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Threshold tensile strength and modulus of carbon-black-filled rubber vulcanizates

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The threshold tensile strength and modulus of carbon-black-filled natural rubber and styrene–butadeine rubber vulcanizates have been determined. N-220, N-330, N-375, N-550 and N-660 carbon blacks at various loadings have been used. The threshold strength varies between 0.4 MPa for gum vulcanizate to ~3 Mpa for 50 phr loaded samples. Both the threshold strength and modulus are dependent on the nature and loading of the filler. The theoretical and experimental values of threshold strength and modulus are in good agreement.

1. Introduction

It is well known that carbon black fillers usually enhance the strength of natural rubber (NR), styrene-butadiene rubber (SBR) etc. significantly. The exact reason why carbon blacks reinforce these rubbers is still obscure. It is usually mentioned that this is due to high hysteresis and interaction. One of the ways to analyse such problems is to understand the contributions of each of the factors discussed above. As a first step then, it is logical to suppress the contributions arising out of energy dissipation and investigate whether the intrinsic strength is improved by using carbon black. Though the fracture of rubber, especially that filled with carbon black, is widely studied [1–5], such an attempt is rarely made. Only a preliminary investigation describes rough values of the threshold tearing energy of carbon-black-filled polybutadiene rubber and ethylene–propylene diene rubber [6]. In the absence of energy dissipation and stress-induced crystallization, the strength of rubber is termed the "threshold" strength. The subject has been reviewed recently by one of the authors [7].

The threshold tensile strength and modulus of NR and SBR filled with several carbon blacks, i.e. N-220, N-330, N-375, N-550, N-660 and china clay are determined. The effects of the loading and nature of fillers on threshold strength and modulus are described here.

2. Experimental procedure

2.1. Material used

The formulation of various mixes is given in Tables I to III. NR- and SBR-based formulations were used in this study. Five different carbon blacks and china clay were used. They were characterized and the results are given in Tables I to III. Mixing and vulcanization were carried out according to the usual procedure.

2.2. Determination of threshold tensile strength and modulus

The tensile strength and modulus of various rubber vulcanizates were determined using dumb-bell samples cut from 1.5 mm thick sheets. The specimens were swollen in xylene, toluene and paraffin oil. The unswollen samples were also tested at 125° C. The samples swollen in paraffin oil were tested at 100° C and those in xylene and toluene were tested at room temperature. For swollen samples the values, which are usually lower even for room-temperature testing, were corrected by multiplying by λ_s^2 (the linear swelling ratio) to take care of the reduced number of chains on the fracture plane. All the samples were tested in a Zwick UTM 1445 at various rates or temperatures. The testing rate for swollen samples was 3.3×10^{-3} m sec^{-1}. A few unswollen samples were also tested at 150° C but there were signs of degradation.

2.3. Measurement of E and V_r

Values of E were determined from tensile stress–strain relations at small strains, using unswollen samples. All the vulcanizates were also characterized by the values of V_r in benzene; V_r, the volume fraction of rubber in the swollen gel, is calculated from

$$V_r = \frac{(D - FT)/\rho_r}{[(D - FT)/\rho_r] + (A_0/\rho_s)}$$

where D = deswollen weight, F = weight fraction of insoluble components, T = sample weight, $\rho_r \rho_s$ = density of rubber and solvent, respectively, $A_0 = S_x - D$ where S_x = swollen weight.

