

# Polyisoprene, Poly(styrene-cobutadiene), and Their Blends. I. Vulcanization Reactions with Tetramethylthiuram Disulfide/Sulfur

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**ABSTRACT:** Polyisoprene (IR), poly(styrene-cobutadiene) (SBR) and IR-SBR blends were vulcanized with tetramethylthiuram disulfide/sulfur in a differential scanning calorimeter (DSC) at a programmed heating rate and isothermally in a press at 130°C. The reaction was stopped at various stages, and the crosslink densities were measured. Residual curatives and extractable reaction intermediates were analyzed by high-pressure liquid chromatography (HPLC). IR crosslinked more rapidly than SBR, and the difference was attributed to the greater reactivity of the accelerator polysulfides in initiating reaction with IR than with SBR. In blends, the greater reactivity of IR led to the earlier crosslinking of IR, the depletion of curatives in the IR phase, and the diffusion of curatives from SBR to IR. Consequently, a zone of highly crosslinked material developed in IR close to the interface. The freezing point of a solvent, imbibed into a gel, is decreased as crosslinking proceeds, and dissimilarities in the crosslink densities of the phases in blends were demonstrated by comparing the crosslink density, calculated from swelling experiments, with the depression of the freezing point of the imbibed solvent. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 1250–1263, 1999

**Key words:** polyisoprene; poly(styrene-cobutadiene); blends; tetramethylthiuram disulfide; covulcanization.

## INTRODUCTION

The tetramethylthiuram disulfide (TMTD) accelerated sulfur vulcanization of polyisoprene (IR) has been studied in detail.<sup>1</sup> Studies include the reactions of accelerator and sulfur in the absence of rubber,<sup>2–6</sup> the reactions of rubber,<sup>7,8</sup> and reactions that occur with model compounds, such as 2,3-dimethyl-2-butene (TME)<sup>9,10</sup> and 2-methylpent-2-ene.<sup>11</sup> The vulcanization reactions in poly(styrene-cobutadiene) (SBR) have, however, not been studied to the same extent.

The structural units in the SBR chain that will take part in the crosslinking process are the butadiene units. A number of studies have been conducted on the TMTD-accelerated vulcanization of polybutadiene (BR). Cassem and McGill<sup>12</sup> did a comparative study on the TMTD-accelerated sulfur vulcanization of BR and IR and found that the overall reaction mechanism for BR was similar to that of IR. However, higher crosslink densities were obtained in BR vulcanizates, and there was a lower percentage polysulfidic crosslinks in the BR vulcanizates. The crosslinking reaction, once initiated, was faster in BR than in IR, and there was a lesser degree of reversion in the BR compounds. It was suggested that tetramethylthiuram monosulfide (TMTM), formed during the crosslinking

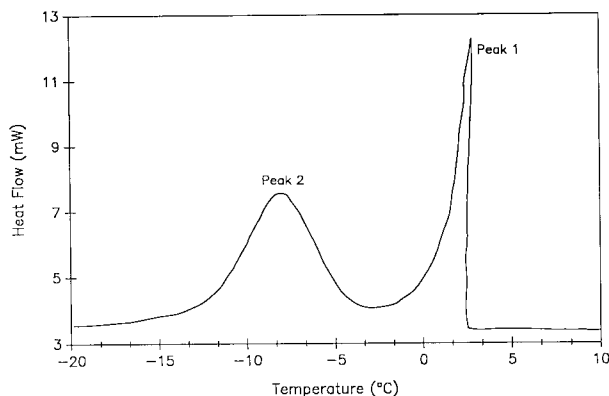
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**Figure 1** Typical DSC curve obtained on cooling a gel vulcanizate, swollen in cyclohexane, at a rate of 5°C/min.

process, could act as a desulfurating agent. Wolfe<sup>13</sup> used cyclohexene as a model olefin for BR vulcanization.

SBR can be expected to react in a similar way to BR, though the crosslinking may be slower due to the lower diene content of the polymer chain. The large styrene groups along the polymer main chain may also effect the reaction. A comparative study of the vulcanization of SBR and IR was conducted with a view to better understand the crosslinking processes that occur in each rubber and in a blend of the two rubbers, in particular, the interfacial crosslinking process.

