

Evaluation of Physical and Dielectric Properties of Chloroprene and Styrene Butadiene Rubber Blends

Amit Das, Dipak Kumar Basu

Polymer Science Unit, Indian Association for the Cultivation of Science, Jadavpur, Calcutta, India

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ABSTRACT: The influence of bis(diisopropyl) thiophosphoryl disulfide, a multifunctional rubber additive, on the curing characteristics and physical properties of polychloroprene rubber and styrene butadiene rubber blends was studied. It is evident from the study that covulcanization of SBR and CR following a two-stage process leads to the development of improved physical properties of the vulcanizates.

Dielectric and scanning electron microscopy study supports the occurrence of coherence of the dissimilar rubber blends. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1492–1504, 2005

Key words: blends; crosslinking; compatibility; dielectric properties; two-stage vulcanization

INTRODUCTION

Blends of SBR and CR used primarily for lower cost¹ offer some technical advantages. They have better crystallization resistance, lower brittleness temperature, and better resistance to sunlight discoloration than CR alone. But some important properties of CR, such as oil, weather, heat, flex, flame, and ozone resistance, decrease as the amount of SBR is increased.² The aim of the present work is to study the effect of a multi functional rubber additive like thiophosphoryl disulfide as accelerator on the properties of CR-SBR blends both in the absence and presence of reinforcing carbon black. The present endeavor is a novel approach towards a vulcanization technique to cocure SBR-CR blends with a view to studying the cure behavior as well as the physical and dielectric properties of the resulting blend vulcanizates. Furthermore, SEM studies have also been carried out to confirm the results obtained so far.

EXPERIMENTAL

Materials used

Polychloroprene rubber (Bayprene 215; precrosslinked XD grade; ML [1 + 4]@100°C, 50 ± 6; total ash content, max 1%; density, 1.23 g/cm³) was obtained from Bayer. SBR (Plioflex 1502) used in the present investigation was obtained from the Goodyear Tire and Rubber Co. Sublimed sulfur (Merck India, Mumbai, m.p.

118°C), A.R grade zinc oxide (Merck India, Mumbai), and precipitated magnesium oxide (Merck India, Mumbai) were used. Extra-pure grade stearic acid (Merck India, Mumbai) was used as received. Carbon black (N-774, semireinforcing furnace, Phillips Carbon Black Ltd., Durgapur, West Bengal, India) and process oil (Elasto-710, IOC, Faridabad, India) were used in this study. Bis(diisopropyl)thiophosphoryl disulfide (DIPDIS) was prepared and purified according to the procedure used by Pimblott and coworkers.³ Iso-octane (2,2,4-trimethyl pentane, S. D. Fine Chemicals Ltd., India) and toluene (Merck India, Mumbai) were used as received.

Preparation of vulcanizates

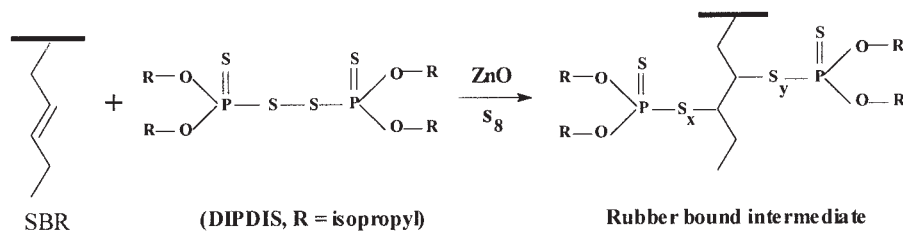
One-stage rubber vulcanizates

Zinc oxide, stearic acid, filler, and oil were added sequentially in previously masticated SBR (for pure SBR compound) or masticated and preblended rubbers (for the blend system) on a Berstorff laboratory size (203 × 102 mm) two-roll mixing mill. Finally, curatives (DIPDIS and sulfur) were added to the mix after cooling the mill. For pure CR, the compounding sequence was MgO, stearic acid, filler, process oil, sulfur, accelerator, and finally zinc oxide was added. The stocks thus obtained were cured under pressure at 160°C to optimum cure (t₉₀).

Two-stage rubber vulcanizates

In this procedure CR and SBR were first masticated separately. The requisite amounts of ZnO, stearic acid, DIPDIS, and sulfur were incorporated in SBR. The time (t) for the commencement of cure for the mix was

Correspondence to: A. Das (psuamit@yahoo.com).



Scheme 1 Formation of rubber bound intermediate.

calculated from a rheograph obtained at 160°C in a Monsanto Rheometer (R-100). The compounded SBR mix was then heated at 160°C in the hydraulic press for the predetermined time (t) to get the modified (grossly undercured) mix. The modified SBR was mixed with previously masticated CR, containing MgO to maintain the desired ratio of SBR and CR. Finally, fillers and process oil were added. The compounds were vulcanized under pressure at 160°C to optimum cure (t_{90}). In the case of pure SBR compounds, modified SBR was mixed with filler and process oil and then the compound was cured.

Measurements of physical properties

Physical properties, like modulus at 200% elongation, tensile strength, etc., of the vulcanizates were measured according to ASTM D412-92 after one-day maturation of the vulcanizates. The hardness was determined using a Shore A durometer according to ASTM D2240-85.

In the aging experiment, the samples were aged for 72 h at $100 \pm 1^\circ\text{C}$ in a forced air circulated oven. Before measuring the physical properties, the samples were kept for another 24 h.

In the crosslinking value measurement experiment, the procedure was discussed by earlier workers.⁴

The solvent used for the bound rubber determination was toluene. All compounds were stored at room temperature for one week before extraction, and the values were determined according to the procedure by Wolff et al.⁵

Scanning electron microscope studies

Scanning electron microscopy (SEM) studies were carried out on the fractured surfaces of specimens derived from tensile testing. Fractured surfaces were then carefully cut from the failed test pieces without touching the surfaces. These specimens were stored in a desiccator and then sputter-coated with gold within 24 h of testing. The SEM observations were made using a Hitachi, Model S-415A Scanning Electron Microscope.

Dielectric measurements

Rubber samples were cured in a mold with a spacer about 0.5 mm thick and 3.8 cm diameter to the corresponding t_{90} . Dielectric measurements were carried

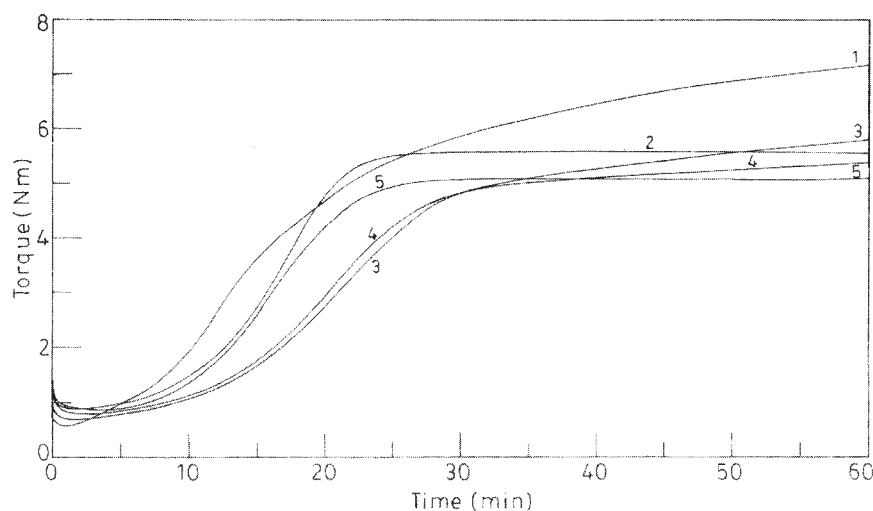


Figure 1 Rheographs of mixes 1-5 cured at 160°C (one-stage).

