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Fracture toughness of polybutadiene at cryogenic temperatures

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An estimate of fracture toughness of crosslinked polybutadiene rubber at − 180° C has been made using the double torsion method. By using suitable specimen dimensions and strain rates, controlled crack propagation can be achieved, together with a constant compliance to crack length ratio. Strain energy release rates for this polymer, crosslinked with either dicumyl peroxide or sulphur, were found to be an order of magnitude higher than for linear, glassy thermoplastics. Crazing is considered to contribute to the high toughness observed.

1. Introduction

At room temperature crosslinked elastomers are widely used as tough engineering materials because of their high elongation at break, coupled with unique elastic recovery properties. When chilled below its glass transition, rubber loses much of its toughness, as indicated by brittle, shattering behaviour when impacted at liquid nitrogen (− 180° C) temperatures. This embrittlement process has been commercially exploited in cryogenic comminution [1–3]; fine powders can be produced with low energy expenditure. Despite widespread recognition of this transformation in behaviour, no attempts to measure Mode I fracture toughness at cryogenic temperatures have previously been recorded for elastomers.

Fracture toughness (K), and energy release rates (G) have been measured for both ductile and brittle polymers using a variety of configurations [4]. From this compilation it is noted that for polybutadiene rubbers in tearing Mode III, G_{Ic} ranges from threshold values of about $20\,\mathrm{J\,m^{-2}}$ (highly swollen and at elevated temperatures) [5] to a maximum of approximately 1 [5] to $3\,\mathrm{kJ\,m^{-2}}$ [6]. As crosslink density increases (i.e. as average molecular weight between crosslinks, M_{c} decreases), threshold fracture energy decreases [5].

For a linear thermoplastic with a glass transition temperature T_{g} above 20° C, many methods are available for convenient measurement of K and G; no serious constraints upon specimen geometry exist, and crack length parameter a can be readily measured *in situ*. For many temperatures and strain rates, polymethyl methacrylates (PMMA's) of varying molecular weight show a quite narrow range of toughness values, with G_{Ic} ranging from 100 to $1000\,\mathrm{J\,m^{-2}}$ and K_{Ic} between 1 and $3\,\mathrm{MN\,m^{-3/2}}$ [4, 7, 8]. Unfilled thermosetting resins including epoxy and unsaturated polyester resins also show similar toughness values [4]; tougher polymers include higher impact engineering grades (for example, acrylonitrile-butadiene-styrene (ABS) and polycarbonate) for which crack bluntening contributes to G_{Ic} values of around 3 to $20\,\mathrm{kJ\,m^{-2}}$ and filled composites with G_{Ic} often greater than $10\,\mathrm{kJ\,m^{-2}}$ [4].

For materials including glass [9], alumina [10, 11] and rigid thermoplastics (PMMA [8, 12, 13], polycarbonate [14] and epoxy resins [15–20] a convenient method for determining fracture energy and toughness is the double torsion technique. Uncertainty exists as to whether failure is of Mode III type (as crack growth is in the x direction) or Mode I (plausible from crack propagation being nearly parallel to z direction) but Jayatilaka [21] considers despite the good agree-

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ment with G_{Ic} data obtained by other methods that the issue is still unresolved.

In practice the double torsion method is potentially ideal for cryogenic fracture toughness measurement. Two major advantages exist: G_{Ic} can be measured independent of crack length, thus reducing much tedius effort and secondly, the compact compression mode of load application is easily adapted to incorporate unusual environments. Alternative crack opening displacement (COD) methods would entail much more elaborate and less direct techniques.

In this study polybutadiene rubbers crosslinked with either dicumyl peroxide or sulphur were fractured in liquid nitrogen using the double torsion method. From a structural viewpoint, these materials are more readily characterized compared with crosslinked epoxy polymers. The latter, essentially multicomponent materials, are not easily defined because linear polymerization and other uncontrolled side reaction occur concurrently with curing.

Elastomers are initially well above T_g and so thermodynamically at equilibrium. Molecular weights and chain architecture can be readily determined. Crosslinking is in the absence of concommittent linear polymerization, and the degree of crosslinking in essentially homogeneous material can be accurately monitored and controlled. Hence it should be possible for the effects of M_c upon fracture energy to be unambiguously determined.

