

Cut Growth and Fatigue Properties of Cellular Polyurethane Elastomers

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Synopsis

The tearing energy theory developed to describe the failure properties of vulcanized rubbers is shown to be applicable to the cut growth and fatigue properties of cellular polyurethanes. The effective inherent flaw size to initiate cut growth in the cellular polyurethane predicted from fatigue results has been found to be similar to the measured size of the largest pore in the material. The cut growth properties of the cellular polyurethane have been compared with solid polyurethane of the same type, crosslinked polyurethanes, and vulcanized rubbers. It is found that the minimum value of tearing energy (T_0) under which no fatigue failure occurs in the absence of chemical effects is far higher in polyurethanes than vulcanized rubbers. It is thought that this is due to the segmented structure of the polyurethane which has highly hysteretical tensile properties.

INTRODUCTION

A number of investigations have been undertaken in recent years into the tear,¹ cut growth, and fatigue²⁻⁴ properties of vulcanized rubbers. Most of the studies have assessed these failure properties by use of the parameter termed tearing energy (T).

The use of artificial leather materials such as poromerics^{5,6} which are permeable to water vapor has increased in the footwear industry during the last few years. Most of these materials either incorporate or are totally composed of a microporous polyurethane layer. Tensile measurements^{7,8} on cellular polyurethanes used in poromerics show that they have high strength, high hysteresis, and wide distribution of relaxation times when compared with vulcanized rubbers.

One of the most important properties of poromerics for their use in footwear is that they have a high resistance to cut growth when used in wear. This paper examines the cut growth and fatigue properties of two cellular polyurethanes used in poromerics in terms of the tearing energy theory and compares the results with those obtained from vulcanized rubbers.

CUT GROWTH

Tearing Energy Theory

Cut growth in polymers, like that in metals, begins at individual points or flaws where the stress is locally very high.²⁻⁴ The determination of the

TABLE I
Values of Parameter K^a

Strain	K	Strain	K
0	π	0.80	2.15
0.10	2.85	1.00	2.05
0.20	2.66	1.50	1.85
0.40	2.43	2.00	1.67
0.60	2.27	>2.00	1.67

^a After Greensmith.¹²

magnitude of the stresses at and around the tip of a flaw in a piece of highly strained rubber is a complex problem. It has been shown, however, for vulcanized rubbers that the consequences of this high stress concentration can be assessed by use of a simpler parameter known as tearing energy (T).

The concept of "tearing energy" was originally developed by Rivlin and Thomas⁹ to describe the tear behavior of rubber and is an extension of the classical theory for the strength properties of glass developed by Griffiths¹⁰ in 1920.

Tearing energy (T) is defined for a strained test piece containing a crack as

$$T = -\left(\frac{\partial U}{\partial A}\right)_e \quad (1)$$

where U is the total elastically stored energy in the test piece and A is the area of the two sides 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.¹¹

The dependence of T on flaw size, applied force, or deformation can be deduced for various types of test piece. For example, the tearing energy⁹ for the "trouser" tear test piece shown in Figure 1a is approximately given by

$$T = 2F/h \quad (2)$$

where F is the applied force and h is the test piece thickness.

For a test piece in the form of a strip with a small cut of length (c) in one edge deformed in simple extension, as shown in Figure 1b, the tearing energy is given by

$$T = 2KUC \quad (3)$$

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 empirically¹² and has values given in Table I for strains up to

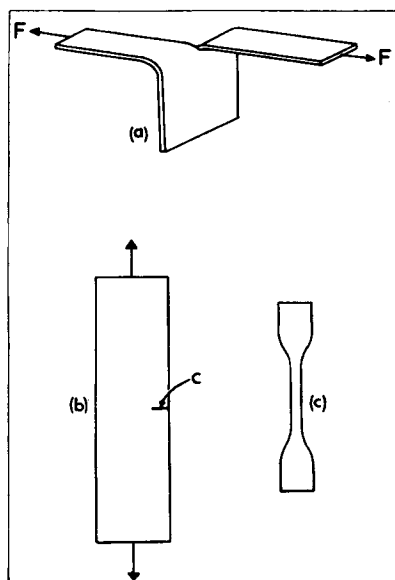


Fig. 1. Cut growth and fatigue test pieces: (a) "trousers" tear piece; (b) tensile strip (cut growth test piece); (c) dumbbell (fatigue test piece).

