Cut Growth Properties of Styrene-Butadiene Copolymers

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Synopsis

The cut growth properties of styrene–butadiene block and random copolymers are considered in terms of the tearing energy theory. It is found that the value of T_0 (the minimum value of tearing energy below which no cut growth takes place in the absence of chemical effects) is far higher for a styrene–butadiene resin copolymer system with a high amount of bound styrene resin than for a conventionally vulcanized SBR elastomer. Similarly, it is shown that the value of T_0 for a butadiene–styrene block copolymer (thermoplastic rubber) is considerably reduced when the material is crosslinked. It is proposed that the value of T_0 is influenced by the hysteresial properties of the rubber.

INTRODUCTION

A number of papers[1-3] have been published during recent years dealing with the cut growth properties of vulcanized rubbers, in particular, natural rubber (NR) and styrene–butadiene rubber (SBR). Most of these studies have assessed the cut growth properties of elastomers by expressing the results in terms of the parameter, tearing energy T.

Tearing energy T is defined for a strained test piece containing an edge crack as follows:

$$T = -\frac{\delta U}{\delta A}\bigg)_e \tag{1}$$

where U is the total elastically stored energy in the test piece and A is the area of one side of the cut surface. The derivative must be taken under conditions that the applied forces do not move and hence do no work. The suffix e denotes that the differentiation is carried out at constant deformation. It thus represents the rate of release of strain energy as the crack propagates and can, therefore, be considered as the energy available to drive the crack through the material. It has been found that, if tear or crack growth measurements are expressed in terms of T, the results obtained from test pieces of different shapes can be correlated.[4]

The dependence of T on flaw size, applied force, or deformation can be deduced for various types of test piece.

For a test piece in the form of a strip with a small cut of length C in one edge, deformed in simple extension, the tearing energy is given by

$$T = 2KUC \tag{2}$$

where U is the strain energy density in the bulk of the test piece (i.e., away from the cut) and K is a slowly varying function of strain which has been determined empirically.[5]

This type of sample was used for the cut growth results described in this paper. It has the advantage that the stress-concentrating effect of both flaw size and deformation (which governs K and U) are expressed in terms of the single parameter T. The tearing energy theory has been successfully applied to tear,[6] cut growth, fatigue,[1-3] and to a limited extent to tensile failure[7] of conventional vulcanized rubbers.

The amount of cut growth per cycle (dc/dn) for a tensile test piece[1-3] containing an edge crack in repeated extension at a particular frequency depends on the maximum value of T attained in each cycle and can be expressed by an equation of the following form:

$$\frac{dc}{dn} = \frac{T^m}{G}. \tag{3}$$

The value of the constant G and the power m are dependent on the type of polymer.

Payne and Whittaker[8] have shown that the constant G can be related to hysteresial properties of the polymer in the case of vulcanized rubbers. James[9] has recently shown that the fatigue properties of unfilled elastomers can be treated as a viscoelastic process, and this is inferred in the theoretical work of Lake and Thomas.[10]

The minimum value of tearing energy (T_0) under which no cut growth takes place in the absence of chemical effects has always been considered a fundamental property of the material. Most of the previous investigations, however, have been on vulcanized rubbers which are relatively elastic at low strains. A theory[10] based on the chemical bond strengths in a polymer chain lying across the path of a crack satisfactorily explains the measured values of T_0 for vulcanized rubbers.

The theory does not make any allowance for hysteresial effects in the rubber although it was known some time ago that the value of T_0 for a styrene–butadiene rubber vulcanizate is increased by 50% when a reinforcing (fine-particle) carbon black[2] is added to it. This considerably increases the hysteresis in the rubber. Nonreinforcing fillers which have little influence on hysteresial properties were found[2] to have a negligible effect on the value of T_0.