3. Results and discussion

3.1. Threshold tensile strength and modulus of elastomers

Experimental values of tensile strength of the samples swollen in xylene, toluene and paraffin oil corrected

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TABLE I Formulation in parts per hundred of rubber (phr) and characterization of mixes

Mix	N0	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*	–	–	–	–	–	–	–	50	–	–	–
N-550	–	–	–	–	–	–	–	–	50	–	–
N-660	–	–	–	–	–	–	–	–	–	50	–
China clay	–	–	–	–	–	–	–	–	–	–	50
Process oil	–	6	6	6	6	6	6	6	6	6	6
PBNA†	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†	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Sulphur	2	2	2	2	2	2	2	2	2	2	2
Optimum cure time at 150° C (min)	11.25	10.75	10.25	10.2	10.1	10.1	10.1	10.1	10.0	10.2	11.75
Tensile strength (MPa)	22.5	23.3	25.9	26.6	26.1	24.6	24.74	23.90	21.6	22.81	18.60
Elongation at break (%)	1100	790	760	690	620	500	480	500	490	600	840

*Variation of loading of N-330 is same as N-375 but only one composition is given.
†Supplied by IEL Limited, Rishra, India: PBNA = phenyl-beta-napthylamine, CBS = cyclohexyl benzthiazyl sulphenamide.

TABLE II Formulation in parts per hundred of rubber (phr) and characterization of mixes

Mix	S0	S1 (N-375)	S2 (N-375)	S3 (N-375)	S4 (N-375)	S5 (N-375)	S5 (N220)	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*	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Sulphur	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	30.25
Tensile strength (MPa), RT	2.05	4.0	9.59	19.5	20.99	22.58	23.12	16.21	13.85	3.28
Elongation at break (%), RT	400	390	470	530	480	450	445	450	470	667

*Supplied by IEL Ltd, Rishra, India.

TABLE III Formulation in parts per hundred of rubber (phr) and characterization of mixes

Mix	N5(N-375)/DCP*	S5(N-375)/DCP
NR	100	–
SBR	–	100
N-375	50	50
Process oil	6	5
PBNA	1	–
Wax	1	–
DCP	1	1
Optimum cure time at 150° C(min)	30	16
Tensile strength (MPa), RT	11.25	13.68
Elongation at break (%), RT	470	370

*DCP = dicumyl peroxide (98%).

TABLE IV Values of tensile strength (T.S.) of gum and filled natural rubber

Sample code	Xylene		Toluene		Paraffin oil (100° C)		Unswollen (125° C)	
	Mod 50%* (MPa)	T.S. (MPa)	Mod 50% (MPa)	T.S. (MPa)	Mod 50% (MPa)	T.S. (MPa)	Mod 50% (MPa)	T.S. (MPa)
N0	0.42	0.60	0.42	0.72	0.35	1.70	0.40	2.85
N1 (N-375)	0.55	1.30	0.51	1.08	0.43	2.00	0.54	3.49
N2 (N-375)	0.66	1.78	0.64	1.76	0.53	3.05	0.70	4.95
N3 (N-375)	0.84	2.10	0.86	2.34	0.62	3.89	0.76	6.68
N4 (-N-375)	1.02	2.52	1.03	2.46	0.68	4.28	0.85	7.68
N5 (N-375)	1.19	2.61	1.22	2.61	0.81	3.99	1.03	7.86
N1 (N-330)	0.52	0.94	0.48	0.76	0.50	1.46	0.46	2.03
N2 (N-330)	0.63	1.66	0.63	1.61	0.55	2.85	0.55	4.52
N3 (N-330)	0.78	1.95	0.76	2.04	0.66	3.58	0.71	5.72
N4 (N-330)	0.99	2.10	0.89	2.71	0.78	4.08	0.76	7.13
N5 (N-330)	1.15	2.44	1.09	2.68	0.94	3.96	1.00	7.83
N5 (N-220)	1.07	2.90	1.01	2.75	0.86	6.82	1.08	7.36
N5 (N-550)	1.67	4.29	1.71	3.18	1.08	8.90	1.24	8.60
N5 (N-660)	1.06	2.33	1.21	2.61	0.74	3.58	0.90	5.52
N5 (China clay)	0.57	1.36	0.62	1.41	0.41	1.95	0.48	3.10
N5 (N-375)/DCP	0.78	1.69	0.77	1.67	0.64	2.63	0.68	3.80

*Modulus at 50% elongation.

for swelling are given in Tables IV and V. The tensile strength of unswollen samples at 125° C is also reported in Table IV. The values obtained for swollen samples are low and are corrected by multiplying by λ_s^2. The modulus at 50% elongation is also reported in the same tables. Table VI shows the values of tensile strength of samples swollen in paraffin oil at different temperatures. At above 100° C, the sample shrinks during the conditioning period. The tensile strength of unswollen samples at different temperatures is reported in Table VII. As usual, the tensile strength decreases at high temperature due to the higher segmental mobility of the chains.

