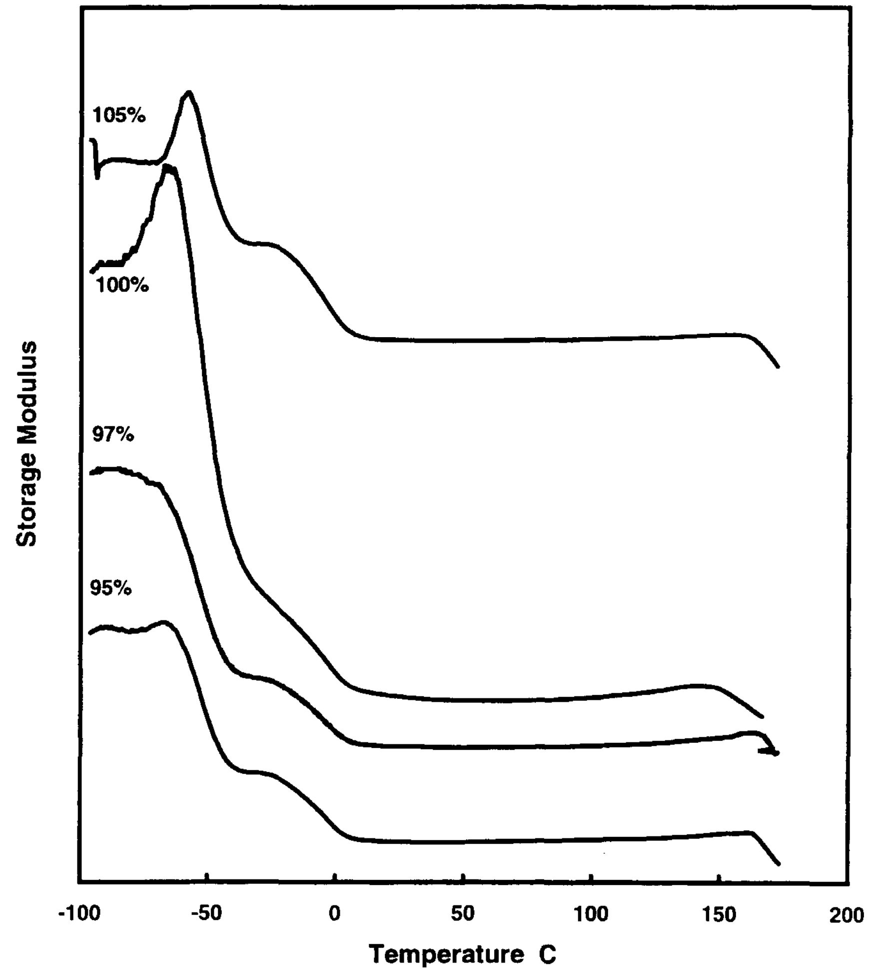

Fig. 1. DMTA Storage modulus as a function of temperature for the different polyurethanes used. (The individual curves have been displaced along the y axis for clarity).

with increasing increments of strain of 50% was continued until the strain was 500%. The time between unloading and subsequent reloading was kept to the minimum time required to reset the recorder and loading machine. Fracture studies were conducted on similar dumbbell samples to those above with a side notch in the centre of the gauge length made by a sharp scalpel blade. The notch length was less than 1 mm which was less than 10% of the gauge width. The notched samples were then subjected to a similar loading sequence to that described earlier for the unnotched samples.

4. Results

Fig. 2 displays the nominal stress–strain curve for the elastomer with the 95% stoichiometry. The material showed significant anelastic behaviour and suffered a degree of permanent set which increased with strain. The stress–strain curves for all of the materials were of similar shape to those of Fig. 2. The main difference was that at high extensions, the stress at a given strain was slightly lower in the materials with stoichiometries of 100% and 105% than for those at 95% and 97%. The amount of permanent set also increased for the materials with the higher stoichiometry as shown in Fig. 3.

The recoverable energy, measured as the area under the unloading curve and expressed in terms of strain energy density, is shown in Fig. 4. In all cases, the strain energy density increased non-linearly with increasing strain. Again the results can be split in two with the 95% and 97% stoichiometry materials having a slightly higher strain energy density than the 100% and 105% materials particularly at high strains.

