Effect of reptation on fracture mechanics of rubber networks

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End-linked hydroxyl-terminated polybutadiene containing unattached linear polybutadiene was used to study the effect of reptating species on the fracture mechanics of rubber networks. The concentration of reptating species in the networks ranged from 0 to 100%. The fracture mechanics of the networks was described using the critical strain energy release rate in mode III testing, i.e. the tearing energy. The tearing energy was measured at room temperature using a 'trouser' specimen at a strain rate spanning five logarithmic decades. When the strain rate was as low as $10^{-4}\,s^{-1}$, the tearing energy of the networks increased with reduction in reptating species. In this case the reptating species did not contribute to the tearing energy of the networks due to relaxation. Hence, the tearing energy increased with the number of crosslinked chains per unit volume in the networks. At a strain rate ranging from 10^{-3} to $10^{-1}\,s^{-1}$, the tearing energy of the networks was governed by local viscosity. The tearing energies of the networks containing various amounts of reptating species were superimposed to give a master curve based on the Williams–Landel–Ferry equation.

(Keywords: reptation; fracture mechanics; rubber networks)

INTRODUCTION

The most fruitful studies of the ultimate properties of polymeric materials have been those based on fracture mechanics. The energy release rate, G, is one of the parameters in fracture mechanics used to describe the ultimate properties of materials. The energy release rate is defined as

$$G = -\partial U/\partial A \qquad (1)$$

where U is the total elastic stored energy in a body and A is the area of the crack interface. In equation (1) the partial differential is used to exclude changes in U arising from causes other than propagation of the crack and the negative sign indicates constant deflection. The criterion for fracture is that the available energy in a body must equal or exceed the energy requirement in equation (1). Extensive verification of the fracture criterion in equation (1) was first given for the tearing of elastomers by Rivlin and Thomas[1]. In the case of the tearing test, i.e. mode III test, the critical energy release rate was conveniently named the tearing energy. It has been found[2,3] that at a given speed a crack in a rubber sheet propagated at a particular value of tearing energy, regardless of the geometry of the test piece and the system of stresses applied. The so-called 'trouser' specimen is especially used, since in steady tear (with inextensible legs) the work done is equal to the applied force, F, times the length of the new crack, Δc, while the new area is Δc times the thickness, t. In this case the tearing energy is

$$G = 2F\,\Delta c/t\,\Delta c = 2F/t \qquad (2)$$

Recently, many studies on the tearing of rubber have focused attention on the effect of additives on the tearing energy of rubber networks[4–6]. The additives here refer to fillers (e.g. carbon black), crosslinked bonds (e.g. S–S or O–O bonds) and reptating species (i.e. the secondary unattached linear component in a network). The various factors which influence the tearing energy include the threshold tearing energy[7], energy dissipation[8] and tear deviation[9].

So far most studies have focused on the reinforcement of carbon black in rubbers. To our knowledge there is only one paper discussing the effect of reptating species on the tearing energy of rubber networks[6]. However, the samples used in that study are too complex, for example, strain-induced crystallizable polyisobutylene butyl rubber and polyisobutylene chains attached to butyl rubber networks were used. Therefore, it is impossible to clarify the effect of the reptating species. In this work, a system of end-linked networks formed by hydroxyl-terminated polybutadiene (HTPB) containing unattached linear polybutadiene (ULPB) was used to study the effect of reptating species. The fraction of reptating species in the system ranged from 0 to 100%. The effect of reptating species on the tearing energy was discussed based on the change in relaxation of the reptating species and local viscosity.

EXPERIMENTAL

The molecular weights of the HTPB and ULPB, used as reptating species, are, respectively, 3800 and $1.8 \times 10^4\,g\,mol^{-1}$. The hydroxyl end group content in HTPB is 5.8×10^{-4} g eq. The ratios of *cis*-1,4/*trans*-1,4/vinyl for HTPB and ULPB are, respectively, 39/41/20 and 48/39/13. The ULPB was first dissolved in toluene for a few days and then mixed with HTPB quantitatively. The weight per cent of ULPB in the mixture was 100, 80, 60, 40, 20 and 0% (100% refers to neat linear polybutadiene and 0% to neat end-linked HTPB). The mixture was then reacted with a stoichiometric amount of tolylene diisocyanate (TDI) in an open Teflon dish. The reaction was

