

TABLE I
Stock Formulation and the Physical Data of the Vulcanizate Obtained at 140°C

Ingredients stock no.	1	2	3	4	5	6	7	8
NR, RMA 1 × (g)	100	100	100	100	100	100	100	100
Silica (g)	10	10	10	10	—	—	—	—
Zinc oxide (g)	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
MBT (g)	2.0	—	2.0	—	2.0	—	2.0	—
OBTS (g)	—	2.0	—	2.0	—	2.0	—	2.0
DIPDIS (g)	—	—	1.5	1.5	—	—	1.5	1.5
Sulfur (g)	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Maximum torque								
R_{∞} (N m)	3.60	5.05	8.35	8.90	5.25	6.10	5.75	6.25
Scorch time t_2 (min)	2.50	23.50	5.75	15.50	3.0	14.50	3.0	11.50
Optimum cure time	18.00	33.50	16.50	24.50	10.50	22.50	11.25	23.00
t_{90} (min)								
Modulus at 200% elongation (MPa)	1.89	2.03	3.04	2.91	2.31	2.49	2.39	2.52
Tensile strength (MPa)	10.73	12.76	16.92	16.88	13.33	14.01	14.77	14.90

(DIPDIS) was prepared according to the procedure as reported by Pimblott and co-workers.⁶ Analytical grade zinc oxide and extrapure stearic acid were used as rubber additives. Technical grade silica filler was heated at 105–106°C for 16 h before use.

Preparation of Vulcanizates and Measurement of Physical Properties

Zinc oxide, stearic acid, DIPDIS, silica, OBTS/MBT, and finally sulfur were incorporated in the extracted rubber (acetone extraction for 72 h) on a Berstorff laboratory mill of size 203 × 102 mm. The whole compounding cycle was 18 min. The mix formulations are given in Table I. The cure characteristics of the different stocks were obtained using the Monsanto Rheometer R-100 at 140°C, and the results are also presented in Table I. The stocks were cured under pressure at 140°C, and the vulcanizates were kept for 24 h at ambient temperature before the measurement of modulus at 200% elongation and tensile strength according to ASTM D 412-51T using dumbbell-shaped test pieces in an Amsler (Sweden) tensile tester.

Reaction of DIPDIS with Silica

For the reaction carried out in the absence of NR, 1.50 g of DIPDIS and 10 g silica were placed in a 100 cm³ round-bottomed flask which was fitted with a condenser and a receiver. The mixture was moistened with CCl₄ so as to facilitate the reaction between DIPDIS and silica. The distilling unit was connected to a vacuum pump. Ice cold water was circulated through the condenser, and the receiver was covered with freezing mixture. The flask was heated at 140°C in an oil bath, and soon drops of a liquid began to collect in the receiver. One portion of the distillate responded to the iodoform test, thus indicating the presence of isopropyl alcohol. To another portion of the distillate red hot copper wire was dipped, and the process was repeated several

times. The treated liquid then tested for acetone through HPLC using a 25 cm Waters, C₁₈ Bondapack, reverse phase chromatography column by retention time as well as co-injection of the authentic sample. Acetonitrile–water (70 : 30 v/v) solvent mixture served as the eluent for the HPLC system. A Varian UV detector operating at 254 nm was used. On heating DIPDIS in the absence of silica, no such products could be detected.

Five grams of NR containing DIPDIS (1.5 phr) and silica (10 phr) was heated in the manner as described above. CCl₄ was not used in this case. The distillate was found to contain isopropyl alcohol. The same experiment was performed in the absence of silica where isopropyl alcohol could not be detected.

Infrared Absorption Spectra to Determine the Chemical Linkage between DIPDIS and Silica

DIPDIS (1.50 g) and silica (10 g) were heated at 140°C for 15 min. These proportions of rubber additives correspond to those actually used in the recipe as presented in Table I. From the GLC analysis of the acetone extract of the product, it was observed that DIPDIS completely reacted with Silica.

The IR spectrum (using KBr disc) of the product was obtained in Perkin-Elmer instrument (Model 783).

For the investigation with rubber, 100 g of extracted rubber (acetone extraction for 72 h) were mixed in a mill with 1.50 g of DIPDIS and 10 g of silica. The mix thus obtained was vulcanized at 140°C for 2 min. A portion of this grossly undercured rubber in the form of a thin film was employed for the IR study.

