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The effect of curative on the fracture toughness of PTMEG/TDI polyurethane elastomers

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The mechanical properties and fracture behaviour of polyurethanes with two hardness levels have been measured. The polyurethanes were based on polytetramethylene ether glycol (PTMEG) and toluene diisocyanate (TDI) and two different curatives, or chain extenders – methylene-bis-orthochloroaniline (MBOCA) and dimethylthiotoluene diamine (Ethacure E300). The polyurethanes made using MBOCA as the curative were found to have a lower initial modulus and less permanent set than polyurethanes of similar hardness but made using Ethacure E300. Moreover, the Ethacure E300 materials showed crack growth when the strain energy density in the sample was low, and a period of slow stable crack advance. The MBOCA cured material of lower hardness also showed slow crack growth, but crack growth started at much higher strain energy densities than for the Ethacure E300 materials. The harder MBOCA cured material did not show slow crack growth and failed rapidly. The strain energy density to cause fracture was higher than that required to initiate slow crack growth in the other materials. The reasons for the differences in the fracture behaviour are discussed in terms of the structure of the polyurethanes.

(Keywords: polyurethanes; fracture toughness; structure)

INTRODUCTION

As part of a study of the wear behaviour of polyurethane elastomers used in mining applications, work was undertaken to investigate their fracture behaviour. This was motivated by the observation of Friedrich[1] that the erosive wear of some polymer materials was related directly to the hardness of the polymer and inversely to the fracture toughness. The wear behaviour of the polyurethanes of interest in this study will be reported elsewhere. It is of interest to note, however, that the elastomer in this study that was cured with methylene-bis-orthochloroaniline (MBOCA) and had a Shore hardness of A83 has performed successfully in service. Unfortunately, the MBOCA curative is being phased out because of health considerations, and alternative agents are required. Polyurethanes using other curing agents have shown inferior wear performance. Various curing agents for polyurethane elastomers are used in practice and the effects of these agents have been reviewed by Lee[2]. Lee does not, however, address the issue of the effect of the curative on the fracture behaviour of the rubber. The work reported in this paper describes the effect of two curatives, or chain extenders, on the mechanical behaviour of otherwise similar polyurethanes.

Measurement of the fracture toughness or tear resistance of rubbers was developed by Rivlin and Thomas[3] based on the energy balance concepts of Griffith[4]. Simply stated, 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

$$-\mathrm{d}U/\mathrm{d}A = \mathcal{T} \qquad (1)$$

where $\mathrm{d}U/\mathrm{d}A$ is the change in total potential energy of the system per unit area of new crack, and $\mathcal{T}$ is the characteristic energy required to produce a crack. The theory was later 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

$$\mathcal{T} = kaW \qquad (2)$$

where k is a factor which depends on the crack length and the extension ratio. Greensmith[5] developed an experimental method for determining the value of k, and showed for natural rubber that k varied from around 3 at low extensions to approximately 2 at an extension ratio of 3. Greensmith suggested that the constant k could, as a first approximation, be related to the extension ratio, λ, by

$$k = \pi/\sqrt{\lambda} \qquad (3)$$

This relationship allows equation (2) to reduce to the familiar form for linear elastic fracture mechanics as λ approaches 1. Andrews and Fukahori[6] measured k as a function of strain energy density for a number of rubbers and polymers, and showed that k rose from the classical

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value of π to a maximum at low strain energy densities and then decreased to a relatively constant value or slightly decreasing value at large values of W. For a styrene–butadiene rubber (SBR) at high values of W, the value of k estimated from equation (3) approximated the values of k measured by Andrews and Fukahori. However, for an ethylene propylene diene monomer rubber, polyethylene and plasticized poly(vinyl chloride), the values of k were higher than predicted by the Greensmith formula and approached a relatively constant value slightly higher than π with increasing strain energy density. The polyurethane elastomers used in this work showed values of hysteresis intermediate between that of the natural rubber of Greensmith and the SBR of Andrews and Fukahori. Moreover, crack growth occurred at relatively high values of W where Andrews and Fukahori showed the value of k to be relatively constant. Consequently, a value of π was taken as an estimate of the value of k in this work.

The quantity U in equation (1) should rightly be considered as the stored elastic energy released by propagation of the crack. In highly elastic rubbers, U is normally taken as the energy expended in loading the elastomer to the point of crack propagation. Many highly extensible rubbers show significant hysteresis and creep when loaded and unloaded. This implies that some of the energy input to the rubber on loading will not be available for crack growth. Ahagon *et al.*[7] and Kadir and Thomas[8] used the recoverable strain energy density, defined as the area under the load–extension curve on unloading, to give a measure of stored elastic energy for rubbers that showed significant internal energy dissipation away from the immediate crack tip region. The work of Kadir and Thomas on unvulcanized natural rubber showed that the value of $\mathcal{T}$ calculated in this way was independent of specimen geometry. This approach takes little account of the processes that are occurring at the crack tip; it merely assumes that there is some characteristic energy required to produce the crack and that this quantity can be obtained from measures of the elastic energy stored in regions remote from the crack tip. A more fundamental approach to the problem may be to use the generalized fracture mechanics theory of Andrews[9]. However, the aim of this work was to compare two somewhat similar elastomers and consequently the more simplified method of Kadir and Thomas was adopted.