In tests of notched samples, crack growth was observed in the first cycle at strains lower than 50% in all the materials. Subsequent stable crack growth occurred with increasing extension until catastrophic failure. The extension at which failure occurred for each of the samples was different. The material with 95% stoichiometric ratio displayed the least crack growth before failure. This failure was typically around 200% extension, with crack growth of less than 1 mm. The material with 97% stoichiometry displayed a slightly higher amount of stable crack growth than the

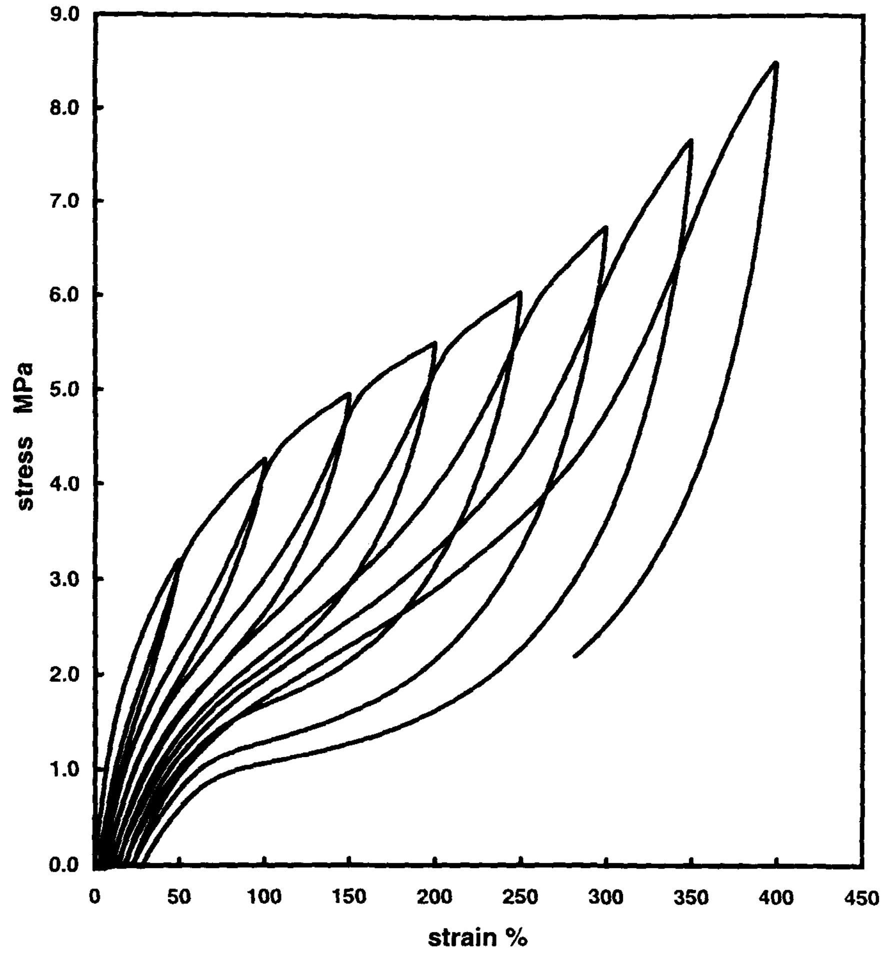

Fig. 2. Nominal stress–strain curve for the 95% stoichiometry material. Other materials showed similar stress–strain curves.

95% material with catastrophic failure occurring around 200%–250% extension with crack growth of up to 1.5 mm. The 100% and 105% stoichiometry materials displayed the highest degree of stable crack growth with extensions of up to 350% before failure. The degree of crack growth before failure was quite extensive with crack lengths over 3 mm being obtained.

The fracture surface of the failed samples examined under an optical microscope showed arrest lines for each loading cycle. Using the recoverable strain energy densities in Fig. 4 and the measured crack lengths at the end of each loading cycle, $\mathfrak{I}$ can be calculated using equation 2 with k being taken as π. In Fig. 5, $\mathfrak{I}$ is plotted as a function of crack growth Δa for each material. In all materials, the value of $\mathfrak{I}$ increased non linearly with crack extension. By fitting a second order polynomial regression through the data, a value for the initiation fracture toughness at $\Delta a = 0$ was obtained. The values of the initiation fracture toughness for the different materials varied from 0.8 kJ m^{-2} to 1.2 kJ m^{-2}. These values were all within experimental error of the value reported previously for the 100% material of 0.9 kJ m^{-2}.