Whittaker[11,12] has recently shown that the value of T_0 is considerably higher for linear polyurethane elastomers than for NR and SBR vulcanizates as shown in Figure 1. Polyurethane elastomers[13-15] have a segmented structure consisting of polyester or polyether soft segments

joined to minute, hard urethane segments.   These hard segments are only approximately 25 Å in diameter and act as very minute filler particles to produce a very effective "self reinforced" elastomer.   These polyurethane elastomers[11,16] have very high tensile strengths (approximately 500–600 kgf/cm^2), and consequently are highly hysteresial in nature.[11,17,18]   The latter point is demonstrated by the very broad distribution of relaxation times measured for polyurethane elastomers compared to other polymer systems.

The results shown in Figure 1 suggest that the value of T_0 could be affected by the hysteresial properties of the rubber.   In order to investigate this phenomenon further, some cut growth experiments were undertaken on both random and block styrene–butadiene copolymers, and the results of these investigations are reported in this paper.   These materials[19,20] are known to be highly hysteresial in character.

MATERIALS

Thermoplastic Rubber (Styrene–Butadiene Block Copolymer)

Shell Chemicals Grade TR3200 (now Kraton 3200) was used.   The chips were consolidated into sheets by pressing in a hot mold at 120–130°C
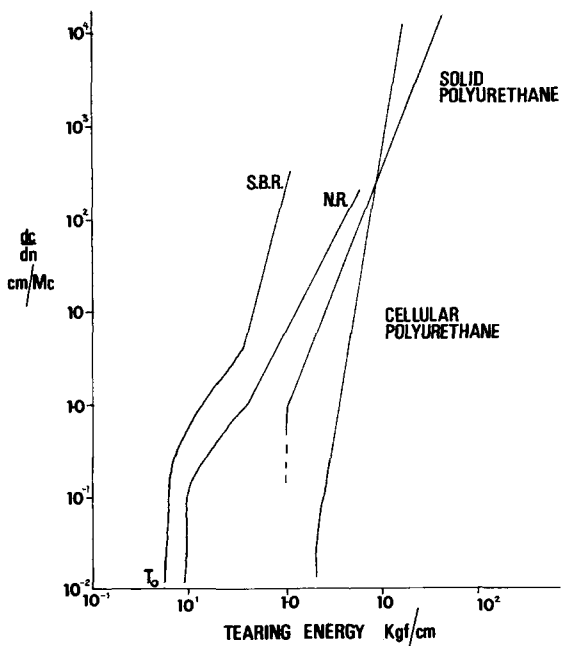

Fig. 1. Variation of rate of cut growth with tearing energy of NR and SBR (from published data[1–3]) and solid and cellular polyurethane[11,12] (results corrected to take account of tension set developed during course of test).

with subsequent cooling. The sheet material was milled on a two-roll laboratory rubber mill with rolls at 100–120°C and sheeted off at 0.75–1.00 mm thickness.

Stress–strain properties, determined both across and along the sheet, showed that there was substantial anisotropy in this material. It was, therefore, plied up, with alternate layers at 90°, to a suitable thickness to produce 3-mm molded sheets substantially free from anisotropy. The molding cycle was 5 min in a mold under pressure between steam-heated platens at 120–140°C, followed by 5 min with water cooling of the platens. The molding temperatures, in this range, had no significant effect on the modulus of the material.

These sheets, of which the physical properties are given in Table I, were used for the fatigue and cut growth experiments described below.

Crosslinked Thermoplastic Rubber

Dicumyl peroxide (as Dicup 40C, 40% active ingredient), 2% by weight, was added to the TR 3200 on a hot mill and the material subsequently molded and crosslinked at 150°C for 20 min. The physical properties are given in Table I.

Butadiene–Styrene Resin Rubber (Random Copolymer Blend)

A blend of two styrene–butadiene copolymers with ratios 23.5/76.5 and 86/14 was compounded with 0.2 phr stearic acid and 2.00 phr dicumyl peroxide (as Dicup 40C), and vulcanized for 20 min at 150°C. (The blend was a 50/50 by weight mixture of Polysar Krylene and Polysar SS250; the latter is a blend of two copolymers, one containing 23.5% bound styrene and the other 86% bound styrene, giving a styrene butadiene ratio 55/45.)