200%. It is assumed that this will be the same for the cellular materials considered in this paper.

This latter 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) is expressed in terms of the single parameter T .

The tearing energy theory has been successfully applied to tear,¹ cut growth, fatigue,²⁻⁴ and to a limited extent to tensile failure¹³ of conventional vulcanized rubbers. A recent paper by Payne and Whittaker¹⁴ has shown that the fatigue behavior of polymers is closely related to their hysteretical properties.

Little work has, however, been reported on the use of the theory to determine the failure properties of either polyurethane rubbers or cellular materials in general, and this particular problem is discussed in this paper.

Cut Growth Properties

It has been found for vulcanized rubbers that when the tearing energy exceeds a minimum value denoted by T_0 , which is discussed later, the amount of cut growth per cycle (dc/dn) for a tensile test piece²⁻⁴ containing an edge crack in repeated extension test 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:

$$\frac{dc}{dn} = \frac{T^m}{G} \quad (4)$$

where G is a constant. The actual value of the power m is unfortunately dependent on the type of polymer, and it was, therefore, necessary initially to determine this value of m for the cellular polyurethane.

Experimental Determination of Cut Growth Properties

The tensile stress strain curve for a linear polyester cellular polyurethane from a poromeric material of density 0.55 g/cc used in this investigation is shown in Figure 2 compared with the corresponding solid material from which the cellular material was manufactured. It was not possible, however, to obtain the solid material direct from the manufacturers, and hence it was necessary to dissolve the foam in a suitable solvent and cast the solid material while drawing the solvent off under heat.

The most noticeable feature of the stress-strain curves shown in Figure 2 is the large difference in modulus and strength between the solid and the foam material. An earlier investigation⁷ showed that the mechanical properties of the foam material could be derived from the solid polyurethane by use of a model consisting of struts of square cross section joined together to form a cubical lattice which was initially proposed by Gent and Thomas¹⁵ to explain the properties of natural rubber latex foam materials.

By graphically integrating the stress-strain curve in Figure 2 at various strains, and using published values¹² of K shown in Table I, the variation of $2KU$ with strain was determined, and this is shown in Figure 3.

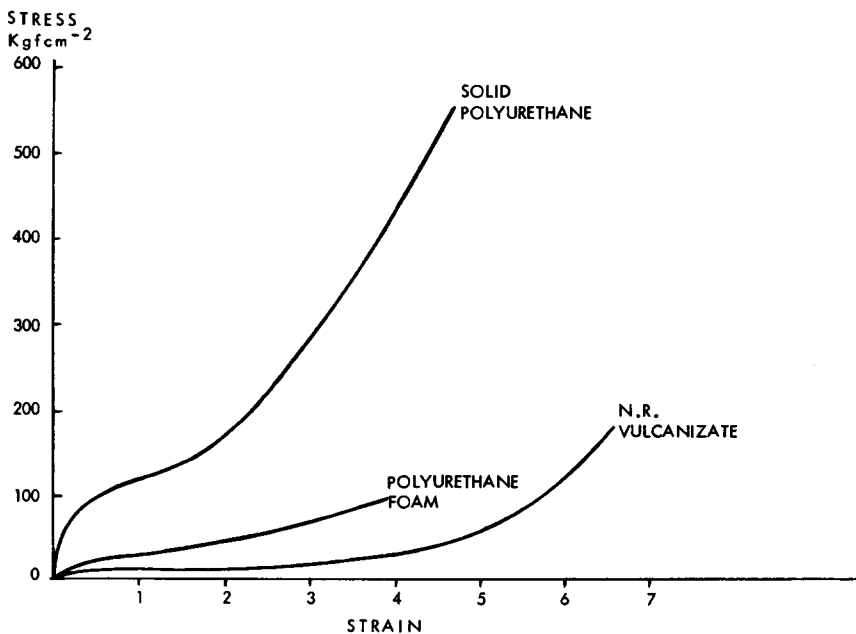


Fig. 2. Tensile stress-strain curves of cellular polyurethane and solid materials (cross-sectional area of foam taken as polymer including holes).

