A New Synergistic Combination of Safe Accelerators for the Improvement of Physical Properties in Gum and Filled Vulcanizates

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SYNOPSIS

The synergistic activity of bis(diisopropyl) thiophosphoryl disulfide (DIPDIS) in the presence of dithio bis(N-β-OH ethyl piperazine) (DTEP), a safe amine-based accelerator, has been studied both in gum and filled stock vulcanization of NR. This study, concerning the effect of variation of sulfur concentration on the gum vulcanization of NR, reveals that, although modulus values of the vulcanizates increase with the level of sulfur, the tensile strength values attain a maximum at 1.5 phr sulfur for an equimolar (4.5 : 4.5) concentration of DIPDIS and DTEP. The concentration of accelerators was varied from 6 mmol to 18 mmol phr, keeping the molar ratio at 1 : 1. It was noticed that, although the torque and modulus values increased, the tensile strength values decreased after attaining a maximum at 12 mmolar concentration of DIPDIS and DTEP accelerators, when the sulfur concentration was fixed at 1.5 phr. The synergistic activity of DIPDIS–DTEP accelerated mixes is considered to arise from the generation of some intermediate accelerators that are governed by the proportion of accelerators, sulfur, filler, etc., present in the mix. Some investigations were also carried out to optimize the amount of carbon black at these fixed levels of accelerators and sulfur. A regarding tensile strength, it increased up to a loading of 50 phr carbon black, but beyond this level a gradual fall in the value was noticed. However, modulus, torque, and hardness increased with the concentration of carbon black. The optimum dispersion of carbon black for this system was obtained following Lee's method. © 1995 John Wiley & Sons, Inc.
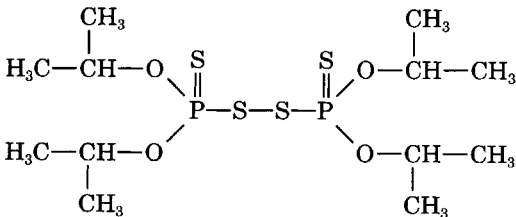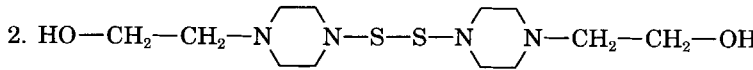
INTRODUCTION

Carcinogenic effects of most of the conventional rubber chemicals have become a matter of great concern in recent years. Literature reports[1-3] carcinogenic effects of different amine-based rubber chemicals, and a series of safe amine-based rubber accelerators have been listed[4] in this regard. Their objective is to develop new, safe accelerators in order to avoid the generation of carcinogenic nitrosamines during and after vulcanization of rubber compounds. Recently, we reported[5-7] synthesis and technical performance of some safe accelerators singly as well as in combination with other accelerators, and eval-

uated their performance by comparing them with other conventional accelerators. The synergistic activity of bis(diisopropyl) thiophosphoryl disulfide (DIPDIS) in the presence of dithiodimorpholine (DTDM), thiazole and thiazole sulfenamide accelerators and the mechanism of synergism have been reported.[8-10] However, it appears that nothing has been reported regarding synergistic activity of DIPDIS with safe amine-based accelerators. In this article, the synergistic combination of DIPDIS with dithio bis(N-β-hydroxy ethyl piperazine) (DTEP) has been chosen because both of them can produce safe rubber accelerators.[4,11] In the present study, an attempt has been made to understand the mode of cure first in gum vulcanizates and then to investigate the physical properties of filled vulcanizates at an appropriate ratio of DIPDIS, DTEP, S, and carbon black.

Table I   List of Compounds Used

Structure	Abbreviation	Chemical Name
1. (see structure below)	DIPDIS	Bis(diisopropyl) thiophosphoryl disulfide
2. HO—CH₂—CH₂—N◯N—S—S—N◯N—CH₂—CH₂—OH	DTEP	Bis(N-β-hydroxyethyl piperazine) disulfide

Structure 1:

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        CH3                        CH3
         |                          |
  H3C—CH—O   S              S   O—CH—CH3
          \  ||             ||  /
           P—S—S—P
          /  \
  H3C—CH—O    O—CH—CH3
         |             |
        CH3           CH3
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EXPERIMENTAL

Material

Bis(diisopropyl) thiophosphoryl disulfide (DIPDIS)[9] and dithio bis(N-β-hydroxyethyl piperazine) (DTEP)[7] were prepared in the laboratory. A list of chemical compounds, their structures, and abbreviations used in the present investigation are given in Table I.

