

# Effect of Vulcanizing System on the Crosslink Density of Nitrile Rubber Compounds

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**ABSTRACT:** The synergistic activity of binary accelerator systems in rubber vulcanization is well known. Binary accelerator systems are being widely used in industry and are becoming increasingly popular because of the fact that such mixed systems can produce a vulcanizate with superior mechanical properties compared to those of stock cured with a single accelerator. The authors have studied the performance of a binary accelerator system based on cyclohexyl benzothiazole sulfenamide (CBS), tetramethyl thiuram disulphide (TMTD) in the sulfur vulcanization of nitrile rubber. The amount of sulfur and accelerator was varied to change

the network crosslink density of vulcanizates. The observed mutual activity has been discussed based on the mechanical properties and crosslink density. The physical crosslink density of the various nitrile rubber mixes was estimated using the Kinetic Theory of Elasticity. The mechanical properties of the various rubber compounds were related to the corresponding crosslink density estimated for each compound. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 2440–2445, 2005

**Key words:** rubber; accelerator; vulcanization; crosslinking; mechanical properties

## INTRODUCTION

Vulcanization increases the reactive force and reduces the amount of permanent deformation remaining after removal of the deforming force. It is generally accomplished by the formation of a crosslinked molecular network.<sup>1</sup> Characteristics related to the vulcanization process are the time elapsing before crosslinking starts, the rate of crosslink formation, and the final extent of crosslinking. There must be sufficient delay or scorch resistance to permit shaping, forming, and flowing in the mold; then crosslink formation should be rapid.<sup>2</sup> Accelerated vulcanization gives both improved efficiencies and rate.<sup>3</sup> Binary accelerator systems can effectively prevent prevulcanization, permitting the vulcanization to be carried out at a lower temperature in a shorter time.<sup>4</sup> The accelerator reacts with sulfur to give monomeric polysulfides of the structure Ac-Sx-Ac, where Ac is an organic radical derived from the accelerator (e.g., 2-benzothiazyl). The monomeric polysulfides interact with the rubber to form polymeric polysulfides, such as rubber-Sx-Ac (sulfurated rubber). During this reaction, MBT (mercaptobenzothiazole) is formed when a benzothiazole-derived accelerator is used and the elastomer is natural rubber. In SBR, the MBT becomes bound to the elastomer molecular chain, probably as thioether rub-

ber-S-Ac. Finally, the rubber polysulfides react, either directly or through an intermediate, to give crosslinks (rubber-Sx-rubber). The chemistry of the accelerated vulcanization of BR, SBR, and EPDM has much in common with that of NR.<sup>5,6</sup> It is reported that the disulfides forms a synergistic combination with thiazole and thiazole-based accelerators.<sup>7</sup>

Three curing agents, CBS, TMTD, and sulfur, were used to study their crosslinking efficiency at different concentrations on nitrile rubber compounds. The physical crosslink density and microphysical network structure can be estimated from the stress–strain data. The statistical theory of rubber-like elasticity relating the force  $F$ , per unit area  $A$ , required for straining a perfectly elastic network at a small extension ratio,  $\lambda$ , is given by

$$F/A = \frac{\rho RT(\lambda - \lambda^{-2})}{M_c} = 2C1(\lambda - \lambda^{-2}) \text{ dyn cm}^{-2} \quad (1)$$

where  $\rho$  is the density of rubber,  $T$  is the absolute temperature,  $R$  is Boltzman's constant, and  $M_c$  is the number of average molecular weight of the network chains. This is sometimes known as the molecular weight between two crosslinks. The  $C1$  is known as the conventional elastic constant at a given temperature. The crosslink density  $\nu = \frac{1}{2} M_c \text{ g}^{-1} \text{ mol}$ . Mooney-Rivlin modified eq. (1) and showed the stress–strain behavior of any network up to moderate strain (20%) to be

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TABLE I  
Rubber Mix Formulations