5. Discussion

The polyurethane elastomers studied here contained the same soft segment, di-isocyanate and curative/chain extender but varied only in the ratio of the isocyanate to amine reactive groups. The elemental analysis suggested that this variation did not alter the hard segment content to any great extent. This observation was consistent with those of Hartmann et al. [10] who measured a ~2% change in the hard segment wt% with changes in stoichiometry of 90% to 110% in a similar polyurethane-urea system. However, altering the stoichiometry would be expected to create a number of changes in the structure of the polymer. Cross-linking reactions in polyurethane-ureas occur by the reaction of isocyanate with ureas and urethane to form biruet and allophane linkages. Thus, those elastomers with a higher isocyanate content, the 95% and 97% materials, would be expected to form cross-links while the cross-linking reactions would be expected to be less evident in the 100% and 105% materials. The swelling results listed in Table 1 clearly indicate this effect. Both the 100% and 105% materials dissolved in the DMF indicating that these materials

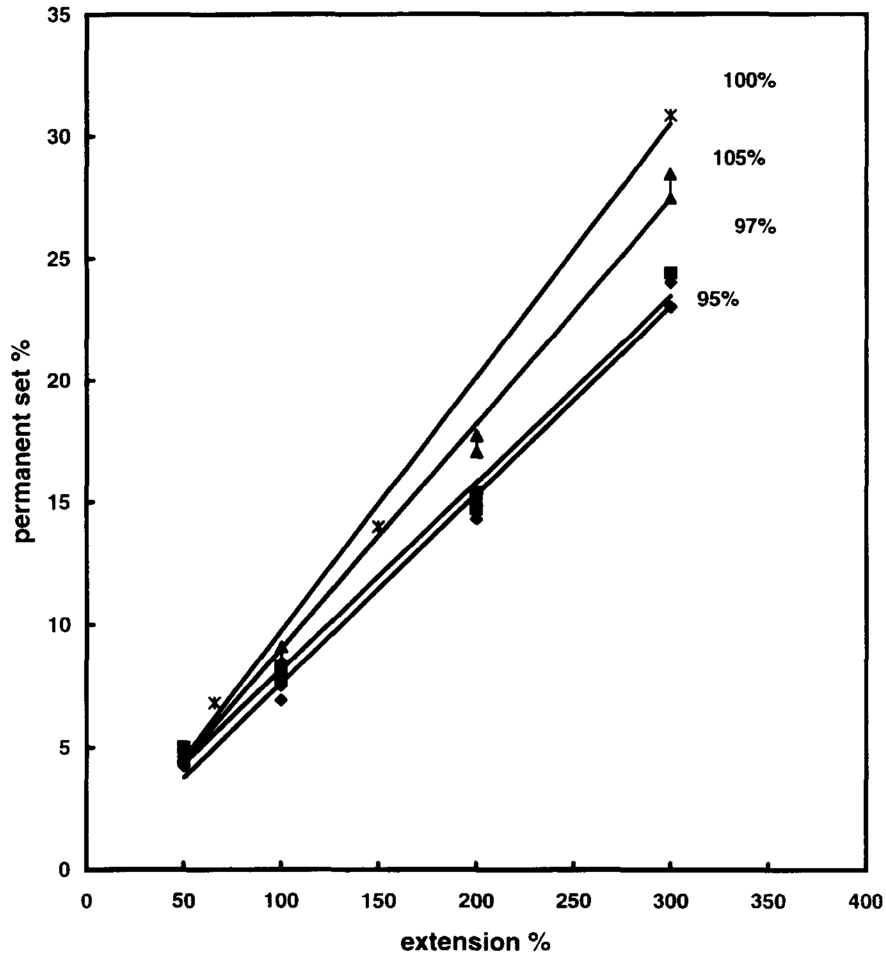

Fig. 3. Permanent set as a function of strain for the materials with different stoichiometry.

had not cross-linked, while the two lower stoichiometry ratio materials showed the presence of cross-links.

However, the formation of chemical cross-links would limit alignment of the chains in the hard domains and consequently may limit hydrogen bond formation. Materials with high stoichiometry would thus be expected to have a greater tendency to form hydrogen bonds in the hard domains. Hydrogen bonds would give some strength to the hard domains but would be expected to dissociate at high temperatures and to allow some plastic deformation of the hard domain as they break and reform. Permanent set has been related to deformation of the hard domains and consequently strengthening of the hard domains by chemical cross links would be expected to decrease the amount of permanent set while the presence of hydrogen bonding would allow for some permanent set to develop. This is consistent with the results shown in Fig. 3 for the different materials tested here. The secondary biuret and allophane linkages can dissociate at high temperatures [4] but would be more stable than the hydrogen bonds. This was consistent with the DMTA data, Fig. 1, which showed a slightly higher hard domain softening point in the two cross-linked materials

The formation of cross-links during polymerisation also has implications for the microstructure of the polymer. The cross-links generally form within the hard domains and if cross-links formed during phase separation, they would be expected to limit phase separation and trap soft segments in the hard domains. Tobolsky and Narkis [11] have argued that this results in a decrease in the slope of the tan δ curve in the region of the soft segment T_g. A broadening of the transition was observed in Fig. 1 for the 95% and 97% material where cross-links existed.