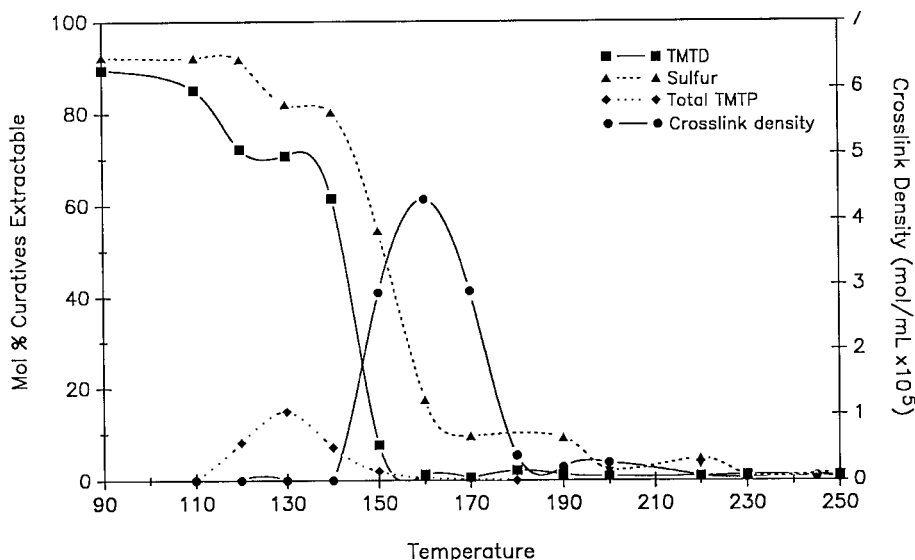
## EXPERIMENTAL

### Materials

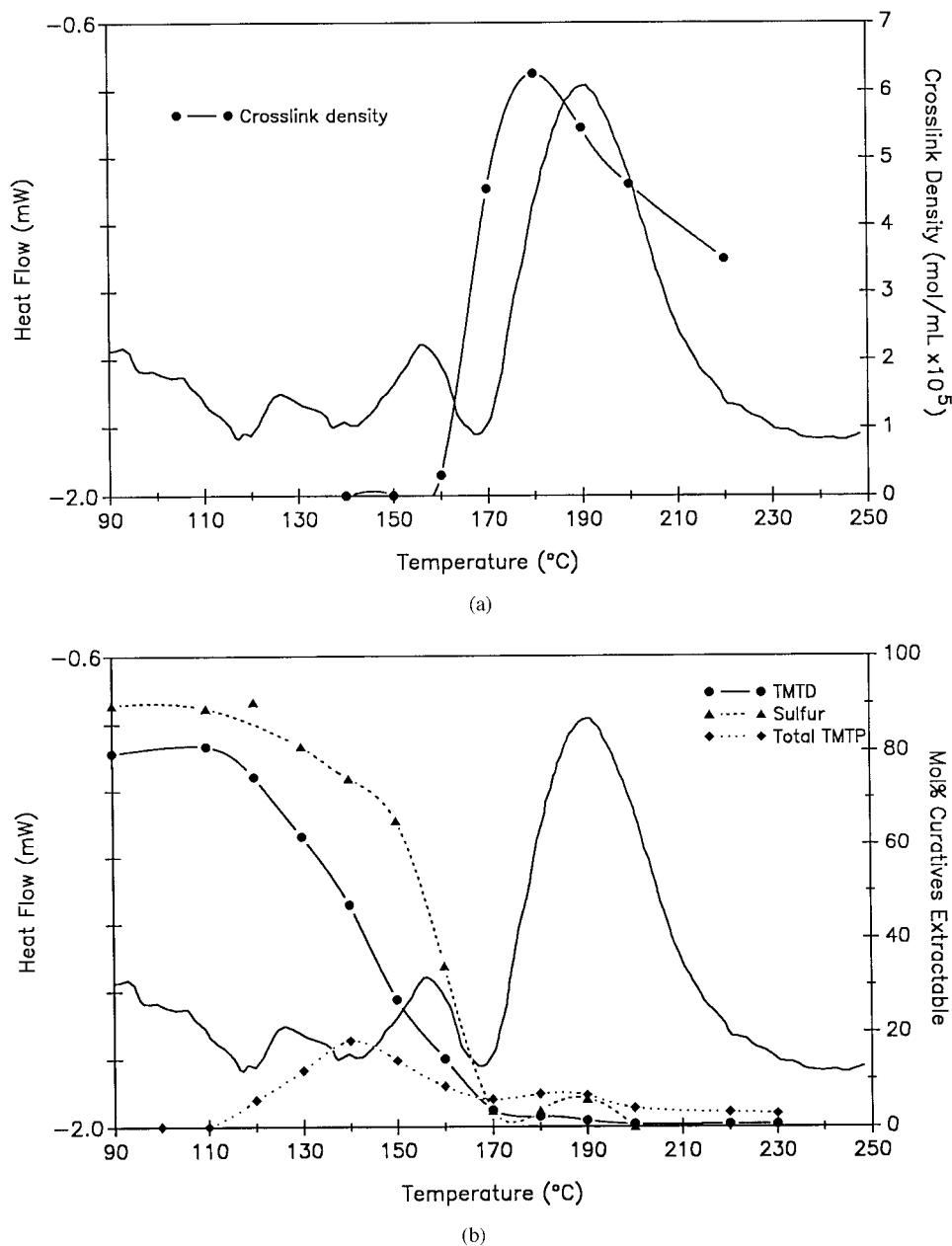
IR and SBR Afpol 1502ST were supplied by Karbochem, South Africa. Orac TMTD (97% chemical purity) was supplied by Orchem, South Africa. Sulfur (98% soluble in CS<sub>2</sub>) was supplied by AECl, South Africa.

