Threshold Tear Strength of Carbon Black Filled Rubber Vulcanizates

ANIL K. BHOWMICK,* and CHANCHAL NEOGI, *Rubber Technology Centre, Indian Institute of Technology, Kharagpur-721302, India,* and S. P. BASU, *Phillips Carbon Black Ltd., Durgapur-713201, India*

Synopsis

Threshold tear strength of unfilled and filled Natural Rubber (NR) and Styrene-butadiene Rubber (SBR) vulcanizates has been determined. Carbon black (N-220, N-375, N-330, N-550, and N-660) and china clay are used as fillers. Threshold tear strength varies from 80 J/m^2 to 1200 J/m^2. Threshold tear strength is found to be dependent on filler loading, nature of filler, and small strain modulus. The results are explained with the help of strain energy density, tear tip diameter, and the excess energy required to stress the many bonds before breaking one of them.

INTRODUCTION

Threshold tear strength of an elastomer is the tear strength when all the dissipative processes are minimized. Threshold values of tear strength of several gum vulcanizates have been reported earlier,[1-4] and the values lie between 50–200 J/m^2. They appeared to be approximately proportional to $E^{-1/2}$ where E is the small strain modulus. Lake and Thomas[1] predicted a dependence of threshold tear strength on molecular weight between crosslinks and this is found to be followed by a wide variety of elastomeric networks. The threshold tear strength is also dependent on the nature of the crosslink, being higher for polysulfidic networks. The threshold fracture of elastomers has been recently reviewed by Bhowmick.[5] In actual formulation, carbon black fillers are used for reinforcement. The introduction of carbon black filler may influence tear behavior in three ways: (a) by influencing the basic tear process, (b) by affecting crystallization, and (c) by contributing a strengthening structure. Greensmith[6] concluded that the main effect of carbon black is the contribution of a strengthening structure. The mechanism of reinforcement has been treated by several workers and summarized by Kraus,[7] Medalia,[8] and Gent.[9] It was concluded from these reviews that tear mechanism of carbon black filled rubber vulcanizates is not established.

This study reports on measurement of threshold tear strength of several carbon black filled natural rubber and styrene-butadiene rubber vulcanizates. A preliminary study on polybutadiene and EPDM rubber has been reported by Bhowmick et al.[9] These values were almost three to four times higher than the simplest unfilled vulcanizates under similar conditions.

* To whom correspondence should be addressed.

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EXPERIMENTAL

Mix formulations and vulcanization conditions are given in Tables IA and IB. In all cases, about 2 cm wide and 6 cm long test strips were cut from 1.5 mm thick vulcanized rubber sheets. Mixing and vulcanization were carried out as per usual procedure.

Measurement of Threshold Tear Strength

The threshold tear strength is attained when all dissipative processes are minimized. Measurements were therefore carried out at high temperature (125°C) and using samples swollen with mobile liquids. Toluene, xylene, heptane, benzene, and paraffin oil were chosen for this purpose. It may bé pointed out that Ahagon and Gent[3] measured threshold values using m-xylene and paraffin oil. Test strips were scored along a central line to a depth of about one half of the thickness, having the other half to be torn through as shown schematically in Figure 1. The tear strength G_o was calculated from the tear force as follows

$$G_o = 2\lambda_s^2 F/w \tag{1}$$

where λ_s is the linear swelling ratio of the sample and w is the measured width of the torn path (Fig. 1). The factor λ_s^2 takes into account the reduced number of network strands crossing a unit area in the swollen material. For the unswollen specimen λ_s becomes 1. Such a method was used earlier by other authors.[2-4]

Measurement of V_r and E

Volume fraction of rubber (V_r) in the swollen gel is calculated using the following relation

$$V_r = \frac{(D - FT)/\rho_r}{(D - FT)/\rho_r + A_o/\rho_s} \tag{2}$$

to characterize various filled vulcanizates. Values of small strain modulus E of unswollen and swollen samples were also found out in Zwick UTM 1445.

Measurement of Strain Energy Density

Strain energy density (W) was determined by measuring the area under the extension curve in Zwick UTM 1445 at various strain rates.