EXPERIMENTAL

Materials

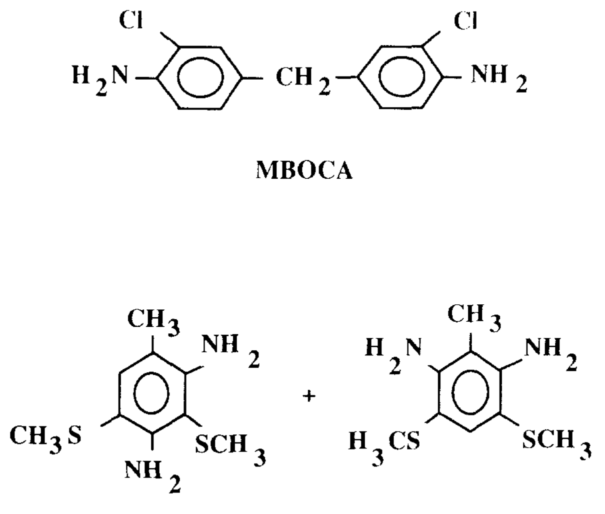
The polyurethane polymers used in this study were based on polytetramethylene ether glycol (PTMEG) soft segments and 2,4-toluene diisocyanate (TDI). Two aromatic chain extenders were used, namely 4,4-methylene-bis-orthochloroaniline (MBOCA) and a mononuclear aromatic diamine based on isomeric 3,5-dimethylthio(80%2,4; 20%2,6)toluenediamine, Ethacure E300 (Ethyl Corp.). Materials with a Shore hardness of A83 were made in which the stoichiometry was 100%. Materials of Shore hardness A90 were also made in which the stoichiometry was 95%. The molecular weight of the PTMEG segments in the Shore hardness A83 materials was approximately double that of the PTMEG used in the harder materials. The structures of the two chain extenders are shown in *Figure 1*.

The polyurethanes were cast into sheets approximately 2 mm thick between glass plates. The curing conditions were different for the two hardnesses. Materials of Shore hardness A83 were cured at 100°C for 1–2 h followed by post-curing at 100°C for a period of 16 h. The Shore hardness A90 materials were cured at 100°C for 1 h followed by two post-curing stages. The first stage of post-curing was conducted at 100°C for 3 h while for the second stage, the temperature was lowered to 70°C for the remaining 13 h.

Methods

Mechanical testing. The mechanical tests were conducted on an Instron model 1026 tensile testing machine fitted with an external recorder. Tests were conducted at room temperature (~23°C) and at a crosshead speed of 50 mm min^{-1}. The specimens were dumbbell shaped with a gauge length of 50 mm and a gauge width of 10 mm cut from the 2 mm thick cast sheets. The dumbbells were cut with a very small radius of curvature from the gauge length to the shoulders and gripped between pieces of emery paper in wedge action grips right on the line of the shoulders, so as to minimize the effect of the shoulder region on the load extension curves. Strain was then calculated from the movement of the crosshead. 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 with increasing increments of strain of 50% was continued until the strain was 400%. The time between unloading and subsequent reloading was kept to the minimum time required to reset the recorder and loading machine. The exception was for a series of tests conducted to examine the effect of relaxation time, in which the relaxation time was varied from a few seconds to several hours.

Fracture studies were conducted on similar dumbbell specimens to those described above. They were given a side notch in the centre of the gauge length using a sharp scalpel blade. The notch was limited to less than 1 mm, which was less than 10% of the gauge width. The notched



MBOCA

ETHACURE E300

Figure 1 Molecular structure of the chain extenders used in production of the polyurethanes specimens were then subjected to a similar loading sequence to that described above for the unnotched specimens.

Characterization techniques. Thermal analysis of the polymers was conducted on a Perkin–Elmer differential scanning calorimeter (DSC 7). Two scans were run over a subambient temperature range of −100 to 40°C to effectively observe the transitions for each sample. The heating rate for the first scan was 40°C min^{-1}. Upon completion of the first scan, the sample was cooled at 200°C min^{-1} to −100°C and a second scan at the same heating rate was commenced immediately. These are the reported thermograms. High temperature scans were also completed over the range 130 to 240°C at a heating rate of 10°C min^{-1}. The sample size for all scans ranged from 9 to 12 mg.

Gel contents of the polyurethanes were measured by placing samples weighing approximately 25–35 mg into individual stainless steel mesh baskets which were suspended in a solution of xylene containing a small amount of antioxidant, Irgonox 1010 (Ciba Geigy). The samples were left in the refluxing solution for 12 h before being washed with acetone and dried in a vacuum oven at 80°C until a stable weight was attained. The samples were reweighed and the gel content was calculated as the end weight to initial weight ratio.