These observations on the structure of these polyurethane-ureas can now be applied to the fracture toughness results of Fig. 5. First, there did not appear to be significant differences in the initial fracture toughness of the different materials. Moreover, the values were all quite small suggesting that flaws in these materials will grow at low strain energy densities and that abrasive wear mechanisms which involve crack growth in response to surface frictional forces would be expected to occur quite readily. In previous work [1] using the same polyol and isocyanate as in this work but with different curatives, differences in the initial fracture toughness were observed. It was argued that the initiation fracture toughness consisted of an intrinsic term

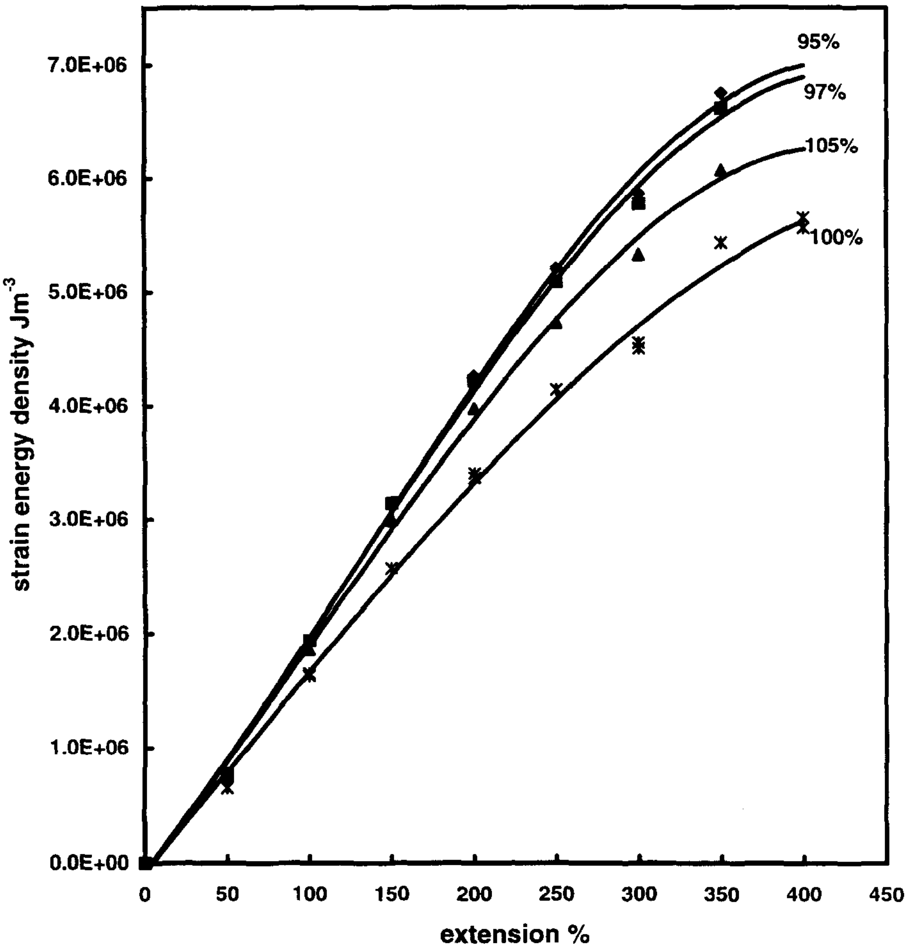

Fig. 4. Recoverable energy, measured as the area under the unloading curve and expressed in terms of strain energy density, for the different polyurethane-ureas.

and a term related to viscoelastic processes at the tip of the crack. Lake and Thomas [3] and Ahagon and Gent [2] have shown that the intrinsic tearing energy of rubbers varies with cross-link density. However, although the cross-link density varied between these polyurethanes, Table 1, the cross-links would have occurred within the hard domains and the effective cross-links for the elastomers would have been the hard domains themselves. The elemental analysis indicated that there was little variation in the hard segment content among these materials. In addition, although there may have been some soft segment trapped in the hard domains as indicated by the DMTA data mentioned above, the similarity in the soft segment T_g's suggested that the rubbery phase was similar for all the materials. Variation in the size and distribution of the hard phase might be expected to change the constraint on the soft segments and therefore change their T_g. Thus, the effective cross-links in the different materials were likely to be similar, implying similar intrinsic tearing energies.