RESULTS AND DISCUSSION

Difficulties were experienced in determining the threshold values of tear energy of filled samples. Unlike gum vulcanizates of SBR or BR, threshold value could not be obtained from measurement at high temperatures (125°C). The values obtained for filled samples are unexpectedly high. At above this temperature, the samples degrade during conditioning. When the samples were swollen with paraffin oil and the measurement was carried out at 100°C, the observed values were lower (Table II). At a still higher temperature of testing, there is an odor of burnt oil. Hence, the samples were swollen in xylene, tolouene, heptane, and benzene, which give swelling ratio λ_s of vulcanizates larger than that when the vulcanizates were swollen in paraffin oil. The measurements were also carried out at lower temperatures. The values measured at various rates are as shown in Figure 2. A constant value is obtained. Ahagon and Gent used m-xylene for measurement of threshold tear strength of gum vulcanizates.[3] Figure 3 shows the force chart when the samples were swollen in various liquids as compared to the one for unswollen samples tested at 125°C. The force-chart clearly shows that the stick-slip process is greatly reduced as the swelling ratio is increased. Moreover, at lower swelling of vulcanizates, it is difficult to do the testing. Though it starts from the crack, it is difficult to control the tear path.

Values of tear strength of highly swollen samples were found to be much lower and comparable to those for the elastomeric materials reported earlier[4] and they did not vary with the nature of the swelling liquid after proper correction. These values have therefore been taken as the minimum values. These are reported in Table II.

Effect of Loading of Filler on Threshold Tear Strength of Carbon Black Filled Vulcanizates

The effect of loading of filler on the threshold tearing energy of NR and SBR vulcanizates filled with 10, 20, 30, 40, 50 phr of carbon black is shown in Figure 4. The threshold tear strength increases with the increase in loading of black for all the systems. The values lie between 150 J/m^2 to 730 J/m^2 for N330 filled NR vulcanizates. N375 filled systems have higher tearing energy. SBR vulcanizates show marginally lower threshold tear strength compared to NR vulcanizates at all loadings of filler. The tear strength varies from 360 J/m^2 for 10 phr N375 filled SBR to 1050 J/m^2 for 50 phr filled SBR. In all the cases these values are much higher than those for gum vulcanizates. There is approximately a five to tenfold increase in strength with 50 phr loading of filler.

The higher tearing energy with higher amount of carbon black under conditions when dissipative processes are minimized may be ascribed to higher strain energy density, higher excess energy for deformation of neighboring bonds, higher tear tip diameter and more colloidal tear deviation as discussed later. It is also interesting to see that the straight line passing through the data points for filled systems when extrapolated to the y-axis (tearing energy) gives a value of threshold tearing energy of gum rubber very close to the experimentally determined value. The higher strength of NR with N375 compared to N330 arises from better interaction of rubber and high structure of N375 black as reported earlier.[10]

It is also interesting to note that the slopes of the plot in Figure 4 are different. N375 black shows a steeper slope (21) than N330 (14). The empirical relation between the tear energy and loading of black may be described as follows: $G_{of} = G_{og} + m \times \phi \times G_{og}$, ϕ = volume fraction of filler, m = constant characteristic of the black, G_{og} = threshold tearing energy of corresponding gum compound, and G_{of} = threshold tearing energy of filled compound. The values of m are 45 $\pm$ 5 and 25 $\pm$ 5 for N375 and N330 respectively in NR. m can characterize a black. It has been pointed out before by Kraus that the slope of the plot between

TABLE IA
Formulations Parts per Hundred of Rubber (phr) and Characterization of Mixes