Determination of DIPDIS through GLC

Free DIPDIS remaining after its reaction with silica filler and NR was estimated using a Hewlett-Packard (Model 5710A) gas chromatograph equipped with a flame ionisation detector and a Hewlett-Packard 3380 A integrator. All GLC analyses were conducted at 170°C using a UCW column (508 × 3 mm).

It has been observed by us that DIPDIS is unreactive towards carbon black. Hence the black filler was impregnated first with a known amount of DIPDIS and then extracted with dry ethanol in a Soxhlet apparatus. Experiments showed that 1.5 h extraction of the test specimen containing DIPDIS at the reflux temperature quantitatively removed DIPDIS. This is also true for the NR vulcanizates extracted with dry ethanol since we could not find any change in the concentration of DIPDIS beyond 1.5 h.

(i) Estimation of Free DIPDIS in the Reaction between DIPDIS and Silica. DIPDIS (0.0128 g) was heated with 0.0666 g of silica filler at 100–170°C for 2 min. These proportions represent the ratio of silica filler (10 phr) to DIPDIS (1.5 phr) used in the present investigation. The residue after heating was extracted with dry ethanol for 1.5 h. Ethanol was removed in vacuum, and 2.5 cm³ of chloroform was added to the residue. The mixture was thoroughly shaken and then filtered. An aliquot of 2 mm³ of the solution obtained from the filtrate was injected onto the column and the chromatograms were obtained.

(ii) **Estimation of Free DIPDIS in the Reaction between DIPDIS and NR.** Thinly sheeted compounded stock (0.649 g) containing NR 100 and DIPDIS 1.5 phr was heated at different temperatures ranging from 140 to 170°C for 2 min. The specimen obtained in each case was extracted with dry ethanol for 1.5 h. The solvent was then removed from the extract, and the dry residue was dissolved in 2.5 cm³ of chloroform. This test solution (2 mm³) was injected onto the GLC column, and the chromatograms were obtained.

The same procedure, excepting the heating of the test pieces, was followed for studying the reaction of DIPDIS with NR during mixing operation.

RESULTS AND DISCUSSION

The Reaction of Bis(diisopropyl) Thiophosphoryl Disulfide with Silica

In this investigation the mixture of DIPDIS and silica was heated at various temperatures, and the chromatograms for the free DIPDIS are depicted in Figure 1(A). Chromatogram (a) of Figure 1(A) obtained at 100°C is identical with that obtained from similar concentration of DIPDIS and thus provide a basis for comparing the degree of disappearance of DIPDIS as observed at other temperatures. It can be seen from the figure that DIPDIS is unreactive towards silica up to 120°C. But at 140°C the coupling reaction sets in (curve c) and the concentration of free DIPDIS gradually diminishes with further rise of temperature from 150 to 170°C (curves d, e, and f). These facts

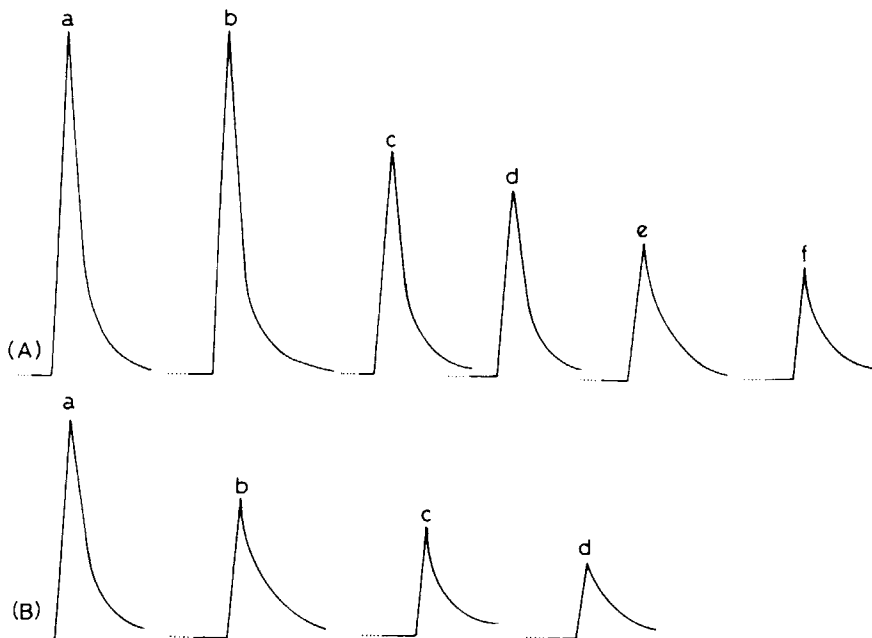
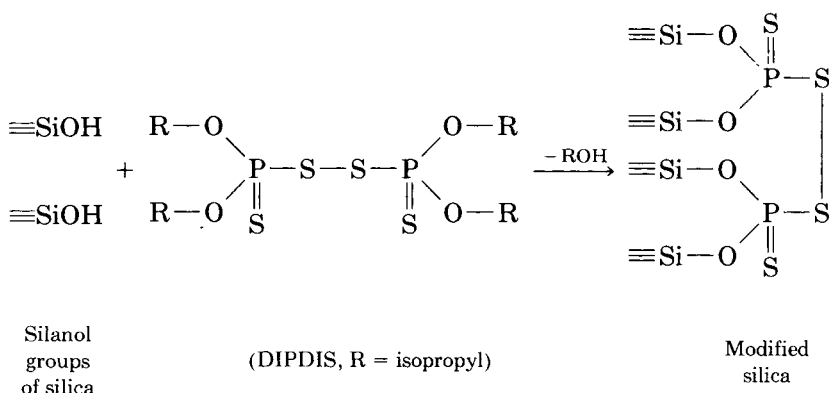


