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Tear strength of elastomers over a range of rates, temperatures and crosslinking: tearing energy spectra

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Measurement of tear strength of polyphosphazene (PNF), polychloroprene (CR) and styrene–butadiene rubber (SBR) has been carried out over a wide range of rates, temperatures and crosslinking. Data on strength of PNF have been found to be superimposable on a single master curve with the help of the WLF shift factor, indicating that enhancement of strength at high rates or low temperatures arises from simple viscoelastic loss mechanisms. The master curve may be termed as tearing energy spectra for a particular crosslinking density. Master curves at different elastic modulii are not superimposable. Strength of PNF is also much lower than that of SBR at a similar degree of crosslinking. This shows that mass per chain atom, which was important for predicting threshold strength is equally important under non-equilibrium conditions. Tearing energy spectra of filled SBR has also been obtained with the help of restricted tearing tests. Strength values obtained at various temperatures and rates for CR are, however, not superimposable on a master curve even with the help of special tests such as: (a) by partial swelling, (b) by doubling the curing agents, or (c) by peeling two layers apart. This anomaly is attributed to strain-induced crystallization of neoprene rubber on a molecular level.

1. Introduction

Tearing of an elastomer involves two processes (i) initiation from small flaws and (ii) propagation of these flaws due to development of an instability at the crack tip when the product of crack length and the density of elastic stored energy somewhat away from the crack attains a critical value. The tear behaviour of rubbers can be conveniently described by a characteristic energy or tearing energy, G_c, of the material, which is defined as [1]

$$G_c = -\frac{1}{h}\left(\frac{\partial W}{\partial c}\right)_l \qquad (1)$$

where W is the elastically stored energy in the test piece of thickness h, c the length of the crack and l the overall length so that partial derivative means that the external forces do not move. The tearing energy (G_c) is, however, dependent on the rate, temperature, and crosslinking because of the dependence of W on these factors. G_c as defined by Andrews [2], is a function of the above parameters and can be expressed as

$$G_c = G_{c0}\phi\,(T, \dot{c}, \varepsilon_0) \qquad (2)$$

where ε_0 is the applied strain, $\dot{c}$ is the crack velocity, and T is the temperature. G_{c0} is the threshold tearing energy below which the crack does not propagate in the absence of chemical attack. Only with great care can the effects of rate and temperature be minimized to get this threshold limit.

Under normal conditions, however, viscoelastic processes come into play. The cracks grow at a rate dependent on the dissipation of stored elastic energy through viscoelastic processes associated with slow crack growth. The rate of crack growth is further slowed down by strain induced crystallization or deviation of the tear tip. All these above processes are actually controlled by temperature of the test, rate of tearing and crosslinking density of the material.

Kadir and Thomas [3] studied the behaviour of rubbers over a wide range of rates and observed three kinds of tearing over the rates studied (a) rough tearing (b) stick slip tearing and (c) smooth tearing. The data obtained for each rubber–nitrile rubber (NBR), styrene–butadiene rubber (SBR) and polybutadiene rubber (BR) could be shifted using a universal WLF shift factor. A composite curve was obtained for NBR, BR and SBR in the smooth tearing region. Similar master plot of tearing energy against effective rate of tearing was done previously for BR by Ahagon and Gent [4]. Bhowmick and Gent [5] studied tearing of natural rubber (NR) and polychloroprene (CR) over a wide range of temperatures. Kelley and co-workers [6] have observed that tearing energy data for fluoroelastomers, obtained at wide range of rates and temperatures could be superimposed to form smooth master curves using a shift factor temperature relationship derived from creep measurements. Harwood *et al.* [7] investigated the strength and reinforcement of natural rubber at different crosslink densities and temperatures.

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Correlation between structure or molecular parameters and tearing of elastomers is not well understood. Attempts have been made to study the same when the viscoelastic processes are minimized [8, 9]. From these studies, two interesting rubbers were chosen for the present study. Polyphosphazene, an inorganic rubber containing phosphorus and nitrogen in the backbone with a high average mass per chain atom, and polychloroprene with its polar nature and crystallizing ability were selected. Strength of these rubbers measured at different rates and temperatures was compared with that of styrene–butadiene rubber, a non-crystallizing rubber. All these rubbers were crosslinked to different extents using either a dicumyl peroxide or a sulphur-based cure system.