Mix	N (O)	N1 (N-375)	N2 (N-375)	N3 (N-375)	N4 (N-375)	N5 (N-375)	N5 (N-220)	N5 (N-330)	N5 (N-550)	N5 (N-660)	N5 (China clay)
NR	100	100	100	100	100	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2	2	2	2
N-375	—	10	20	30	40	50	—	—	—	—	—
N-220	—	—	—	—	—	—	50	—	—	—	—
N-330[a]	—	—	—	—	—	—	—	50	—	—	—
N-550	—	—	—	—	—	—	—	—	50	—	—
N-660	—	—	—	—	—	—	—	—	—	50	—
China clay	—	—	—	—	—	—	—	—	—	—	50
Process oil	—	6	6	6	6	6	6	6	6	6	6
PBNA[a]	1	1	1	1	1	1	1	1	1	1	1
Paraffin wax	1	1	1	1	1	1	1	1	1	1	1
CBS[b]	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Sulfur	2	2	2	2	2	2	2	2	2	2	2
Optimum cure time at 150°C (min)	11.2	10.7	10.2	10.2	10.1	10.1	10.1	10.1	10.0	10.2	11.7
Tensile strength (MPa)	22.5	23.3	25.9	26.6	26.1	24.6	24.3	23.8	21.6	22.8	18.6
Elongation at break (%)	1100	790	760	690	620	500	480	500	480	600	840

[a] Variation of loading of N-330 is same as N-375 but only one composition is given.
[b] Supplied by IEL Limited, Rishra, India. PBNA, Phenyl-beta-napthylamine; CBS, Cyclohexyl benzthiazyl sulphenamide.

TABLE IB
Formulations Parts per Hundred of Rubber (phr) and Characterization of Mixes

Mix	S (O)	S1 (N-375)	S2 (N-375)	S3 (N-375)	S4 (N-375)	S5 (N-375)	S5 (N-220)	S5 (N-550)	S5 (N-660)	S5 (China clay)
SBR	100	100	100	100	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2	2	2
N-375	—	10	20	30	40	50	—	—	—	—
N-220	—	—	—	—	—	—	50	—	—	—
N-550	—	—	—	—	—	—	—	50	—	—
N-660	—	—	—	—	—	—	—	—	50	—
China clay	—	—	—	—	—	—	—	—	—	50
Process oil	5	5	5	5	5	5	5	5	5	5
CBS[a]	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Sulfur	2	2	2	2	2	2	2	2	2	2
Optimum cure time at 150°C (min.)	28.5	25.0	25.0	24.5	24.5	24.5	26.0	24.5	25.5	30.2
Tensile strength (MPa)	2.0	4.0	9.6	19.5	21.0	22.6	23.1	16.2	13.8	3.3
Elongation at break (%)	400	390	470	530	480	450	445	450	470	660

[a] Supplied by IEL Limited, Rishra, India.

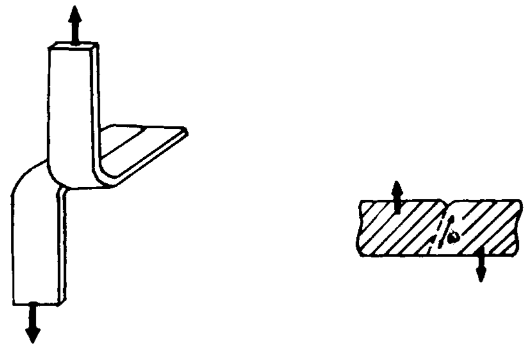

Fig. 1. Measurement of tear strength of rubber.

V_{ro}/V_{rf} against $\phi/1\text{-}\phi$ characterizes a carbon black. For example, a value of 1.17 indicates N330 black in NR.[11]

Effect of Nature of Filler on Threshold Tear Strength at 50 phr Loading

The influence of the nature of filler on threshold tear strength of NR and SBR vulcanizates at 50 phr loading is shown in Figures 5 and 6. For comparison, clay-filled vulcanizates were also tested. It is observed that clay shows the minimum value in the series and for SBR vulcanizate this value is comparable to that for gum compound. With the decrease in particle size of the black filler, the threshold tear strength increases systematically. NR and SBR vulcanizates show similar strength for various sizes of filler. It may be mentioned that a similar trend is followed at room temperature testing for unswollen samples. The relative increase in strength with increase in surface area of filler at constant loading is due to increased polymer–filler interaction. Figure 7 shows a plot of V_{ro}/V_{rf} against $\phi/1\text{-}\phi$ which explains above point. Hence, carbon black reinforces rubber even under threshold conditions. In previous studies by Bhowmick et al.,[4] the value reported for N765 filled BR vulcanizates was also shown to be higher than that for the gum compound and it was described that an extra energy dissipating mechanism is operative for filled vulcanizates. With the present systems this could be confirmed and the filler which shows better interaction (proportional to lower particle size) with rubber shows higher tearing energy.