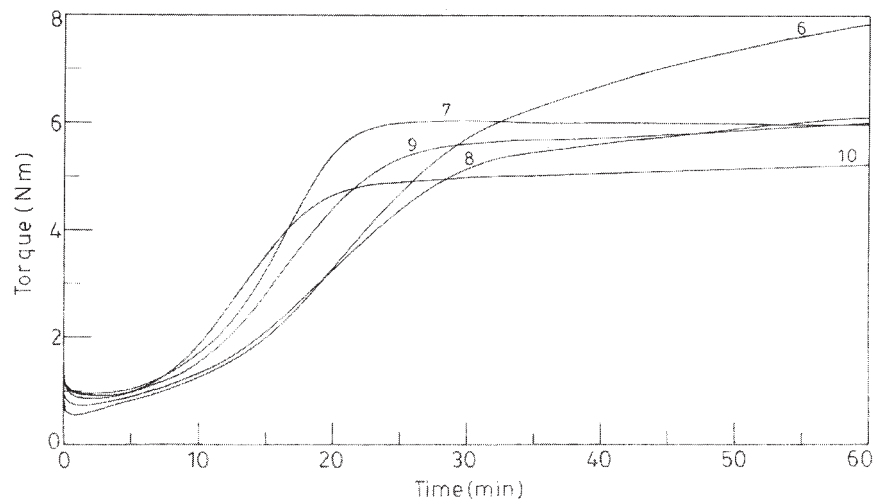


Figure 2 Rheographs of the black filled mixes 6–10 cured at 160°C (one-stage).

out by a Dielectric Spectrometer (model DS100U, Seiko Instruments Inc, Japan) at room temperature in a three terminal parallel plate with working electrode diameter 35.6 mm, allowing adequate overlap of the guard ring by the centrally placed specimen. Dielectric constant and loss factor was measured over the frequency range 10 Hz to 100 k Hz at room temperature.

RESULTS AND DISCUSSION

Owing to the large difference in polarity between SBR and CR, curatives as well as filler diffusion in the blend matrix play an important role during the vulcanization.^{6,7} Cocuring of the SBR-CR blend is effected in the present investigation using DIPDIS, which is expected to form rubber bound intermediates (as shown in Scheme 1). An effective inter-rubber

crosslinking is contemplated by restricting the curatives and filler migration across the phase boundaries. The physical properties obtained from different weight ratios of dissimilar rubbers used in the vulcanization have been effected in the presence of sulfur.

One stage vulcanization

A Monsanto oscillating disk rheometer has been used to determine the minimum viscosity, scorch time, rate of cure, optimum time of cure, and maximum torque (reflecting the modulus of the vulcanized samples). The results are presented in Figures 1 and 2 and also in Table I. It can be seen that development of maximum torque is very much dependent upon the type of investigated rubbers and their blends. Also, the optimum cure and scorch time depend markedly on the nature of the rub-

TABLE I
Formulation and the Cure Characteristics of One-Stage Vulcanizates at 160°C

| Mix | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|--|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| CR | 100 | — | 75 | 50 | 25 | 100 | — | 75 | 50 | 25 |
| SBR | — | 100 | 25 | 50 | 75 | — | 100 | 25 | 50 | 75 |
| ZnO | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
| MgO | 4 | — | 3 | 2 | 1 | 4 | — | 3 | 2 | 1 |
| Stearic acid ^a | 0.5 | 2 | 0.875 | 1.25 | 1.625 | 0.5 | 2 | 0.875 | 1.25 | 1.625 |
| DIPDIS ^b | 3.834 | 3.834 | 3.834 | 3.834 | 3.834 | 3.834 | 3.834 | 3.834 | 3.834 | 3.834 |
| S | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| N774 | — | — | — | — | — | 30 | 30 | 30 | 30 | 30 |
| Process oil | — | — | — | — | — | 5 | 5 | 5 | 5 | 5 |
| Maximum rheometric torque, R_{∞} (Nm) | 6.8 | 4.75 | 5.1 | 4.6 | 4.2 | 7.3 | 5.0 | 5.3 | 4.8 | 4.3 |
| Scorch time, t_2 (min) | 4 | 7 | 4.5 | 5 | 6 | 3 | 5 | 1.5 | 2 | 2.5 |
| Optimum cure time, t_{90} (min) | 43 | 19 | 40 | 30 | 22 | 45 | 20 | 38 | 31 | 22 |

^a Weight corresponds to 9 m mol DIPDIS.

^b 2 phr with respect to SBR and 0.5 phr with respect to CR stearic acid was added.