In this paper the fracture energy of high-*cis*-polybutadiene is measured when immersed in liquid nitrogen. Details concerning the experimental procedure and its validity are included, together with a brief description of fracture morphology.

2. Experimental procedure

2.1. Elastomers

In this study the base polymer was "*cis*-4 1203" polybutadiene (BR) provided by Phillips Petroleum Co., Bartlesville. Typically this polymer has a 92% *cis* content, a weight average molar mass M_w of about 380 000 and a polydispersity of 2.1 [22].

"Dicup R" dicumyl peroxide (Hercules Chemical Co., Wilmington) was dispersed into thin BR crepe, milled and massed. From cure rheometer traces, vulcanization at 150° C for 2 h was chosen. Sheets 3 to 5 mm in thickness were made between polyester film, using suitable plate dies. Crosslink densities were then determined by swelling in *n*-heptane, using the Flory–Rehner equation [23] and constants from Kraus [24]. Details of this group of polymers are summarized in Table I. Increase in Monsanto torque has been listed at an arbitrary 60 min cure time to reflect modulus changes at each level of peroxide.

Sulphur crosslinked BR samples were prepared using basically the formulation of Henry and Gent [25]. The rubber was premixed at 60 rpm in a Braebender RE-6 instrument for 2 min, followed by addition of zinc oxide, stearic acid, TBBS accelerator and sulphur, each at 1 min intervals. After a total mix time of 6 min, the off-white polymer was passed 10 times on a Farrell mill, before massing and vulcanization. Details of samples at three sulphur levels (chosen to centre about a typical, commercial value) are provided in Table II.

Strips approximately 13 mm wide and 60 mm long were guillotined for flexural modulus determination at −180° C. Other samples, from 25 to 30 mm wide and from 80 to 100 mm long were prepared for double torsion testing, as described below.

2.2. Double torsion test method

Established procedures (for example, described in [9, 10]) were varied in that a steel "U" frame was used instead of rollers to support the test piece and the load was applied by a 6.5 mm diameter ball bearing attached via a slender probe to the descending Instron crosshead. Cryogenic experi-

TABLE I Peroxide crosslinked BR – formulation and properties

Dicup level (parts/100 rubber)	Change in Monsanto torque after 60 min (lb inch^{-1})	M_c (using = $0.32 + 0.57 V_R$)	SG
0.05	29	61 300	–
0.20	40	6200	0.90
0.40	55	3800	0.91
0.60	64	3300	0.91
1.00	75	3000	–

TABLE II Sulphur-cured BR – formulation and properties

Sample code (Based on 100 parts hydrocarbon)	Sulphur	Change in Monsanto torque after 60 min (lb inch^{-1})	M_c	SG
A	1.0	38	4900	0.95
B	1.5	50	3700	0.95
C	2.0	57	3200	0.94

ments were conducted with specimens resting in liquid nitrogen, contained in a flat bottomed aluminium bowl, separated from the compression cell by a 12.5 mm thick PVC/gypsum insulating sheet. This assembly was shown by prior compression trials not to yield significantly under the load range of interest (i.e. up to about 1 kN). The double torsion test apparatus is illustrated in Fig. 1.

Fracture toughness data were obtained in the following manner. Each rubber specimen had a crack guidance groove inserted using a jewellers saw and then prenotched with a sharp, lubricated blade. A "sandwich" of the test-piece clamped between 1 mm thick steel plates (to prevent distortion during cooling) was immersed in liquid nitrogen for about 5 min. The then "liberated" test-piece was held temporarily on the U frame using a small weight. Once the bearing began to deform the test-piece at a controlled crosshead speed, the positioning weight was removed. Using suitable crosshead speeds and specimen dimensions, the load recorded will increase and then plateau.

Often a fine "saw-tooth" trace is obtained, reflecting at a microscopic level crack initiation and arrest; the difference in load is normally small and unimportant when approximate G_{Ic} values are being considered. Care needs to be taken to ensure that the test-piece deforms in the correct manner; plate hinging can arise when the guidance channel is too deep, and trouser tear mode operates when the load is not evenly distributed onto the two "tines" of the test specimen.