Extension of the Lake and Thomas Concept

Lake and Thomas[1] pointed out that many bonds on a fracture plane must be stressed in order to break one of them. Thus, when the molecular length between two points of crosslinking in a gum vulcanizate is greater, there will be larger number of bonds that should be stressed. But fewer of them will cross the fracture plane. Similarly the higher density of crosslinking will allow for a larger number of molecules on the fracture plane and a lesser number of bonds to be stressed. The net effect is a dependence of threshold strength on the molecular length. A very similar concept can be extended to the carbon black filled rubber vulcanizates. The stronger interaction between rubber and filler will increase the anchorage points along with the usual crosslink sites. In ad-

TABLE II
Values of Tear Strength of Gum and Filled NR and SBR

Sample code	Tearing energy (J/m^2), unswollen sample tested at 125°C	Tearing energy (J/m^2), paraffin oil swollen sample tested at 100°C	Tearing energy (J/m^2), xylene/toluene swollen sample tested at 25°C (after correction)	Tearing energy (J/m^2), heptane swollen sample tested at 25°C (after correction)	Tearing energy (J/m^2), benzene swollen sample tested at 25°C (after correction)
N(O)	1200	950	120	—	—
N1(N-375)	—	1437	410	470	430
N2(N-375)	—	2670	560	—	—
N3(N-375)	18000	4100	700	790	710
N4(N-375)	—	4745	950	—	—
N5(N-375)	34000	5650	1100	—	—
N5(China clay)	3000	—	440	—	—
N1(N-330)	—	970	150	—	—
N2(N-330)	—	—	340	—	—
N3(N-330)	—	3620	540	—	—
N4(N-330)	—	—	—	—	—
N5(N-330)	—	—	730	—	—
S(O)	690	—	80	—	—
S1(N-375)	—	—	360	430	400
S2(N-375)	—	—	500	—	—
S3(N-375)	1100	—	600	660	620
S4(N-375)	—	—	860	—	—
S5(N-375)	1500	—	1060	—	—
S5(China clay)	800	—	120	—	—

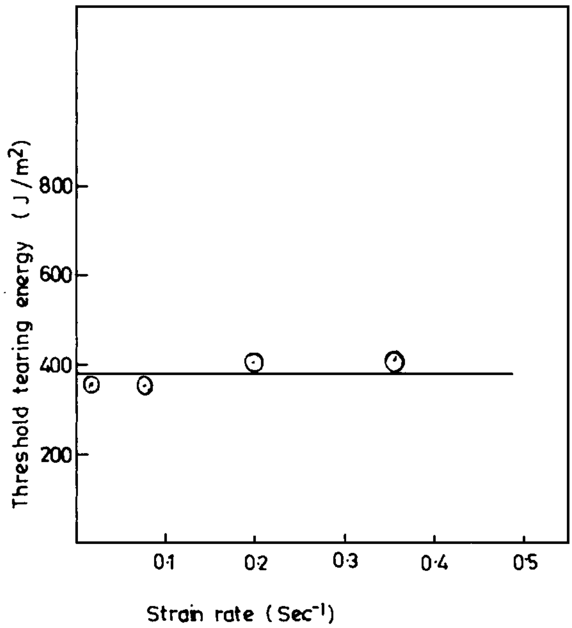

Fig. 2. Plot of threshold tearing energy vs. strain rate ⊙: N2 (N-330).

dition to this effect, since carbon black particles are aggregate in structure, and bond between rubber and filler is mainly physical in nature, any force imposed on the system will deform the aggregates and detach the carbon black from polymer molecules before actual rupture of the main chain. The combined effect of rubber–filler interaction, breakdown of carbon black structure, and deformation of rubber on threshold fracture energy is complicated unlike that of gum compound. However, the addition of carbon black increases the intrinsic strength of filled vulcanizates in the absence of an energy dissipating mechanism.