It is observed that the tensile strength measured either in paraffin oil at 100° C or for unswollen samples tested at 125° C is higher than that measured in xylene or toluene. Moreover, the values obtained in xylene and toluene after correction are similar for all the samples and hence these values are taken as the "threshold" value. Ahagon and Gent [8] measured the threshold fracture energy of polybutadienes in *m*-xylene and paraffin oil. The threshold values are reported in Table V. The modulus at 50% is also treated in the same way and found to achieve the lower limit. However, the "minimum" value of modulus could be obtained in high-temperature experiments. The experiments at various rates of testing shown in Fig. 1 show that the values of tensile strength in xylene or toluene are indeed minimum. Though slightly lower values could be obtained at still higher temperature for unswollen samples (> 125° C) and for samples swollen in paraffin oil (> 100° C) there are signs of rapid degradation during conditioning and shrinkage in paraffin oil. These threshold values are, however, much lower than the tensile strength measured at room temperature when both a viscoelastic effect and strain-induced crystallization for NR are operative.

3.2. Threshold strength and modulus of vulcanizates as a function of filler loading

Threshold strength $\sigma_{b,0}$ is plotted in Fig. 2 as a function of loading of carbon black. For both N-375 and N-330 in NR, the threshold strength increases rapidly with loading up to a certain point and then levels off or shows a slowly increasing value. $\sigma_{b,0}$ for N-375 is higher at all loadings of filler than $\sigma_{b,0}$ for N-330. The critical value at which $\sigma_{b,0}$ shows a slow increase or levelling is calculated as follows: (i) tangents on the two portions of the curves (as shown) are drawn, (ii) the points at which the tangents are drawn are

TABLE V Values of tensile strength of gum and filled SBR

Sample code	Xylene		Toluene	
	Mod 50% (MPa)	T.S. (MPa)	Mod 50% (MPa)	T.S. (MPa)
S0	0.41	0.44	0.49	0.52
S1 (N-375)	0.57	0.62	0.55	0.83
S2 (N-375)	0.64	1.12	0.65	0.89
S3 (N-375)	0.92	2.19	0.98	1.61
S4 (N-375)	1.14	2.99	1.27	2.07
S5 (N-375)	1.78	3.01	1.66	2.24
S5 (N-220)	1.58	2.96	1.63	2.90
S5 (N-550)	1.17	2.59	1.54	3.03
S5 (N-660)	1.25	2.98	1.31	3.03
S5 (China clay)	0.14	0.56	0.17	0.61
S5 (N-375)/DCP	1.04	1.49	0.99	2.16

TABLE VI Values of tensile strength and modulus of gum and filled natural rubber in swollen condition (paraffin oil)

Sample code	75° C		100° C	
	Mod 50% (MPa)	T.S. (MPa)	Mod 50% (MPa)	T.S. (MPa)
N0	0.42	2.20	0.42	1.52
N1 (N-375)	0.42	2.92	0.43	2.00
N2 (N-375)	0.54	5.79	0.53	3.05
N3 (N-375)	0.68	6.06	0.62	3.89
N4 (N-375)	0.80	6.16	0.68	4.28
N5 (N-375)	0.96	6.17	0.81	3.99
N1 (N-330)	0.50	2.51	0.50	1.46
N2 (N-330)	0.55	2.63	0.55	2.85
N3 (N-330)	0.70	7.11	0.66	3.58
N4 (N-330)	0.88	7.32	0.78	4.08
N5 (N-330)	1.03	9.47	0.94	3.96