RESULTS

Stress–strain curves

Figures 2 and *3* show the nominal stress–strain curves for the two polyurethanes with nominal Shore hardness of A83 and the MBOCA and Ethacure E300 curatives, respectively. The initial slope of the stress–strain curve for the MBOCA cured material was higher than that of the Ethacure E300 material, but by the time extensions of 100% were reached the stress levels on both materials were comparable. The stress–strain curves for both materials showed significant anelastic behaviour, with the Ethacure E300 material showing slightly higher hysteretic losses than the MBOCA cured polymer. The Ethacure E300 material also showed significantly higher permanent set. At high extensions, the nominal stress in the MBOCA material was higher than that in the Ethacure E300 polymer. This was probably a result of calculating the stresses and strains on the initial dimensions of the specimen and not compensating for the permanent set in the Ethacure E300 material. Similar results were obtained for the harder polyurethanes with, of course, the stresses being commensurately higher.

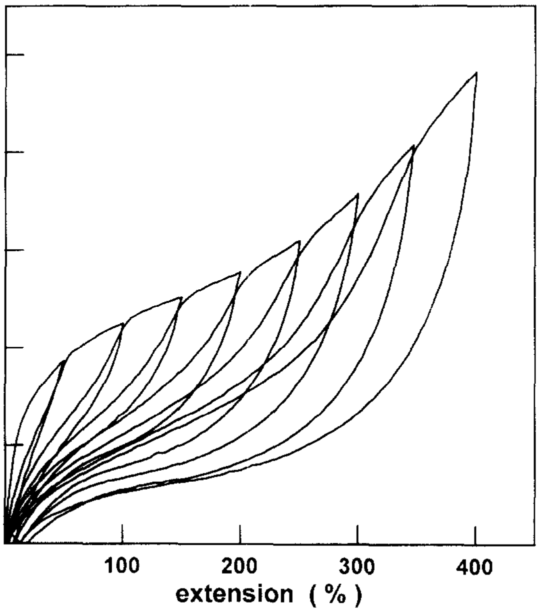


Figure 2 Nominal stress–strain curves for the polyurethane cured with MBOCA with a Shore hardness of A83

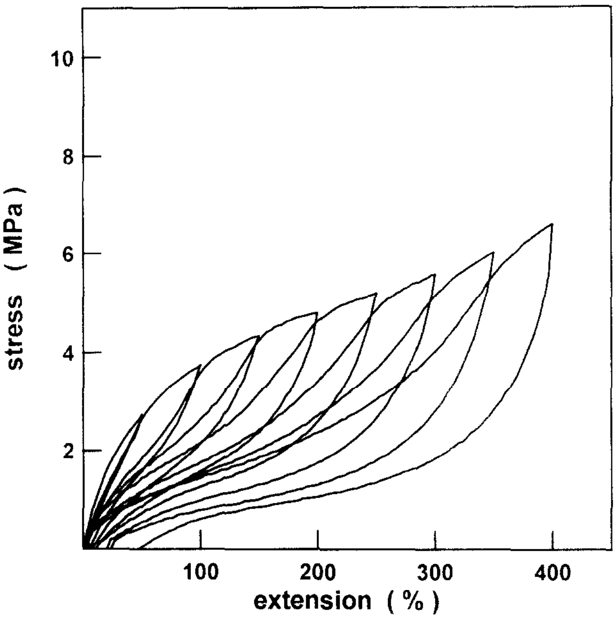


Figure 3 Nominal stress–strain curve for the polyurethane cured with Ethacure E300 with a Shore hardness of A83

The recoverable energy measured as the area under the unloading curves in *Figures 2* and *3* and expressed in terms of the strain energy density are shown in *Figures 4* and *5* for the Shore hardness A83 and A90 materials, respectively. The recoverable energy at a given strain did not appear to depend on loading history prior to that strain provided each loading cycle was continued to a higher strain than that previously experienced by the sample. This was confirmed by a number of tests where the loading histories differed from that described in Mechanical testing above. When the specimen was taken to a strain of 300% in a single cycle, the recoverable strain energy was the same as that measured when the specimen was subjected to several cycles of increasing strain up to 300%. Equally, increasing the time interval between the end of one unloading cycle and the start of the next, from a few seconds to several hours, had no effect on the measured recoverable strain energy. This was in contrast to the input energy which was clearly dependent on both the previous strain history and the relaxation time between loading cycles.