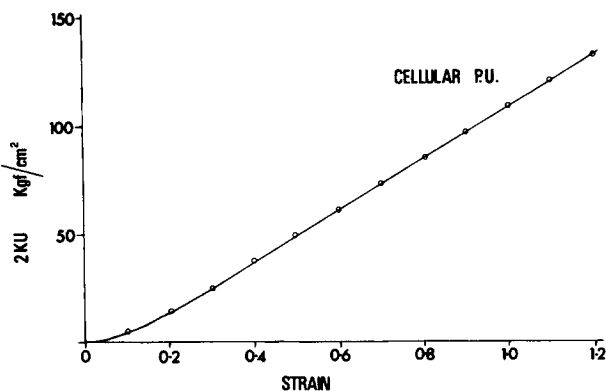


Fig. 3. Variation of $2KU$ with strain for the cellular polyurethane.

The cut growth experiments were carried out on tensile strips (shown in Fig. 1b) of approximate dimensions $15\text{ cm} \times 2.5\text{ cm}$ and about 2 mm thick. A cut about 0.5 mm long was made in the center of one edge of the sample by use of 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 length (C) was measured with a magnifying micrometer eye piece, the strip being slightly strained to facilitate observations. Readings were taken at intervals corresponding to approximately a 10% increase 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. A typical example of the variation of cut length with number of cycles is shown in Figure 4 for a test piece strained to 70%.

Several cut growth tests were carried out at a number of extensions up to 100% maximum strain for the polyurethane, and a number of graphs similar to Figure 4 were produced. 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 Figure 3 at the maximum initial strain of the cycle. 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 $2KU$.

No correction was made in any experiment for permanent set developed in the test piece. Provided that all the measurements were referred to the initial stress-strain curve of the material, the correction was not necessary. (This procedure differs slightly from that adopted in the published work on solid rubbers,²⁻⁴ where set is usually allowed for in both the cut growth and in the stress-strain measurements.)

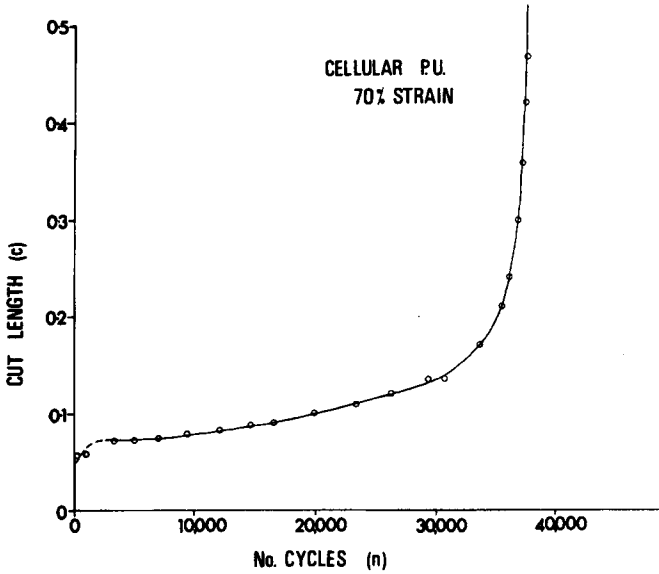


Fig. 4. Increase in cut length with number of cycles in a cut growth test for cellular polyurethane test piece cycled to 70% strain. Dotted line shows initial rapid growth due to razor cut.

The variation of the rate of cut growth (dc/dn) with tearing energy for the cellular polyurethane is shown in Figure 5. The lowest recorded value of tearing energy at which some cut growth was observed was 2.4 kgf./cm.

Cut growth samples put on the repeated extension machine at values of tearing energy less than 1.7 kgf./cm showed no cut growth after repeatedly being stretched for 3 million cycles. It was therefore assumed that the value of T_0 for the cellular polyurethane was approximately 2 kgf./cm.

Above T_0 , however, as shown in Figure 5, a relationship of the power 6 is obeyed between cut growth rate and tearing energy, and hence eq. (4) can be written for this material as

$$\frac{dc}{dn} = \frac{T^6}{G} \quad (5)$$

This power is much higher than is normally found in a solid rubbery polymer²⁻⁴ but can vary according to the cellular structure and degree of crosslinking, as discussed later.