TABLE VII Values of tensile strength of gum and filled natural rubber at different temperatures

Sample code	Tensile strength (MPa)			
	25° C	75° C	100° C	125° C
N0	22.50	–	3.74	3.00
N1 (N-375)	23.30	10.81	7.61	3.49
N2 (N-375)	25.90	12.90	10.00	4.95
N3 (N-375)	26.60	15.90	13.60	6.68
N4 (N-375)	26.10	16.00	10.26	7.68
N5 (N-375)	24.60	16.90	14.29	7.86
N1 (N-330)	23.00	8.12	4.24	2.03
N2 (N-330)	24.80	12.80	7.76	4.52
N3 (N-330)	26.00	15.90	9.55	5.72
N4 (N-330)	25.70	16.00	9.26	7.13
N5 (N-330)	23.90	16.40	11.76	7.83

joined together and the midpoint of the line is found, (iii) the midpoint and the intersecting point of two tangents are joined, and (iv) the point at which this line intersects the curve is determined as the critical value. A similar procedure is followed for finding the optimum cure-time of synthetic rubbers as reported earlier [9].

It is interesting to note that N-375 shows a similar critical value as N-330 in NR. It has been reported that NR shows an optimum in strength at around 30 phr loading and SBR at around 60 phr loading for room-temperature testing [10]. We have observed a similar trend (Tables I to III). This is due to the fact that two opposing factors are in action when a reinforcing filler like carbon black is added in rubber. One is the increase in tensile strength and modulus dependent on the particle size of the carbon black, and the other is the reduction in properties at higher loading due to the dilution effect and to a diminishing volume fraction of rubber in the composite. However, the threshold value $\sigma_{b,0}$ for SBR continuously increases with an increase in carbon black loading. At similar loading SBR vulcanizates always show lower strength than natural rubber under threshold conditions.

It is interesting that a substantial degree of reinforcement still remains when dissipative processes

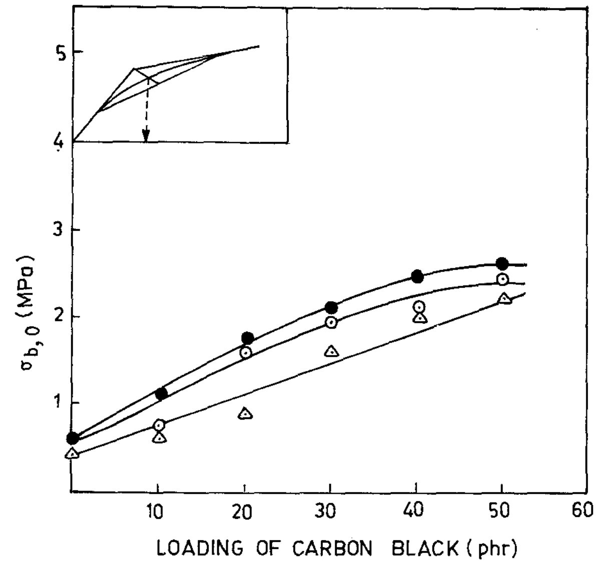

Figure 2 Relationship between threshold tensile strength ($\sigma_{b,0}$) and loading of carbon black for NR and SBR: (●) NR/N-375, (⊙) NR/N-330, (△) SBR/N-375.

are minimized. One possible mechanism of reinforcement may be that there is detachment of polymer molecules from particles of carbon black, which requires energy. The higher the number of contact points, which increases when the particle size of the carbon black is smaller or the surface area larger, the higher is the reinforcement. As the fracture surfaces observed under a microscope are rough even under threshold conditions, the increase in threshold tensile strength may also be due to colloidal tear deviation. In order to understand the degree of reinforcement, a Kraus plot (V_{ro}/V_{rf} against $\phi/(1 - \phi)$) has been made. Fig. 3 shows such a plot. It is observed that N-375 is slightly more reinforcing than N-330 under swollen conditions.