The compounds were mixed in the Brabender Plasticorder, as described earlier.<sup>8,14,15</sup> A mixing head volume of 85 mL and a fill factor of 0.85 were used. The loadings were 100-phr elastomers, 4-phr TMTD, and 3-phr sulfur. Compounds involving master batches, in which all the curatives were added to one of the rubbers before compounding with the second rubber, are indicated in the text with square brackets around the master batch.

In the dynamic heating study, individual samples of approximately 20 mg were weighed on a microbalance and encapsulated in differential scanning calorimetry (DSC) pans. The samples were heated in the DSC calorimeter at a rate of 2.5°C/min to various temperatures.<sup>14</sup> At the pre-selected temperature or degree of vulcanization, the samples were removed from the DSC calorimeter and immediately placed in liquid nitrogen to quench the reaction. The mass of the samples used to obtain the DSC curves are indicated on the legends to the diagrams as  $M_D$ . Isothermal vulcanization was conducted by heating samples



**Figure 2** Crosslink density and HPLC analysis of extractable curatives for IR-TMTD/sulfur heated in a DSC at 2.5°C/min.



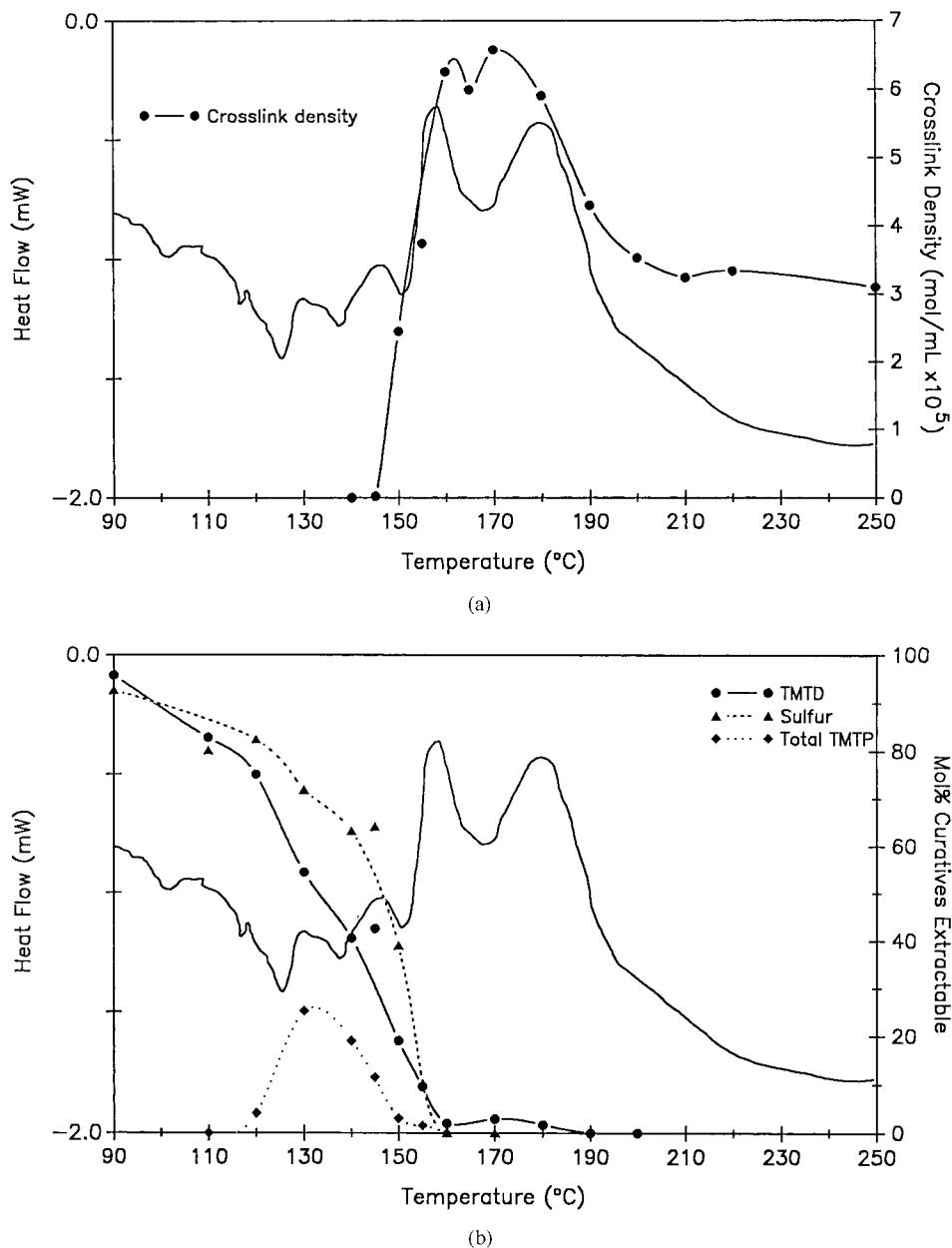
**Figure 3** (a) DSC cure curve and crosslink density for SBR-TMTD/sulfur ( $M_D = 18.5835$  mg) heated at  $2.5^\circ\text{C}/\text{min}$ . (b) DSC cure curve and HPLC analysis of extractable curatives for the SBR-TMTD/sulfur heated at  $2.5^\circ\text{C}/\text{min}$ .

in a small mold in a press for various times at  $130^\circ\text{C}$ .

