JOURNAL OF MATERIALS SCIENCE 22 (1987) 1651–1656

The fracture toughness of polybutadiene and other elastomers in cold nitrogen gas

R. P. BURFORD, A. POTOK
School of Chemical Engineering and Industrial Chemistry, University of New South Wales, PO Box 1, Kensington, New South Wales 2033, Australia

The fracture toughness of crosslinked polybutadiene was measured using the double torsion method, with chilled nitrogen gas as the environment. High fracture energies were found as the gas temperature approached the nitrogen boiling point (77 K). As temperature increased to 115 K, G_{Ic} decreased from about 7 to 1 kJm^{-2}. Above this temperature, fracture toughness increased again, but no reliable data could be gained by this method, when the temperature exceeded 135 K. The range of fracture toughness observed for this polymer is about one half that previously recorded, using liquid nitrogen. Crosslink density has a modest effect upon fracture toughness. Strain crystallizing natural rubber and non-strain crystallizing polyisobutylene rubber were either lightly or heavily crosslinked, and the fracture toughness also measured in nitrogen at 95 and 125 K. Again, G_{Ic} decreased at the higher temperature for both polymer types, but the natural rubber was significantly tougher than the polybutadiene, whilst the polyisobutylene was more fragile.

1. Introduction

When thermoplastics are cooled to cryogenic temperatures, one anticipates brittle behaviour, consistant with polymer chains being far below their glass transition temperature. Whilst this indeed occurs in "inert" environments including helium gas and *in vacuo*, Brown and coworkers [1–6] and others (e.g. [7–9]) have shown that in nitrogen and argon at 80 K many amorphous and crystalline polymers exhibit environmental crazing. Here, breaking strains are considerably larger than the 5% maximum otherwise predicted.

The reason for this was proposed to be a reduction in the polymer surface free energy by physisorption, leading to plasticization and the subsequent promotion of craze initiation [3]. As the relative pressure of the gas, P_{r}, defined by Equation 1

$$P_{\mathrm{r}} = P \exp\left[-\frac{Q_{\mathrm{v}}}{R}\left(\frac{1}{T_{\mathrm{b}}} - \frac{1}{T}\right)\right] \qquad (1)$$

(from [5], where P is in atmospheres, Q_{v} is the heat of vaporization and T_{b} is the boiling point) increases, solubility and adsorption of the gas into the polymer also increase.

The tensile behaviour of rubbers strained at temperatures far below their glass transition, T_{g}, has been studied in detail by Reed and coworkers [10–15]. A variety of crosslinked poly (dienes) were shown to craze when certain conditions were met. The rubber needed to be prestrained, tested at temperatures below their glass transition temperatures, and be in an environment at temperatures approaching liquefaction or sublimation temperatures. Substantial uptake of environmental matter into the polymer was observed, as revealed by analysis of evolved gases when the strained polymers were allowed to warm. Possible mechanisms for gas storage within the polymer cited by Reed *et al.* [15] include free volume accommodation, and monolayer storage in craze cavities.

The fracture toughness of polymeric materials at low temperatures has only been measured fairly recently. Scott and coworkers [16] were one of the first groups to use the double torsion method, this being with epoxide resins in the temperature range 80 to 300 K. At lower crosshead speeds the fracture energy varied with temperature as shown in Fig. 1 (Fig. 7 from [16], reproduced with permission).

At high and low temperatures, stick-slip behaviour was observed, contrasting with continuous behaviour between 140 and 250 K, when slow crosshead speeds were employed. Whilst various types and concentrations of curing agents, crosshead speeds and temperature were examined in detail, the general effect as shown by the EDA cured material is that arrest fracture energy is low (≈ 100 to 150 Jm^{-2}) decreasing slightly (to below 100 Jm^{-2}) as temperature decreases below 175 K. Initiation fracture energies, however, increase dramatically at $T < 115$ K, and $T > 270$ K. These limiting temperatures are designated by Scott *et al.* [16], as high temperature (T_{H}) and low temperature (T_{L}) transitions. As the temperature falls below T_{H}, the polymer becomes too rigid to allow rapid plastic deformation and continuous crack propagation is observed. Fracture initiation energy is said to be controlled by plastic flow behaviour above T_{H}. The reversions to stick-slip behaviour below T_{L} were unexpected and the reasons for their occurrence not yet understood [16].