In order to confirm whether eq. (5) was correct for the cellular polyurethane and secondly to obtain a value for the minimum flaw size C_0 at which cut growth occurs, conventional fatigue tests where no cuts were placed in the sample were undertaken, and the results of these experiments are described in the next section.

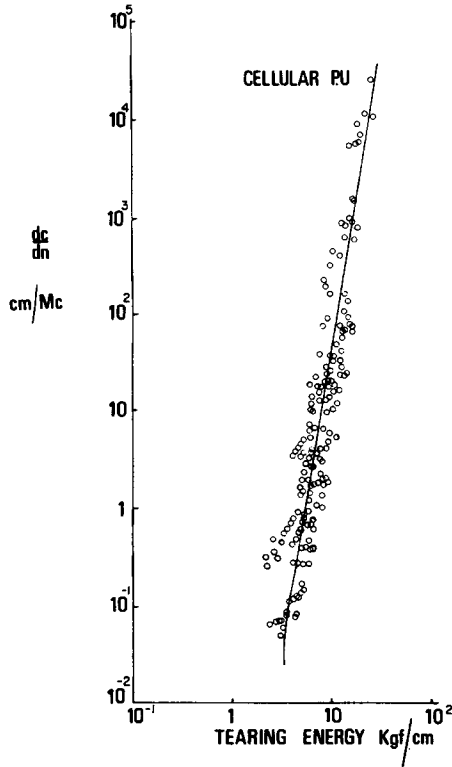


Fig. 5. Variation of rate of cut growth with tearing energy for cellular polyurethane material.

FATIGUE PROPERTIES

Theory

Failure of rubber test pieces containing no artificially inserted cracks can be deduced from the cut growth behavior³ by assuming that naturally occurring flaws of length C_0 are present in the rubber. In the case of a cellular material, C_0 would be expected to be in the same order as the largest pore size.

It is possible to eliminate from eqs. (3) and (5) the parameter T and hence form the differential equation

$$G \frac{dc}{dn} = T^6 = (2KU)^6 C^6. \quad (6)$$

This equation can be solved to give the number of cycles n to increase the crack from its initial value C_0 to C_1 :

$$n = \frac{G}{5(2KU)^6} \left(\frac{1}{C_0^5} - \frac{1}{C_1^5} \right). \quad (7)$$

When failure occurs the final crack length (C_1) is much larger than the initial flaw size (C_0), and hence the number of cycles to failure or fatigue life (N) is given by

$$N = \frac{G}{5(2KU)^6} \cdot \frac{1}{C_0^5} \quad (8)$$

Experimental Results

Dumbbell samples of the type shown in Figure 1c were cut from the microporous polyurethane foam used in the cut growth investigation. The samples with no inserted cuts were then placed on the repeated extension machine. The average number of cycles to failure for 12 samples repeatedly strained to the same initial strain was then recorded. The strains were calculated as a function of the original length of the parallel side center section of the dumbbell with no allowance being made for set in a similar manner to that described for the cut growth experiments. These experiments were repeated at a number of initial strains between 200% and 350%. The average values of fatigue life (N) are plotted as a function of strain in Figure 6.

In order to confirm that eq. (8) and the cut growth theory outlined are applicable to cellular polyurethanes of the type used in poromerics, the average number of cycles to failure of the 12 samples used at each strain was plotted as a function of $2KU$ on logarithmic scales as shown in Figure 7. The sixth power line drawn through the results in Figure 7 indicates that eq. (8) is obeyed.

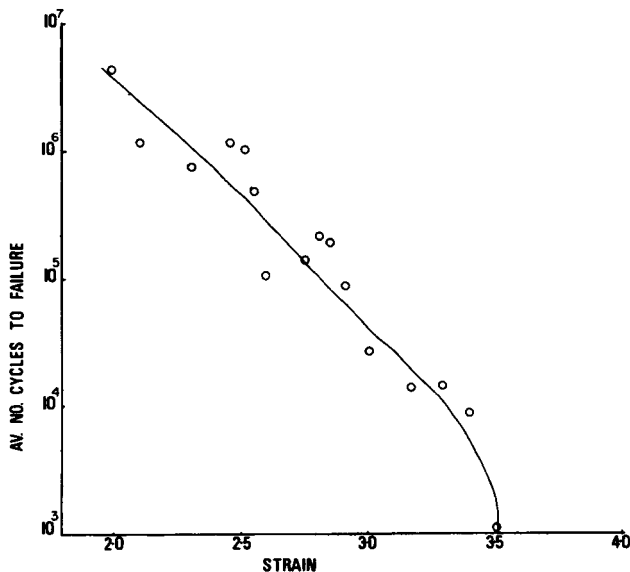


Fig. 6. Variation of fatigue life with strain for cellular polyurethane material.