The modulus values show higher values at higher carbon black loading (Fig. 4). SBR vulcanizates show higher modulus values than NR vulcanizates and N-375 shows higher values than N-330 as usual. It is

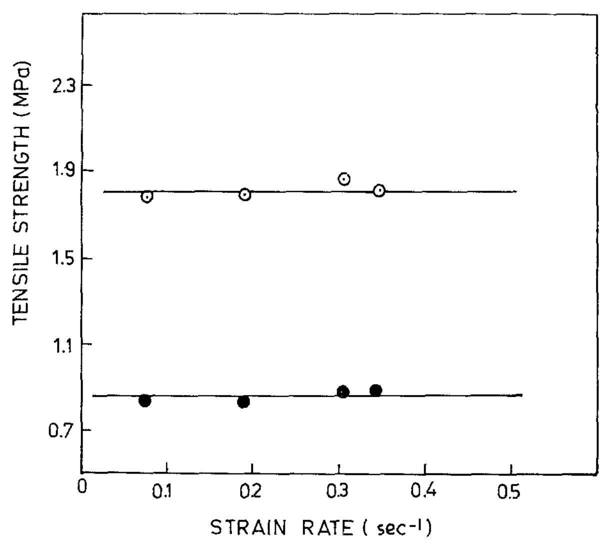

Figure 1 Variation of tensile strength with strain rate of swollen rubber vulcanizates: (⊙) N2 (N-375) in xylene, (●) S1 (N-375) in toluene.

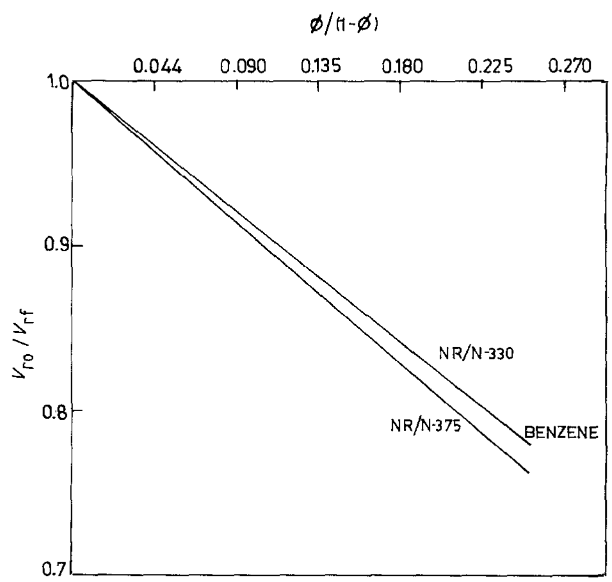

Figure 3 Plot of V_{r0}/V_{rf} against $\phi/(1 - \phi)$ for N-375 and N-330 black-filled NR vulcanizates (ϕ is the volume fraction of the filler).