The fracture toughness of polybutadiene rubber has been measured in liquid nitrogen by the double torsion procedure [17] and was found to be in the range 5 to 20 kJm^{-2} depending upon deformation rate and crosslink type and density. Here the onset of crazing and

0022–2461/87 $03.00 + .12 © *1987 Chapman and Hall Ltd.*

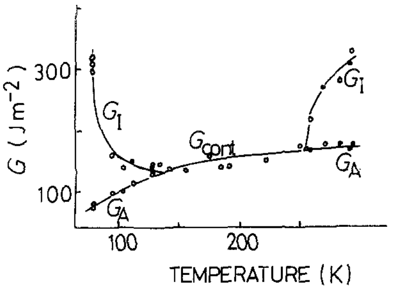

Figure 1 The variation of fracture energy with temperature for EDA-cured resin at a crosshead speed of 0.25 mm min^{-1} (redrawn from Fig. 7 of Scott *et al.* [16])

corresponding high toughness is caused by the liquid nitrogen environment. A limitation of this work was that only one temperature (i.e. boiling point of nitrogen, 77 K), was used.

The purpose of the present paper is to indicate how the fracture mode and toughness are altered by varying temperature in the range 77 to 150 K. Changes in behaviour found with gaseous rather than liquid environment are also described.

This is of some industrial relevance, as cryogenic grinding processes used to recycle rubber may utilize either liquid or gaseous nitrogen: substantial differences in fracture toughness resulting from either temperature or nitrogen relative pressure would be significant.

2. Experimental procedure

2.1. Elastomers

Most experiments were conducted using "Austrapol BR 1220" polybutadiene provided by Australian Synthetic Rubber Co., Altona, Victoria. This polymer has a *cis* content in the range 96 to 98%, a weight average molecular weight of about 2.5 to 3.0 × 10^5 and a poly dispersity of about 3.5 [18]. Sheets of peroxide crosslinked polymer were prepared in the following manner. 40% dicumyl peroxide ("Dicup 40", Hercules Chemical Co., Wilmington) was dispersed in the BR in a "Haake 600" mixing head operating using "Banbury" rotors at 60 r.p.m. and an initial temperature of 40° C. After adiabetic mixing for 8 min, the crumb was massed by passing it five times through an unheated two roll mill with a nip setting of 3 mm and vulcanizing at 140° C for 1 h to produce sheets about 2 to 3 mm thick. Crosslink densities were determined by swelling in *n*-heptane, using the Flory–Rehner equation [19, 20] with constants from Kraus [21]. Similarly, natural rubber (SMR-20) was crosslinked with dicumyl peroxide using the same procedure. Specific gravities were determined pycnometrically. Details of the peroxide crosslinked elastomers are summarized in Table I.

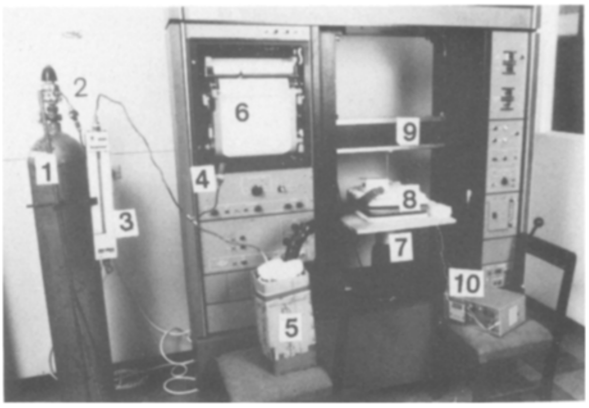

Figure 2 Experimental equipment. 1–Nitrogen gas supply, 2–gate valve, 3,–rotameter, 4–pressure relief valve, 5–cooling bath, 6–recorder, 7–compression cell, 8–test chamber, 9–crosshead and 10–temperature indicator.