Preparation of Vulcanizates and Measurement of Physical Properties

Zinc oxide (5 phr), extra pure stearic acid (2 phr), varying amounts of sulfur, carbon black, and accelerator(s) were incorporated in 100 g of rubber on a Berstorff laboratory mixing mill of size 203 × 104 mm using an 18 min compounding cycle. The cure characteristics of different stocks were obtained using the Monsanto Rheometer R-100 at 140°C, and the cure data are presented in Tables II, III, IV, and V. The stocks were cured under pressure at 140°C for the optimum cure time, and the vulcanizates were kept for 24 h at ambient temperature before measuring modulus at 200% elongation and tensile

strength according to ASTM D 412-51T using dumbbell-shaped test pieces in an Amsler (Sweden) tensile tester. The physical data concerning modulus, tensile strength, and elongation at break of the vulcanizates are also provided in Tables II, III, IV, and V.

RESULTS AND DISCUSSION

For the study of cure synergism of the binary system comprising DIPDIS and DTEP, the accelerator proportions were varied. The rheometer data and physical properties of the vulcanizates are recorded in Table II. Figure 1 depicts the cure behavior of DIPDIS, when it is progressively replaced by DTEP, keeping the total mmolar concentration of accelerators at a constant but arbitrary level of 9 mmol phr. The synergistic activity with respect to maximum torque (R_α) and physical properties of vulcanizates, like modulus, tensile strength, etc., are conveniently presented by plotting them against relative concentrations of accelerators as shown in Figures 2(A) and 2(B). The dotted lines (additive line) are indicative of theoretical weight average values if one

Table II   Physical and Cure Data of Stocks[a] (Gum) Cured at 140°C

Mix No.	1	2	3	4	5
Composition mmol	DIPDIS-9	DIPDIS-6 DTEP-3	DIPDIS-4.5 DTEP-4.5	DIPDIS-3 DTEP-6	DTEP-9
Maximum torque, R_α, Nm	3.60	3.65	3.75	3.45	2.60
Scorch safety t_2, min	9.0	4.0	5.0	4.0	11.0
Optimum cure time, t_{90}, min	40.0	16.0	14.0	16.0	33.5
Modulus at 200% elongation, MPa	0.61	0.64	0.68	0.47	0.22
Tensile strength, MPa	13.6	14.7	15.8	14.6	9.5
Elongation at break, %	700	740	740	780	850

[a] Stock composition: NR 100 g, zinc oxide 5 phr, stearic acid 2 phr, and sulfur 0.5 phr.

Table III   Physical and Cure Data of Stocks[b] (Gum) Cured at 140°C

Mix. No.	1	2	3	4	5
Composition phr	S[c]-0.5	S-1.0	S-1.5	S-2.0	S-2.5
Maximum torque, R_α, Nm	3.75	4.55	5.05	6.00	6.45
Scorch safety, t_2, min	5.0	4.0	3.5	3.5	3.0
Optimum cure time, t_{90}, min	14	12	14	15	18
Modules at 200% elongation, MPa	0.68	0.82	1.05	1.30	1.60
Tensile strength, MPa	15.8	16.5	18.7	16.0	15.4
Elongation at break, %	740	640	600	550	500

[b] Stock composition: NR 100 g, zinc oxide 5 phr, stearic acid 2 phr, DIPDIS 4.5 mmol and DTEP 4.5 mmol.
[c] Sulfur.