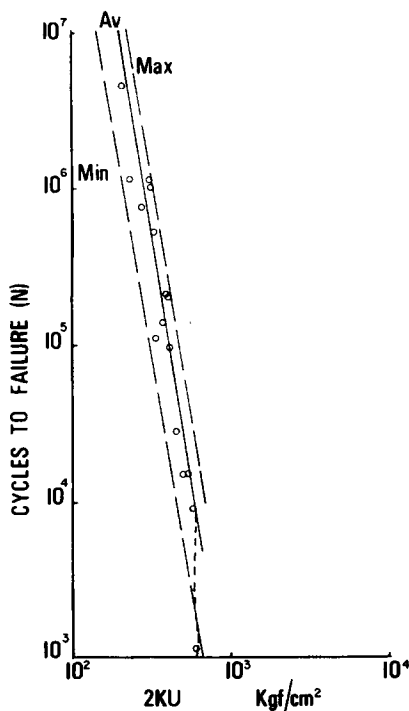


Fig. 7. Variation of average fatigue life of 12 test pieces with $2KU$ for cellular polyurethane material. Dotted lines indicate maximum and minimum fatigue life of 12 samples at each $2KU$ value.

From the intercept (N^*) of the line on the $2KU = 1$ ($\log 2KU = 0$) axis, it is possible to derive a value for the effective flaw size C_0 from

$$N^* = \frac{G}{5 C_0^5} \quad (9)$$

The value of $G = 2.86 \times 10^{10}$ cgs cycle units is obtained from the line shown in Figure 5. Using the value of $N^* = 4.6 \times 10^{20}$ from Figure 7, the value of C_0 is found to be 6.6×10^{-3} cm.

The scanning electron microscope photograph (Fig. 8) of the cellular polyurethane used in this investigation shows the average pore diameter to be approximately 2×10^{-3} cm; the scanning electron microscope photograph (Fig. 9), however, shows odd pores can be up to 2×10^{-2} cm in diameter. The calculated value for C_0 appears to be well within the range of cell diameters found in commercial cellular polyurethane materials.

The results shown in Figures 6 and 7 are the average number of cycles to failure for 12 samples of the microporous polyurethane foam at various strains, but the actual number of cycles for the first and last samples of the 12 to fail were very different. Lines representing the sixth power law have been included (dotted) in Figure 7 passing through the points for the first and last of the 12 samples to fail. From the respective N^* values,

TABLE II
Values of Effective Flaw Size C_0 from Fatigue Data

No. of cycles to failure	N^*	C_0 , cm
Max.	10^{21}	5.6×10^{-3}
Av.	4.5×10^{20}	6.6×10^{-3}
Min.	8×10^{19}	9.3×10^{-3}