A smaller number of fracture toughness determinations were made using sulphur crosslinked BR, natural rubber and polyisobutylene. The amount of each ingredient used in the formulation, together with density, hardness (Durometer Shore A) and nominal crosslink density, are summarized in Table II. Appropriate levels of zinc oxide, stearic acid and accelerator were used in each case.

Specimens for double torsion testing were prepared by cutting the vulcanized rubber sheets into strips 100 mm long and 25 mm wide, and machining a 1.5 mm deep grove lengthwise along the centre, using a rotary blade attached to an electric drill. Sample dimensions including specimen thickness, B, and thickness under groove, B_c, were determined at the test temperature.

2.2. Double torsion test method

The main details of the procedure, using liquid nitrogen as the environment, have been previously described [17]. In the present study, a somewhat different chamber and cooling device was used.

Nitrogen gas was regulated using a gate valve through a 100 mm diameter 12 turn coil of 6.4 mm copper tubing immersed in liquid nitrogen. The chilled gas emerging from this "heat exchanger" was then delivered onto the sample surface, contained within a well insulated chamber. A copper constant type "T" thermocouple adjacent to the sample was connected to a temperature controller, which in turn controlled the gate valve. By adjusting the flow rate of the gas, this crude feedback system allowed temperature to be maintained within ±5 K of the desired value. The equipment used is illustrated in Fig. 2.

The testing chamber comprised a stainless steel

TABLE I Peroxide crosslinked elastomers – formulation and properties

Polymer type	Code No	Dicup level (parts/rubber)	*SG*	Hardness (Durometer A)	*Mc*
Polybutadiene rubber	BP-A	0.02	0.91	28	> 20 000
	BP-B	0.18	0.93	45	6 000
	BP-C	2.0	0.95	75	750
Natural rubber	NP-A	0.4	0.93	29	21 000
	NP-B	2.0	0.94	47	6 500

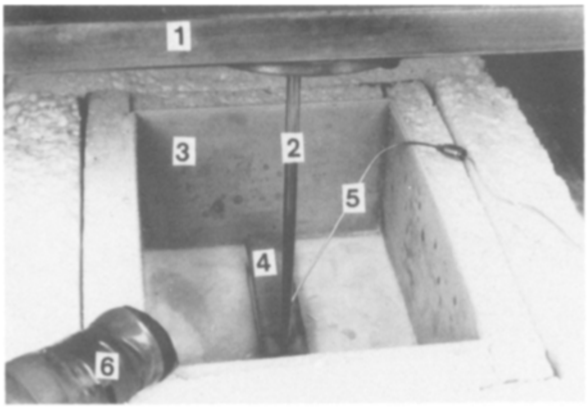

Figure 3 Testing chamber. 1–Instron crosshead, 2–probe, 3–stainless steel box, 4–sample resting on U-frame, 5–thermocouple and 6–insulated copper tube.

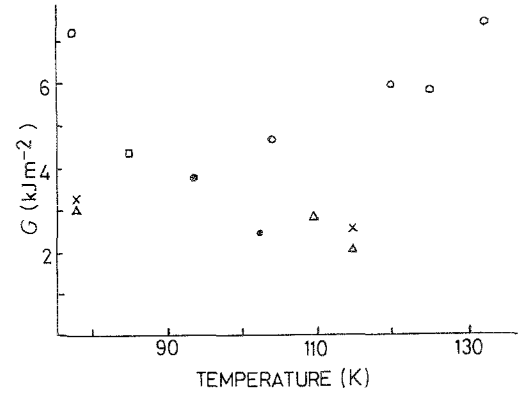

Figure 4 Fracture energy, G, against temperature in a nitrogen gas environment; highly crosslinked, peroxide-cured polybutadiene (BP-C) (X) initiation, (△) arrest, (□) average, (○) unstable and (●) nearly stable.

box with sides insulated by polystyrene foam, and supported on a 15 mm thick asbestos board. This rested on a compression cell of an Instron 1115 Universal testing machine and was shown by prior compression trials not to yield significantly under the load range of interest. The load was applied via a 5 mm diameter, round-ended stainless steel rod, with the crosshead descending at 1 mm min^{-1} to encourage controlled crack growth. During each experiment the chamber was covered by a sheet of polystyrene foam, pivotting about the copper nitrogen feed tube at one corner of the bath. A slit to facilitate cover rotation past the central probe, and a transparent PMMA viewing port were also incorporated in the cover sheet. Particular attention was paid to ensure that the specimen geometry relative to both probe and support promoted deformation in the correct manner. The compression testing chamber, without cover, is illustrated in Fig. 3.