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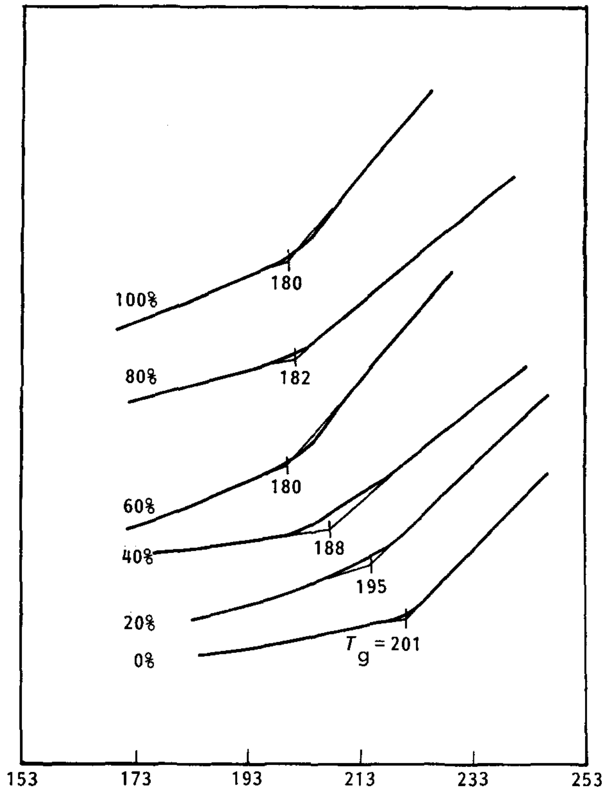


Figure 1 Thermal expansion behaviour of the end-linked HTPB containing ULPB (shown as a percentage). The single T_g suggests little phase separation

carried out at room temperature while solvent was slowly evaporated.

The tear test was carried out using trouser specimens at room temperature. Specimens of ~15 mm × 150 mm were cut from a sheet of crosslinked sample, which was backed with cloth to minimize deformation of the legs. Specimens with a thickness of ~2 mm were scored with a razor blade along the centre line to a depth of about one-third of the original thickness from both sides. The specimens were then torn by using an Instron Universal testing machine model 1121 at 10 rates spanning five logarithmic decades. The rate of crosshead was from 8.3×10^{-7} to 1.7×10^{-2} m s^{-1}. The strain rate is approximated as follows[10], although difficult to determine precisely at the tip of a tear:

$$\varepsilon = R/2t \tag{3}$$

where R is the crosshead rate and t the thickness of the unscored region of the specimens. Hence, G was calculated from the force required to propagate a tear according to equation (2).

A Rheovibron dynamic viscoelastometer (model DDV-II-EA) was used to determine the temperature-dependent storage Young's modulus at frequencies ranging from 3.5 to 110 Hz. Those moduli were then shifted to a master curve by the Williams–Landel–Ferry (WLF) equation.

The equilibrium moduli for the samples with various amounts of ULPB were determined from stress relaxation measurements. They were measured at room temperature and under a stretch ratio of 1.1 using a laboratory-made instrument. The modulus at a relaxation time of 10^4 s was taken as the equilibrium modulus because at that time the contribution of ULPB chains to the networks was quite small[11].

The glassy transition temperatures, T_gs, of the samples were measured at a heating rate of 5°C min^{-1} using a computerized Du Pont thermal mechanical analyser (model 943).

RESULTS AND DISCUSSION

The solubility parameters at 25°C for ULPB and TDI-linked HTPB were calculated as follows[12–14]:

ULPB

$$\delta = \rho(9.2394W_c + 9.1215W_t + 8.6215W_v) \tag{4}$$

TDI-linked HTPB

$$\delta = \rho[8.7150W_u + W_B(9.2394W_c + 9.1215W_t + 8.6215W_v)] \tag{5}$$

where W_B and W_u are the weight fractions of butadiene and urethane, respectively, and the subscripts c, t and v refer to *cis*-1,4, *trans*-1,4 and vinyl in the butadiene composition. The density, ρ, is taken as 0.889 and 0.890 g cm^{-3} for ULPB and TDI-linked HTPB, respectively, and their solubility parameters are 16.49 and 16.47 (kJ m^{-3})$^{1/2}$. This indicates that there is little phase separation in TDI-linked HTPB containing ULPB. The single T_g value shown in *Figure 1* and the previous work of Taylor *et al.*[15] also support this suggestion.