accelerator does not activate the other and vice versa. The distance between the dotted line and additive line signifies the extent of synergism, i.e., mutual activity between the two accelerators. It is evident from the rheographs (Fig. 1) and data for mixes 1–5 (Table II), that a fast rate of cure and enhanced torque are obtained when an equimolar ratio (4.5 : 4.5) of DIPDIS and DTEP is used. The scorch safety (t_2) of all the binary systems is less than that of the single accelerator system. But the system containing equimolar ratio of the accelerators shows a slightly higher t_2 value than that obtained in each of the other two intermediate compositions. The optimum cure times (t_{90}) also follow the same trend as found in the case of t_2. The t_{90} values of the binary mixes are again lower than that of the DIPDIS or the DTEP-accelerated stock. Out of three binary mixtures, the equimolar combination (mix. 3, Table II) records the lowest t_{90} value, and this indicates the optimum vulcanization reaction among the binary combinations.

Synergism, with regard to modulus, is projected in Table II and Figure 2(A). It is evident from the figure that, like torque, the modulus at 200% elongation also exhibits maximum value for the

stock containing equimolar amount of each of the accelerators. As expected, the modulus value in each case is proportional to corresponding torque value (R_α).

The tensile strength values are plotted in Figure 2(B) with respect to relative proportions of accelerators. From Table II and Figure 2(B) it is seen that, keeping in harmony with torque and modulus, highest tensile strength is exhibited by the vulcanizates obtained from the equimolecular combination of accelerators (4.5 : 4.5). However, a significant change in elongation at break is observed through the incorporation of dithio bis(N-β-hydroxyethyl piperazine).

The synergistic activity[12–16] of two or more different accelerators arises from the interaction of the accelerators to form new intermediate compounds, which, again, actively take part in the vulcanization reaction leading to enhancement of crosslink density and the rate of vulcanization reaction. As maximum synergism and highest reaction rate are exhibited by the equimolar mixture of accelerators, it is reasonably expected that maximum amounts of intermediate active components are formed at this proportion. By analogy with the reaction products of the DIPDIS–OBTS,[10] DIPDIS–OBDS,[10] DTDM–

Table IV   Physical and Cure Data of Stocks[c] (Gum) Cured at 140°C

Mix. No.	1	2	3	4	5
Composition, mmol	DIPDIS-3 DTEP-3	DIPDIS-4.5 DTEP-4.5	DIPDIS-6 DTEP-6	DIPDIS-7.5 DTEP-7.5	DIPDIS-9 DTEP-9
Maximum torque, R_α, Nm	4.25	5.05	5.80	6.55	6.80
Scorch safety, t_2, min	7.0	3.5	6.0	7.0	7.5
Optimum cure time, t_{90}, min	16.0	14.0	18.0	15.0	14.5
Modulus at 200% elongation, MPa	0.74	1.05	1.34	1.45	1.76
Tensile strength, MPa	16.9	18.7	21.56	15.5	14.5
Elongation at break, %	700	600	610	550	480

[c] Stock composition: NR 100 g, zinc oxide 5 phr, stearic acid 2 phr, and sulfur 1.5 phr.

Table V Physical and Cure Data of Stocks[d] (Filled) Cured at 140°C

| Mix. No.	1	2	3	4	5	6	7
Composition, phr	CB.[e]10	C.B.20	C.B.30	C.B.40	C.B.50	C.B.60	C.B.70
	P.O[f]2.5	P.O.5	P.O.7.5	P.O.10	P.O.12.5	P.O.15	P.O.17.5
Maximum torque, R_a, Nm	6.3	6.9	7.4	8.0	8.35	8.3	7.9
Scorch safety, t_2, min	4.5	4.5	5.0	5.0	4.5	4.25	4.0
Optimum cure time, t_{90}, min	11.0	12.0	12.5	13.25	11.25	10.5	9.0
Modulus at 200% elongation, MPa	2.2	3.5	4.1	6.3	6.7	7.5	7.9
Tensile strength, MPa	22.0	22.8	23.5	23.8	24.5	20.2	18.3
Elongation at break, %	550	530	500	420	380	360	350
Shore A hardness	45	50	60	62.5	65	70	73

[d] Stock composition: NR 100 g, zinc oxide 5 phr, stearic acid 2 phr, sulfur 1.5 phr, DIPDIS 6 mmol, and DTEP 6 mmol.
[e] Carbon black
[f] Paraffin oil.