2. Experimental details

Formulations of the mixes are given in Table I. Mixing and vulcanization were carried out as per the usual procedure.

2.1. Materials

2.1.1. Polyphosphazene

Phosphonitrilic fluoroelastomer, PNF 200, was supplied by Firestone Tire & Rubber Company, USA. This was mixed with various amounts of dicumyl peroxide (Di Cup R, Hercules Chemical Co.) and crosslinked by heating for 1 h at 150° C.

2.1.2. Neoprene

Neoprene WRT, supplied by EI du Pont de Nemours & Co., was crosslinked by various curing agents to yield only oxide, only sulphur and mixed interlinks.

2.1.3. SBR

SBR 1502, obtained from Firestone Tire & Rubber Company, USA was crosslinked to various levels with dicumyl peroxide. One mix using carbon black and sulphur was also prepared.

TABLE I Mix formulations and vulcanization conditions employed for preparing test specimens

A PNF
  PNF-200, 100; dicumyl peroxide, 0.5,1,3; vulcanized at 150° C for 1 h.

B(i) SBR
  FR-S 1502, 100; dicumyl peroxide 0.5; vulcanized at 150°C for various cure times.

B(ii) SBR-filled
  SBR-1502, 100; HAF black-50; zinc oxide 5; stearic acid, 2; sulphur 1.25; CBS, 1.0; vulcanized at 150° C for 1 h.

C Neoprene
  (i) Neoprene WRT, 100; sulphur, 1; tetramethyl thiuram monosulfide (TMTM), 1.0; diorthotolyl guanidine (DOTG), 0.5; magnesium oxide, 4.0; zinc oxide, 5; stearic acid, 1.0; vulcanized at 150° C for 2 h.
  (ii) Neoprene WRT, 100; sulphur, 2; TMTM, 1.0; DOTG, 1.0; magnesium oxide, 8.0; zinc oxide, 10.0; vulcanized at 150° C for 2 h.
  (iii) Neoprene WRT, 100; magnesium oxide, 2; zinc oxide, 5; vulcanized at 150° C for 90 min.
  (iv) Neoprene WRT, 100; sulphur, 2.0; DOTG, 0.5; tetramethyl thiuram disulfide (TMTD), 1.5; vulcanized at 150° C for 80 min.

2.2. Measurement of elastic modulus and V_r

Values of Mooney–Rivlin constants C_1 and C_2 were determined from stress–strain relations in tension at room temperature. Small strain elastic modulus, E, was obtained from

$$E = 6(C_1 + C_2) \qquad (3)$$

Volume fraction of rubber in the swollen vulcanizate (V_r) was also measured with the help of the following relations and using benzene for SBR and methyl ethyl ketone for CR and PNF as the solvents for swelling. ASTM # 3 liquid was also used for partial swelling of CR.

$$V_r = \frac{[(D - BH)/\varrho_r]}{[(D - BH)/\varrho_r] + (A_0/\varrho_s)} \qquad (4)$$

where D is the deswollen weight; B is the fraction insoluble; H is the sample weight; ϱ_r, ϱ_s are the density of rubber and solvent, respectively; and A_0 is the weight of solvent absorbed.

2.3. Measurement of tear strength

Rectangular strips about 6 cm long, 1 cm wide and 0.15 cm thick were scored along a central line to a depth of about half of the thickness. A peel test as shown in Fig. 1 was used. The tearing energy was calculated with the help of the following relationship

$$G_c = 2F/w \qquad (5)$$

when F is the applied force and w the width of the torn path.

A few samples of carbon black filled SBR were tested using a restricted tearing test (Fig. 1). The steel foils (0.05 cm thick) were bonded to the rubber (~0.02 cm) on both sides with the help of a bonding agent (Chemlok 220, Hughson Chemical, USA).

In the case of polychloroprene, strength of the interface between two CR layers was measured according to the method shown in Fig. 1. The strength of the interface was calculated using the same relation (Equation 5), but w now being the width of the interface.