The recoverable strain energy density at a given strain for the MBOCA cured materials increased linearly with strain (*Figures 4* and *5*). In contrast, the recoverable strain energy density for the Ethacure E300 materials showed a non-linear increase with strain. This non-linearity was probably a result of permanent deformation occurring in the sample. If the strain in *Figures 4* and *5* was calculated

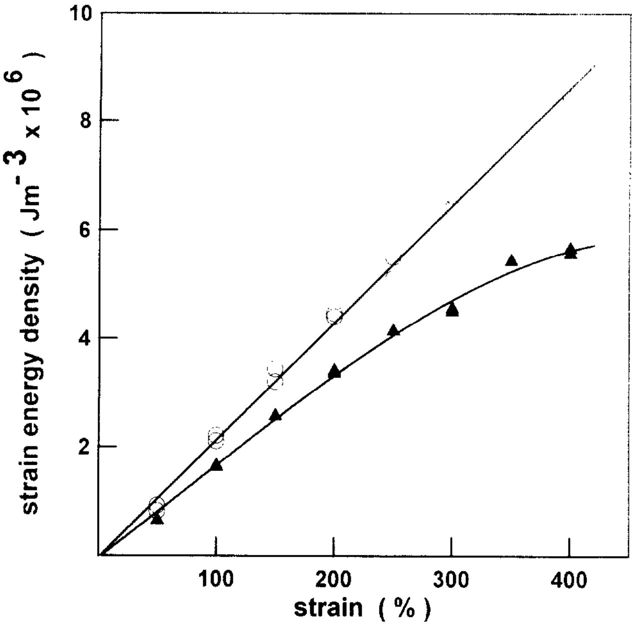


Figure 4 Recoverable strain energy density at different strains for the polyurethanes with Shore hardness A83: ○, MBOCA; ▲, Ethacure E300

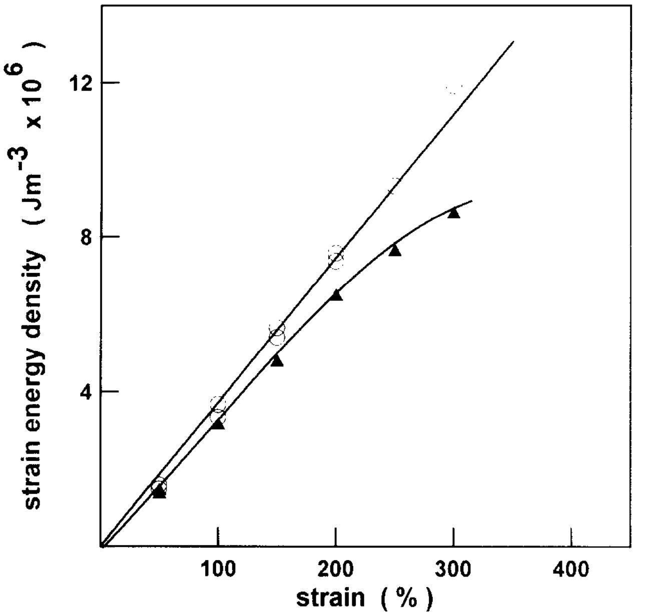


Figure 5 Recoverable strain energy density at different strains for the polyurethanes with Shore hardness A90: ○, MBOCA; ▲, Ethacure E300

on a gauge length which was adjusted from the permanent set, a more linear dependence of recoverable strain energy density on strain was obtained for the Ethacure E300 materials.

Fracture tests

In the Shore hardness A83 Ethacure E300 cured polyurethane, extension of the crack occurred in the first cycle at strains lower than 50%. In subsequent cycles, the crack was seen to extend stably for several millimetres before the specimen failed catastrophically. This was at nominal strains as large as 400%. The Shore hardness A83 MBOCA cured material also showed some stable crack growth. However, the strain at which crack growth started was higher and the crack length at final failure was generally less than in the Ethacure E300 material. Examination of the fracture surfaces after final failure in both materials showed distinct arrest marks as the growth of the crack stopped on reversal of the load. The position of these arrest lines was measured using a travelling microscope.

The Shore hardness A90 Ethacure E300 polyurethane also showed crack growth at quite low strains which extended to some millimetres before final failure. The Shore hardness A90 MBOCA cured material, however, did not exhibit any measurable slow crack growth before failure, but failed rapidly in the second or third loading cycle.

Using the recoverable strain energy densities in *Figures 4* and *5* and the measured crack lengths at the end of each loading cycle, $\mathcal{T}$ was calculated using equation (2), with k being taken as π. In *Figures 6* and *7*, $\mathcal{T}$ is plotted as a function of crack extension for the different materials. A curve is not shown for the Shore hardness A90 MBOCA material as it failed without observable crack extension. For this material, the fracture toughness was determined directly using the initial notch depth and the appropriate strain energy density associated with the strain at failure. This gave a fracture toughness of $5.5 \times 10^3\,\mathrm{J\,m^{-2}}$. All of the other materials showed an increase in the value of $\mathcal{T}$ with crack extension. For the Shore hardness A83 MBOCA material, the increase in $\mathcal{T}$ with crack extension was approximately linear. A linear regression through the data points gave an intercept on the $\Delta a = 0$ axis of $3.2 \times 10^3\,\mathrm{J\,m^{-2}}$. The Ethacure E300 materials both showed crack growth at quite low strain energy densities, with the value of $\mathcal{T}$ increasing non-