The dependence of the tearing energy on the amount of reptating species and on the strain rate is shown in *Figure 2*. An increase in strain rate is associated with a higher tearing energy. At moderate strain rate there are deviations in the curves of tearing energy *versus* strain rate, which are attributed to unstable tearing. In the whole strain rate range, the networks without reptating species give the highest tearing energy compared with networks containing various amounts of reptating species. The case of networks with reptating species is complex. At a low strain rate, e.g. at 10^{-4} s^{-1}, the lower the amount of reptating species, the higher the tearing energies. At a high strain rate, e.g. at 10^{-1} s^{-1}, the tearing energy of the network with 40% reptating species is higher than for other networks.

According to the theory of Lake and Thomas[16], the

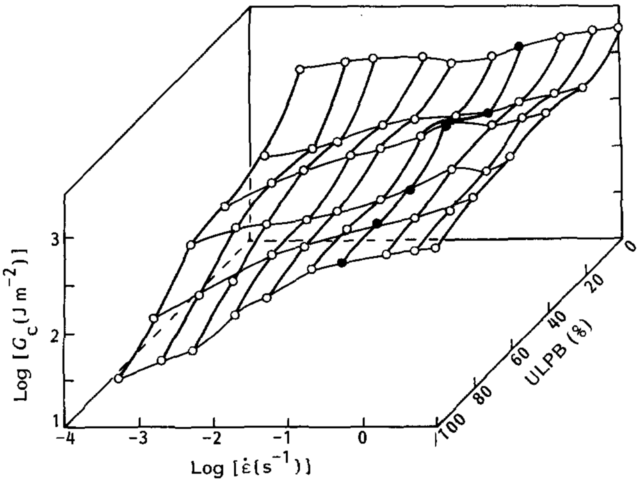


Figure 2 Room temperature tearing energy content of the ULPB–strain rate relationship for end-linked HTPB containing ULPB

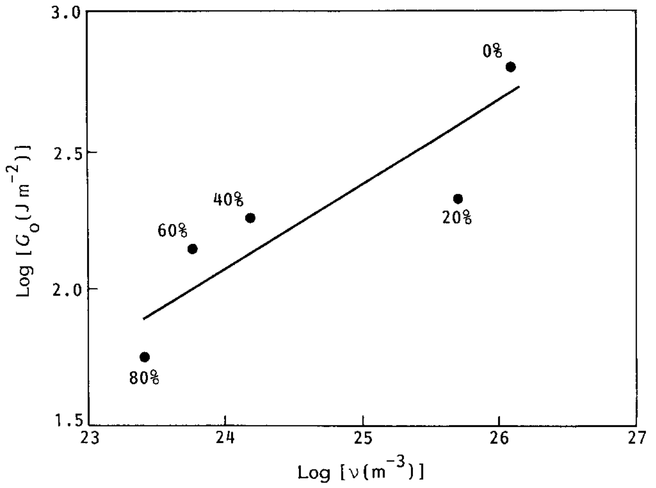


Figure 3 Room temperature tearing energy at a strain rate of $4.2\times10^{-4}\,\mathrm{s^{-1}}$. The value of G_0 increases with the number, ν, of crosslinked chains per unit volume for end-linked HTPB containing ULPB

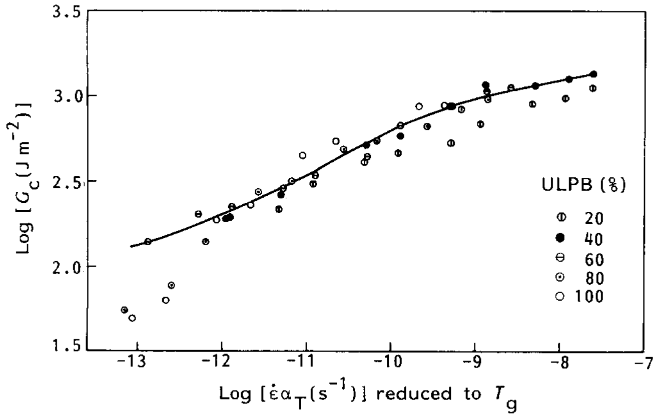


Figure 4 Master curve of room temperature tearing energy *versus* strain rate at the reference temperature of T_g for end-linked HTPB containing various amounts of ULPB