Tear strength was measured in an Instron fitted with a temperature cabinet capable of measuring from − 100 to + 200° C. Tear strength was also measured at different rates. The width of the torn path was measured using a travelling microscope.

3. Results and discussion

3.1. Tearing energy spectra of polyphosphazene rubber

Values of tearing energy G_c for samples crosslinked to different extents are plotted against the reduced rate Ra_T of tear propagation in Fig. 2. The results have been obtained at several temperatures in the range of − 25 to + 100° C and at several rates from 10^{-3} to 10^{-6} m sec^{-1}. Three different samples having small strain modulus (E) 50, 97 and 121 kPa have been used. All the tear rates have been multiplied by the universal WLF rate temperature shift factor a_T [10] so as to convert all the data to equivalent rates at the glass temperature. a_T is given by

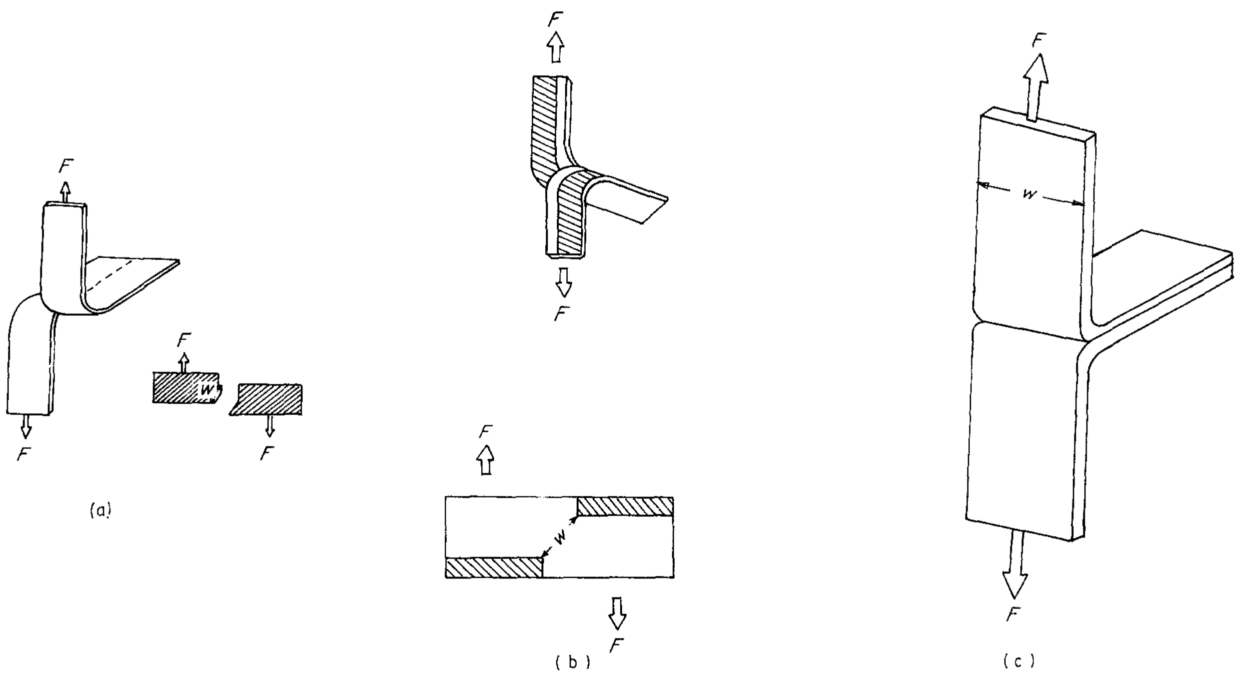

Figure 1 (a) Method of measurement of tear strength (b) tear strength measurement by restricted tearing test, (c) peel test using two elastomer layers.