Ingredients (phr)	S1	S2	S3	S4	S5
Nitrile 34.4	100	100	100	100	100
Zinc oxide	5	5	5	5	5
Stearic acid	2	2	2	2	2
6PPD <sup>a</sup>	3	3	3	3	3
GPF <sup>b</sup>	40	40	40	40	40
CBS <sup>c</sup>	0.75	1	-	0.25	-
TMTD <sup>d</sup>	1.25	2	1.25	1	2
S	1	0.5	1	1.50	1
Minimum torque (lb-in)	1.68	0.99	1.62	0.88	1.21
Maximum torque (lb-in)	10.48	10.68	9.14	14.74	14.49
Scorch time (min)	1.67	1.32	1.58	1.15	1.23
Cure time $t_{c90}$ (min)	4.46	4.01	4.53	4.36	3.91
Tear (N/mm)	108.86	110.86	112.17	106.62	96.29
Tensile strength at break (MPa)	3.33	3.70	3.75	3.33	3.11
Elongation at break (%)	658	703	734	508	476
Force at 100% strain (MPa)	0.55	0.53	0.46	0.68	0.57
Force at 200% strain (MPa)	0.92	0.92	0.76	1.24	1.08
Crosslink density $\times 10^4$ , $\text{g}^{-1} \cdot \text{mol}$	1.690	1.907	2.102	2.600	2.860
$M_c$ value ( $\text{g} \cdot \text{mol}^{-1}$ )	2958.6	2621.9	2378.7	1923.1	1748.3

<sup>a</sup> 6-PPD, *N*-(1,3) dimethyl butyl *N'*-phenyl-*p*-phenylene diamine.

<sup>b</sup> GPF, general purpose furnace black.

<sup>c</sup> CBS, *N*-cyclohexyl benzthiazyl sulphenamide.

<sup>d</sup> TMTD, tetramethyl thiuram disulfide.

$$F = 2(C_1 + C_2 \lambda^{-1}) (\lambda - \lambda^{-2}) \quad (2)$$

where  $C_1$  and  $C_2$  are constants characterizing the vulcanizate. By plotting the stress-strain data in the form  $\frac{1}{2} F (\lambda - \lambda^{-2})^{-1}$  as a function of  $\lambda^{-1}$ , the values of  $C_1$  and  $C_2$  can be obtained graphically.

## EXPERIMENTAL

### Processing

Mixing of (acrylo-butadiene copolymer) of grade 34 was carried out on a two-roll laboratory open mixing mill (152.4  $\times$  330.2 mm) at a friction ratio 1: 1.4. The machine was water cooled during the mixing operation. These mixes were compounded according to the basic formulations given in Table I. The mixing was carried out according to ASTM D3182.89.

To ensure a fair comparison between the various mixes a masterbatch was prepared. Sulfur, CBS, and TMTD were added in different concentrations to each portion of the masterbatch.

### Testing

Samples for testing were compression molded in a laboratory hydraulic press (Mackey Bowley, C1136199) at 152°C, to their respective optimum cure time as determined by means of a Monsanto Rheometer (Alpha Technologies MDR 2000).

Tensile testing machine Z010/TH2A with a cross-head speed 500 mm/min was used to measure tensile

strength and elongation at break. The forces at 100 and 200% strain were also recorded. The tear resistance was also measured.

### Relaxed stress-strain measurements

The Zwick tensile testing machine was run at a speed 10 mm/min to obtain stress-strain curves for each rubber mix. These results were recorded up to 20% strain. From these curves, the stresses at 2, 4, . . . up to 20% were detected. The extension ratios,  $\lambda$ , were calculated.

For each extension ratio  $\lambda$ , the value  $(\lambda - \lambda^{-2})$  was calculated and plotted against the applied stress  $F/A$ , where  $A$  is the cross-sectional area of the straight part of a dumbbell test piece. The stress-strain curves showed almost straight lines. This indicates that the kinetic theory of elasticity is valid for this specific rubber mix, as long as the stress-strain curve is carried out below 16% strain. The slopes of these lines were calculated (Fig. 1); this represents the ratio  $(F/A)/(\lambda - \lambda^{-2})$ .

Substituting these values in eq. (1), the  $M_c$  value (molecular weight between two crosslinks) can be calculated. Consequently the crosslink density  $(1/2M_c)$  can also be calculated.