EXPERIMENTAL METHODS

Estimation of Crosslink Density of Crosslinked Thermoplastic and Butadiene–Styrene Rubbers

Swelling tests were carried out in toluene to equilibrium at room temperature, and the percentage of toluene absorbed by the rubber was calculated on the weight of the dried vulcanizates (to allow for extractable non-

TABLE I

	Tensile stress at break, kg/cm²	Elongation at break, %
Thermoplastic Rubber	105	650
Crosslinked thermoplastic rubber	70	135
Butadiene–styrene resin rubber	102	485

rubber ingredients). The crosslinked thermoplastic and high styrene–butadiene copolymer mixes gave values of 145% and 227%, respectively. The uncrosslinked thermoplastic dissolved in toluene.

Stress–strain measurements were carried out on the resin rubber; the stresses at strains up to 200%, allowing a relaxation time of 90 sec at each increment of strain, were recorded λ, the extension ratio, was calculated and the value of C_1 in the Mooney Rivlin equation obtained by plotting,

$$f[2A_0(\lambda - \lambda^{-2})]^{-1} = C_1 + C_2\lambda^{-1} \tag{4}$$

where f = force to extend sample of cross-sectional area A_0 to extension ratio λ. If ρ = density of rubber, R = gas constant, and T = absolute temperature, the crosslink density $C_1/\rho RT$ is calculated to be 0.62×10^{-4}.

From the volume fraction of rubber in the swollen jelly, v_r, and the C_1 value, the interaction constant of the Flory-Rehner equation, χ, is found to be 0.53 by using eq. (5):

$$-RT\ [\ln\ (1 - v_r) + v_r + \chi v_r^2] = C_1V\left(v_r^{1/3} - \frac{v_r}{2}\right). \tag{5}$$

Due to the high modulus and low extensibility of the crosslinked thermoplastic rubber, a satisfactory value of C_1 could not be obtained. Therefore, the above determined value of χ and the v_1 for the crosslinked thermoplastic rubber were used to calculate its crosslink density, which was found to be 1.9×10^{-4}. This value is open to question as a true chemical crosslink density because of the contribution of the styrene domains.

Cut Growth Measurements

The cut growth experiments were carried out in a similar manner to that described for polyurethane elastomers[12] using tensile strips of approximate dimensions 15 cm $\times$ 2.5 cm and about 2 mm thick. A cut about 0.5 mm long was made in the center of one edge of the sample with a razor blade, and the test piece was then clamped into position on a repeated extension machine, extended to a suitable strain, and cycled.

During the test, the cut length C was measured with a magnifying micrometer eyepiece, the strip being slightly strained to facilitate observations. Readings were taken at intervals corresponding to approximately 10% increases in cut length. Razor cuts tend to have very sharp tips, and a small amount of rapid growth often occurs before the tip of the cut roughens to its steady state. This period of initial rapid growth was usually ignored.

Cut growth tests were carried out at a number of extensions up to 150% maximum strain. For each graph, the rate of cut growth, dc/dn, was determined from the difference in cut length divided by the number of cycles between the two readings. This rate was then referred to the tearing energy calculated from the average of the two cut lengths and the $2KU$ value obtained from tensile stress–strain curves. The test was stopped when the cut reached about 20% of the test piece width as the theory is inapplicable

above this cut width.   It was possible, however, to cover a decade of tearing energy values with one test piece.   A different range of T was covered by cycling another sample to a different maximum strain, hence changing $2KU$.

The tearing energy values for polyurethane shown in Figure 1 were calculated in a similar manner to the previous investigations on vulcanized rubbers[1–3] (i.e., on the basis that U was measured from the stress-softened extension curve but making allowance for the changed dimensions of the testpiece due to permanent set effects).   In an earlier investigation,[12] it was found that little difference occurred in tearing energy values between this method and the more easily calculated basis used in this paper of taking the initial stress–strain curve and calculating U from the original dimensions of the testpiece.