MBTS,[7] and DIPDIS-DTEP[17-19] systems, the reaction between DIPDIS and DTEP is expected to yield the following active accelerators *in situ.* (i) Bis(diisopropyl)thiophosphoryl disulfide; (ii) Dithio bis(N-β-hydroxyethyl piperazine); (iii) Bis(diisopropyl)thiophosphoryl monosulfide; (iv) Diisopropyl thiophosphoryl-N-β-hydroxyethyl piperazino disulfide; (v) Diisopropyl thiophosphoryl-N-β-hydroxyethyl piperazino sulfenamide; (vi) Monothio bis(N-β-hydroxyethyl piperazine); (vii) Bis(diisopropyl) thiophosphoryl tetrasulfide; (viii) Tetrathio bis(N-β-hydroxyethyl piperazine); where R = isopropyl group.
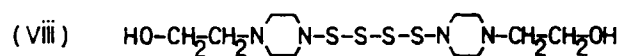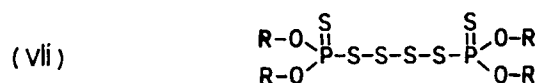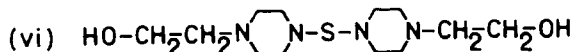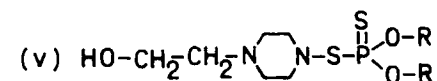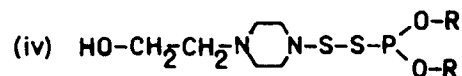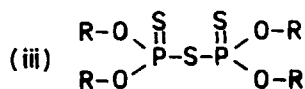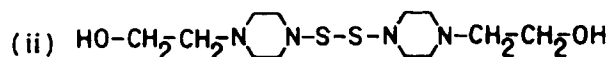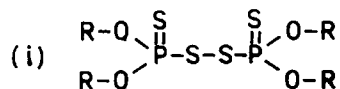
These compounds (i), (ii), (iii), (iv), (v), (vi), (vii), and (viii) can be considered as the intermediate vulcanizing aids in the complex reactions, which ultimately end with crosslinked rubber vulcanizates. The process of vulcanization is, thus, directed by the combined effect of these compounds. It is now well established that the proportions of sulfur, accelerator(s), and reinforcing fillers have a profound effect upon the physical and chemical properties of the vulcanizates, and our attention is, thus, focussed upon the optimization of sulfur, accelerator, and carbon black in order to obtain vulcanizates exhibiting good physical properties.

Effect of Variation of Sulfur Concentration on the Vulcanization of NR

After establishing the fact that maximum synergism of physical properties is exhibited by the stock containing the equimolar concentration of each accelerator, some studies were made to observe the effect of sulfur concentration upon the physical properties of the vulcanizates. In this study, efforts to optimize the concentration of sulfur are stressed with a view to produce technical vulcanizates where tensile strength plays the most vital role. With this in mind, the concentration of sulfur was varied from 0.5 phr to 2.5 phr so as to find out the optimum concentra-
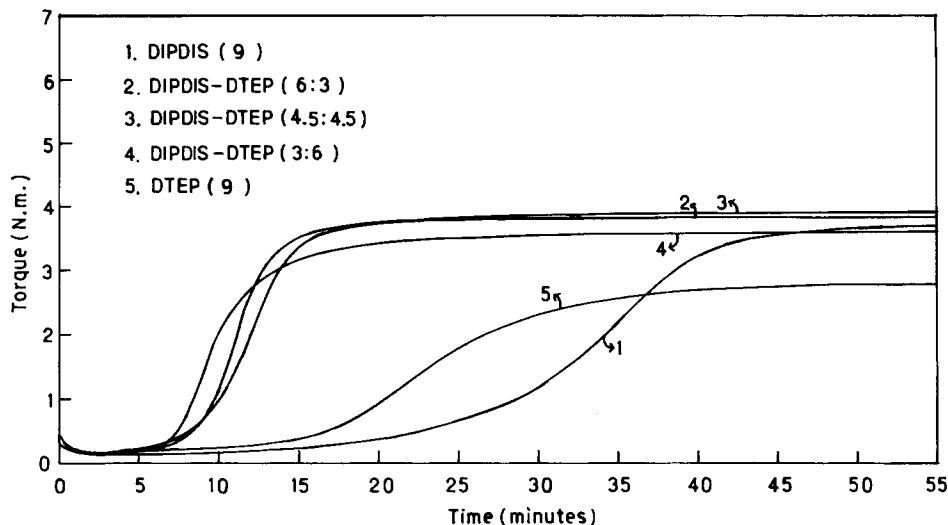
Figure 1   Rheographs of NR gum stocks cured at 140°C.