Young and Lovell [12] have argued that as the crack grows, the material in the region of the crack tip is deformed and relaxed viscoelastically. Measurement of the bulk hysteresis in these materials indicated that there was little difference in the energy lost during cycling at low strains. If the behaviour of the material at the tip of the crack was similar to the bulk behaviour, then the viscoelastic component of the initial fracture toughness would also be expected to be similar for all four materials.

The most significant effect of stoichiometry was in the ability of the materials to undergo stable crack growth. Chemical cross-linking in 95% and 97% materials appeared to inhibit stable crack growth causing catastrophic failure to occur at lower extension. The materials without chemical cross-links but with a high degree of hydrogen bonding in the hard domains, such as the 105% material, were able to sustain a large degree of stable crack growth with final failure not occurring until 350% extension. Although hydrogen bonding gives some extra rigidity to the hard domains, they would have the ability to break and reform allowing more deformation of the hard domains than chemical cross-links. This was consistent with the permanent set data of Fig. 3 which indicated that greater deformation was occurring in the high stoichiometry materials. It was reported previously [1] that significant plastic deformation was occurring at the tip of the crack in these materials and the extent of the deformation zone increased as crack growth occurred.

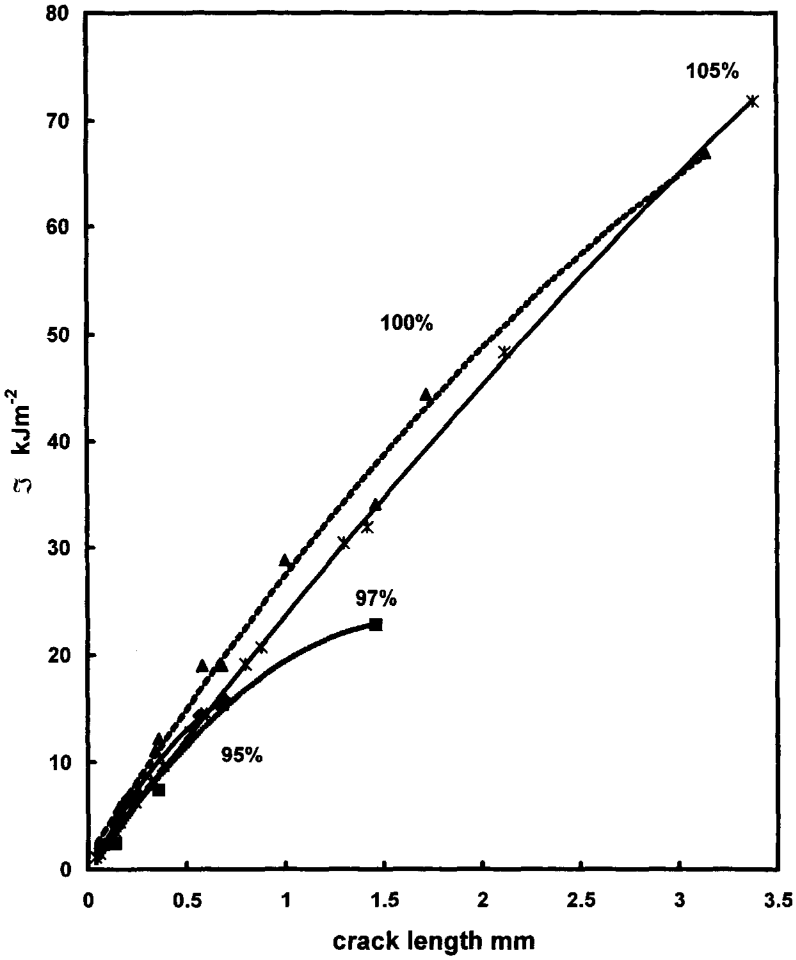

Fig. 5. Fracture toughness, τ, as a function of crack growth Δa for each material.

Energy dissipated by plastic deformation at the crack tip adds to the energy required for crack growth and this may account for the crack stability in the hydrogen bonded material.

6. Conclusions

The fracture toughness of a series of polyurethanes using the same polyol, isocyanate and curative, but with varying ratio of the isocyanate to curative, have been measured. Varying the stoichiometry was found to change the amount of cross-linking in the hard domains of the polymer but this had little effect on the initial fracture toughness. The major difference observed was in the degree of stable crack growth which decreased with the presence of cross-links.

Acknowledgements

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