EXPERIMENTAL RESULTS

The variation of cut growth per cycle with tearing energy for the random butadiene–styrene resin rubber (containing approximately 40% of styrene) is shown in Figure 2.   These results are compared in the figure with a conventional pure gum-vulcanized styrene–butadiene rubber (SBR) (23.5%
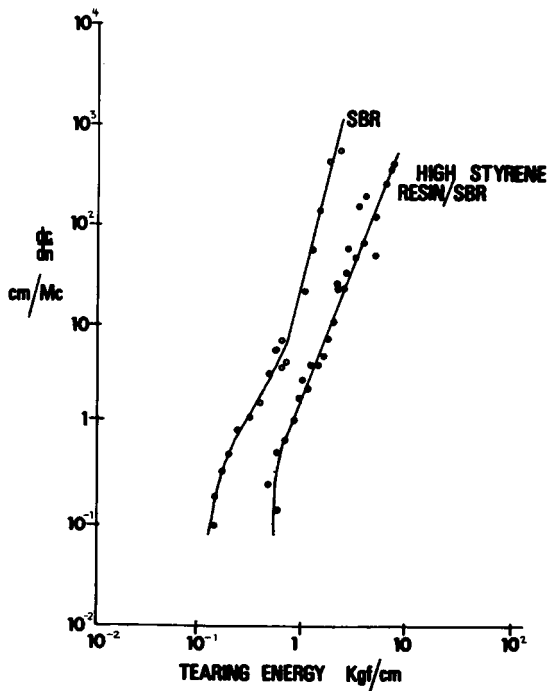

Fig. 2. Variation of rate of cut growth with tearing energy of random styrene–butadiene copolymer containing high amount of styrene resin and conventional vulcanized SBR elastomer (both results uncorrected for tension set developed during test).

styrene) calculated in the same manner (i.e., not taking account of set). It is clearly seen that the addition of a high styrene–butadiene resin to the rubber increases the value of T_0.   High butadiene–styrene resin rubber is known to be highly hysteresial in character.   This effect is found in practice as microcellular resin-rubber soling materials are commonly manufactured from a mix consisting of styrene–butadiene copolymers with a high styrene resin content, and these have excellent resistance to cut growth in wear.

The variation of rate of cut growth with tearing energy for the styrene–butadiene block copolymers (thermoplastic rubber) is shown in Figure 3. A number of investigations[19,20] have shown that the structure of thermoplastic rubbers consists of long, flexible polybutadiene chains attached randomly to hard polystyrene blocks of approximately 300 Å in diameter and hence are highly hysteresial in character.   It is interesting to note that the value of T_0 is high compared with conventional vulcanized rubbers and is similar in magnitude to polyurethane elastomers.   The cut growth properties of the crosslinked thermoplastic rubber are also shown in Figure 3.   It is seen that the introduction of crosslinks into the material and hence a reduction in its hysteresial properties considerably reduces the value of T_0.   This is thought to be due to the crosslinking preventing the formation of the typical thermoplastic rubber domain structure.[19]   The nonformation of this domain structure reduces the strength and hysteresis in the
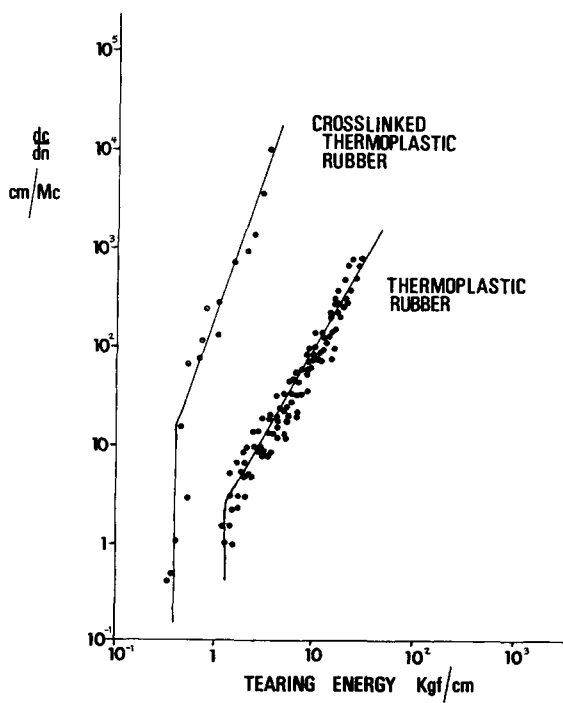