Relation between E and G_o

G_o, the threshold tear strength has been plotted against E for all the vulcanizates (Fig. 8). It is interesting to note that as E increases, the value of threshold tear strength increases for NR or SBR. In the earlier experiment with gum vulcanizates, it has been found that an increase in E reduces the value of G_{og}, the threshold tear strength. Hence the increased value of G_o due to increased loading may be due to enhanced colloidal tear deviation and more resistance to tearing. It is perhaps more appropriate to use a relationship involving the tear tip diameter (d), strain energy density (W) and tearing energy (G_o) as pointed out by Thomas.[12]

$$G_o \approx d \times W \tag{3}$$

for incision with a semicircular tip. Table III shows the value of G_o and W and d for various filled systems. It is observed that for SBR vulcanizates there is an increase in G_o with W at all loadings up to 50 phr, whereas for NR, the increase holds good up to 30 phr beyond which strain energy density decreases

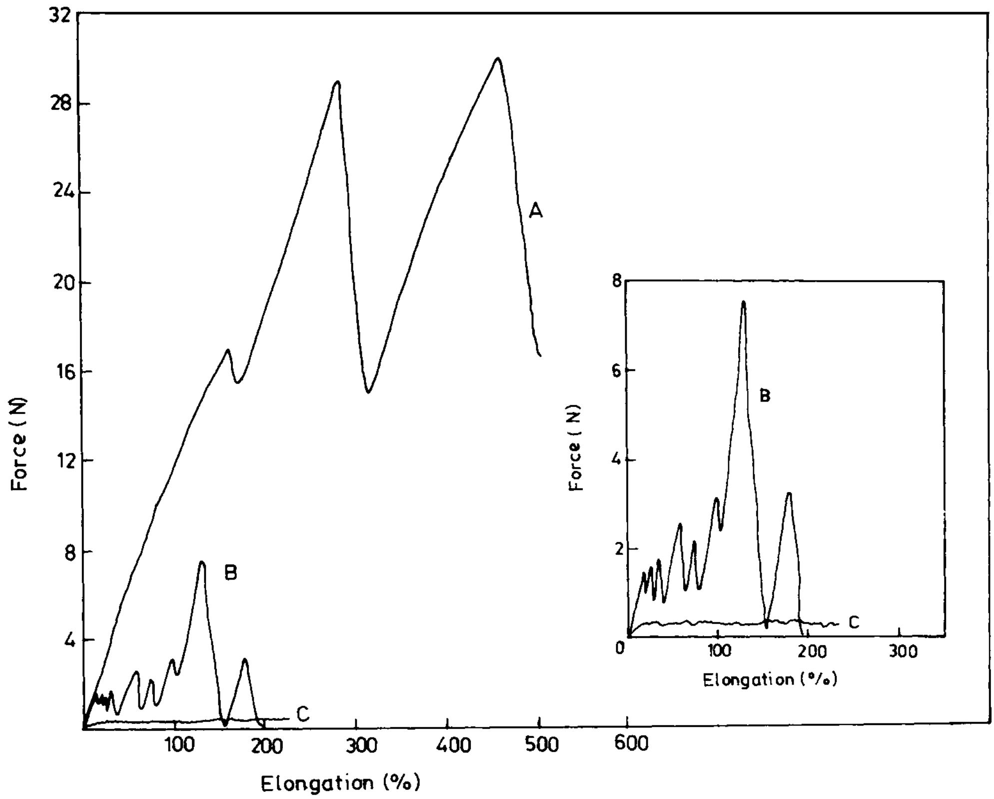

Fig. 3. Force chart of unswollen and swollen N5 (N-375). (A) Unswollen sample tested at 125°C. (B) Paraffin oil swollen sample tested at 100°C. (C) Xylene swollen sample tested at 25°C.