Fracture toughness data were obtained in the following manner. The rubber testpiece, with a 10 to 15 mm "starter notch" inserted using a scalpel blade, was placed on the support frame and the cold nitrogen allowed to fill the chamber until thermal equilibrium at the desired temperature was reached. This typically took 10 to 15 min and so the specimen was not subjected to the same thermal shock associated with immersion in liquid nitrogen. Here the steps required to prevent warpage previously recorded [17] were not necessary. Cold specimen dimensions were then recorded, followed by careful positioning under the lowered probe. After cooling again to the test temperature, the probe was lowered at 1 mm min^{-1} and a load against crosshead travel trace was continuously recorded. Under some conditions samples showed stick-slip behaviour, so values of load for crack initiation and arrest, P_i and P_a, respectively, were obtained. In other cases, more continuous crack propagation occurred, with only a fine "sawtooth" load trace being recorded. Fracture toughness, G_{Ic}, was determined using Equation 2, where constants correspond to those used by Williams [22].

$$G_{Ic} = \frac{3P^2 l^2}{2DB_c B^3 G} \tag{2}$$

No correction was made for crack front geometry as described by Levers [23]. Modulus G was taken to be 3×10^9 Pa, and l, half the U-frame width, remained constant at 8.7 mm.

3. Results and discussion

3.1. Peroxide crosslinked polybutadiene

Highly crosslinked polybutadiene (code BP-C) was fractured at temperatures ranging from 78 to 128 K and strain energy release rates (G_{Ic}) are found generally to be in the range 2 to 4.5 kJ m^{-2} at the lower temperature (Fig. 4). The load trace for these experiments is typically that represented by Fig. 5, in which load builds up at the notch until essentially unstable fracture occurs. However, this arrests at a lower but finite load, and more controlled, continuous crack growth then occurs. Examination of the fractured specimen in these cases reveals the numerous evenly spaced rib markings, but unambiguous evidence for craze matter

TABLE II Sulphur crosslinked elastomers – formulation and properties

Polymer type	Code	Sulphur (parts/100 rubber)	*SG*	Hardness (Durometer A)	*Mc*
Polybutadiene	BS-A	0.22	0.93	23	12 000
	BS-B	3.4	0.97	47	3 000
Natural rubber	NS-A	0.1	0.97	21	≈ 120 000
	NS-B	5.0	0.99	44	7 000
Butyl rubber (polyisobutylene)	IS-A	0.2	0.94	25	sample dissolved
	IS-B	5.0	0.96	46	8 000

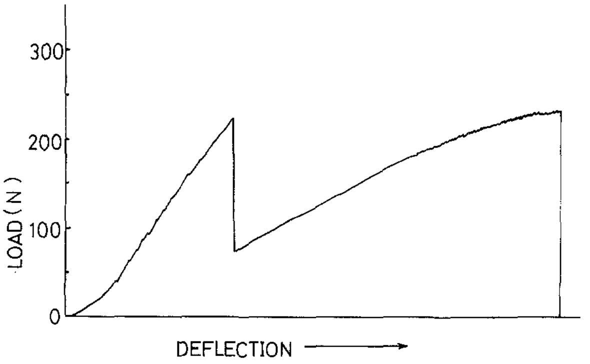

Figure 5 Load against deflection for highly crosslinked, peroxide cured polybutadiene (BP-C) at 85 K.