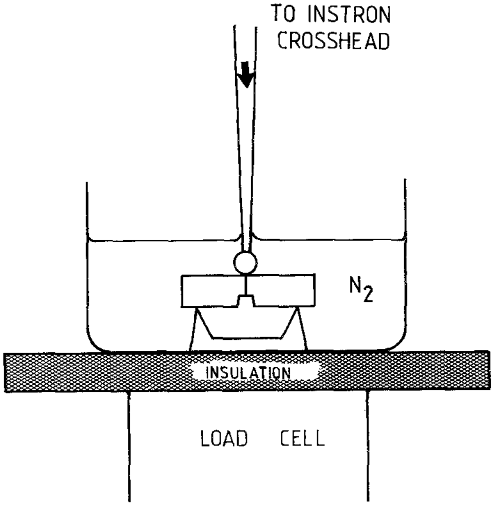

Figure 1 Double torsion test apparatus.

Dimensions of the cold, fractured test-piece are then taken, and G_{Ic} is determined from value of constant load, P, specimen dimensions l, D, B, B_c, and modulus G (estimated by 3 point flexing at −180° C, in separate experiments), using Equation 1, where constants correspond to those used by Williams [26].

$$G_{Ic} = \frac{3P^2l^2}{2DB_cB^3G}\,. \tag{1}$$

In most cases duplicate measurements of G_{Ic} were obtained. Crosshead speeds ranging from 0.5 to 50 mm min^{-1} were employed.

2.3. Morphology of fracture surfaces

High resolution examination of fracture morphology during and just after testing was impractical. Macrographs were obtained of fractured specimens in both the liquid nitrogen and in the cold gaseous environment just above the liquid surface. Subsequently test pieces were equilibrated at 20° C, gold coated and examined both optically and by SEM (using a Jeol SM2 instrument).

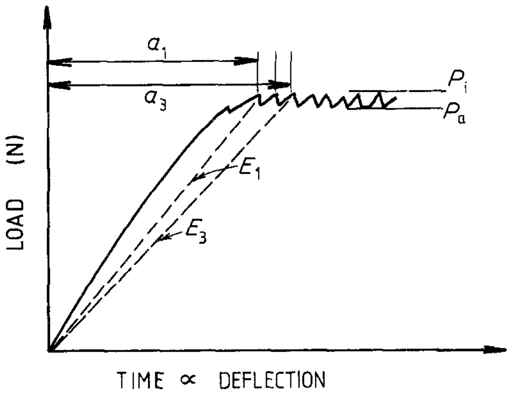

Figure 2 Load against deflection trace.

Figure 3 Evenly spaced crack arrest lines on fracture surface of peroxide-crosslinked polybutadiene.

3. Verification of the test procedure

As indicated by Marshall *et al.* [8] and Williams [26], a necessary condition for legitimate results is that compliance C must be proportional to crack length a. Calibration can be undertaken to show that

$$C = \frac{K(1+\nu)}{E} a + C_0$$

where C is the compliance at crack length, C_0 is the compliance at crack length $a = 0$, K is the constant incorporating specimen dimensions, E is the tensile modulus, and ν is the Poisson's ratio.

Where a load against deflection trace takes the form shown in Fig. 2, and where subsequent examination of the fracture surface reveals evenly spaced crack arrest lines (for example, Fig. 3), the conditions of proportionality between C and a are met.

4. Results and discussion

4.1. Load against displacement (or time) traces

Before examining chilled rubber samples, PMMA test pieces of varying dimensions were tested at 20° C using crosshead speeds ranging from 0.5 to 100 mm min^{-1}. This was undertaken to check that G_{Ic} values consistent with those already published were obtained, and also to choose convenient conditions which would be suitable for the cryogenic studies. From Fig. 4 it can be see that toughness increases as strain rate increases for PMMA at 20° C, in much the same way as indicated by Williams and Hodgkinson (Fig. 2 in [27]). Although test specimen thickness, channel depth and length of starter notch were varied, the relatively narrow range of values shown in Fig. 4 indicate that substantial departures in fracture mechanism are absent. In essence, results including fracture morphology agreed closely with those of Hakeem and Phillips [13].

From these preliminary studies, rubber specimens were prepared with dimensions of B typically 3 to 4 mm, B_c 1 to 2 mm (with channel width being about 1 mm) l was generally fixed at about 12 mm and D ranged from 14 to 20 mm (all dimensions are of rubber at cryogenic temperatures). Occasionally the channel was replaced by a sharp lengthwise incision, again to give B_c about 1.5 mm, but this procedure provided no advantage over the sawn channel method. Finally, starter notches of varying length were tested, but as a steady load was only obtained after the crack had grown substantially, no sensitivity to notch length was observed. Unduly long starter notches were avoided as this merely encouraged specimen warpage during cooling and thus caused experimental difficulties.