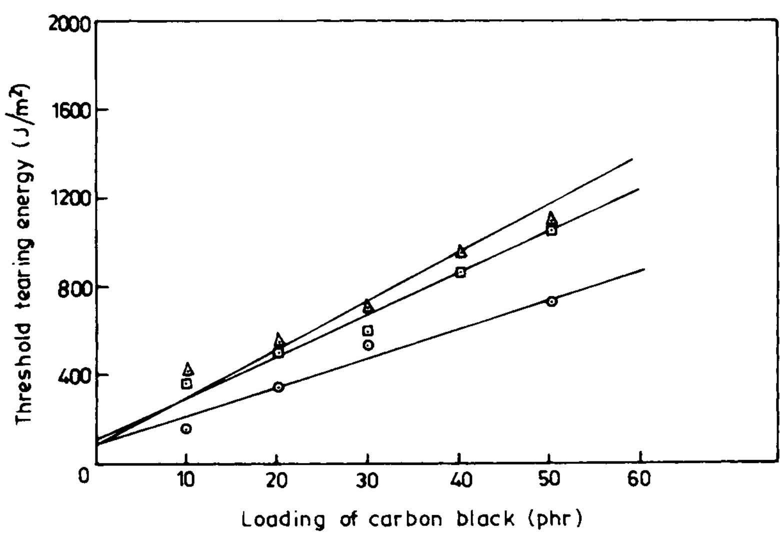

Fig. 4. Effect of loading of carbon black on threshold tear strength. (⊙) NR/N-330, (△) NR/N-375, (⊡) SBR/N-375.

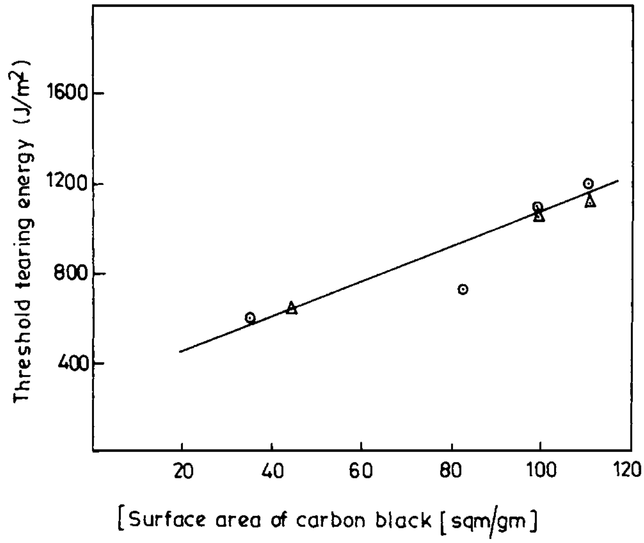

Fig. 5. Effect of surface area of carbon black on threshold tear strength. (⊙) NR/N-375, (△) SBR/N-375.

and tearing energy increases. By dividing G_0 with W an approximate idea of tear tip diameter shows that for SBR vulcanizates average diameter is approximately 2 mm whereas for NR it is 1.2 mm up to 30 phr. These results suggest that the reasons for strengthening structure for NR and SBR are different. It is also different for NR samples loaded above and below 30 phr filler. In one case the tear tip diameter as well as the modulus are increased whereas in the other the strain energy density is increased. The increase in the value of d is associated with knotty tearing. However the knotty tearing does not occur for rubber filled with clay.

CONCLUSIONS

1. Threshold tear strength have been obtained for NR and SBR vulcanizates swollen in xylene, toluene, heptane, and benzene.

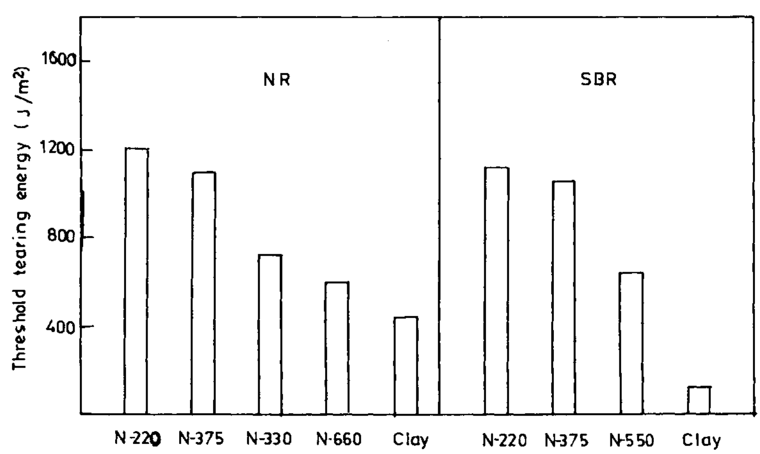

Fig. 6. Bar diagram of threshold tear strength for samples with different types of fillers.