$$\log a_T = \frac{-17.4\,(T - T_g)}{52 + T - T_g} \qquad (6)$$

It has been observed that the results at different temperatures and rates superpose to give a master curve. This may be called the tearing energy spectra of elastomers, since it gives an idea about the behaviour of elastomers over a wide range of rates and temperatures. It is also evident that the dependence of tear energy upon rate of tearing and temperature of testing arises from a simple viscoelastic energy dissipation mechanism. The strength at higher E values (121 kPa) is lower than that obtained at lower E values (97 and 50 kPa) over the whole tearing region. Lake and Thomas [11] point out that under the threshold conditions, tearing energy, G_{c0}, is proportional to molecular weight between crosslinks (M_c) or

$$G_{c0} \propto M_c^{1/2} \qquad 7(a)$$

and

$$G_{c0} \propto (1/E)^{1/2} \qquad 7(b)$$

since

$$E = \frac{3\varrho R'T}{M_c} \qquad 7(c)$$

according to the theory of rubber elasticity. Hence, a plot of $\log G_{c0} - \frac{1}{2} \log M_c$ against M_c should give a horizontal line while G_{c0} is independent of rate of tearing. Similar plot of $\log G_c - \frac{1}{2} \log M_c$ against the reduced rate of tearing for the time dependent tearing energy was attempted to get a universal master curve as if G_c were normalized with respect to M_c. Though qualitatively, the tear strength decreases with increase in E or decrease in M_c, a quantitative fit using the above concept is not possible. This indicates that the fractional tear strength being contributed from the viscoelasic energy loss mechanism at a given rate of tear is not constant. It depends on the degree of crosslinking, being greater for lightly crosslinked materials. This is again due to the fact that stress relaxation mechanisms at long times are most effective when the small strain modulus is small i.e. around the gel point due to relaxation of entanglements. Andrews [2] has observed that the tearing energy consists of two terms – a threshold value and a loss function. Of the two, the contribution of the loss function exceeds far more than that of the other term and hence the latter controls the value of G_c. Fracture energy of different rubbers does not reach a threshold limit even at 10^{-19} m sec^{-1} reduced rate in the present experiment.

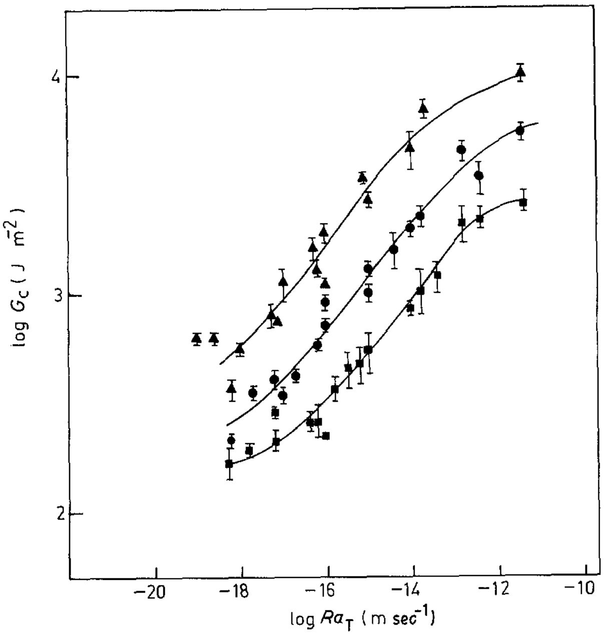

Figure 2 Tearing energy G_c against effective rate Ra_T of tear propagation at T_g for PNF samples crosslinked to various extents: (▲) 0.5% DCP (E = 50 kPa); (●) 1% DCP (E = 97 kPa); (■) 3% DCP (E = 121 kPa).

It was shown previously [8] that tear strength of PNF was much lower that that of cis-BR or cis-PI under threshold conditions. To know the behaviour under non-threshold conditions, samples of PNF, CR

TABLE II Comparison of strength of PNF, SBR and CR, measured at 103 ± 2° C test temperature

Sample No.	Elastic modulus, E (kPa)	Rate (m sec^{-1})	Cohesive strength, G_c (J m^{-2})
PNF	97	2×10^{-5}	210
SBR	100	2×10^{-5}	600
NR	300	2×10^{-5}	1400
CR	200	2×10^{-5}	1550

and SBR have been compared at similar elastic modulus (Table II). It is interesting to note that even under non-threshold conditions, the strength of polyphosphazene is lower than that of SBR or CR rubber, indicating the fact that the large mass per chain atom mentioned in Lake and Thomas theory [11] is also important in deciding the strength under normal conditions.