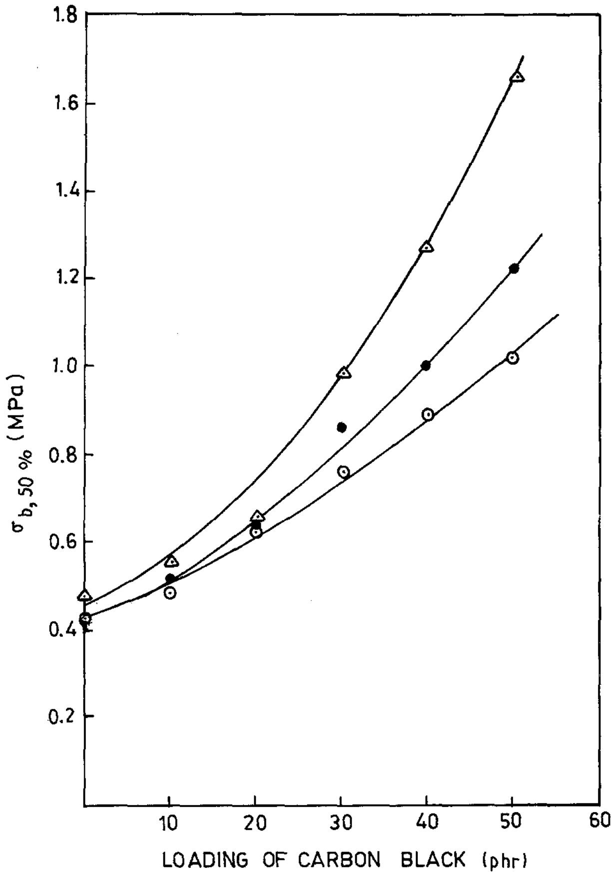

Figure 4 Relationship between modulus and loading of carbon black for NR and SBR: (●) NR/N-375, (△) SBR/N-375, (⊙) NR/N-330.

interesting here also that the relative trend for room-temperature measurements for these vulcanizates is followed even under threshold conditions [10].

3.3. Effect of nature of black at 50 phr loading on threshold tensile strength, modulus and elongation at break

The effect of the nature of the carbon black on the threshold tensile strength, modulus and elongation at break has been studied for NR and SBR vulcanizates and is reported in Figs 5 to 7. At 50 phr loading, the improvement in tensile strength for NR (Fig. 5) follows the order

N-220 > N-375 > N-330 > N-660

This is in line with the total surface area, which is highest for N-220. The elongation at break values without correction are also reported in the figure. These values are similar. The trend of tensile strength measured at room temperature for unswollen samples is identical. N-550 black at the same loading, however, gives the highest modulus and tensile strength due to higher structure. The comparable 300% modulus at room temperature for unswollen samples is also found to be in line with earlier observations ([10] and Tables I to III). The tensile strength measured at room temperature for unswollen samples of N-550 filled compound is, however, much lower than for the rest of the carbon blacks.

For SBR vulcanizates filled with N-220 and N-375 (Fig. 6) the tensile strength is highest for N-220 black while it is lowest for N-375 black. The modulus values are comparable. N-550, however, shows the lowest modulus and a tensile strength higher than N-375.

For comparison, 50 phr china clay-filled samples have been tested. Both NR and SBR vulcanizates show the lowest tensile strength and modulus (Tables IV and V).

It is apparent from the above data that under threshold conditions the strength and modulus are guided by the surface activity and surface area of the filler.

3.4. Effect of nature of crosslinking in filled vulcanizates

The effects of sulphur and dicumyl peroxide crosslinks on the threshold tensile strength of carbon-black-filled vulcanizates is given in Tables IV and V. It is observed that the sulphur crosslinking gives higher tensile strength values even under threshold conditions than for DCP-cured samples. This is a general trend, as observed in rubber vulcanizates tested at room temperature and for unswollen vulcanizates [11]. Cross-link rearrangement or scission before rupture of the main chain is responsible for such strengthening features [6].