## RESULTS AND DISCUSSION

### Crosslink density and $M_c$ values

Random concentration selection of accelerators CBS, TMTD, and the vulcanizing sulfur agent were used

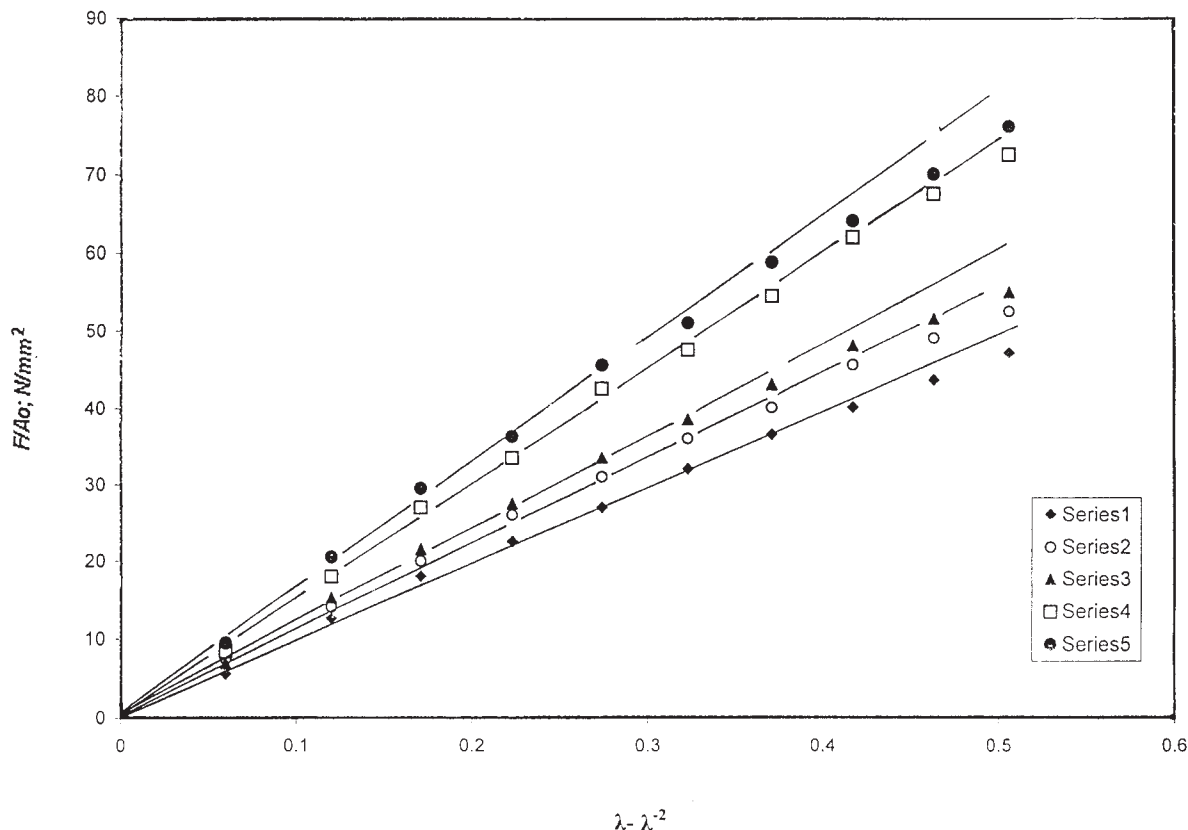


Figure 1 Relations between  $\lambda - \lambda^{-2}$  versus  $F/A_0$ ,  $N/mm^2$ . Stress-strain curves of rubber vulcanizates.

with the nitrile rubber compounds. By using the stress-strain measurement, the crosslink density of the various compounds could be obtained. The mixes were ordered according to their crosslink density as shown in Table I. It is clear that the concentration of each ingredient individually cannot be used as a base to examine the crosslink density trend of the vulcanizates. But the mentioned agent groups act together to form the chemical and physical crosslinks with the used rubber. Meanwhile, comparing the crosslink density of S1 and S3 containing same amount of TMTD and sulfur, it is clear that the presence of CBS minimize the crosslinks formed. It is known that CBS is a fast delayed action-curing agent.<sup>2,8</sup> Gradwell and McGill<sup>9</sup> used high-performance liquid chromatography (HPLC) to analyze the soluble curatives and reaction intermediate. This technique was used to explain the delayed action of CBS on polyisoprene rubber.<sup>10</sup> The delayed action of the CBS accelerator is explained in terms of an exchange reaction between benzothiazole terminated polysulfidic groups on the polymer chain and CBS to yield unreactive amine terminated pendent groups and 2-bisbenzothiazole-2,2'-disulphide (MBTS). MBTS reacts with sulfur to form 2-bis benzothiazole-2,2'-polysulphides (MBTPs), which also forms pendent groups. The mechanisms and reactions of delayed action vulcanization have been discussed previously.<sup>10,11</sup>