The tearing energy spectra (shown in Fig. 2) can be described by the left half of a Gaussian curve, as reported by Kelley *et al.* [6]

$$G_c = G_{c0} + P_1 \exp\left(-\frac{\log Ra_T - P_2}{W_D}\right) \qquad (8)$$

where W_D is related to half width of the curve; P_1 is the height of the peak above the base line; and P_2 is the centroid position.

The spectra could be divided into three zones: (a) Threshold zone: here the tearing energy value is independent of rate or temperature and depends on molecular parameters as guided by Lake and Thomas theory [11]; (2) Transition zone: the tearing energy increases very sharply with the increase in rate. Molecular relationship with all the fitting parameters (Equation 8) or the correlation between G_c and molecular parameters is not known till to-day; and (3) High tear energy zone: in this zone the tearing energy does not rise so sharply as in the transition zone, but values of tearing energy are quite high.

3.2. Tearing energy spectra of filled rubber

Tear strength of gum SBR rubber are shiftable on a master curve [12]. Preliminary experiments have been done on filled SBR using a special test as shown in Fig. 1b. The strength values obtained at different rates and temperatures are shifted to T_g of SBR using a WLF shift factor (Equation 6). The data points are on the same line (Fig. 3), indicating that the same viscoelastic energy loss mechanisms are operative for the filled materials, if the tear deviation is controlled. Tear strength of filled rubbers has been reported before by Greensmith [13] and it has been found that these values cannot be shifted onto a master curve. It can now be argued that the nature of crack propagation plays a role in determining the strength of filled rubber. It has been demonstrated before [14] that carbon black filled natural rubber or SBR shows knotty tearing which is responsible for the high strength of such materials.

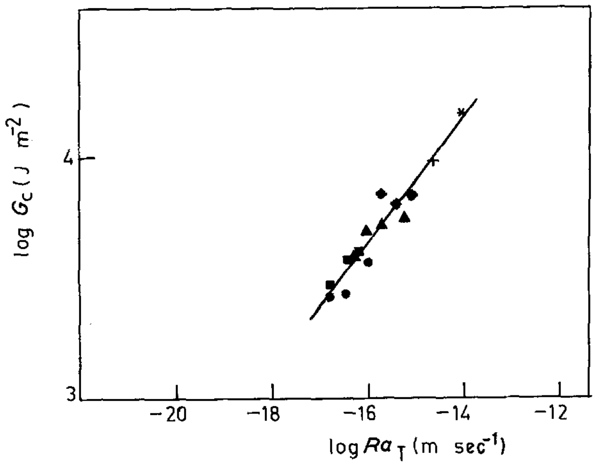

Figure 3 Tearing energy spectra of filled SBR. (+) 22° C; (*) 50° C; (◆) 75° C; (▲) 100° C; (■) 125° C; (●) 150° C.

3.3. Tear energy of polychloroprene rubber

Similar experiments have been done for the measurement of tear strength at different rates and temperatures for polychloroprene rubber crosslinked to different levels by either sulphur, oxide or mixed type of crosslinking system.

Tear strength of mixed crosslinked system (E = 2050 kPa) was measured under a wide variety of conditions and shifted to T_g using the same shift factor (Equation 6). In the case of neoprene, measured fracture energies were found not to obey the WLF superposition relationship, especially at low temperatures and high rates of tearing, indicating that the strain-induced crystallization along with the rough tearing may be important here. Similar observation has been made with a crystallizing, lightly crosslinked cis-1,4 polybutadiene rubber [4].

Three methods have been adopted to remove the crystallization and rough tearing effects.

(1) Partial swelling of the rubber network by a high boiling swelling liquid in order to nullify the effects due to cyrstallization.