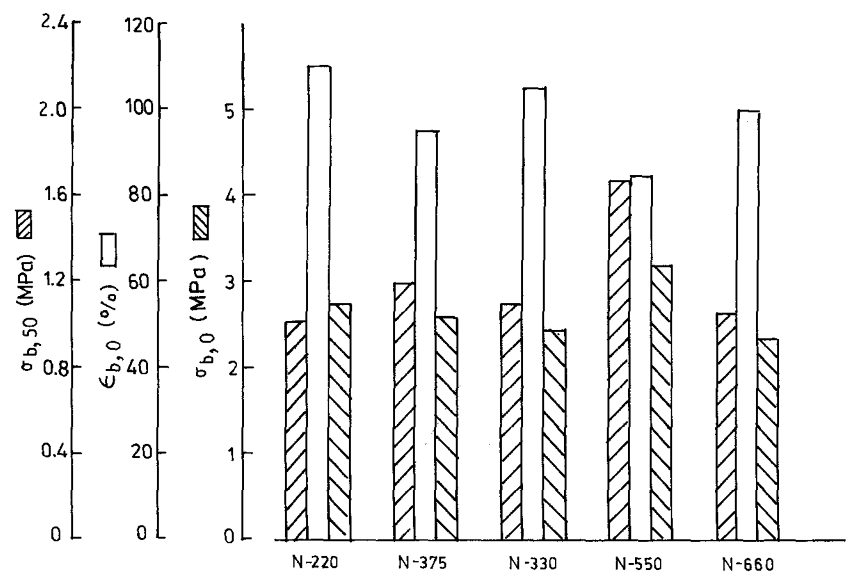

Figure 5 Effect of nature of black at 50 phr loading on threshold strength, modulus and elongation at break for NR vulcanizates.

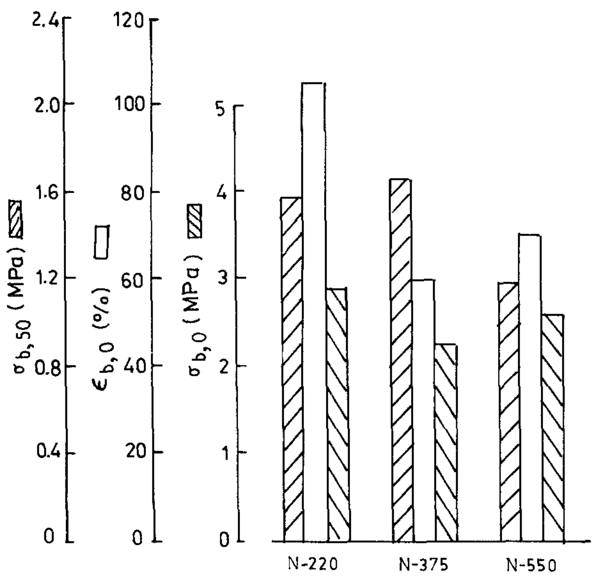

Figure 6 Effect of nature of black at 50 phr loading on threshold strength, modulus and elongation at break for SBR vulcanizates.

3.5. Theoretical values of small-strain modulus and threshold tensile strength

An attempt has been made to calculate the theoretical modulus by using the equations [12, 13]

$$E = E_0 (1 + 2.5\phi' + 14.1\phi'^2)$$

$$\frac{V_{\text{occl}}}{V_c} = \frac{\phi' - \phi}{\phi}$$

$$\phi' = \phi\,(1 + 0.02139\ \text{DBPA})/1.46$$

where V_{occl} and V_c refer to the total volume of occluded rubber and of carbon black, respectively, and ϕ' and ϕ are the volume fraction of filler plus occluded rubber and volume fraction of filler alone, respectively and DCPA is the dibutyl phthalate number. The value of E is now calculated using the crushed DBP value and 50% effective occluded volume. The results are shown in Tabe VIII. It is found that excellent agreement between theoretical and experimental values is obtained.

The threshold tensile strength could be calculated using the relation

$$\sigma_{b,0} = \left(\frac{G_{co} E}{\pi c}\right)^{1/2}$$

where G_{co} is the threshold tearing energy, E is the small-strain modulus; c, the size of the crack, is generally of the order of 5×10^{-3} cm. As an example taking $c = 5 \times 10^{-3}$ cm, E and G_{co} from a previous communication [14] the threshold tensile strengths of a few samples are calculated. These are given in Table VIII and compared with the experimentally observed values. It is observed that a 50 phr N-375 filled NR sample shows a theoretical value of ~2.5 MPa which is in accord with the experimental value. A similar accordance is obtained for the other systems calculated.