tion of sulfur at the most effective DIPDIS : DTEP ratio of 1 : 1. The variation of physical properties with change of sulfur concentration is recorded in Table III (mixes 1–5) and pictorically presented in Figure 3(A). It is seen from Table III that, with the increase of sulfur concentration, the t_2 values decrease very slowly, whereas t_{90} values increase to some extent.

As can be seen from Table III, both torque (R_α) and modulus increase with the increase of sulfur concentration. The tensile value initially goes on increasing, attains the highest value at the sulfur concentration of 1.5 phr, and again declines [Fig. 3(A), Table III]. So, it is clear from the graph [Fig. 3(A)] that, beyond 1.5 phr of sulfur, an adverse effect for the reinforcing of vulcanizates in respect of tensile strength could be seen for the equimolar combination (4.5 : 4.5) of DIPDIS and DTEP.

Optimization of the Amount of Accelerator at 1.5 phr of Sulfur

Based on the tensile property of the vulcanizates, the maximum effect was found at a sulfur concentration of 1.5 phr and at an equimolar concentration (4.5 : 4.5 of the DIPDIS : DTEP) of accelerator. This observation demands further study of the cure characterization as well as the vulcanizate properties for a higher concentration of accelerators. Because an increasing concentration of sulfur has a deleterious effect upon tensile properties of the vulcanizates, the study is restricted, for convenience, to the use of 1.5 phr of sulfur. For this purpose, the total accelerator concentration was varied from 6 mmol
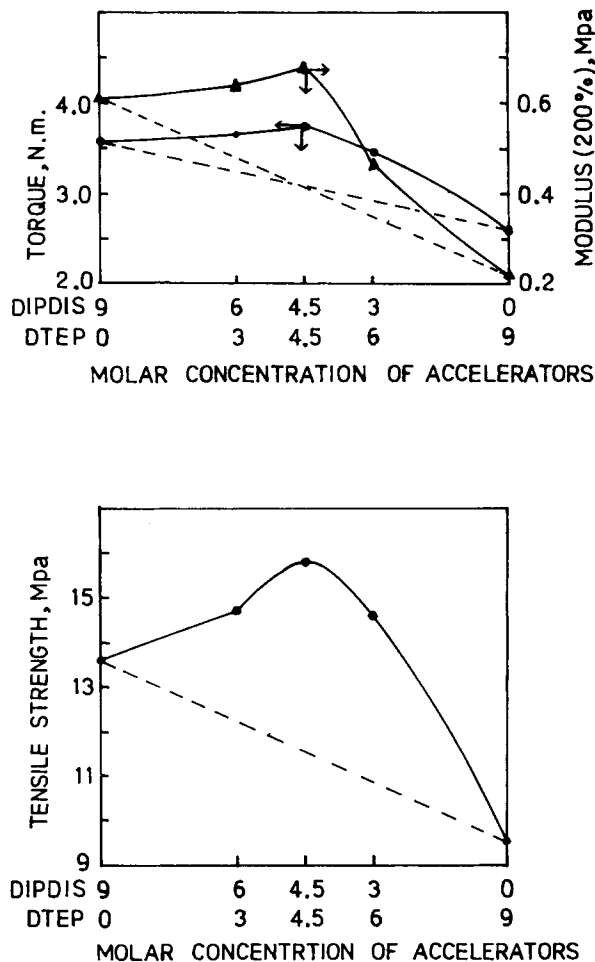