(2) Use of a high level of crosslinking agent to achieve a high degree of crosslinking which will hinder the strain-induced crystallization, and

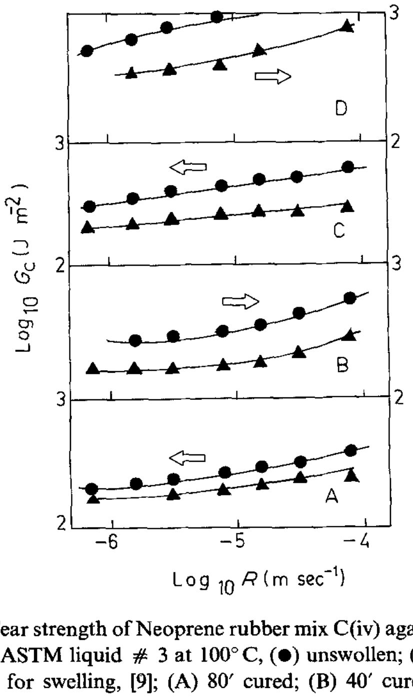

Figure 4 Tear strength of Neoprene rubber mix C(iv) against rate of tearing in ASTM liquid # 3 at 100° C, (●) unswollen; (▲) swollen (corrected for swelling, [9]; (A) 80′ cured; (B) 40′ cured; (C) 30′ cured; (D) 25′ cured.

TABLE III Tear strength, G_c(J m^{-2}) of Neoprene having high crosslink density as compared to one with normal crosslinking at 1.0 cm min^{-1} rate of tearing

Sample No.	Temperature (° C)					
	45	65	85	105	125	150
Neoprene (ZnO + S excess) Mix C(ii) in Table I (V_r = 0.54)	3200	1400	800	480	360	240
Neoprene (ZnO + S normal) Mix C(i) in Table I (V_r = 0.45)	2060	1250	930	650	500	260

(3) A special experiment has been done using the test piece shown in Fig. 1c, so that the fracture surface obtained will be smooth in nature. Two layers of partially crosslinked rubber (crosslinked to equal degree) are brought in contact with each other and then interlinked in contact for a further period of time so as to achieve the final degree of crosslinking. The force to separate the fabric-backed rubber layers was noted. The crosslink density at the interface was obtained from differences in crosslink denisty or elastic constant C_1 in the Mooney–Rivlin equation of the fully crosslinked samples and that of the partially crosslinked ones.

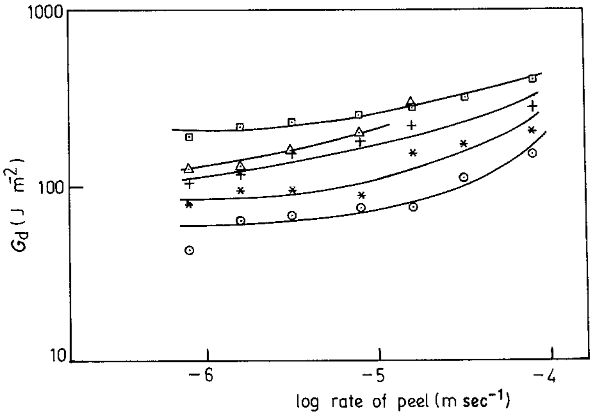

Figure 5 Work of detachment *Gd* at 100° C for interlinked layers of CR compound, C(iv) against rate of peel R. (□) G_c at 80′ cure at 140° C; (△) 50′ bonding; (+) 40′ bonding; (∗) 30′ bonding; (⊙) 20′ bonding.

It has been shown in Fig. 4 that tearing energy decreases when the samples are swollen with ASTM oil # 3. If the samples are swollen to a larger extent with tri-chlorobenzene (λ_{TCB} = 2.17 as compared to λ_{ASTM} = 1.32), the strength decreases further [9]. Although the viscoelastic effect would be minimized with the help of solvent, the effect of crystallization would still persist in presence of ASTM liquid. It has been observed earlier that the threshold strength of neoprene varies from 50 to 120 J m^{-2} over E values of 3200 to 370 kPa. Measurement at very high temperature and/or low rate of tearing yields an equilibrium value, which is far away from the threshold value [9].

The effect of using densely crosslinked neoprene on tear strength has been demonstrated in Table III. The amount of curing agent is almost double, but the values of tear strength are still high even at a high temperature (150° C), which may be ascribed to strain induced crystallization along with the rough fracture surface obtained on tearing. Hence, the third experiment has been designed to nullify the effect of the rough surface.