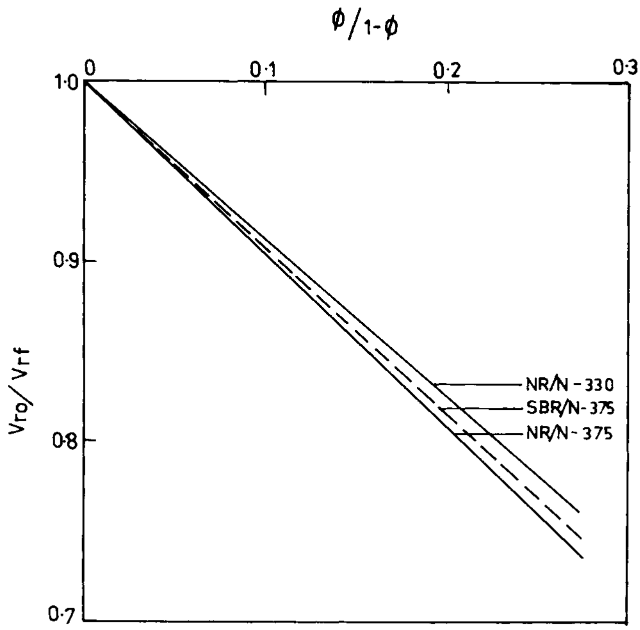

Fig. 7. Plot of V_{ro}/V_{rf} against $\phi/1\text{-}\phi$.

2. Threshold values vary from 80 J/m^2 for gum to 1200 J/m^2 for filled system.
3. Threshold tear strength increases with increase in filler loading and decrease in particle size of the filler.
4. SBR samples show marginally lower threshold tear strength than NR.

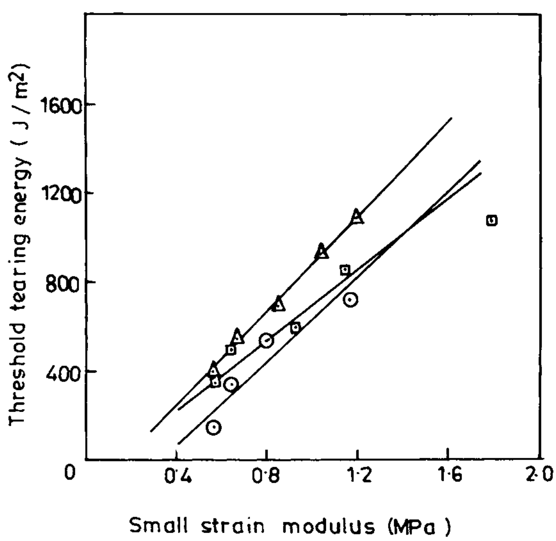

Fig. 8. Relationship between threshold tearing energy and small strain modulus. (△) NR/N-375, (⊙) NR/N-330, (⊡) SBR/N-375.

TABLE III
Values of Threshold Tearing Energy and Strain Energy Density of Gum and Carbon Black Filled NR and SBR Vulcanizates

Sample code	Threshold tearing energy (G_0) (J/m^2)	Strain energy density (W)(J/m^3) $\times 10^{-4}$	Tear tip diameter (mm)
N(O)	120	9	1.3
N1(N-375)	410	26	1.6
N2(N-375)	560	43	1.3
N3(N-375)	700	90	0.8
N4(N-375)	950	75	1.3
N5(N-375)	1100	64	1.7
S(O)	80	3	2.7
S1(N-375)	360	14	2.6
S2(N-375)	500	26	1.9
S3(N-375)	600	42	1.4
S4(N-375)	860	48	1.8
S5(N-375)	1060	50	2.1

5. China clay filler gives lowest threshold tear strength for both NR and SBR filled systems.
6. The tear tip diameter for SBR vulcanizates is more (~ 2 mm) than NR vulcanizates (~ 1.2 mm) up to 30 phr loading.

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