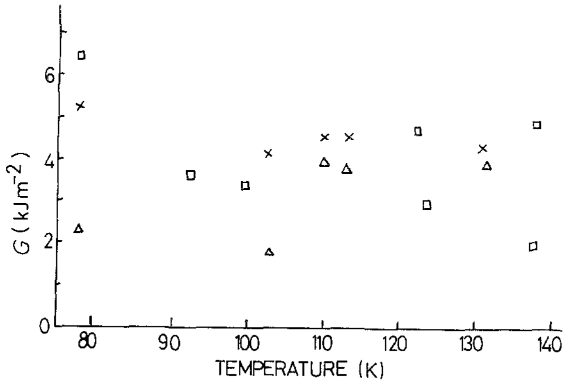

Figure 6 Fracture energy, G, against temperature of nitrogen gas, medium crosslinked polybutadiene (BP-B). (×) initiation, (△) arrest, (□) average.

was not able to be clearly resolved, due to surface frosting. The toughness of this material appears to be above one half that for similarly crosslinked 92% *cis* polybutadiene tested in liquid nitrogen [17], this being attributable to reduced sorption of the nitrogen. However, measurement of nitrogen uptake in the polymer has not yet been attempted. At highest crosslink density, the pronounced increase in opacity normally observed after immersion was not found, although this is difficult due to inherent turbidity of the original sample.

At higher temperatures (> 110 K) unstable behaviour occurred, with high loads being reached before catastrophic rupture of the sample occurred. The load against time trace comprised the first part of Fig. 5, with load falling to zero after the first maxima. Thus the nominal G_{Ic} values shown in Fig. 4 do not reflect continuous fracture. It is envisaged that the notch tip bluntens considerably at these higher temperatures. At still higher temperatures specimen buckling without fracture occurred.

Polybutadiene of medium crosslink density (BP-B) showed similar toughness, with G_{Ic} again ranging from 2 to 5 kJ m^{-2} (Fig. 6). A less pronounced increase in toughness occurs at both temperature extremes than for BP-C, although toughness at 78 K closely approach that found for samples in liquid nitrogen environments (4 to 6.5 kJ m^{-2}). For many samples, a region of unstable crack growth ("stick-slip") preceded more continuous fracture (Fig. 7). This is not due solely to starter notch effects, as the trace is quite dissimilar to Fig. 5, and the fracture topography also differs from previous specimens.

Lightly crosslinked polybutadiene (BP-A) generally gave load–deformation traces shown typically in Fig. 8 where crack arrest (G_a) and initiation (G_i) values each remains fairly constant with crack length. G_a and G_i were often of the same magnitude (as reflected in Fig. 10, later). However, at higher temperatures (for example, at 130 K, Fig. 9), a starter notch effect was still apparent, although not as pronounced as previously described for the highly crosslinked polybutadiene. In several tests an "end effect" was found, being represented by an increase in load after stable propagation. This preceded fracture, and was associated with distinctive fracture surface morphology. This change in fracture mode may be due to slight crack path deviation or bluntening due to changes in stress distribution about microscopic flaws or inclusions.

The effect of temperature upon fracture toughness for the lightly crosslinked samples is shown in Fig. 10. At temperatures near the boiling point of nitrogen high toughness is observed, being of the same order as that previously found for a similarly crosslinked polybutadiene in liquid nitrogen [17]. However, G_{Ic} rapidly falls as temperature rises to 95 K, and then remains essentially constant to around 130 K. Low values of G at around 120 K are consistent with Olf and Peterlin's findings [8]. Toughness in this temperature regime (0.5 to 0.75 kJ m^{-2}) is somewhat lower than that found for the more highly crosslinked samples BP-C and BP-B ($\geqq 2$ kJ m^{-2}). As temperature begins to approach the polymer glass transition, fracture toughness again rises markedly. At temperatures above 135 to 140 K the samples were again too ductile to allow double torsion measurements to be made.

3.2. Peroxide crosslinked natural rubber

Samples of high and lower crosslink density natural rubber (NP-B and NP-A) were tested in gaseous

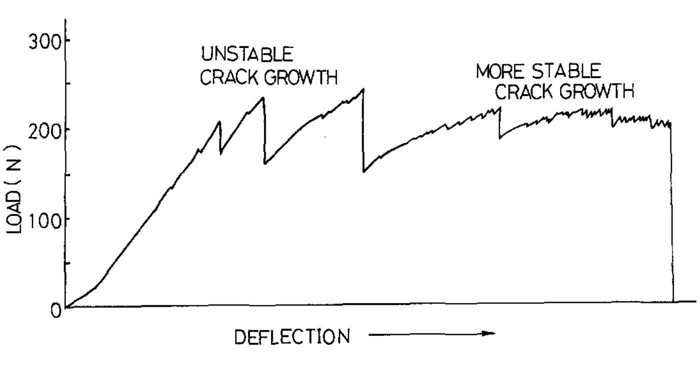

Figure 7 Load against deflection for medium crosslinked, peroxide cured polybutadiene (BP-B) at 110 K.