With rubber specimens very deep channels had also to be avoided, as this led to "hinging", an inappropriate mode of deformation. It was found that slower crosshead speeds (≤ 5 mm min^{-1}) gave controlled crack propagation; a slip-stick trace was

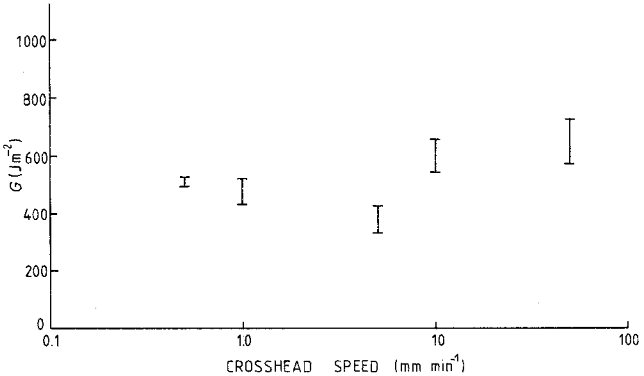

Figure 4 Fracture energy G_{Ic} against strain rate, for PMMA.

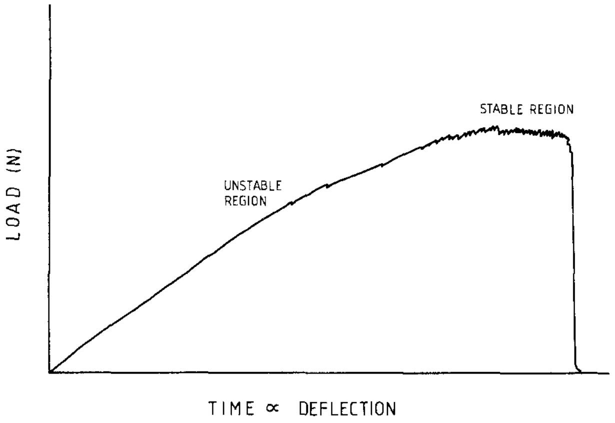

Figure 5 Slip-stick trace for *cis*-BR with 1 phr sulphur, crosshead speed 0.5 mm min^{-1}.

often obtained, as shown for "Cis 4" BR cured with 1 phr sulpur in Fig. 5. As differences between crack initiation load P_i and arrest load P_a were generally small (less than 5%), for the purposes of estimating G for internal comparison an average can be taken.

In some experiments a smoother trace was obtained (for example Fig. 6). This suggests that the mode of failure is changing slightly, but the emphasis here is to compare the magnitude of G with compound variables and so discussion on this point will come later. It is noted that these two load against displacement traces correspond to those shown in Figs. 12d and f of Scott *et al.* [19]. However, one would not expect to see major changes in fracture mechanism in our case, as temperature and polymer type are fixed. Those traces from which G data are presented as "legitimate" also include those corresponding to Figs. 12c and occasionally g [19].

When higher crosshead speeds (typically $50\,\text{mm}\,\text{min}^{-1}$) are used, fracture often occurs before stable crack propagation. In these circumstances, a load against time trace of the type shown in Fig. 7 is obtained. Maximum loads sustained by specimens in these circumstances were thus recorded, and in principle corresponding G_{Ic} value can be calculated. However, these generally low ($\leqq 5\,\text{kJ}\,\text{m}^{-2}$) results are invalid as no stable crack growth has occurred.

4.2. Fracture energy against compound variables

4.2.1. Peroxide cured polymer

The effect of crosslink density (reflected by M_c) upon G_{Ic} is shown in Fig. 8. It can be seen that there is little sensitivity with G_{Ic} remaining high even at high crosslink densities. This would suggest that crack-bluntening can still arise by some localized plastic deformation process. As the specimens are tested slowly at temperatures as much as 80° C below T_g, it is unlikely that thermal effects are significant (if compared with data for PMMA by Kambour [28]).