The fracture surface obtained by this experiment was smooth as compared to that obtained from the tearing experiment. As shown in Figs 5 and 6, the variations of interfacial strength with either rate or temperature are similar to those of tear strength. It decreases with increasing temperature or decreasing rate. An attempt has now been made to obtain the tearing energy spectra using the same WLF shift factor (Equation 6) and using data over a range of rates and temperatures. The data still do not fit onto one single curve (Fig. 7), especially at high rates and low temperatures. This behaviour is again due to strain induced crystallization which is present at these rates and temperatures. Hence, the present study indicates that tearing energy spectra could not be obtained for polychloroprene, probably due to the molecular parameter, i.e. crystallization at the crack tip per unit volume of the material, because the volume of materials deformed at the crack tip is different over the range of rates and temperatures.

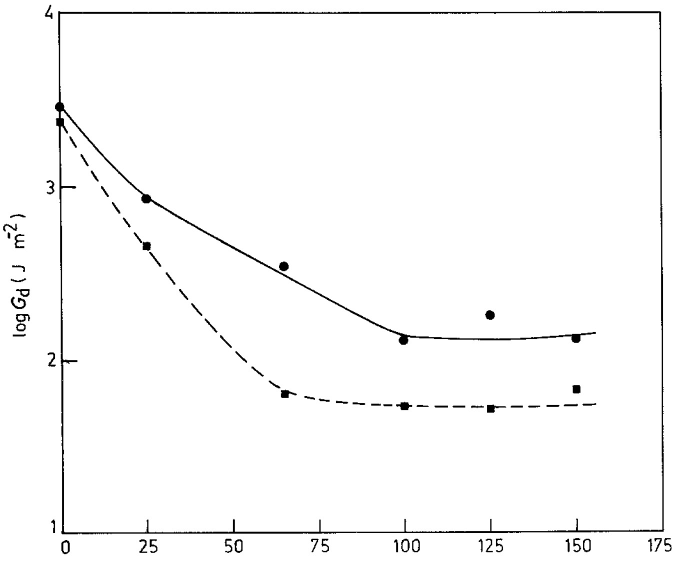

Figure 6 Work of detachment of interlinked layers of CR compounds against test temperature. Rate of peel was 8 μm sec^{-1}. (●) Mix C(iv), 50′ bonded in contact; (■) Mix C(iii), 10′ bonded in contact.

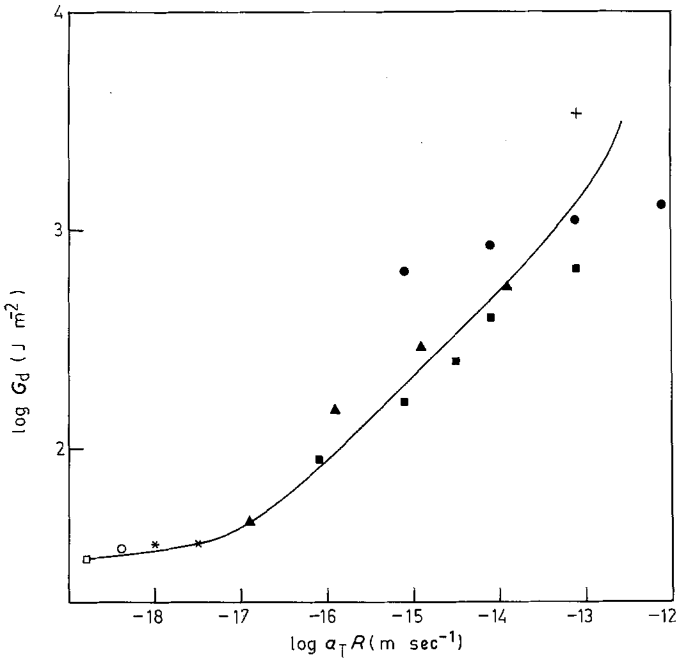

Figure 7 Detachment energy Gd against reduced rate Ra_T of crack propagation at T_g for neoprene rubber C(i). $\log a_T = [-17.4(T - T_g)]/[52 + (T - T_g)]$. (+) 0° C; (●) 25° C; (■) 45° C; (▲) 65° C; (x) 85° C; (∗) 105° C; (○) 125° C; (□) 150° C.

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