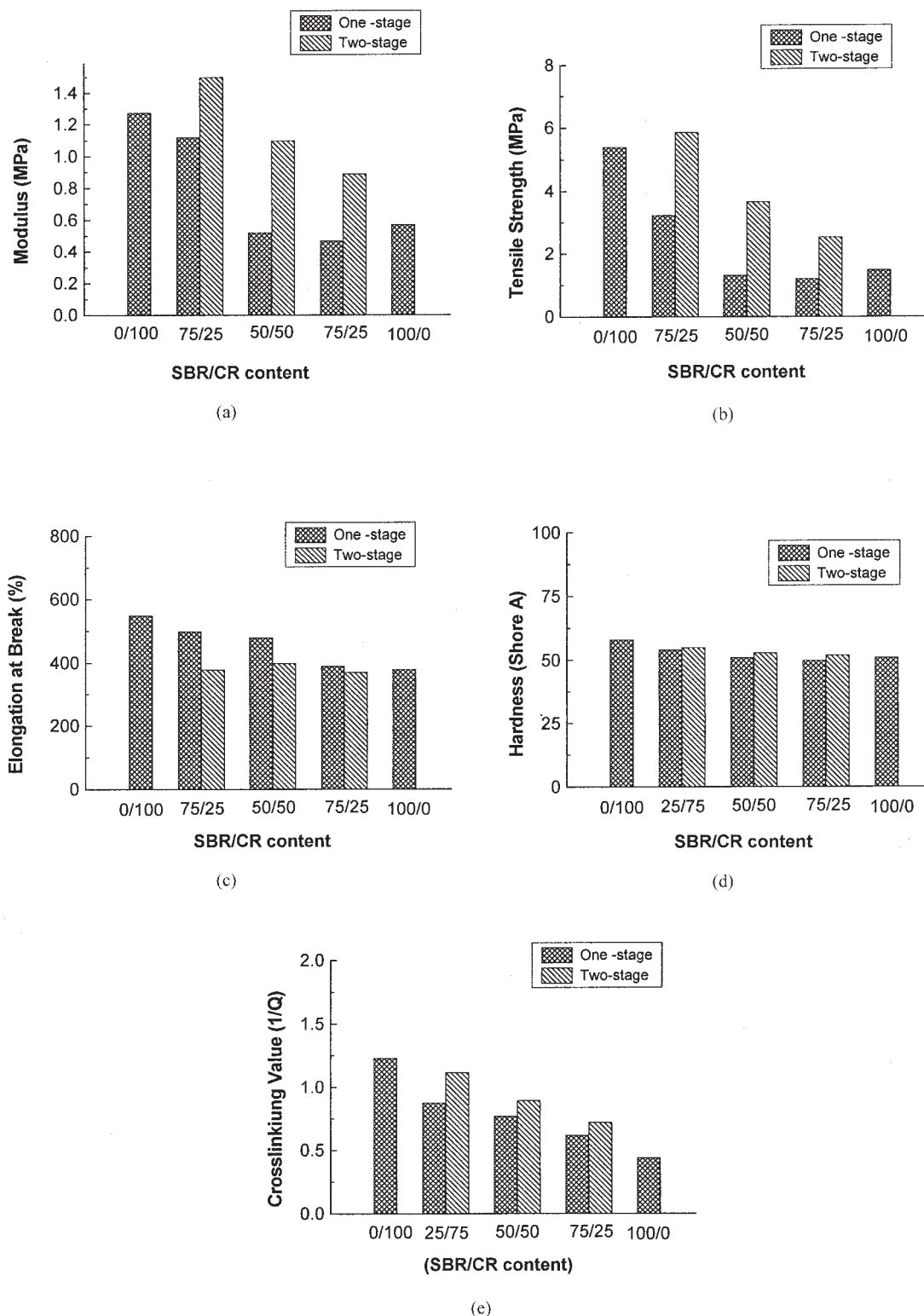


Figure 3 Comparison of (a) tensile strength, (b) 200% modulus, (c) elongation at break, (d) hardness, and (e) crosslinking value versus blend composition for SBR and CR blends (gum) derived from the one-stage and two-stage processes.

ber used. It has been found from Table I that ultimate torque and optimum cure time are maximum for CR compounds cured by DIPDIS, and so far as the blends are concerned, the values decrease as CR content decreases

creases. The physical properties of the blend vulcanizates are shown in Figures 3 and 4. It is evident from Figure 3 that elongation at break, tensile strength, and hardness values also decrease as CR content decreases

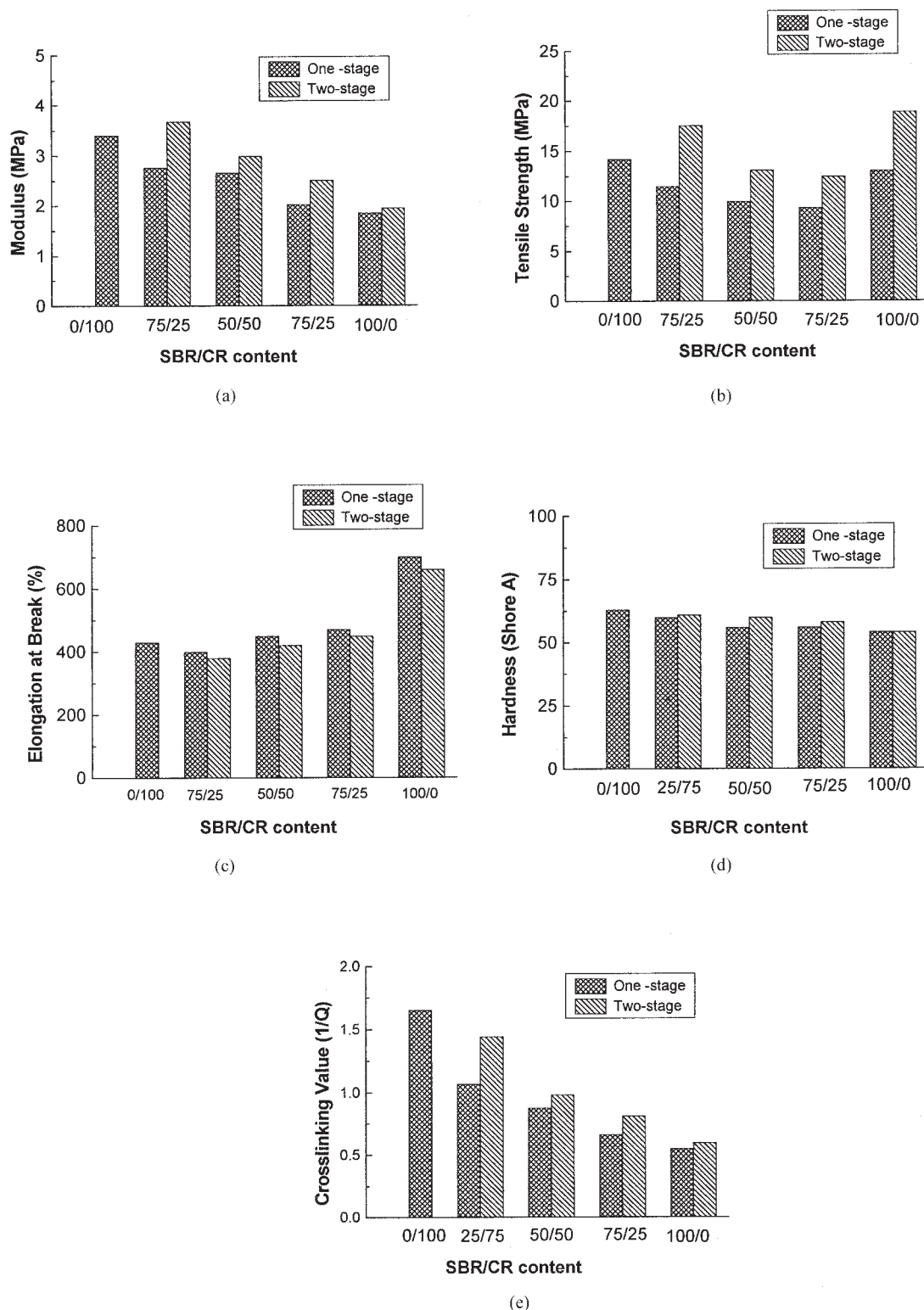


Figure 4 Comparison of (a) tensile strength, (b) 200% modulus, (c) elongation at break, (d) hardness, and (e) crosslinking value versus blend composition for SBR and CR blends (black filled) derived from the one-stage and two-stage processes.

for the blend of gum vulcanizate. The same trend is observed for tensile strength and modulus as well as hardness values for the black filled vulcanizates, as shown in Figure 4. However, the reverse trend is ob-

served for elongation at break values for black filled vulcanizates (compare Fig. 3c with Fig. 4c). As the proportion of SBR is increased in the blend, physical properties are lowered due to the nonuniform distribution of

TABLE II
Formulations and the Cure Characteristics of Two-Stage Vulcanizates at 160°C

| | Mix | 3' | 4' | 5' | 7' | 8' | 9' | 10' |
|---|---------------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| First stage | SBR | 25 | 50 | 75 | 100 | 25 | 50 | 75 |
| | ZnO | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
| | Stearic acid ^b | 0.87 | 1.25 | 1.62 | 2 | 0.87 | 1.25 | 1.62 |
| | DIPDIS | 3.834 ^a | 3.834 ^a | 3.834 ^a | 3.834 ^a | 3.834 ^a | 3.834 ^a | 3.834 ^a |
| | S | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| | Preheating time | 3.5 | 4.5 | 6 | 6 | 3 | 3.5 | 4.5 |
| Second stage (after preheating compounded SBR at first stage) | N 774 | — | — | — | 30 | 30 | 30 | 30 |
| | process oil | — | — | — | 5 | 5 | 5 | 5 |
| | MgO | 3 | 2 | 1 | 0 | 3 | 2 | 1 |
| | CR | 75 | 50 | 25 | 0 | 75 | 50 | 25 |
| Maximum rheometric torque, R_{∞} (Nm) | | 5.3 | 4.7 | 4.4 | 5.8 | 6.0 | 5.0 | 4.8 |
| Scorch time, t_2 (min) | | 1.50 | 2.00 | 2.50 | 2.00 | 3 | 1.25 | 1.50 |
| Optimum cure time, t_{90} (min) | | 30 | 17.5 | 15 | 13.5 | 35 | 22 | 13 |

^a Weight corresponds to 9 m mol DIPDIS.