Figure 2   (A) Effect of DIPDIS to DTEP molar ratio on the torque and the modulus at 200% elongation. (B) Effect of DIPDIS to DTEP molar ratio on the tensile strength.
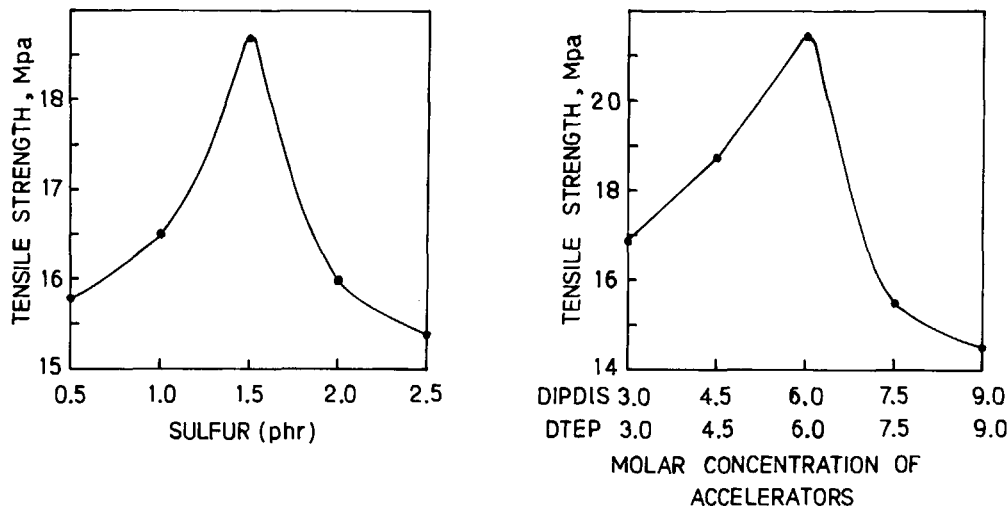
Figure 3   (A) Variation of tensile strength (MPa) of the vulcanizates with the change of sulfur concentration (0.5–2.5 phr) at DIPDIS : DTEP in the molar ratio of 6 : 6. (B) Variation of tensile strength (MPa) of the vulcanizates with the change of molar ratio of accelerators (DIPDIS : DTEP) at constant level of sulfur (1.5 phr).

phr to 18 mmol phr, keeping other ingredients fixed at the previously observed level. From Table IV (mixes 1–5), it is seen that the scorch safety (t_2) decreases sharply in the initial phase, while accelerator concentration is increased from (3 + 3) to (4.5 + 4.5) mmol phr and, thereafter, it increases gradually up to (9 + 9) mmol of accelerators. The t_{90} value also decreases in the beginning, then increases to attain it's highest value at (6 + 6) mmol accelerator concentrations, and thereafter declines.

From the data of Table IV (mixes 1–5) it is evident that torque and modulus values go on increasing with the increase of total accelerator concentration 6 mmol phr to 18 mmol phr. Figure 3 (B) shows the steep rise of tensile value with the increase of total accelerator concentration up to (6 + 6) mmol phr and which beyond that tends to decline.

From the foregoing studies, it is clear that the DIPDIS–DTEP–S system in gum vulcanization, produces vulcanizates of the highest tensile strength when the DIPDIS : DTEP accelerator ratio is maintained at a 6 : 6 molar ratio at 1.5 phr of sulfur. As we are interested in optimizing the different ingredients to give the highest value of tensile strength, we next attempted to optimize the concentration of filler.