Fig. 3. Variation of rate of cut growth with tearing energy of thermoplastic rubber both uncrosslinked and crosslinked with 2.0 phr dicumyl peroxide.

material.   This effect is similar to that found previously[12] in polyurethane elastomers, as shown in Figure 4 where the cut growth properties of a linear cellular polyester polyurethane are compared with the results from a cross-linked cellular polyether polyurethane of the same density.   It is seen that the introduction of crosslinks, which in this case also prevent the ordered hard/soft segment domain structure being formed and reduce the strength and hysteresis of the material, considerably reduces the value of T_0.

CONCLUSIONS

This paper has considered the variation of the minimum value of tearing energy T_0 (Table II) under which no cut growth will occur in practice in elastomers in the absence of chemical effects for a number of polymer systems.   Earlier investigations[1-3,11,12] have indicated that increasing the hysteresis in a material by adding carbon black or by comparing the cut growth properties of vulcanized rubbers with highly hysteresial elastomers such as linear segmented polyurethanes increases the value of T_0.

These conclusions have been supported by the work in this paper where it has been shown that a highly hysteresial butadiene–styrene resin copolymer system with a high amount of bound styrene resin has a far higher
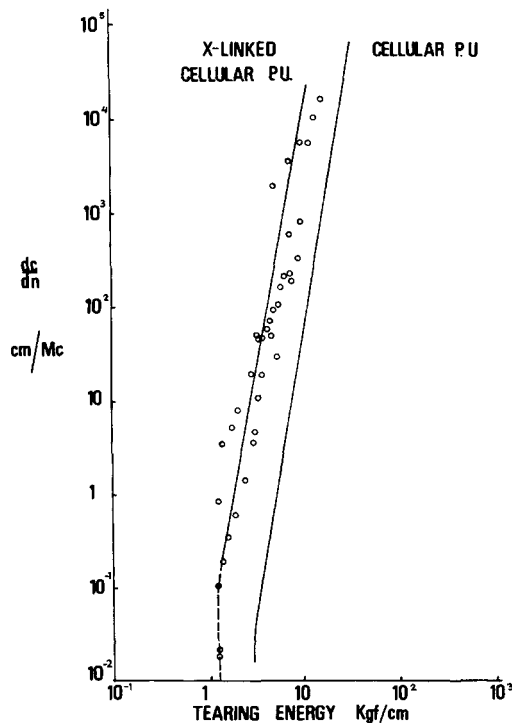

Fig. 4. Variation of rate of cut growth with tearing energy of linear cellular polyurethane compared to cellular crosslinked polyurethane (from previous investigation[12]).

TABLE II
T_0 Values (Uncorrected for Set)

Rubber	T_0, kgf/cm
Pure gum SBR vulcanizate	0.1
Solid polyurethane	1.0
Cellular polyurethane	2.0
Crosslinked cellular polyurethane	1.2
High-styrene resin SBR	0.6
Thermoplastic rubber	1.3
Crosslinked rubber	0.4

value of T_0 than a conventionally vulcanized SBR elastomer. Similarly, styrene–butadiene block copolymer (thermoplastic) rubbers have a large value of T_0, but this is considerably reduced when the elasticity in the materials is increased by crosslinking.

The early theory[10] for T_0 based on chemical bond strengths now require modifying to take account of the hysteresis contribution.

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