Moreover, comparing S3 and S5, in the absence of CBS, one can notice that increasing the TMTD concentration up to TMTD : S weight ratio 2 : 1 enhances the crosslink density up to 36%. This TMTD : S ratio corresponds to 3.8 g atoms of sulfur per mole TMTD.<sup>12</sup> In TMTD-accelerated sulfur vulcanization systems the peak value of zinc dimethyldithiocarbamate (ZnDMDC) formation reaches an end value when the stock contain 4 g atoms of sulfur per mole TMTD. It was found that ZnDMDC is the actual accelerator in TMTD accelerated sulfur systems, which are faster accelerators than thiuram disulfides.<sup>13-15</sup> This may explain the recorded data given in Table I, where S5 showed scorch time and cure time lower than that of S3.

### Tensile strength

Several studies have been reported on the effect of crosslinking on the tensile strength of rubber vulcanizates.<sup>2,16,17</sup> In this article, the degree of crosslinking was expressed in terms of  $M_c$  (the number of average molecular weight of network chains), where  $M_c = 1/2\rho$ . The tensile strength passes through a maximum as the degree of crosslinking increases. This can be seen in Figure 2. The maximum tensile strength value can be taken as a measure of the degree of crystallization.<sup>18</sup> Thus, the tensile strength is governed

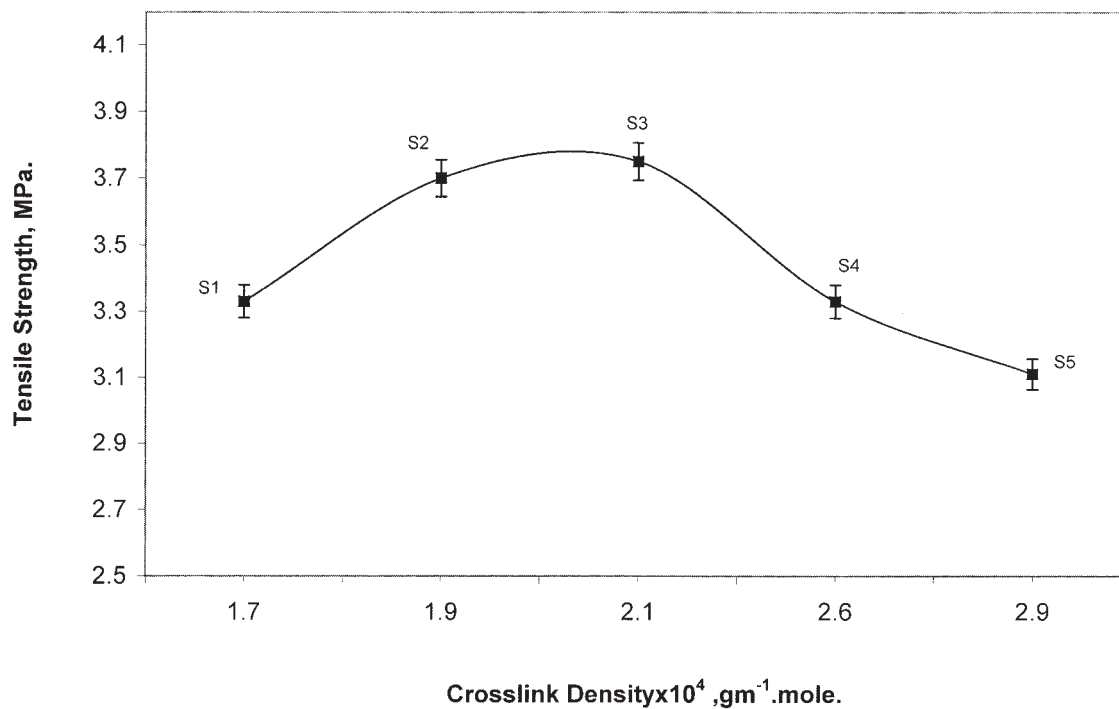


Figure 2 Relation between the crosslink density  $\times 10^4 \text{ g}^{-1} \cdot \text{mol}$  versus tensile strength, MPa.

by the degree of crystallization attained as the breaking point is approached.