It is highly likely that environmental crazing is occurring in these experiments, as the phenomena

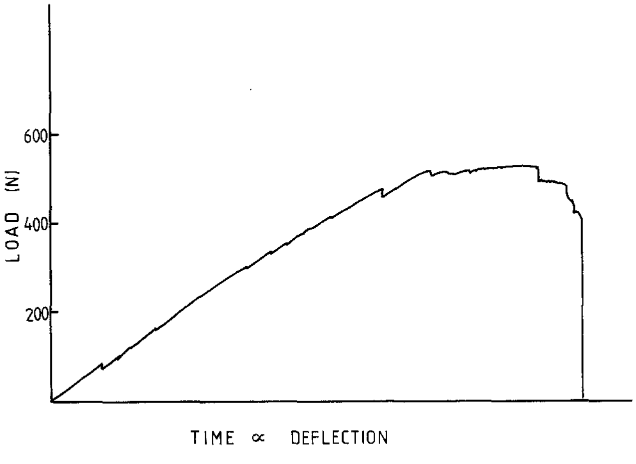

Figure 6 Load against deflection trace showing more continuous crack propagation (1.5 phr sulphur, crosshead speed 0.5 $\text{mm}\,\text{min}^{-1}$).

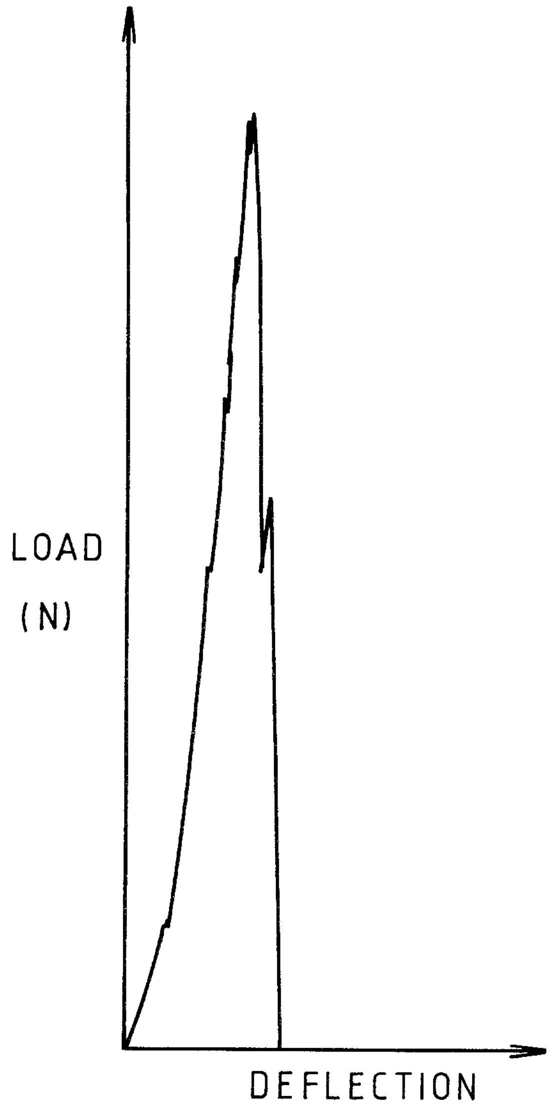

Figure 7 Load against deflection trace – unstable crack growth at high crosshead speeds.

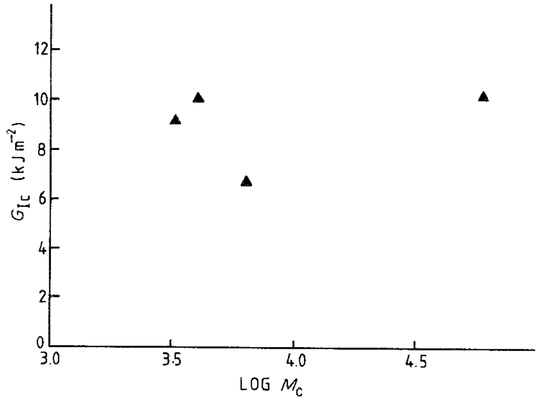

Figure 8 Effect of crosslink density upon G_{Ic}, peroxide cured polybutadiene.

is now well documented for these [29, 30] and related amorphous polymers [31–34]. For polydienes, conditions for crazing are pre-orientation, low strain rates and test temperatures near the liquification temperature of the environment [30]. More recently it was shown [29] that pre-oriented peroxy-crosslinked polybutadiene when strained at 93 K in nitrogen led to prolific, prominent crazing. However when the pre-extension (normally 100–300%) was not undertaken, brittle behaviour was noted with no craze formation. When nitrogen was replaced by helium, no crazing was noted, agreeing with related studies using other polymers [36]. During crazing, large amounts of gas are absorbed, although the hypothesis that storage is in craze voids has not been directly substantiated.