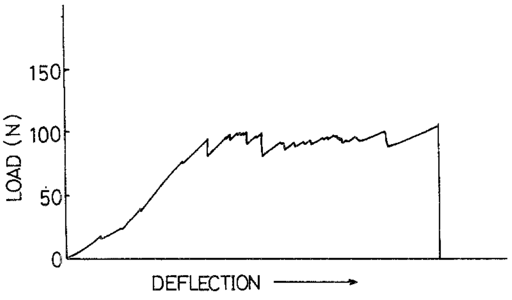

Figure 8 Load against deflection for lightly crosslinked, peroxide cured polybutadiene (BP-A) at 113 K.

nitrogen at 95 and 125 K, these temperatures having been previously found representative of nearing the high toughness/craze regime (in the former case) and minimum toughness regime, in the latter. These initial experiments are useful in identifying major trends and for comparing different polymers under the same test conditions.

The highly crosslinked rubber was quite tough at the lower temperature (Fig. 11) although even at 125 K, G values remained substantially greater than for the peroxide crosslinked polybutadienes. The limited data for the more lightly crosslinked polymer suggests the same trend, but with the lower temperature value of G being even higher than before.

It is envisaged that if the test temperature approached nitrogen T_b, fracture toughness would be much greater than $10\,\mathrm{kJ\,m^{-2}}$.

3.3. Sulphur crosslinked elastomers

Fracture toughness for three elastomer types at two temperatures are shown in Figs 12a, b and c. In all cases these elastomers were tougher at the lower temperature, and so trends consistent with those previously described for the peroxide crosslinked polymers exist. The most highly crosslinked polybutadiene (BS-B) was unable to be satisfactorily tested, but the other samples (BS-A) possessed low fracture toughness (Fig. 12a) this being of the same order as that found for the peroxide cured rubber of lowest crosslink density (BP-A).

The sulphur crosslinked natural rubber was found to be of similar toughness (Fig. 12b) to that crosslinked with peroxide. However, the more highly crosslinked sample appears tougher, as seen previously with peroxide crosslinked polybutadiene, but contrast with the trend seen for the peroxide cured natural rubber counterpart. The reason for the change with crosslinking agent is uncertain although further microstructural characterization of each polymer may provide some illumination.

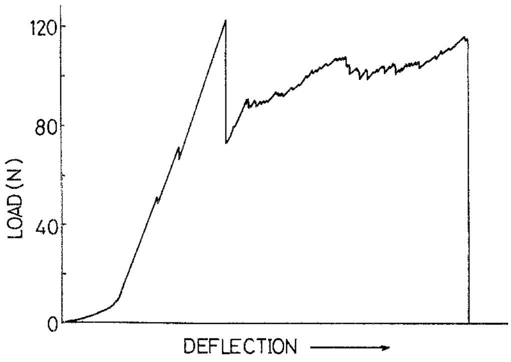

Figure 9 Load against deflection for lightly crosslinked, peroxide cured polybutadiene (BP-A) at 130 K.

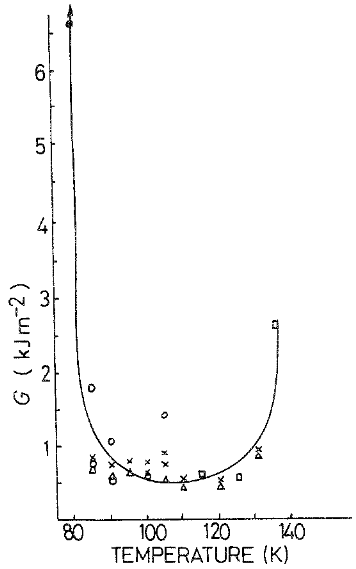

Figure 10 Fracture energy, G against temperature of nitrogen gas, lightly crosslinked peroxide cured polybutadiene (BP-A). (×) Initiation, (△) arrest, (□) average, (○) unstable and (●) nearly stable.