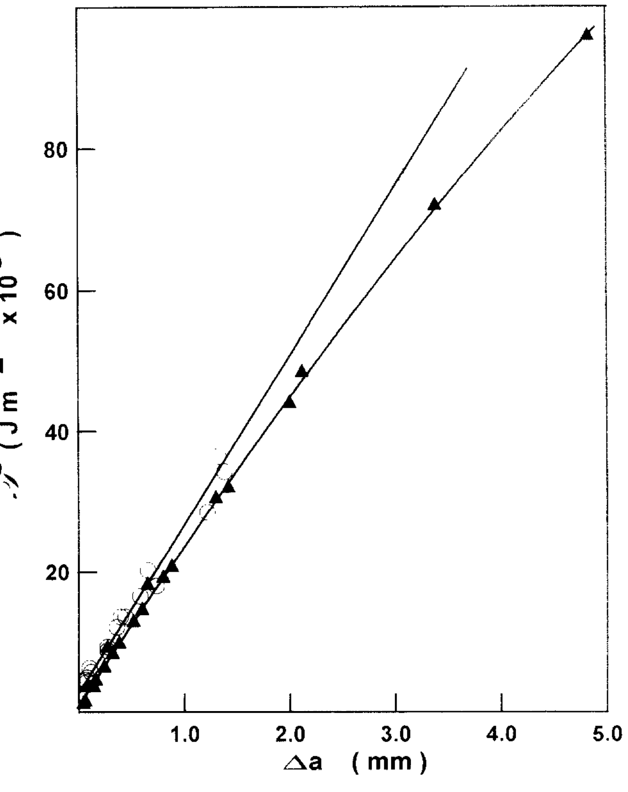


Figure 6 Measured fracture toughness as a function of crack growth for the Shore hardness A83 materials: ○, MBOCA; ▲, Ethacure E300

linearly with crack extensions. The dependence of $\mathcal{T}$ on Δa was fitted to a polynomial and this gave the intercepts on the $\Delta a = 0$ axis for the Shore hardness A83 and A90 materials as $0.9 \times 10^3\,\mathrm{J\,m^{-2}}$ and $1.6 \times 10^3\,\mathrm{J\,m^{-2}}$, respectively.

The data shown in *Figures 6* and *7* are a combination of data from several specimens with varying initial crack depths. There did not appear to be any dependence on the initial crack depth. However, the range of initial notch depths was quite small and restricted to < 1 mm.

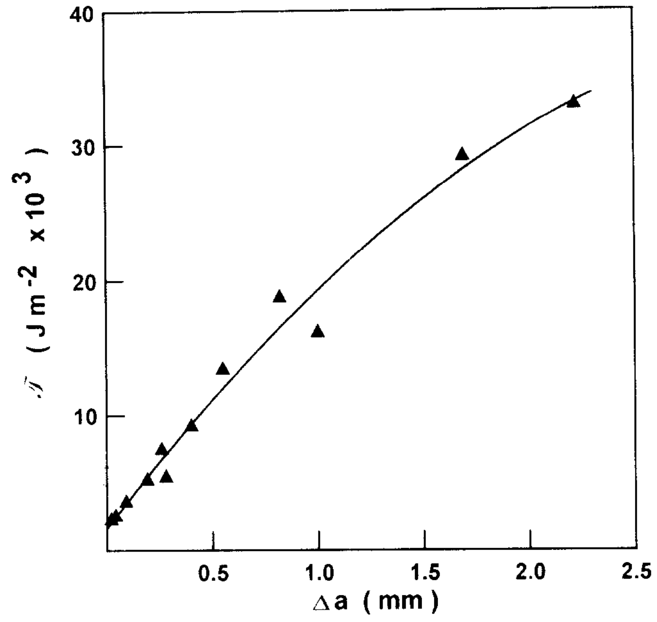


Figure 7 Measured fracture toughness as a function of crack growth for the Shore hardness A90 materials: ○, MBOCA; ▲, Ethacure E300

Slow crack propagation was associated with the development of a large deformation zone at the tip of the crack. To illustrate this, a specimen of Ethacure E300 cured polyurethane with Shore hardness A83 was notched and tested as for the other notched specimens. On each unloading, the specimen was removed from the testing machine and examined in an optical microscope in transmitted cross-polarized light. Although the examination process took some 15–20 min, the $\mathcal{T}$ *versus* Δa data obtained showed excellent agreement with previously obtained data. *Figure 8* shows the deformation zone at the notch as a function of imposed strain. A distinct birefringent zone developed at the notch and grew in size as the crack slowly extended. Similar zones developed in the Shore hardness A90 Ethacure E300 material and the Shore hardness A83 MBOCA cured polyurethane. Examination of the failed Shore hardness A90 MBOCA cured specimens indicated only a very small deformation zone in this material.