In the double torsion testing, conditions are similar to those described by Mead *et al.* [29], except that no intended pre-extension exists (and residual orientation caused by milling and other sample preparation steps would appear to be no greater than in their experiments), and double torsion test geometry is rather more complex than simple uniaxial tensile testing. In several experiments, the test pieces were coated with a silicone grease to try to retard nitrogen penetration, but similar results as for uncoated samples were obtained.

Despite these aforementioned experimental differences, it is most likely that the predominant contributor to high fracture energy is environmental crazing. With the absence of pre-orientation the extent of crazing is not expected to be as great as indicated by Mead *et al.* [29], so that the rubber will be sufficiently embrittled for double-torsion fracture energy measurement to be of some value.

4.2.2. Sulphur-cured polybutadiene

The extremes in practical levels of sulphur are generally from 1 to 2 parts, and this corresponds to a rather narrow range of crosslinked densities (i.e. M_c from 3200 to 4900). Fracture energies are provided for three compounds tested at three crosshead speeds (Fig. 9). Ignoring the suspect high speed data, it will be noted that G_{Ic} ranges from a little over 5 kJ m^{-2} to perhaps about 10 kJ m^{-2}. However, as for the peroxide cured samples, no great sensitivity to crosslink density was again observed. It is considered that at the maximum crosslink density employed, crazing or

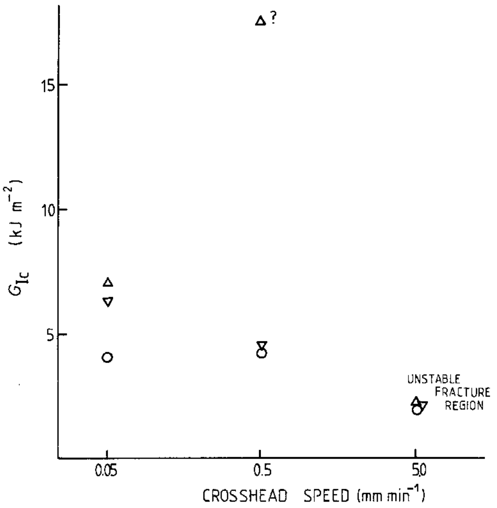

Figure 9 Fracture energy against crosshead speed: sulphur-cured polybutadiene △ = 1.0 phr, ▽ = 1.5 phr, ○ = 2.0 phr.

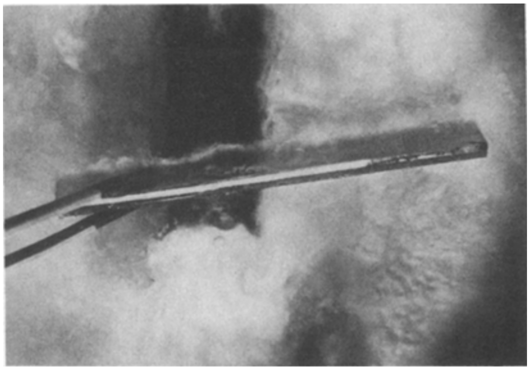

Figure 11 Low magnification fracture morphology of peroxide-crosslinked polybutadiene, in cold nitrogen atmosphere.

other crack bluntening modes of deformation are possible. The use of unusually high levels of sulphur to reduce M_c to below 1000 may cause a change in mode of failure although this step would be of limited practical importance. For environmental crazing, the rate of uptake of nitrogen is undiminished and little change in G_{Ic} is expected.

Strain rate effects for this set of polymers were more pronounced than for the peroxide-cured polymer (Fig. 10). The reason for this departure is not clear.

4.3. Morphology of polymer fracture surfaces

As it was known that liquid nitrogen environmental crazing had already been reported for similar polymers [29, 30] and as fracture energy values obtained were higher than for many brittle linear polymers, the test pieces were examined closely during and after double torsion tensile testing.