As expected, the non-strain-crystallizing polyisobutylene samples were more fragile (Fig. 12c) than natural rubber, but tougher than polybutadiene. As before, toughness decreased as temperature rose, and now increased crosslinking appears to lower toughness, as found for peroxide crosslinked natural rubber.

4. Conclusions

The fracture behaviour of rubber in very cold nitrogen is essentially similar to that observed for the epoxide resins recorded by Scott [16], and as shown in Fig. 1. All rubbers show a high fracture toughness as temperature approaches 77 K and nitrogen relative pressure increases. Toughness values approach those previously recorded for a liquid nitrogen environment.

At temperatures around 100 K, a plateau region of low fracture toughness is found, with polybutadiene having G_{Ic} values typically $\leq 2\,\mathrm{kJ\,m^{-2}}$. As temperature increases further, a tendency to plastic deformation with associated high toughness was indicated. No clear or constant trend with crosslink density could be found.

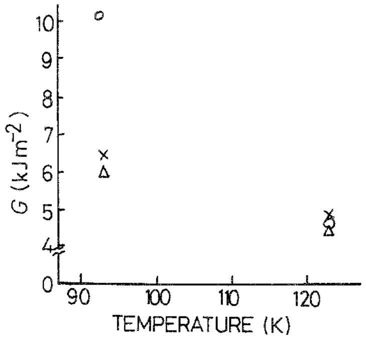

Figure 11 Fracture energy, G against temperature of nitrogen gas, peroxide crosslinked natural rubber. (○) unstable, NP-A (light crosslinking), (×) initiation, NP-B (heavier crosslinking), (△) arrest, NP-B (heavier crosslinking).

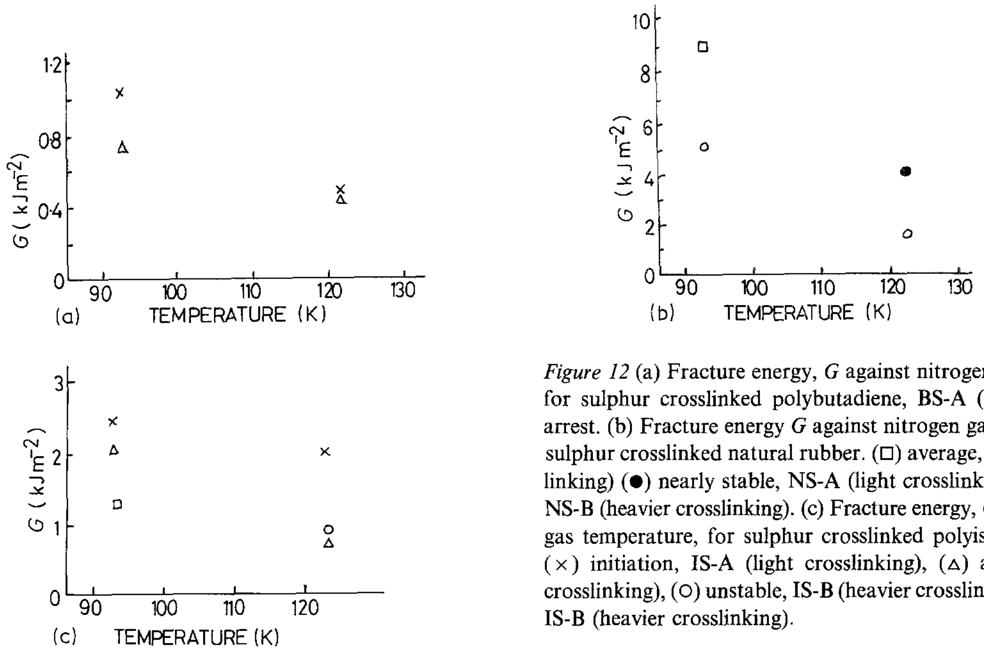

Figure 12 (a) Fracture energy, G against nitrogen gas temperature, for sulphur crosslinked polybutadiene, BS-A (×) initiation, (△) arrest. (b) Fracture energy G against nitrogen gas temperature, for sulphur crosslinked natural rubber. (□) average, NS-A (light crosslinking) (●) nearly stable, NS-A (light crosslinking), (○) unstable, NS-B (heavier crosslinking). (c) Fracture energy, G, against nitrogen gas temperature, for sulphur crosslinked polyisobutylene rubber. (×) initiation, IS-A (light crosslinking), (△) arrest, IS-A (light crosslinking), (○) unstable, IS-B (heavier crosslinking), (□) average, IS-B (heavier crosslinking).