DISCUSSION

Although the polyurethanes studied in this work were made up from similar molecular building blocks, namely PTMEG soft segment and TDI, with only the curative changing, the resultant materials showed some significant variations in mechanical properties. The MBOCA cured materials were stiffer at low strains, showed minimal permanent set on unloading, and initiated crack growth

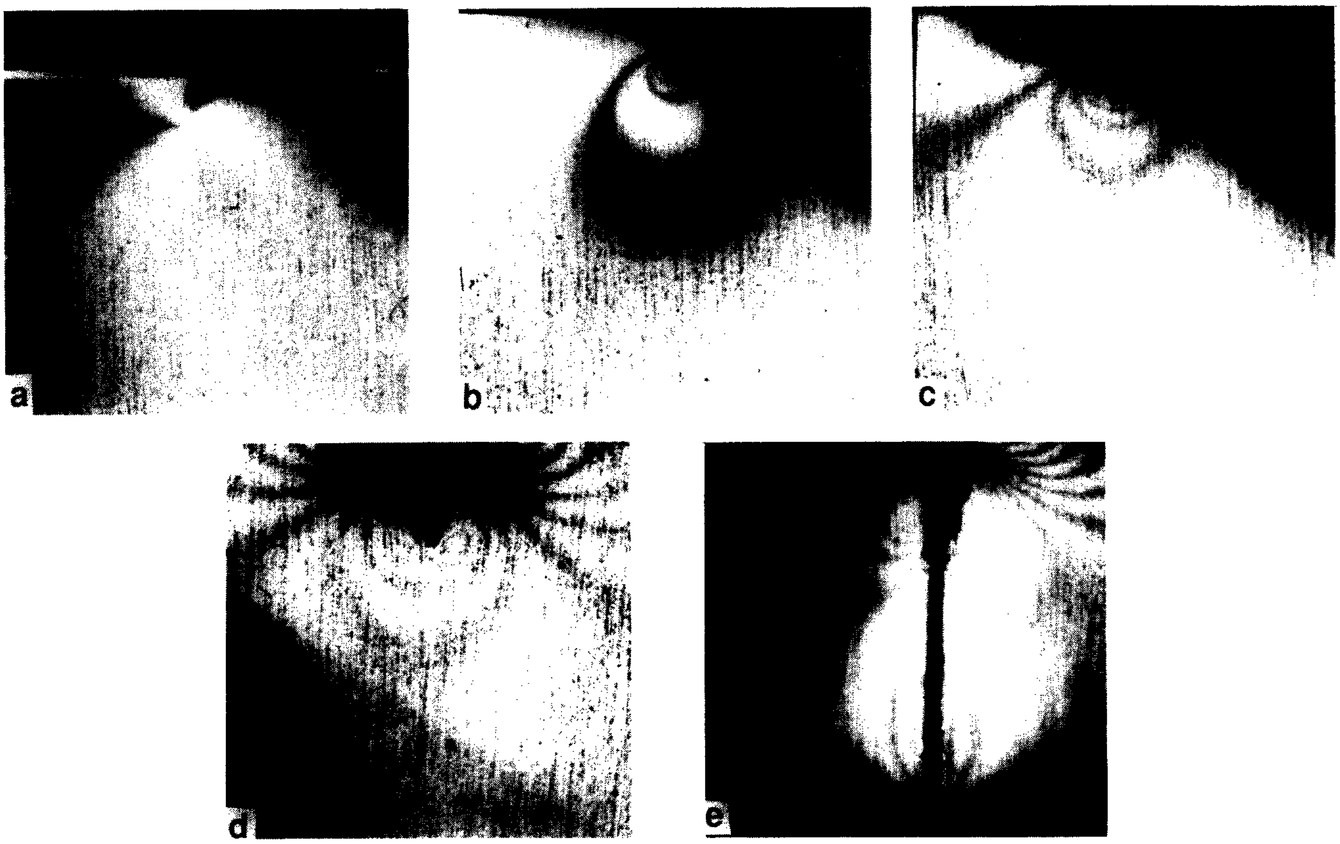


Figure 8 Deformation at the crack tip viewed in the optical microscope under crossed-polarized light in the Ethacure E300, Shore hardness A83 material. The specimen strains were: (a) 50%; (b) 150%; (c) 250%; (d) 350%; (e) final failure

when the material was under a higher strain energy density than for the equivalent hardness Ethacure E300 materials. Moreover, the MBOCA cured materials showed less stable slow crack growth than that observed for the Ethacure E300 cured samples, with the Shore hardness A90 MBOCA polymer fracturing without noticeable slow crack growth.

In polyurethanes, structures capable of producing the network required for rubbery behaviour can be either chemical, in the form of crosslinks, or physical, in the form of hard domains. The amount of chemical crosslinking in the polymers studied here was assessed by measuring the gel content of the polymers, and the results are shown in *Table 1*. The samples cured with MBOCA showed a substantially larger degree of insoluble chemical crosslinks compared to the Ethacure E300 polymers. It was expected that chemical crosslinks in the form of biuret linkages would form only in the Shore hardness A90 samples, since a 95% stoichiometry was used for these materials and biuret linkages generally require an excess of isocyanate to react with the urea groups. The result for the Shore hardness A90 MBOCA material was the expected result, but the Shore hardness A83 MBOCA sample, which should have contained no chemical crosslinks, produced a gel content of 31%, while the Ethacure E300 cured polymers contained little gel in the harder material and none in the softer polymer. The reason for this anomaly is not known but may be due to the effects of temperature on the reaction kinetics of the various reactions that can occur in these systems.