Fig. 1. (A) Gas liquid chromatograms obtained by heating 0.0128 g of DIPDIS with 0.0338 g silica at various temperatures for 2 min: (a) 100°C; (b) 120°C; (c) 140°C; (d) 150°C; (e) 160°C; (f) 170°C. (B) Gas liquid chromatograms showing the disappearance of DIPDIS (1.5 g) in the presence of NR (100 g) when heated for 2 min at various temperatures: (b) 140°C; (c) 150°C; (d) 160°C. Chromatogram (a) is obtained from the compounded stock kept at ambient temperature.



Scheme 1. Reaction of silica with DIPDIS.

are presented in Scheme 1. The scheme depicts the elimination of isopropyl alcohol. Actually, we could detect isopropyl alcohol both in the presence and absence of NR by converting it to iodoform with KOH and iodine and also by transforming it into acetone with red hot copper wire (see Experimental). The experiments provide convincing evidence for the formation of isopropyl alcohol in the reaction of DIPDIS with silica. That DIPDIS reacts with silica both in the absence and presence of NR and forms the chemical bond as depicted in the reaction scheme is more clear from the IR spectrums of the reaction products (see Experimental). The analyses of IR spectrum [Fig. 2(a)] give characteristic peak maxima (cm^{-1}): 812 S (P—O—Si stretching, mainly P—O); 670 S (P—O—Si stretching, mainly O—Si); 640 S (P=S stretching); 500 S (P—S stretching). The peaks corresponding to C—H stretching and

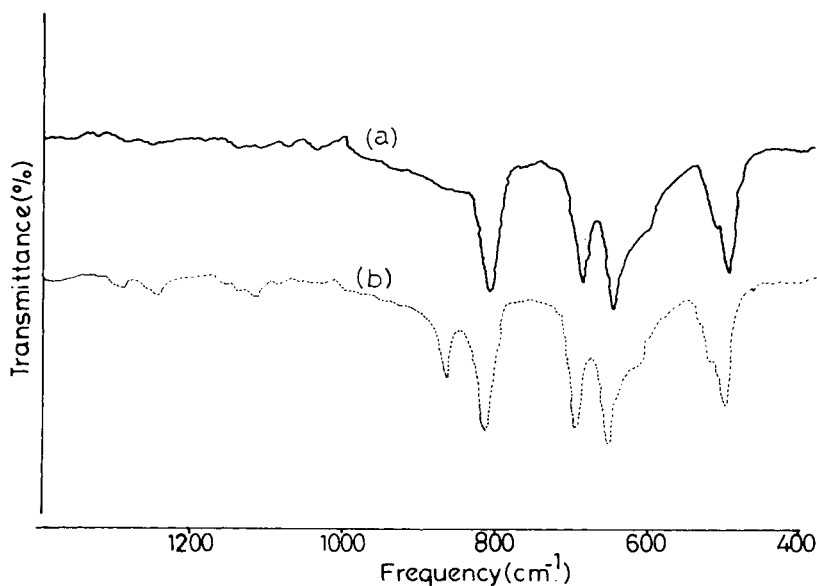


Fig. 2. IR spectrum of the product obtained from the reaction of DIPDIS with silica (a) in the absence of NR and (b) in the presence of NR.

that pendent groups resulting from the accelerator would be of the type $R'(S)_nSP(S)$ (O isoPr)₂ where R' is *cis*-1,4-polyisoprene.