Some circumstantial evidence for nitrogen penetration in *cis*-polybutadiene was that the bulk material changed from transparent bright yellow to a more opaque cream colour upon chilling. This change was reversible, with the exterior recovering first. The cross-section was similar to that shown for polychloroprene (Fig. 6, [29]).

Fracture surfaces (Fig. 11) macroscopically resemble familiar mirror-like craze texture observed in PMMA and polystyrene. This pearl-like or opalescent appearance is caused by the differing refractive index of the essentially spongelike matter compared with the homogeneous uncrazed bulk [37, 38].

When specimens are brought to 20° C, this characteristic craze sheen is lost, and macroscopically all that can be seen are the characteristic double torsion fracture zones (Fig. 12) which correspond to the description by Hakeem and Phillips

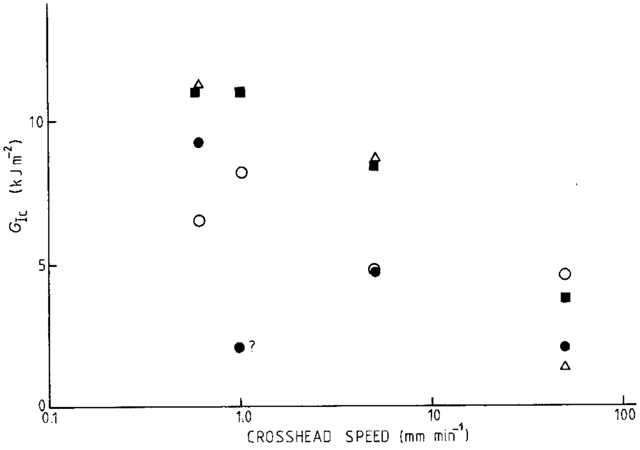

Figure 10 Effect of strain rate upon fracture energy, peroxide-cured polybutadienes, △ = 0.05, △ = 0.2, ■ = 0.4, ● = 0.6 phr.

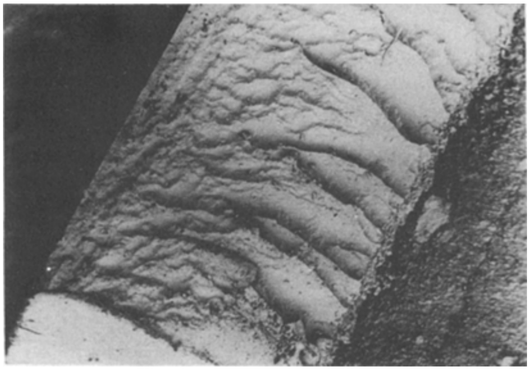

Figure 12 Fracture zones of broken double torsion specimens (peroxide-cured polybutadiene).

[13] for PMMA. At higher magnification no evidence for craze material can be detected (Fig. 13), although this is hardly surprising, as fine oriented remnants will have disappeared during the 200° C increase in temperature. The retention of low temperature structure for the purposes of high resolution microscopy constitutes a major and practical challenge at present.

5. Conclusions

Crosslinked rubbers with no pre-orientation can be tested by the double torsion method and estimates of fracture energy obtained. Under slow strain rate conditions stable crack propagation transpired, and fracture energy values of about 5 kJ m^{-2} were recorded. This high value was rather insensitive to both strain rate, crosslink density and type. The major cause for high toughness is considered to be liquid nitrogen environmental crazing, although direct high resolution morphological data is lacking. Further double torsion studies where inert helium is substituted for nitrogen as the coolant, will be undertaken to establish the contribution made to fracture energy by the environment.

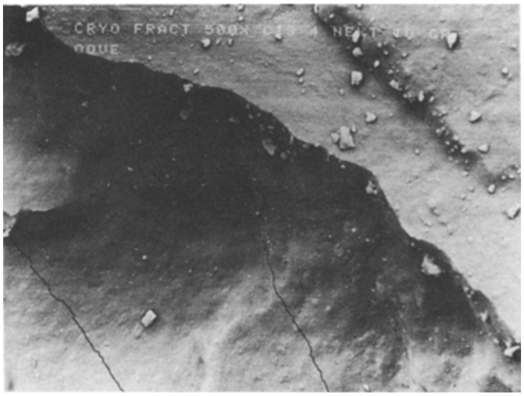

Figure 13 Scanning electron micrograph of fractured double torsion specimen at 20° C.

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