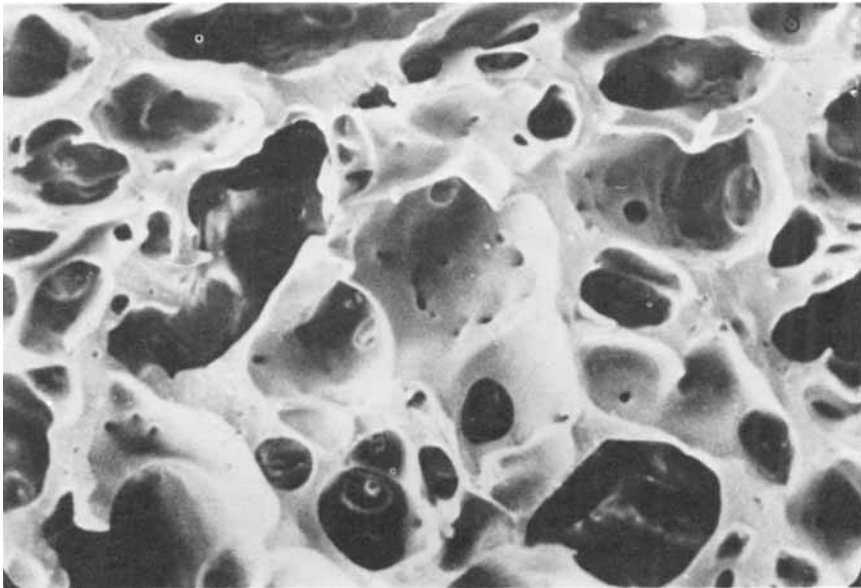


Fig. 8. Scanning electron microscope photograph of cellular polyurethane showing type of cell structure. Magnification 3200 \times .

an indication of the maximum and minimum flaw size could be obtained, and these are shown in Table II. These values of effective flaw size are, therefore, within the range of cell diameters found in cellular polyurethanes used in poromerics in practice.

It is concluded, therefore, that the tearing energy theory developed for vulcanized rubbers appears to be applicable to cellular polyurethanes of the type used in poromerics and that fatigue failure of these materials under repeated straining is due to cut growth from the largest hole in the sample. The fatigue behavior of cellular materials is, therefore, similar to that found in solid vulcanized rubbers, with the size of the largest hole in cellular materials taking the place of the size of natural flaws in solid rubbers.

COMPARISON WITH OTHER MATERIALS

Solid Polyurethane

In this section, the results for the cellular polyurethane discussed in the earlier part of the paper are compared with cut growth results for other

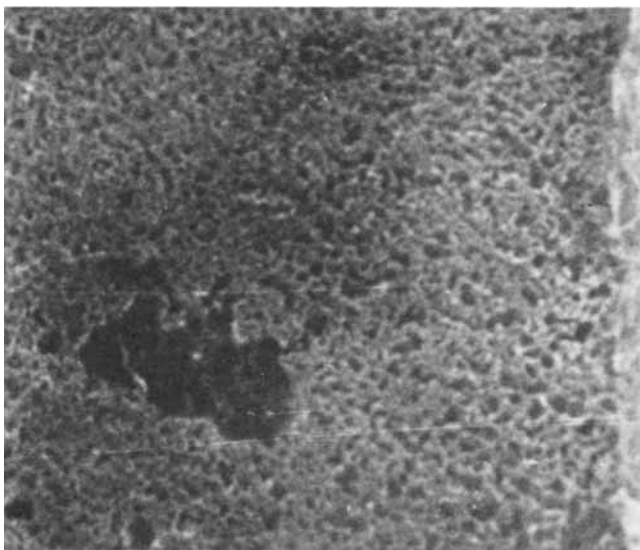


Fig. 9. Scanning electron microscope photograph of cellular polyurethane used in this investigation, showing that odd pores can be of the order of 10^{-2} cm. Magnification $100\times$.

materials. The variation of rate of cut growth with tearing energy for the solid polyurethane of the type used in the cellular material is shown in Figure 10. The line through the results for cellular polyurethane from Figure 5 is also dotted on Figure 10 for comparison.

The line drawn through the results for solid polyurethane has a slope above T_0 on the double logarithmic plot of $5/2$ to give the relationship

$$\frac{dc}{dn} (\text{solid}) = \frac{T^{5/2}}{G'} \quad (10)$$

which is different from that for the cellular polyurethane, eq. (5). This is observed by the difference in slope of the two lines in Figure 10. The higher slope in the case of the cellular polyurethane is to be expected because no allowance has been made for the effect of the holes. The cut growth process in solid materials is also different, as it is a continuous growth of a crack, whereas in the cellular polyurethane it is a repeated process of crack initiation through the polyurethane solid strands and rapid growth through the holes.

The lower value of limiting tearing energy (T_0) at which no cut growth occurs for the solid material is 1.5 kgf./cm, which is approximately the same as found for the cellular polyurethane in the earlier sections of the paper. The effect of generating a cellular structure in a polyurethane material used in poromerics appears to have little effect on T_0 but increases the rate of cut growth with tearing energy.