It has been supposed that the tensile strength is low at a higher degree of crosslinking, because the breaking point attained before the extension is sufficiently high for crystallization to develop. In explanation of

the low tensile strength at a low degree of crosslinking, Gee<sup>16</sup> suggests that, unless the degree of crosslinking is sufficiently high for a coherent network to be formed, plastic flow will occur and will prevent the maximum case of orientation of chains to form crystallization. Flory and coworkers<sup>17</sup> reported, re-

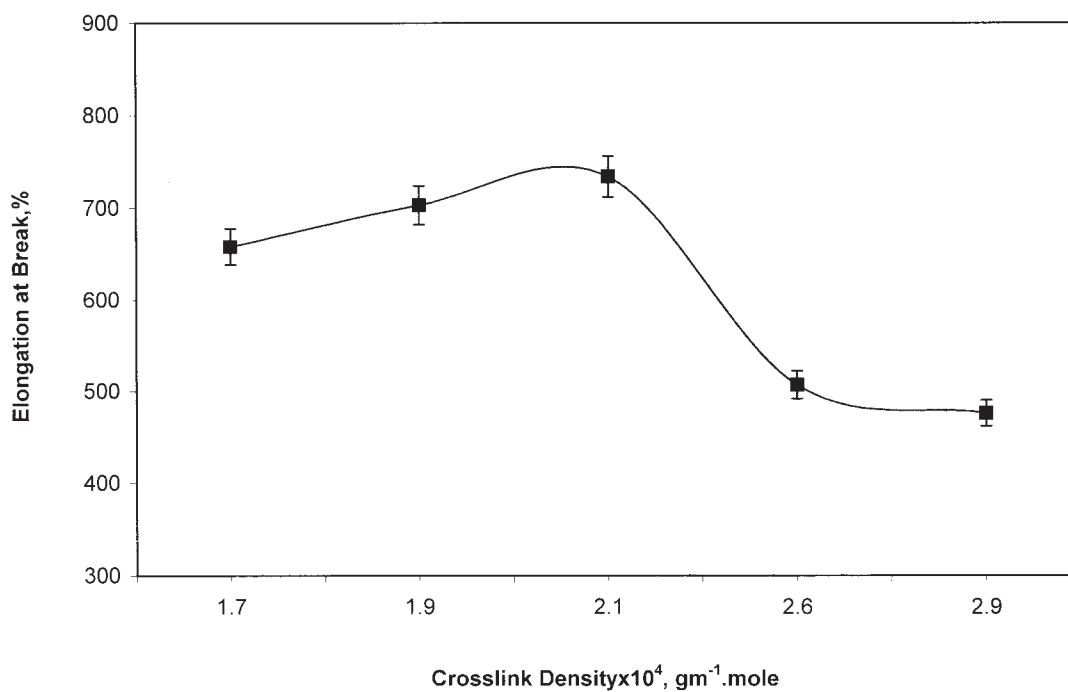


Figure 3 Relation between the crosslink density  $\times 10^4 \text{ g}^{-1} \cdot \text{mol}$  versus elongation at break, %.