^b 0.5 phr with respect to CR and 2 phr with respect to SBR stearic acid was added.

crosslinks between the constituent elastomeric phases. CR being more polar than SBR is favored with more carbon black and curatives distribution. As a result, the SBR matrix is poorly vulcanized. These factors lead to the formation of a poor overall state of cure of the blend vulcanizates.

Two stage vulcanization

In this process the preheating time plays a vital role, and it is likely that adequate rubber bound intermediates are formed.⁸⁻¹⁰ The preheating time is calculated from the rheographs of the compounds where all the ingredients are incorporated into the SBR phase. These mixes are subjected to heating under pressure. The preheating time has been chosen up to the time where the onset of cure just commences.

The rubber bound intermediate (as shown in Scheme 1) formed in the first step of the two stage vulcanization plays an important role in the vulcanization process. Once the intermediate compound is formed (preheated mix), it gets more opportunity to react with the active site of the other rubber molecules or functional groups of the filler particle rather than getting crosslinked with itself (SBR). The curing characteristics are given in Table II, and the corresponding rheographs are depicted in Figures 5 and 6. It is evident from the table that there is significant improvement of the curing characteristics as compared to those obtained from the one-stage process. Ultimate torque has been increased during the two stage vulcanization process as compared to that of the corresponding one stage values, but this effect is less pronounced in the case of gum vulcanizates (compare

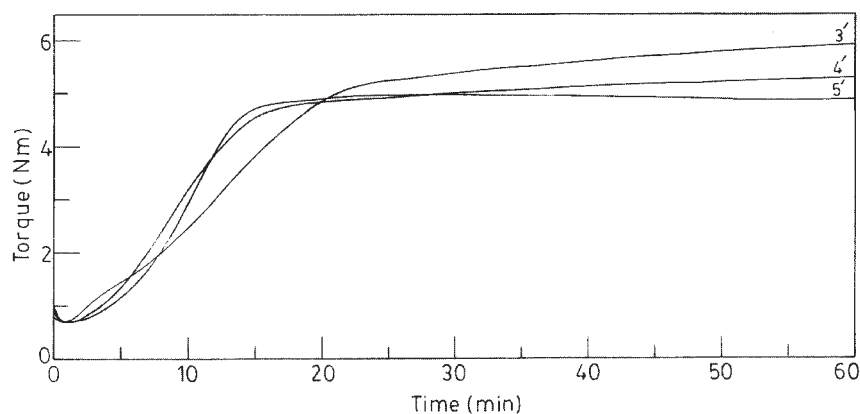


Figure 5 Rheographs of mixes 3'-5' cured at 160°C (two-stage).

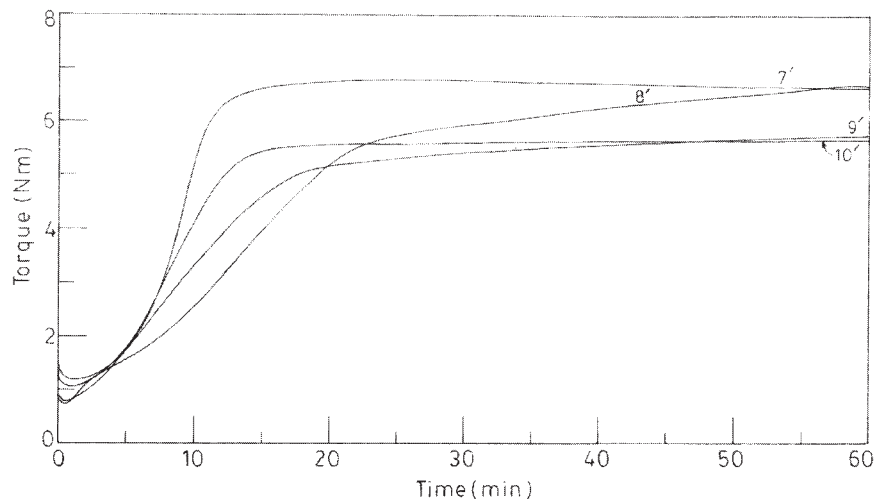
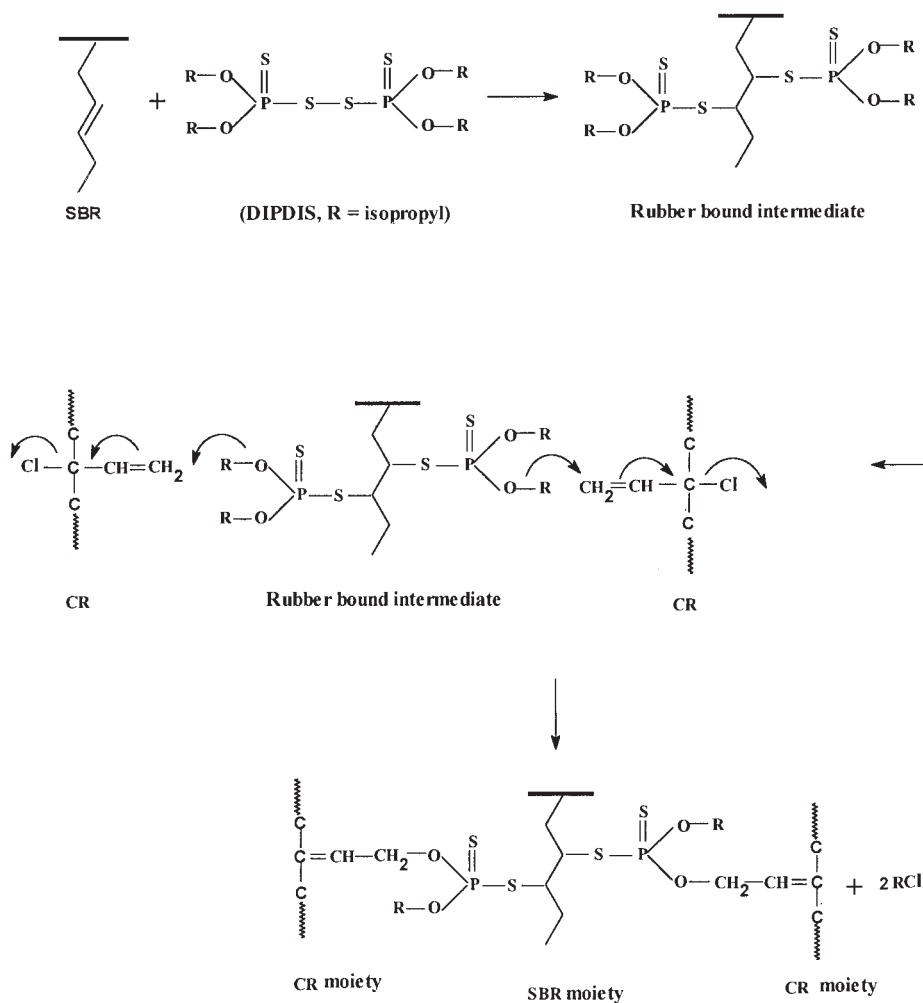