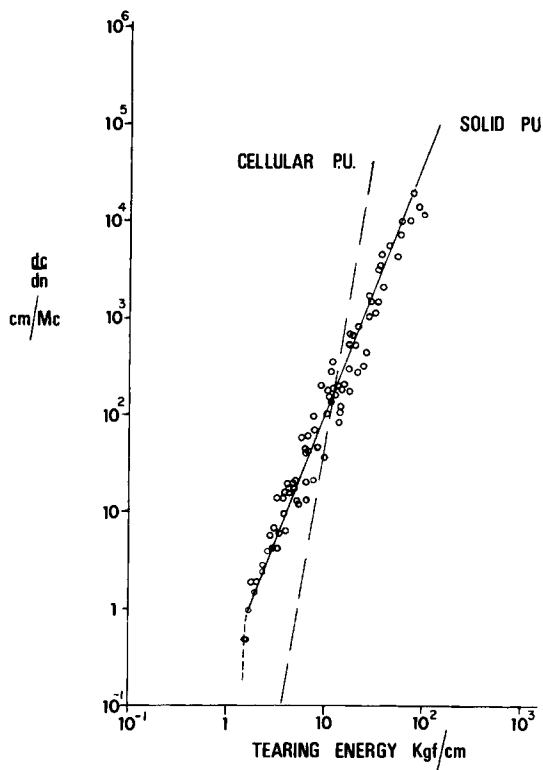


Fig. 10. Variation of rate of cut growth with tearing energy for solid polyurethane compared with results for the cellular polyurethane.

Effects of Chemical Crosslinking

Cut growth measurements were also made on a microporous polyurethane coating stripped from a fibrous-based poromeric. This particular polyurethane coating was different from the cellular material reported on above and the majority of poromerics in that it was based on a polyether polyurethane rather than a polyester, and secondly it was chemically cross-linked.

The variation of rate of cut growth with tearing energy is shown in Figure 11 compared with the cellular polyurethane used in the earlier investigations. Although a sixth power law between cut growth rate and tearing energy is still obeyed, the effect of chemical crosslinking is to decrease the value of T_0 .

Vulcanized Rubbers

The majority of the published²⁻⁴ cut growth test results which are expressed in terms of the parameter "tearing energy" have been confined to vulcanized rubbers such as natural rubber (NR) and styrene-butadiene rubber (SBR). In general, these test results have been calculated on a

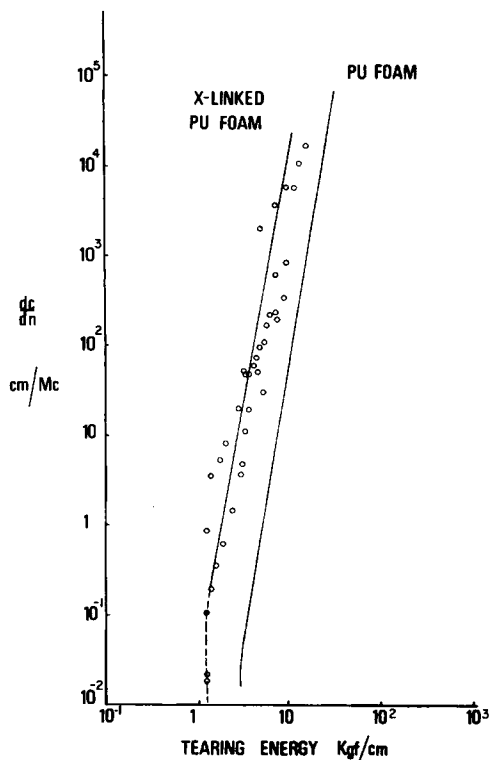


Fig. 11. Variation of rate of cut growth with tearing energy for chemically crosslinked cellular polyether surface layer from a fibrous poromeric with cellular polyurethane material used in earlier sections of paper.

slightly different basis from the measurements discussed in this paper. In the work on vulcanized rubbers, when calculating strain, account has been taken of tension set developed during an experiment. Tearing energy values in this paper are therefore higher than those normally quoted.

The cut growth results for the solid polyurethane elastomer were, however, recalculated to take account of set and in Figure 12 are compared with NR and SBR data from published papers.²⁻⁴ Although the slope of the rate of cut growth-tearing energy curve of polyurethane is similar to that of NR, indicating, as found in practice, that both materials are highly hysterical in character, the polyurethane is displaced along the tearing energy axis resulting in a far higher value for T_0 for polyurethanes than normally obtained for vulcanized rubbers.