The effectiveness of the hard domains as physical crosslinks will also depend on phase separation in the polymer and the structure of the hard blocks, such as their level of crystallinity and hydrogen bonding. Hydrogen bonding between the NH group and the carbonyl group was measured via Fourier transform infra-red spectroscopy and was found to be similar for all of the polymers. The degree of phase separation can be estimated from the values of the glass transition temperature, T_g, of the soft domains, since any incorporation into the soft domains of the aromatic groups that usually associate into the hard blocks would be expected to increase the T_g of the soft domains.

Typical thermograms obtained for all materials are shown in *Figures 9* and *10*. The subambient scans of the Shore hardness A83 materials (*Figure 9b, c*) showed a soft segment T_g for the Shore hardness A83 MBOCA cured sample of −70°C, while the Shore hardness A83 Ethacure E300 cured material had a slightly lower T_g of −73°C. The T_g of pure PTMEG has been reported[10] to be −85°C which suggests that these systems were highly phase separated. The major difference between the thermograms for the softer materials was the degree of soft segment crystallization. The Shore hardness A83 MBOCA sample displayed a broad exotherm at approximately −25°C attributed to soft segment crystallization, while a large endothermic peak at −3.6°C was indicative of soft segment melting. No exothermic peak was observed for the Shore hardness A83 Ethacure E300 sample although a small melting endotherm was measured. The heat of fusion for the Shore hardness A83 MBOCA polymer was 9.0 J g^{-1}, which was six times greater than the value for the Ethacure E300 material (1.5 J g^{-1}). The slightly higher soft segment T_g for the MBOCA material might suggest a higher incorporation of the aromatic

Table 1 Gel contents of the polyurethanes

Polyurethane	Gel content (%)
A90 MBOCA	71
A90 Ethacure E300	0
A83 MBOCA	31
A83 Ethacure E300	~2

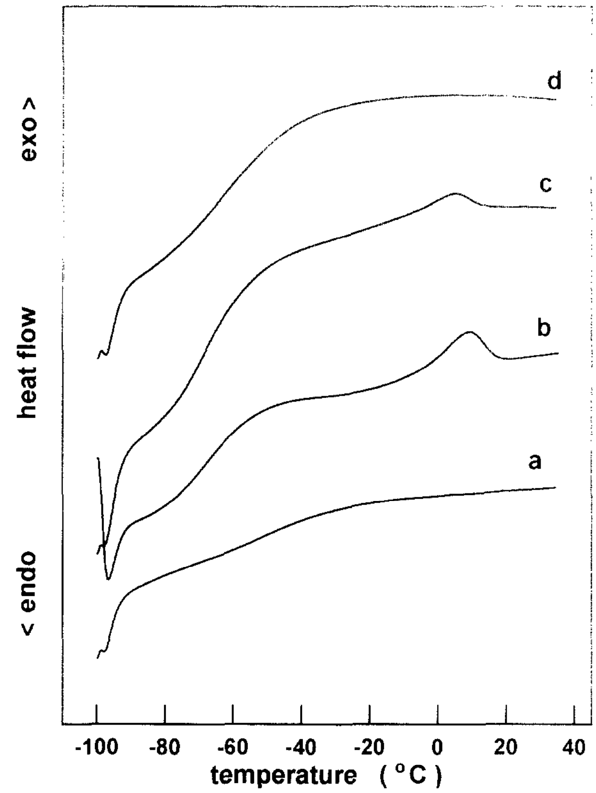


Figure 9 Low temperature d.s.c. curves for the polyurethanes studied: (a) A90 MBOCA; (b) A83 MBOCA; (c) A83 Ethacure E300; (d) A90 Ethacure E300

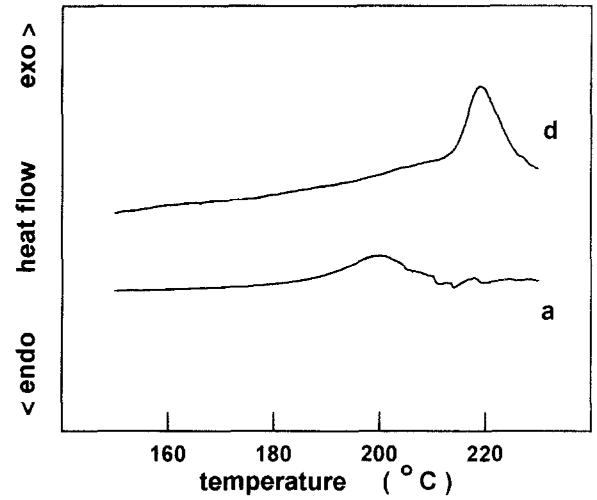


Figure 10 High temperature d.s.c. curves for the polyurethanes studied: (a) A90 MBOCA; (d) A90 Ethacure E300

moieties into the soft domains of the MBOCA material than for the Ethacure E300 cured material. However, this conflicted with the higher ability of the soft segments to crystallize when the MBOCA curative was used, suggesting greater mobility for the PTMEG segments in this material. It is possible that the slightly higher T_g of the soft segments of the MBOCA cured polymers merely reflects the more bulky nature of the MBOCA molecule, rather than the number incorporated in the soft blocks, and that the MBOCA materials are in fact more highly phase separated than the Ethacure E300 polymers.