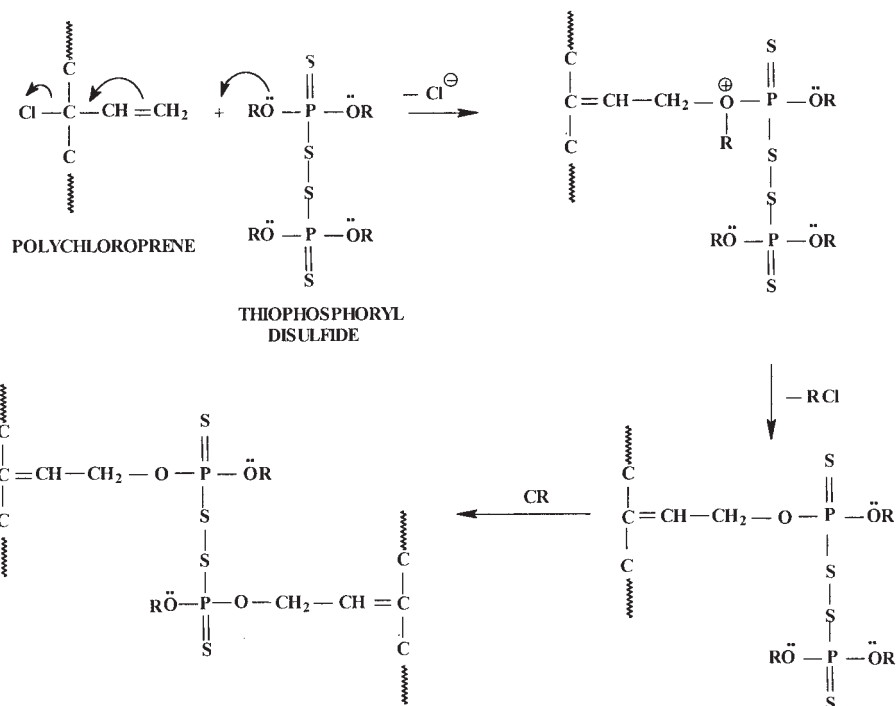
Figure 6 Rheographs of the black filled mixes 7'-10' cured at 160°C (two-stage).

mixes 3', 4', 5' with mixes 3, 4, 5). Scorch time and cure time have been reduced to a considerable extent in both the cases (gum and filled). For better understand-

ing, the physical properties are shown graphically in Figures 3 and 4. The enhancement of physical properties has been observed for the gum vulcanizates. There



Scheme 2 Formation of inter-rubber crosslinking through DIPDIS.



Scheme 3 Reaction between polychloroprene and thiophosphoryl disulfide.

is considerable increment of 200% modulus values and reduction of elongation at break values for the mixes 3', 4', 5' over those obtained from mixes 3, 4, 5 (Figs. 3a and 3c). Tensile values are also increased to some extent. However, in the case of black filled compounds, the results are more encouraging. It is evident from Figure 4 that for all the cases the modulus values are always greater than the vulcanizates obtained from the one stage process. Tensile strength is found to be maximum for the pure SBR vulcanizates (7') obtained from the two-stage process. It is interesting to note that where the blend ratio is 75 : 25 (with respect to CR : SBR, mix 8'), the tensile strength surpasses the values of CR vulcanizates. This phenomenon is, however, absent for the one-stage blend vulcanizates. This may be explained by the formation of reactive rubber bound intermediates along the SBR backbone followed by the reaction of this crosslink precursor with CR molecules in the second stage to produce coherent blend vulcanizates. The inter-rubber crosslinking through the DIPDIS fragment is shown in Scheme 2. In our earlier paper¹¹ it has been shown that alkoxy groups of the DIPDIS molecule can react with the CR molecule through tertiary allylic chlorine atoms (Scheme 3). In this way the rubber bound intermediate having pendant DIPDIS fragments on its backbone gets crosslinked with CR to give interfacial crosslinked coherent blend vulcanizates.

The formation of rubber bound intermediates has been further supported by the bound rubber experiment. Table III shows the corresponding bound rub-

ber of SBR under conventional conditions (one-stage) and two-stage conditions. It is observed that the bound rubber content of DIPDIS accelerated stocks is greater than the control stock where no accelerator was used. However, bound rubber content from stock derived from the two-stage process is greater than that from the one-stage process. The reason behind this fact is that the modified backbone of SBR must have more active reaction sites for black particles in the two-stage process. Since a carbon black particle contains different reactive organic functional groups,¹²⁻¹⁵ it may be reacted with the OR group of the pendant thiophosphoryl moiety to produce covalent linkages. This interaction has been shown in Scheme 4. However, the significant enhancement of tensile strength

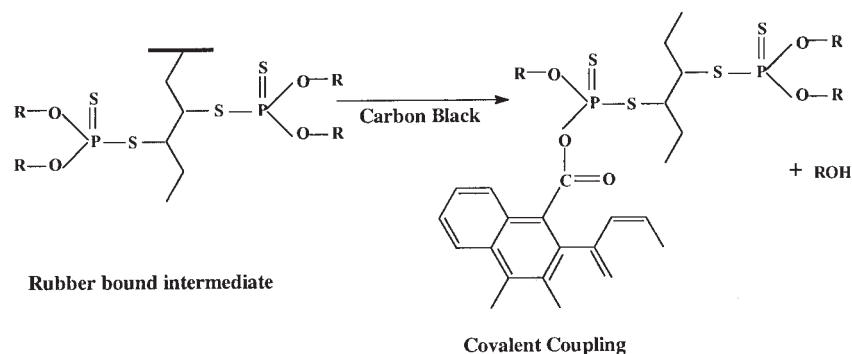
TABLE III
Bound Rubber Content of One-Stage and Two-Stage SBR Mixes

| Type of formulation | Preheating time (min) | Bound rubber (%) |
|----------------------------|-----------------------|------------------|
| Control stock ^a | — | 21.34 |
| One-stage ^b | — | 31.37 |
| Two-stage ^c | 6 | 45.67 |

^a Mix contains SBR 100, ZnO 5, stearic acid 2, and (N 774) 30 phr.

^b Mix contains SBR 100, ZnO 5, stearic acid 2, DIPDIS 9 mmol phr, and black (N 774) 30 phr.

^c Mix containing SBR 100, ZnO 5, stearic acid 2, and DIPDIS 9 mmol phr were preheated, and 30 phr black (N 774) was mixed with the preheated mass.



Scheme 4 Formation of covalent bond between rubber and carbon black.

value and almost unaltered value of 200% modulus of the pure SBR black filled vulcanizates obtained from the two-stage process have been observed as compared with the vulcanizates derived from the one-stage process. Generally, rubber-filler interactions increase the modulus values¹² but in our case the increment is negligible. This may be explained by the formation of polysulfidic type linkages between rubber and fillers as shown in Scheme 4. Here polysulfidic crosslinking¹⁶ plays a vital role to increase the tensile properties without significantly altering modulus at 200% elongation.

Solvent resistance

The solvent resistance property of CR is well known, while that for SBR is rather poor. The interfacial crosslinking between SBR and CR is likely to influence this property. Thus, swelling behavior of CR and SBR and their blends is expected to enlighten in this regard. It is evident from Figures 3 and 4 that the SBR vulcanizates exhibit poor resistance to oil while, as expected, those obtained from CR show quite significant results. It can be seen from Figures 3e and 4e that with the increase in the proportion of CR content of the blends, the crosslinking density (1/Q values) of the SBR-CR blend vulcanizates increases. This solvent resistance property of the vulcanizates is further im-

proved by the two-stage process. The enhanced 1/Q values suggest the formation of more interfacial crosslinks between the rubber phases in the two-stage vulcanization. The two-stage vulcanization not only improves the properties of blend vulcanizates of SBR-CR, but this technique also enhances the physical properties of the SBR vulcanizates, as indicated from the bar graphs presented in Figures 4a–e. The SBR vulcanizate obtained from the two-stage process gives higher crosslinking density, as shown in Figure 4e. These findings indicate that the formation of a rubber filler network is promoted by the two-stage technique.