threshold tearing energy is determined by the number of chains crossing the fracture plane and the length of the chains. The complete theoretical description of the tearing energy based on generalized fracture mechanics[17] further points out that after taking into account the effect of crack velocity, temperature and applied strain, the tearing energy above the threshold value is also dependent on the number of chains crossing the fracture plane and the length of the chains. In the case of end-linked networks containing reptating species, when the strain rate is so low that the reptating species relax, the tearing energy is determined by the crosslinked chains. Since it is known that at a relaxation time of 10^4 s the contribution of reptating species to the modulus of the networks containing them is quite small[11], the tearing energy of end-linked HTPB containing ULPB at a strain rate of $4.2\times10^{-4}\,\mathrm{s^{-1}}$ increases with the number, ν, of crosslinked chains per unit volume (*Figure 3*). The number of crosslinked chains per unit volume in *Figure 3* was calculated from the equilibrium modulus, E_e, of the samples:

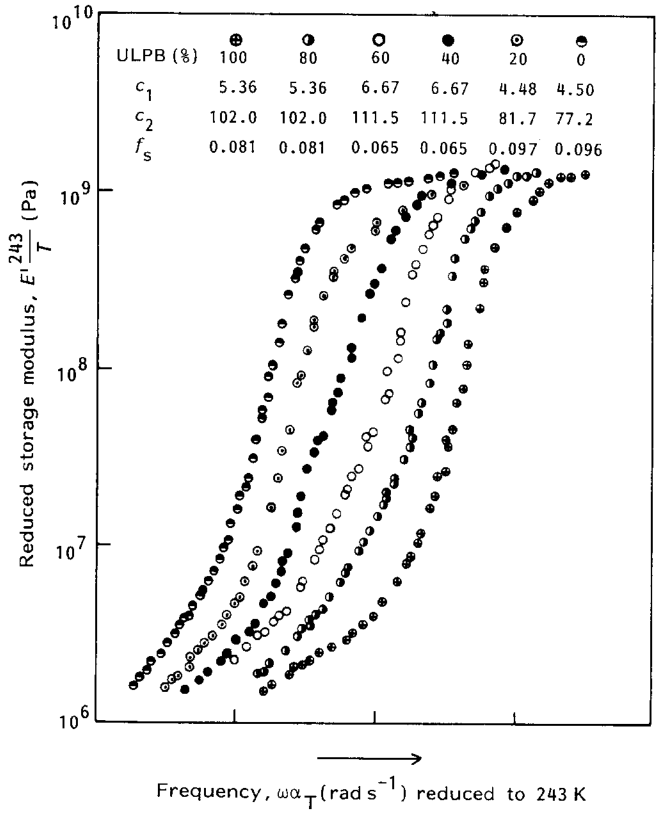
$$\nu = E_e/3kT \tag{6}$$

A double logarithmic plot of the tearing energy *versus* the number of crosslinked chains per unit volume (*Figure 3*) gives a slope of 0.3 rather than unity as predicted by the Lake–Thomas theory[16]. It is seen from *Figure 3* that when the strain rate is as low as the relaxation rate of the reptating species, the tearing energy of the networks containing reptating species is predominantly controlled by the content of crosslinked components provided that the length of crosslinked chains is constant.

The tearing energies of several elastomers measured at many temperatures have been superimposed to give a master curve as a function of the tearing rate[18]. In this study a master curve of the tearing energy *versus* the strain rate for networks containing various amounts of reptating species is shown in *Figure 4*. The shift factors in *Figure 4* were obtained based on C_1 and C_2 in *Figure 5* [from equations (28) and (29) in ref. 19]. In *Figure 4* there was no vertical shift corresponding to a correction to the tearing energy for the temperature dependence of the retractive force of the chains because the regions in which the vertical shift should be applied are not well defined[20].