A smaller number of experiments with crosslinked natural rubber and polyisobutylene allowed the following tentative conclusions to be made:

(a) the similar strong dependence on temperature found for polybutadiene exists for these polymers,

(b) fracture toughness is sensitive to extremes in crosslink density and in particular to the type of crosslinking agent,

(c) natural rubber shows the greater toughness for the two temperatures used, with polyisobutylene being marginally more fragile than the polybutadiene.

It can be concluded that environmental temperature is significant where it does not lie within T_L and T_H. Similarly major changes in chemical composition of rubber will alter fracture toughness. Small changes in crosslink density (i.e. degree of vulcanization) or rubber compound formulation are likely to be less important. The role of major additives including reinforcing filters and plasticizers has yet to be quantified, but is considered to be sufficiently important to justify future studies.

References

1. N. BROWN and Y. IMAI, *J. Appl. Phys.* **46** (1975) 4310.
2. Y. IMAI and N. BROWN, *Polymer* **18** (1977) 298.
3. M. PARRISH and N. BROWN, *J. Macromol. Sci. Phys.* **B8** (1973) 655.
4. J. B. C. WU and N. BROWN, *Mater. Sci. Eng.* **44** (1980) 121.
5. *Idem, J. Mater. Sci.* **17** (1982) 1311.
6. N. BROWN and B. D. METZGER, *J. Appl. Phys.* **48** (1977) 4109.
7. A. HILTNER, J. A. KASTELIC and E. BAER, in "Advances in Polymer Science and Engineering" edited by K. D. Pae, R. D. Morrow and Yu Chen, (Plenum Press, New York, 1972) p. 335.
8. H. G. OLF and A. PETERLIN, *J. Polym. Sci. Polym. Phys. Ed.* **12** (1974) 2209.
9. *Idem, Macromol.* **6** (1973) 470.
10. E. H. ANDREWS and P. E. REED, *J. Polym. Sci. A-2* **5** (1967) 317.
11. *Idem*, "Deformation and Fracture of High Polymers" edited by R. P. Kausch (Plenum Press, New York, 1974).
12. R. NATARAJAN and P. E. REED, *J. Polym. Sci. A-2* **10** (1972) 585.
13. W. T. MEAD and P. E. REED, *Polymer Eng. Sci.* **14** (1974) 22.
14. W. T. MEAD, R. S. PORTER and P. E. REED, *Macromol.* **11** (1978) 56.
15. *Idem, J. Mater. Sci.* **14** (1979) 850.
16. J. M. SCOTT, G. M. WELLS and D. C. PHILLIPS, *J. Mater. Sci.* **15** (1980) 1436.
17. R. P. BURFORD, *ibid.* **18** (1983) 3756.
18. J. A. J. HONIG, R. P. BURFORD and R. P. CHAPLIN, *J. Polym. Sci. Polym. Chem. Ed.* **21** (1983) 2559.
19. P. J. FLORY and J. REHNER Jr, *J. Chem. Phys.* **11** (1943) 521.
20. P. J. FLORY, *ibid.* **18** (1950) 108.
21. G. KRAUS, *J. Appl. Polym. Sci.* **7** (1963) 1257.
22. J. G. WILLIAMS, "Applications of Linear Elastic Fracture Mechanics", in "Failure in Polymers" (Advances in Polymer Science) Vol. 27 (Springer-Verlag, Berlin, Heidelberg, 1978) p. 80.
23. P. S. LEEVERS and J. G. WILLIAMS, *J. Mater. Sci.* **20** (1985) 77.

Received 2 June
and accepted 18 August 1986