Aging characteristics

Polychloroprene rubber is noted for its age resistance owing to the presence of the electronegative chlorine atom, which deactivates the double bond of CR. It is thus expected that the presence of CR would impart some beneficial effect on the aged samples of the rubber blends. So it was our objective to examine the aging behavior of the CR-SBR blend vulcanizates. It can be seen from Table IV that all the aged samples obtained in one stage vulcanization exhibit progressive increment of modulus values as the concentration of CR in the blend is gradually increased. Tensile values diminished rapidly during aging with the increase in CR content of the blend of gum vulcanizates.

TABLE IV
Change in Physical Properties After Air Aging at 100 ± 2 °C during 72 hours

| Mix* | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|-----------------------------|-----|-----|-------|-------|-------|-----|-------|-------|-------|-------|
| Δ TS | -31 | -33 | -35 | -21 | -12 | -10 | -22 | +7 | +5 | +3 |
| (%) | — | — | (-55) | (-36) | (-50) | — | (-44) | (-34) | (-22) | (-36) |
| Δ M 200% | +44 | +52 | +42 | +38 | +34 | +77 | +24 | +54 | +52 | +37 |
| (%) | — | — | (+8) | (+14) | (+21) | — | (+14) | (+32) | (+33) | (+25) |
| Δ Eb | -29 | -28 | -20 | -27 | -46 | -34 | -30 | -20 | -15 | -21 |
| (%) | — | — | (-8) | (-20) | (-37) | — | (-40) | (-37) | (-33) | (-38) |
| Change in hardness (points) | +3 | +3 | +1 | +2 | +1 | +4 | +2 | +5 | +6 | +5 |
| | — | — | (+2) | (+4) | (+5) | — | (+3) | (+6) | (+7) | (+6) |

Values in the parenthesis are aged values of the corresponding two-stage vulcanizates.

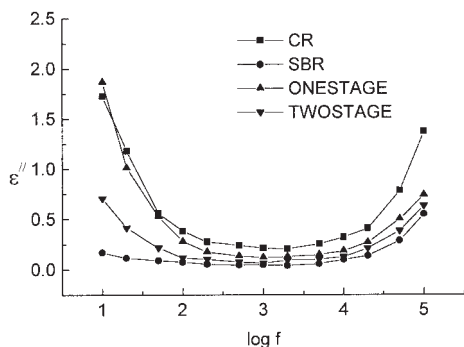


Figure 7 Plot of dielectric loss ϵ'' versus applied frequency f of gum vulcanizates of SBR, CR, and their blends: (●) SBR 100%; (■) CR 100%; (▲) CR(75)-SBR(25) in one stage; (▼) CR(75)-SBR(25) in two stage.

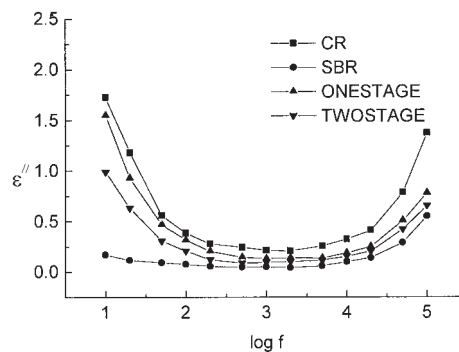


Figure 8 Plot of dielectric loss ϵ'' versus applied frequency f of gum vulcanizates of SBR, CR, and their blends: (●) SBR 100%; (■) CR 100%; (▲) CR(50)-SBR(50) in one stage; (▼) CR(50)-SBR(50) in two stage.

But a remarkable result was observed for the CR enriched black filled blend vulcanizates (mixes 8, 9, and 10). Here the retention of tensile strength value is higher compared to that of the other vulcanizates, which is even higher than that obtained from the two-stage process (compare mixes 8, 9, and 10 with 8', 9', and 10'). For the black filled one-stage vulcanizates, retention of elongation at break values are always greater than the corresponding two-stage vulcanizates. This is because of the fact that a higher amount of ZDP^{3,17} is likely to be formed in the one stage process, and the protective action of ZDP as an antioxidant becomes congenial to retaining the physical properties of the blend vulcanizates. As CR content is increased, the crosslinking sites are also increased, and residual crosslinking occurs during progressive aging.

Dielectric studies

Recently it was reported that dielectric measurements^{18,19} might be a tool to investigate compatibility of different rubber blends. In this regard, dielectric constant ϵ' and dielectric loss ϵ'' for CR, SBR, and their blends were measured over a frequency range from 10 Hz to 100 k Hz at room temperature ($27 \pm 1^\circ\text{C}$). The measured values of ϵ'' versus log of applied frequency are shown in Figures 7, 8, and 9. It is evident from these figures that the loss factor ϵ'' is lowest for SBR in the whole frequency region and is much more pronounced for chloroprene rubber, while the values of ϵ'' for blends remain in between them. In all cases, the values of ϵ'' are decreased to minimum values at frequency around 2 k Hz while these values are increased at the higher frequency region. In the low frequency region, the significant dielectric loss may be due to the Maxwell Wagner¹⁹⁻²² effect and the direct current conductivity,²³ whereas the absorption spectrum in Figures 7, 8, and 9 still show a tail of an absorption region with maxima at frequency higher

than 100 k Hz. This is mainly due to segmental motions of rubber chains. The main cause for dielectric loss at lower frequency is an alternating current, which generates due to differences in the permittivities and the resistivities of the constituent polymers of a heterogeneous system.²⁴ This phenomenon also depends on the impurity level and the thermal prehistory of the sample.²⁵ In our previous paper²⁶ we have noted that two different interfacially crosslinked rubber blends gave less dielectric loss at the low frequency region as compared to those blends that are not microhomogeneous. In this present study we also found that the dielectric loss data are lower, especially in the low frequency region, for the blends derived from the two-stage process as compared with corresponding blends derived from the one-stage process, which means that there is more phase separation for the latter case. There are considerable accumulations of foreign particles (rubber additives) in the interfacial region for the vulcanizates obtained from the one-stage process, which are responsible for high dielectric loss. These preferential accumulations of foreign par-

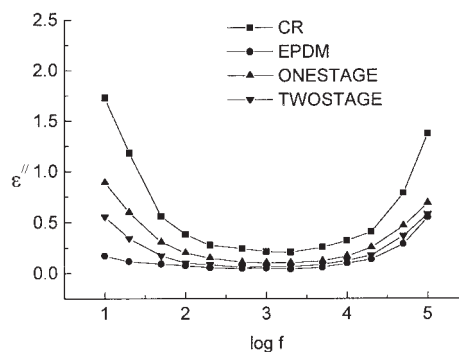


Figure 9 Plot of dielectric loss ϵ'' versus applied frequency f of gum vulcanizates of SBR, CR, and their blends: (●) SBR 100%; (■) CR 100%; (▲) CR(25)-SBR(75) in one stage; (▼) CR(25)-SBR(75) in two stage.