The soft segment T_g values were higher for both Shore hardness A90 materials compared to their A83 counterparts (*Figure 9a, d*). For the Shore hardness A90 MBOCA polymer, the soft segment T_g was approximately $-57°C$, while for Shore hardness A90 Ethacure E300 material it was $-68°C$. Neither Shore hardness A90 material showed any sign of soft segment melting. Hartmann *et al.*[10] noted that the degree of phase separation tends to decrease with decreasing molar mass of the PTMEG. The Shore hardness A90 materials where made with PTMEG of lower molar mass than the softer A83 materials, and the higher soft block T_g values found for the Shore hardness A90 materials were consistent with the observation of Hartmann *et al.*

The d.s.c. traces for the softer Shore hardness A83 polymers showed no evidence of hard segment crystallinity, but there was evidence of crystallinity in the hard domains for the harder materials (*Figure 10a, d*). The heat of fusion for the harder MBOCA cured polymer was $4\,J\,g^{-1}$, which was similar to that for the equivalent Ethacure E300 material ($3\,J\,g^{-1}$). The major difference between the two materials was that the onset temperature for hard segment melting in the MBOCA cured sample ($\sim 193°C$) was lower than that in the Ethacure E300 material (211°C). However, this should have had little effect on the room temperature mechanical behaviour of the polymers.

Since the level of crystallinity of the hard blocks was similar for the two types of polymer, the major effect on the properties of the hard domains must be the presence of the chemical crosslinks in the MBOCA polymers. The chemical crosslinks that occur in polyurethaneureas would be expected to be within the hard blocks. Their effect would be to increase the strength and stiffness of the hard domains rather than to contribute further crosslinks to the rubbery network. Hard domains that are less able to deform, would make permanent deformation of the bulk polymer more difficult. This was consistent with the higher gel content of the MBOCA cured elastomers and the lower permanent set found in these materials. The higher initial modulus of the MBOCA cured materials may also have resulted from this effect, although the modulus would also have been affected by phase separation.

The fracture toughness of a rubber is a combination of two terms – an intrinsic fracture toughness associated with the breakage of chemical bonds, and a second term incorporating energy dissipation by viscoelastic processes at the crack tip. A number of workers[11–13] have attempted to measure the intrinsic fracture toughness of rubbers, including polyurethanes, by testing them under very slow fatigue conditions or testing the swollen rubbers at low rates or high temperatures, where viscoelastic processes could be virtually eliminated. Values for the intrinsic fracture toughness of 40–$100\,J\,m^{-2}$ were obtained. These values are from one to two orders of magnitude less than the values of $\mathscr{T}$ at crack initiation (i.e. at $\Delta a = 0$) measured here. The observed small birefringent zone confirmed that significant energy dissipation processes were occurring at the crack tip in these polymers, even before slow crack growth began.

The MBOCA cured materials showed higher intercepts on the $\Delta a = 0$ axis of the $\mathscr{T}$ *versus* Δa curve than their Ethacure E300 counterparts. The higher intercepts may have been a result of a higher inherent fracture toughness in the MBOCA cured polymers or a reflection of greater energy dissipated in plastic deformation at the crack tip. Lake and Thomas[14] have suggested that the inherent fracture toughness is related to the crosslink density in rubbers, while Ahagon and Gent[13] extended this analysis to include physical crosslinks and variations in the number of molecules crossing the fracture plane with chain length. This gave a complex dependence of the intrinsic fracture toughness on the molar mass between crosslinks in which the intrinsic fracture toughness initially increased as the crosslink density increased, but then decreased as the rubber became more heavily crosslinked. If the arguments of Lake and Thomas[14] and Ahagon and Gent[13] are applicable to these polymers, the different intercepts for the MBOCA cured materials and the Ethacure E300 materials would suggest that the number of hard domains varied between the two materials. Attempts to image the domains in these materials and consequently to assess this option directly have so far not been successful. However, it would be expected that chemical crosslinks present in the hard domains would make them harder to deform and consequently any deformation at the crack tip would absorb more energy.

CONCLUSION

The fracture toughness of a PTMEG/TDI polyurethane elastomer of two hardness levels has been shown to change when the MBOCA curative was replaced by an alternative curative, Ethacure E300. The Ethacure E300 cured polyurethanes showed crack growth at lower applied strain energy density and a greater ability for stable crack growth than their MBOCA cured counterparts. Moreover, the Ethacure E300 materials showed more permanent set, a lower initial modulus and higher hysteresis than rubbers of equivalent hardness made using MBOCA as the curative. These changes in the mechanical properties have been attributed to the hard domains in the MBOCA cured materials being less deformable as a result of the higher gel content in these materials.

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