TABLE VIII Theoretical and experimental values of small-strain modulus and tensile strength

Sample code	Small-strain modulus (MPa)		Tensile strength (MPa)	
	Theor.	Exper.	Theor.	Exper.
S1 (N-375)	0.52	0.57	–	–
S2 (N-375)	0.66	0.64	1.41	1.12
S3 (N-375)	0.82	0.92	1.87	1.61
S4 (N-375)	1.03	1.14	2.50	2.10
S5 (N-375)	1.24	1.78	3.34	2.24
S5 (N-220)	1.26	1.58	3.36	2.96
S5 (N-550)	1.19	1.17	3.30	2.59
S5 (N-660)	1.10	1.25	2.15	2.98
N1 (N-375)	0.51	0.55	1.24	0.94
N2 (N-375)	0.65	0.66	1.51	1.76
N3 (N-375)	0.81	0.84	1.93	2.10
N4 (N-375)	0.99	1.02	2.48	2.46
N5 (N-375)	1.19	1.19	2.50	2.60
N1 (N-330)	0.51	0.52	0.68	0.76
N2 (N-330)	0.64	0.63	1.16	1.61
N3 (N-330)	0.73	0.78	1.61	1.95
N4 (N-330)	0.97	0.99	2.40	2.10
N5 (N-330)	1.16	1.15	2.70	2.50
N5 (N-220)	1.21	1.07	2.85	2.90
N5 (N-550)	1.15	1.67	–	–
N5 (N-660)	1.06	1.12	2.01	2.33

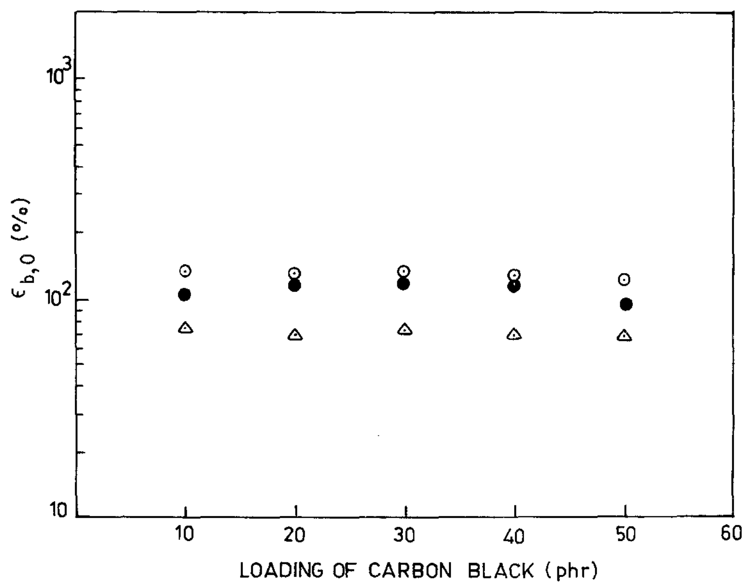

Figure 7 Effect of loading of carbon black on elongation at break for swollen vulcanizates: (●) NR/N-375, (⊙) NR/N-330, (△) SBR/N-375.

4. Conclusions

1. The threshold tensile strength and modulus of carbon-black-filled natural rubber and SBR vulcanizates have been reported here. The threshold strength could be obtained by swelling the vulcanizates in xylene or toluene.

2. The threshold tensile strength lies between 0.4 and 3 MPa for various vulcanizates. For NR it increases up to 30 phr loading of black and then it plateaus. For SBR the increase is up to 50 phr of carbon black.

3. At equal loadings of black filler in NR and SBR, N-220 carbon-black-filled vulcanizate shows the highest tensile strength. The improvement with carbon black follows the order

$$\text{N-220} > \text{N-375} > \text{N-330} > \text{N-660}$$

4. A sulphur crosslinking system shows higher threshold strength than peroxide crosslinking in both NR and SBR.

5. Theoretical values of the threshold small-strain modulus and tensile strength are in accord with the observed values for the systems studied.

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