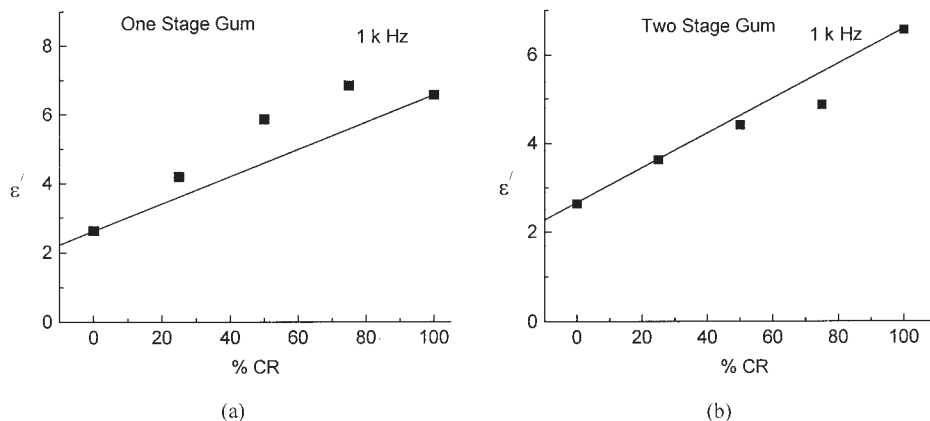


Figure 10 The relationship between the dielectric constant (ϵ') and the proportion of CR in the CR-SBR blend (gum) at frequency 1 k Hz: (a) one stage, (b) two stage.

ticles are minimized in the blends obtained from the two-stage process. This conclusively supports that two-stage vulcanization promotes interfacial cross-linking between two different rubbers according to Scheme 2.

To justify the compatibility, the dielectric constant (ϵ') was measured at the frequency of 1 k, 10 k, and 100k Hz. The chloro group adjacent to the double bonds present in CR is highly polarizable. So it is expected that the dielectric constant will be increased with the increase of CR content in the blends. Figures 10, 11, and 12 represent the variation of dielectric constant with the CR content of the blends at different frequencies. It is evident from these figures that the dielectric constant increases as the CR content increases. The increase in ϵ' values may be due to the increase of orientation polarization of the polar chlorine atom of chloroprene rubber. The blends obtained from the one-stage process have a higher dielectric constant as compared with that of the corresponding blend derived from the two-stage process. This may

be due to the presence of a higher number of dipoles in the interfacial region in one-stage vulcanizates. However, the interfaces are reduced by interfacial crosslinking in two-stage vulcanizates, which causes less dielectric constant. It is also evident from the figures that the dielectric values follow the additive rule for the blends derived from the two-stage process but the values remain below the additive line for the blends obtained from the one-stage process. This result supports the coherence of the blends derived from the two-stage process.

SEM studies

To elucidate the coherence, the tensile fracture surface of DIPDIS accelerated black filled blend vulcanizates of CR and SBR derived from both one stage and two-stage vulcanization processes were studied.

Figures 13a, 13b, and 13c represent SEM micrographs of CR and SBR in the proportions 75 : 25, 50 : 50, and 25 : 75, respectively, derived from one-stage

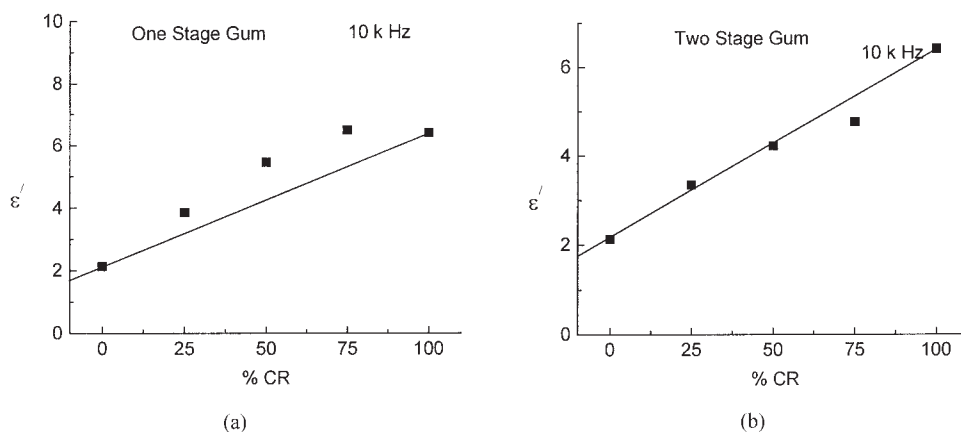


Figure 11 The relationship between the dielectric constant (ϵ') and the proportion of CR in the CR-SBR blend (gum) at frequency 10 k Hz: (a) one stage, (b) two stage.

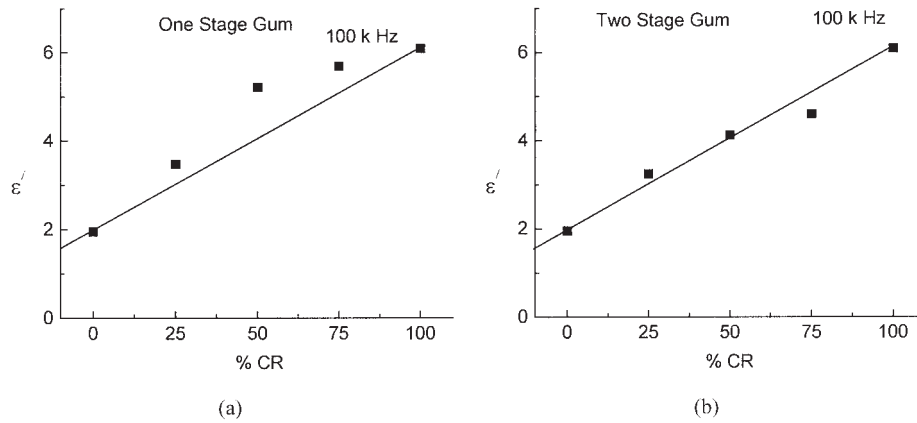


Figure 12 The relationship between the dielectric constant (ϵ') and the proportion of CR in the CR-SBR blend (gum) at frequency 100 k Hz: (a) one stage, (b) two stage.