From the foregoing results it is apparent that DIPDIS can simultaneously combine with NR and silica during cure and thus is likely to influence the physical properties of the vulcanizates like the silane coupling agents.⁸⁻¹⁴ In order to investigate the effect of DIPDIS in the vulcanization of NR several stocks were prepared, and these are presented in Table I. The cure data for mixes 1-8 were obtained with Monsanto Rheometer (R-100) and are designated as maximum torque (R_∞), scorch time (t_2), and optimum cure time (t_{90}). It is apparent from the rheographs (Fig. 3) that DIPDIS greatly activates MBT and the values for R_∞ , t_2 , and t_{90} are significantly increased (compare the cure data of mix 1 with those of mix 3). This activating influence of DIPDIS is also manifested in the modulus and tensile strength of the corresponding vulcanizates (Table I). It may be mentioned at this stage that DIPDIS activated dimorpholyl disulfide (DMDS) in the vulcanization of NR.⁷ A similar effect is also observed with the stocks containing DIPDIS and OBTS (also compare the cure data of mix 2 with those of mix 4). An arbitrary amount of 10 phr silica was used in the investigation only to observe how DIPDIS reacts with it and thus influences the physical properties of the vulcanizates. Comparing the physical data of mix 1 with mix 5 and mix 2 with mix 6 of Table I, it is evident that, in the absence of DIPDIS, silica lowers torque, modulus, and tensile strength of NR vulcanizates to a great extent. However, the picture changes when silica and DIPDIS are simultaneously

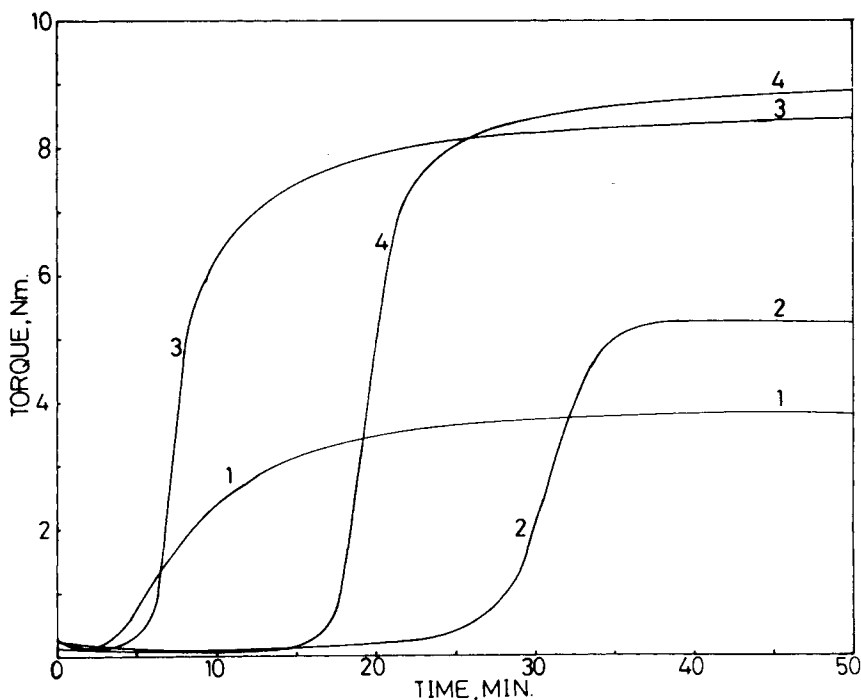


Fig. 3. Rheographs of NR stocks cured at 140°C. Mix formulations are given in Table I. (1) MBT-silica; (2) OBTS-silica; (3) MBT-silica-DIPDIS; (4) OBTS-silica-DIPDIS.

present in the rubber medium. Here, modulus and tensile strength of the vulcanizates are increased. Corresponding torque values, on the other hand, are greatly enhanced in the presence of silica and DIPDIS (compare the data of mix 3 with those of mix 7 and also the data of mix 4 with those of mix 8). From Table I it is evident that t_2 and t_{90} values are increased when the stocks contain both DIPDIS and silica. This phenomenon is indicative of the mutual reaction of the two, thereby causing the scorch delay.

CONCLUSION

DIPDIS, as it appears from the study, can act as a coupling agent for silica filled NR stocks. However, its effectiveness remains to be evaluated. Although the results presented here indicate the reaction of DIPDIS with NR, the exact nature of the reaction remains to be explored.

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