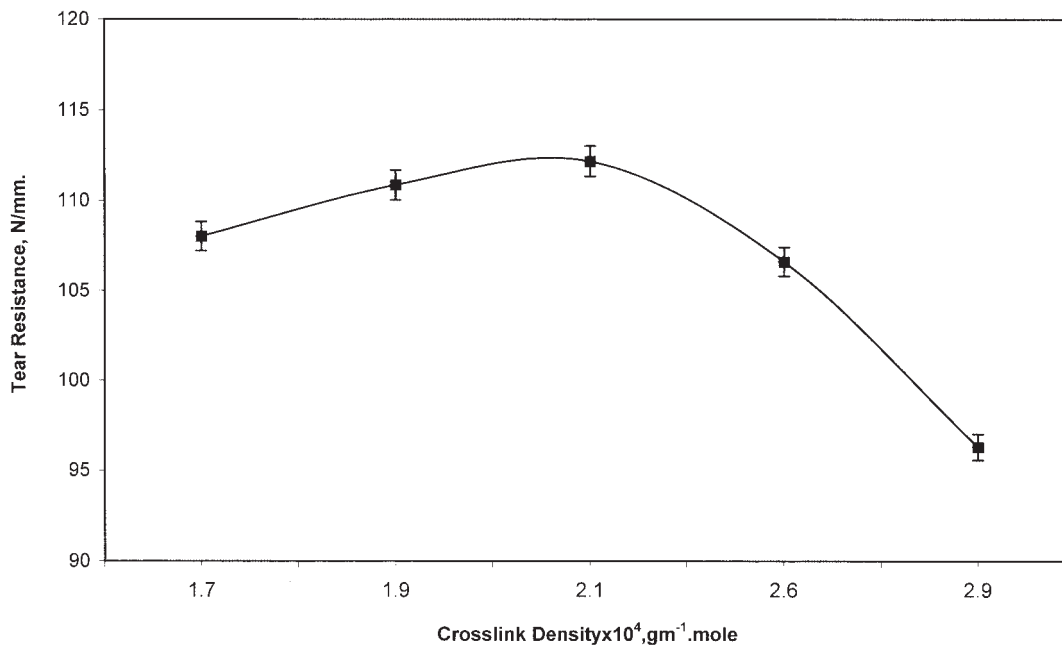


Figure 4 Relation between the crosslink density  $\times 10^4 \text{ g}^{-1} \cdot \text{mol}$  versus tear resistance, N/mm.

garding the tensile strength at the degree below that of maximum tensile strength, the fraction material in the form of active network chains that would form increased as the degree of crosslinking increased.

#### Elongation at break

The ability of rubber to stretch to several times its original length is one of its chief characteristics. Hence, the elongation at break is one important factor in the rubber study, which can be related also to the crosslink density of the rubber samples. This relation is shown in Figure 3. The figure shows similar results to those given in Figure 2, in which the tensile strength is related to the average number of crosslinks. The maximum elongation at break was recorded at almost the same crosslink density as shown in Figure 2 and can also be related to the degree of crystallization of the rubber mix, which is attained as the breaking point is approached.

#### Tear resistance

The initiation and propagation of a rubber tear is a very important factor in the failure of rubber products. It is known that high tensile strength is an indication of good tear resistance. The tear resistance is also an indication for the fatigue and abrasion of rubber as well as the growth of cut when this rubbery material is exposed to a sudden stress. Figure 4 shows a similar relation between the crosslink density and the tear force, expressed as N/mm, to that given in Figures 2 and 3. This was expected, as long as the tensile

strength is an indication for high or low tear force resistance. Coran<sup>2</sup> reviewed the chemistry of vulcanization and its effect on vulcanizate properties. He illustrates the main effect of vulcanization on the use-related properties representing tear strength and other properties. The crosslink density and the vulcanization properties reviewed by Coran can be seen in Figure 5. The figure showed the same pattern as that obtained in our study.

From Figures 2–4, we can deduce that S3 containing sulfur : TMTD in the weight ratio 1 : 1.25 has superior mechanical properties in comparison with the other vulcanizates. This finding is in agreement with Coran,<sup>2</sup> who stated that the best mechanical properties for natural rubber are obtained with long-chain poly-

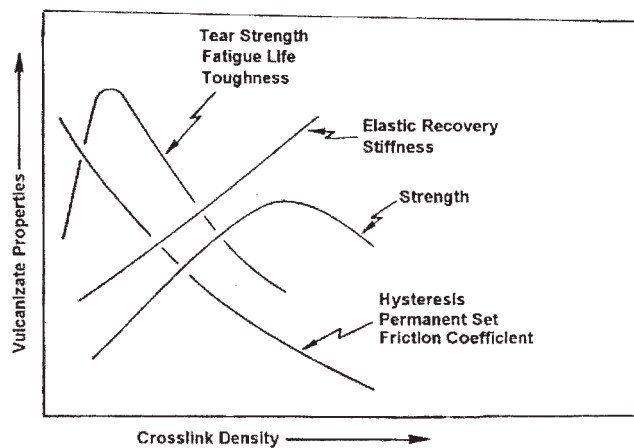


Figure 5 Vulcanizates properties versus crosslink density.<sup>11</sup>

sulfidic crosslinks formed by sulfur. The sulfur also combined with the rubber chains as sulfur containing six-membered heterocyclic rings along the rubber molecular chains.<sup>19</sup>

### CONCLUSION

The kinetic theory of elasticity can be used to estimate the physical crosslinks of a rubber vulcanizate. The validity of this theory holds to a maximum strain of 16%.

Up to certain value of the vulcanizate crosslinks the mechanical properties increase. Beyond this value the mechanical properties began to decrease.

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