Optimization of the Amount of Carbon Black at a Fixed Level of Accelerato

In these experiments, the concentration of carbon black was varied from 10 phr to 70 phr, keeping the concentration of accelerators and sulfur at the op-

timum levels as discussed. The physical properties and rheometer data are recorded in Table V. The reinforcement of physical properties, consequent upon the addition of carbon black, depends on the dispersion of the same in rubber. It is assumed that, at lower loading, there is not enough filler to give adequate reinforcement and, at higher loading, there is a shortage of rubber to fill all the voids in the filler. It is expected that, at optimum loading, the bonding capacity of carbon black by mechanical and/or chemical means is fully exhausted and the vulcanizates are likely to exhibit the highest physical properties. For the determination of optimum loading, we follow the method of Lee.[20] According to Lee,[20] for a well-dispersed filler rubber system, there is a difference in the degree of agglomeration (hydrodynamic volume) of filler in the cured and uncured states. It is proposed that $\eta_r > M_r$, where η_r and M_r are the relative viscosity (ratio of viscosity of loaded and unloaded elastomer) and relative modulus (ratio of modulus of loded and unloded elastomer), respectively. Lee further proposed that η_r and M_r could be determined from the rheographs of the corresponding stocks using a Monsanto Oscillating Disc Rheometer in accordance with the following expression:

$$\eta_r = T_{\min,f}/T_{\min,p}$$
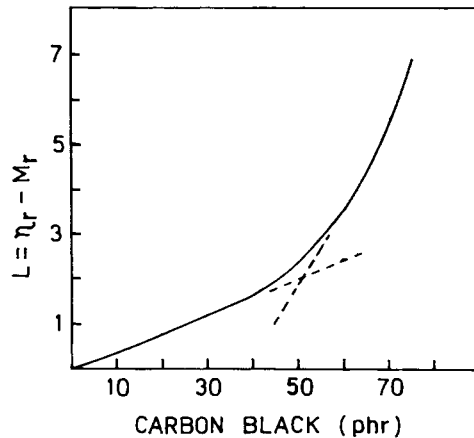
$$M_r = T_{\max,f}/T_{\max,p}$$

Figure 4   Variation of 'L' with the concentration of carbon black (10-70 phr) at DIPDIS : DTEP in the molar ratio (6 : 6) and at constant level of sulfur (1.5 phr).

where T denotes torque and subscripts f and p refer to compounds loaded with filler and unfilled polymer, respectively. In this study, the parameter L has been introduced[20] and this is defined by $L = \eta_r - M_r$.

The value of L changes slowly at low loading, and above a certain loading it increases very sharply, which is ascribed to the predominance of agglomerates. The intersection of the tangents to the curves at the low and high concentrations provide an approximate idea about good dispersion, and this concentration is taken as optimum loading for the particular recipe.

It can be seen from Table V that maximum torque (R_α), modulus, and tensile strength, increase with increasing amount of carbon black up to 50 phr of loading. The stock containing 50 phr of carbon black exhibits maximum values of R_α and tensile strength. Beyond 50 phr loading of carbon black the R_α and tensile strength decrease gradually. The intersection of the tangents of the Lee's curve [$L = (\eta_r - M_r)$ vs. concentration of carbon black (10–70 phr) in Fig. 4] also indicates that the optimum loading of carbon black is very near to 50 phr.