CONCLUSIONS

The tearing energy theory which was derived for determining the failure properties of vulcanized rubbers has been shown to be applicable to the cut growth and fatigue properties of cellular polyurethanes used in poromerics.

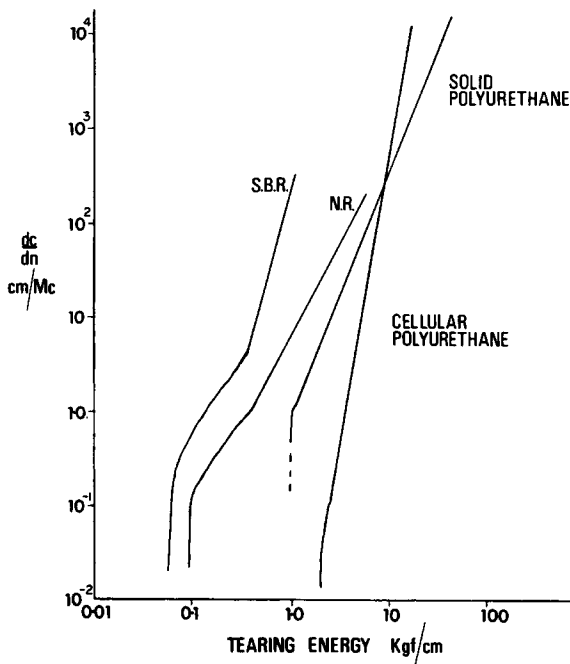


Fig. 12. Variation of rate of cut growth with tearing energy for NR and SBR from published data with solid polyurethane results from this investigation (results for polyurethane corrected to take account of tension set developed during course of test).

The effective inherent flaw size to initiate cut growth for the cellular material was found to be similar to the measured diameter of the largest pore. Similar effects have been shown to occur in polyurethane soling materials.¹⁶

The effect of making a cellular material from a solid polymer is shown to alter the relationship between cut growth and tearing energy but to have little effect on the value of T_0 . Chemically crosslinking the cellular polyurethane results in only a small decrease in the value of T_0 .

The most important factor from the results presented in this paper is the high value of T_0 for polyurethanes of this type when compared with conventional unfilled vulcanized rubbers.

Lake and Thomas¹⁷ have shown that it is possible to calculate from theory a value for T_0 for unfilled vulcanized rubbers by considering the energy required to rupture polymer chains lying across the path of a crack from the strength of chemical bonds. These calculated values agree within a factor of 2 with those found experimentally. Limited work has been published on the cut growth properties of filled vulcanized rubbers, but it has been shown³ that T_0 is increased by about 50% with the addition of a reinforcing carbon black filler to the rubber. Nonreinforcing fillers have been found³ to have little effect on the value of T_0 .

A number of published papers^{8,18-20} have appeared recently which discuss the structure of the type of polyurethanes being used in poromerics or textile coatings. These materials are made up of two segments, the soft segment consisting of long polyester or polyether flexible rubber chains joined to hard urethane segments. These hard urethane segments appear to be very small in size (approximately 25 Å diameter) and act as minute filler particles in the polyester or polyether rubber matrix and effectively reinforce the material to produce what has been termed a "self-reinforced" elastomer.

The dispersion of these urethane inclusions within the polyurethane elastomer is therefore excellent compared to normal carbon black-filled rubbers as it is done chemically. The minute size of the urethane segment compared with normal carbon black particles provides a high degree of reinforcement to the rubber matrix due to the large surface area of the effective filler particle. This leads to high hysteresis⁸ in the material, and it is thought that this gives rise to the high value of T_0 . Similar effects have also been shown in thermoplastic elastomers.²¹

The work described in this paper is part of a Ph.D. Thesis by the author to Loughborough University. The author is indebted to Dr. A. R. Payne (SATRA), Professor R. J. W. Reynolds, and Dr. C. M. Blow (Loughborough University) for their helpful advice and encouragement throughout the course of this work.

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Received September 20, 1973

Revised January 10, 1974