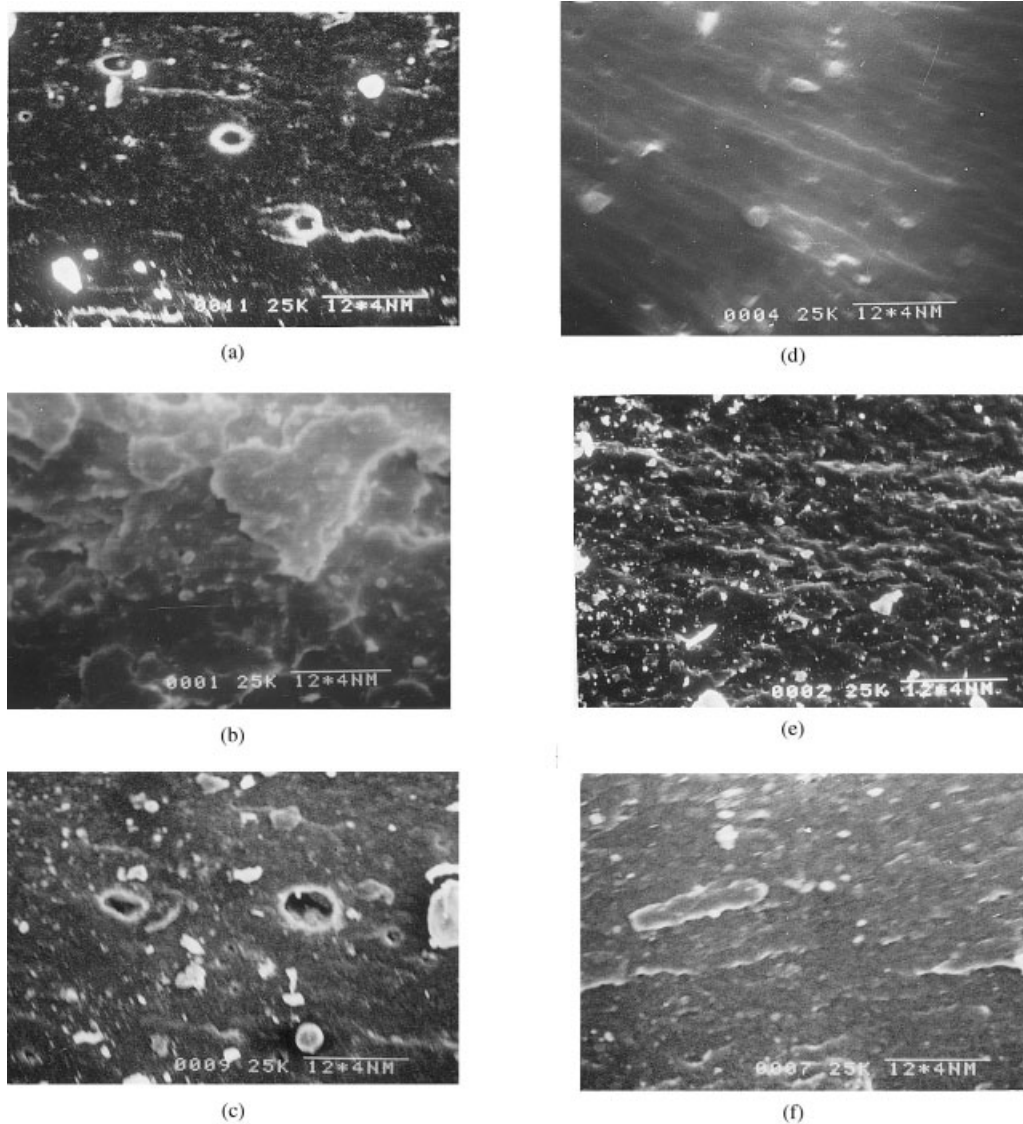


Figure 13 SEM micrographs of tensile fractured surfaces of the black filled vulcanizates cured at 160°C: (a) 75 : 25 CR-SBR blend (one stage) at 250 ×; (b) 50 : 50 SBR-CR blend (one stage) at 250 ×; (c) 25 : 75 CR-SBR blend (one stage) at 250 ×; (d) 75 : 25 CR-SBR blend (two stage) at 250 ×; (e) 50 : 50 CR-SBR blend (two stage) at 250 ×; (f) 25 : 75 CR-SBR blend (one stage) at 250 ×.

vulcanization. It is evident from the self-explanatory micrographs that DIPDIS accelerated blend vulcanizates obtained from one stage vulcanization contain a considerable number of vacuoles, indicating a poor state of dispersion of SBR in CR (Figs. 13a and 13c).

Figures 13d, 13e, and 13f provide SEM micrographs of the corresponding two-stage vulcanization of the above proportions. From these micrographs it is evident that with the increase of CR content of the blends, the state of dispersion is progressively improved. The number of vacuoles is also comparatively less in the vulcanizates obtained from the two-stage process. Moreover, there appears a line of reinforcement as visualized through the development of a network structure in Figures 13d, 13e, and 13f, which are absent in one stage vulcanizates. These findings suggest a good degree of homogeneity for the blend having 75 : 25 CR : SBR ratio in the two-stage process. The homogeneity, coherence, and ordered orientation of Figure 13d as revealed in the micrographs corroborate the observed good mechanical properties of the vulcanizates of mix 8'.

CONCLUSION

Noticeable improvements of physical properties were obtained from the black filled two stage blend vulcanizates. It was revealed that DIPDIS has a role to form more inter rubber linkage in the two-stage vulcanizates. Dielectric properties are very much dependent on the vulcanization technique, and these measurements may be applied to find compatibility of such types of blends. The phase morphology as evident from the SEM micrographs is indicative of the presence of much compact and coherent rubber matrix in the two-stage vulcanizates. However, more studies are needed to reveal the chemistry behind it.

References

1. Murray, R. M.; Thompson, D. C. *The Neoprene; Elastomer Chem Department, E. I. Du Pont De Nemours and Co. (INC): Wilmington, Delaware, 1963.*
2. Ramesan, M. T.; Mathew, G.; Kuriakose, B.; Alex, R. *European Polymer J* 2002, 37, 719.
3. Pimblott, J. G.; Scott, G.; Stuckey J. E. *J Appl Polym Sci* 1975, 19, 865.
4. Parks, C. R.; Brown, R. J. *Rubber Chem Technol* 1976, 49, 233.
5. Wolff, S.; Wang, M. J.; Tan, E. H. *Rubber Chem Technol* 1993, 66, 163.
6. Hess, W. M.; Herd, C. R.; Vegvari, P. C. *Rubber Chem Technol* 1993, 66, 329.
7. Callan, J. E.; Hess, W. M.; Scott, C. E. *Rubber Chem Technol* 1971, 44, 814.
8. Ghosh, A. K.; Basu, D. K. *Polymer International* 2003, 52, 1370.
9. Ghosh, A. K.; Basu, D. K. *Kautsch Gummi Kunstst* 2003, 56, 101.
10. Ghosh, A. K.; Debnath, S. C.; Naskar N.; Basu D. K. *J Appl Polym Sci* 2001, 81, 800.
11. Das, A.; Naskar, N.; Basu, D. K. *J Appl Polym Sci*, to appear.
12. Gonzalez, L.; Rodriguez, A.; Benito, J. L. D.; Marcos, A. *Rubber Chem Technol* 1996, 69, 266.
13. Studebaker, M. L. *Rubber Chem Technol* 1957, 30, 1400.
14. Donnet, J. B.; Voet, A. *Carbon Black, Physics, Chemistry and Elastomer Reinforcement*; M. Dekker: New York, 1976.
15. Schallamach, A. *Rubber Chem Technol* 1958, 31, 892.
16. Hashimoto, K.; Harada, T.; Ando, I.; Okubo, N. *J Soc Rubber Ind Japan* 1970, 43, 652.
17. Pimblott, J. G.; Scott, G.; Stuckey, J. E. *J Appl Polym Sci* 1979, 23, 3621.
18. Younan, A. F.; Abd-El-Messieh, S. L.; Gasser, A. A. *J Appl Polym Sci* 2061 1998, 70.
19. Saad, A. L. G.; El-Sabbagh, S. *J Appl Polym Sci* 2001, 79, 60.
20. Maxwell, J. C. *Electricity and Magnetism Vol. 1*; Clarendon Press: Oxford, 1892; p 452.
21. Wagner, K. W. *Arch Electrotech* 1937, 2, 378.
22. Sillars, R. W. *J Inst Elect Engineers* 1937, 80, 378.
23. Saad, A. L. G.; Aziz, H. A.; Dimitry, O. I. H. *J Appl Polym Sci* 2003, 91, 1590.
24. Abd-El-Messieh, S. L.; Eid, M. A. M.; Hussein, A. I. *J Appl Polym Sci* 2002, 86, 540.
25. North, A. M.; Reid, J. C. *European Polymer J* 1972, 8, 1129.
26. Das, A.; Ghosh, A. K.; Pal, S.; Basu, D. K. *Polym Advn Technol* 2004, 15, 197.