The state of dispersion of carbon black in the rubber medium can also be pictorially presented by Electron Microscopy. The Scanning Electron Microscopy (SEM) study of vulcanizates containing 40, 50, 60, and 70 phr of carbon black were carried out with a view to get an insight on how carbon black dispersion can explain the increase or decrease of tensile strength beyond 50 phr. Figure 5(A–D) pres-
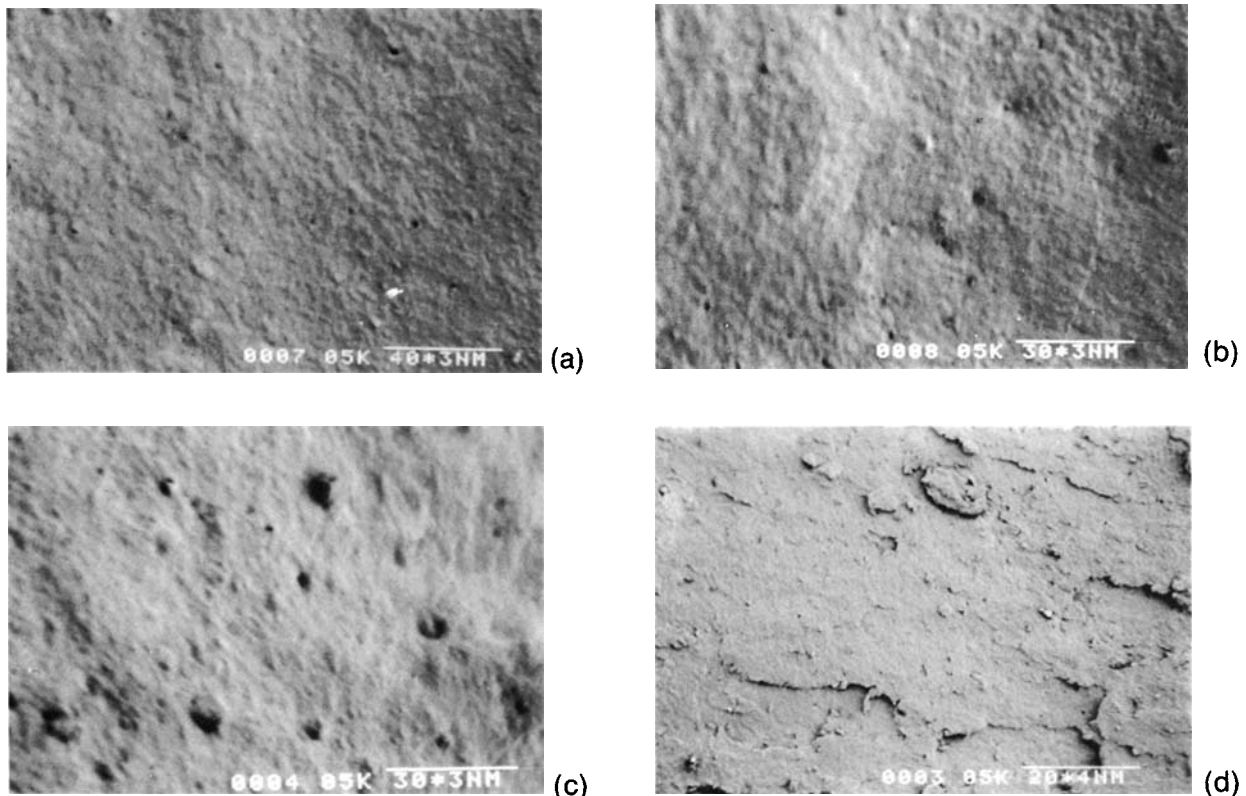

Figure 5   SEM micrographs of tensile fractured surfaces of the vulcanizates at 140°C, (a) 40 phr carbon black at 750×; (b) 50 phr carbon black at 750×; (c) 60 phr carbon black at 750×; (d) 70 phr carbon black at 750×.

ent SEM photographs of different samples containing 40, 50, 60, and 70 phr carbon black, respectively. It is evident from the pictures that stocks containing 40 and 50 phr of carbon black produce vulcanizates showing very little or no vacuole. The use of excess carbon black above the optimum level is apt to cause poor dispersion of carbon black in NR. Evidently, there occur molecular flaws in the rubber matrix and, thus, the vacuoles (as can be seen the SEM micrograph) tend to increase depending upon the concentration of carbon black in NR. Regarding the appearance of the laminas in the tensile fractured surfaces of NR vulcanizates obtained with a large excess of carbon black (70 phr), it is suggested that poor adhesion between carbon black and NR becomes predominant. The poor dispersion of carbon black in rubber, as can easily be seen in the vulcanizates containing 60 and 70 phr of carbon black [Fig. 5(C) and 5(D)], seem to be responsible for the deterioration of tensile strength. The modulus values at 200% elongation and Shore-A hardness go on increasing with carbon black concentration even beyond 50 phr of loading. It is expected that the stiffening effect of carbon black at higher filler : rubber ratio might be partly responsible for the further increases of modulus and hardness beyond 50 phr.

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