It is seen from *Figure 4* that the tearing energies at higher strain rates are superimposed relatively well. This confirms that at these strain rates the tearing energy of the networks containing reptating species is dominantly controlled by local viscosity arising from the friction of sub-molecules. The scatter at the lower strain rate in *Figure 4* is not unexpected since there is no contribution of local viscosity from reptating species due to their relaxation.

The WLF coefficients C_1 and C_2 for the master curves of storage modulus *versus* frequency in *Figure 5* do not vary widely with the amount of reptating species. Thus, the reptating species influence the temperature dependence of the modulus primarily through its effect on T_g. It is



ULPB (%)	100	80	60	40	20	0
C_1	5.36	5.36	6.67	6.67	4.48	4.50
C_2	102.0	102.0	111.5	111.5	81.7	77.2
f_s	0.081	0.081	0.065	0.065	0.097	0.096

Figure 5 Master curves of storage modulus *versus* frequency with WLF coefficients C_1 and C_2; f_s is the fractional free volume at 243 K

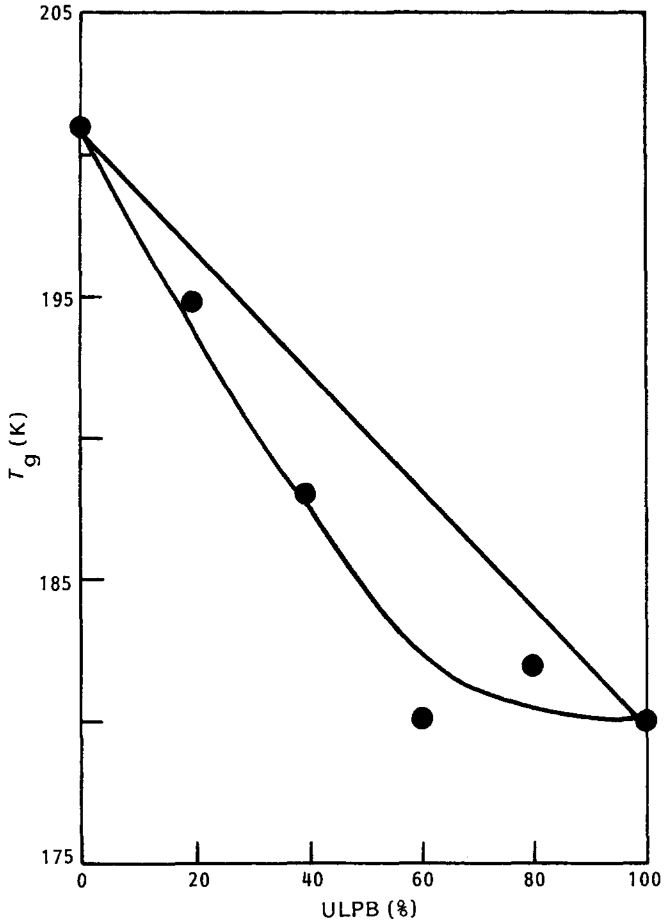


Figure 6 Non-linear dependence of T_g on the content of ULPB. The straight line was obtained using the additive law

shown in *Figure 6* that the dependence of T_g on the content of reptating species does not obey the additive law, which is described by the straight line in the figure. Addition of reptating species into networks depresses T_g, linearly at first and then somewhat concave upwards, which is similar to the polymer system diluted by small molecules[21]. This is attributed to the fact that the fractional free volume, f_s, is not quite additive[22].

The f_s at the reference temperature (243 K) in the master curves in *Figure 6* can be obtained from the WLF coefficient C_1 through the relationship[19]:

$$f_s = 1/2.303C_1 \qquad (7)$$

It is seen from the values in *Figure 5* that f_s does not monotonously change with the content of reptating species. The networks with a moderate amount of reptating species, i.e. 60 and 40%, have the lowest f_s which can be explained by the effect of entanglements. It has been reported[12] that in a network with a lower or higher content of reptating species, there are only entanglements between reptating species themselves or between reptating species and crosslinked components; in a network with a moderate amount of reptating species, both of these entanglements occur.

CONCLUSIONS

In the case of end-linked polybutadiene networks containing ULPBs, when the strain rate of tearing was as low as the relaxation time of the unattached linear species the tearing energy was determined by the crosslinking density. The tearing energies at high strain rate were superimposed relatively well, which indicated that they were controlled by local viscosity.

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