Crosslink densities were determined by swelling. The polymer-solvent interaction parameters used in the Flory-Rehner equation<sup>16</sup> were 0.435 for IR-benzene<sup>17</sup> and 0.370 for SBR-benzene.<sup>18</sup> An average value of 0.403 was used for the polymer blends.

Residual curatives and soluble intermediates were extracted from the rubber at various stages

of the reaction and analyzed by high-pressure liquid chromatography (HPLC).<sup>2,8,14</sup> The extraction was dealt with in one of two ways, depending on whether samples dissolved or swelled in benzene. For samples that did not dissolve in benzene, the solvent was decanted from the swollen samples and was evaporated. The residue was redissolved in dichloromethane-methanol (5/95 *v/v* ratio) and analyzed by HPLC. In the uncrosslinked samples, the benzene was evaporated



**Figure 4** (a) DSC cure curve and crosslink density for IR-SBR-TMTD/sulfur ( $M_D = 18.2563\text{mg}$ ) heated at  $2.5^\circ\text{C}/\text{min}$ . (b) DSC cure curve and HPLC analysis of extractable curatives for the IR-SBR-TMTD/sulfur heated at  $2.5^\circ\text{C}/\text{min}$ . (c) Crosslink density and freezing point of cyclohexane in swollen vulcanizates for IR-SBR-TMTD/sulfur heated at  $2.5^\circ\text{C}/\text{min}$ .

from the sample, leaving a thin rubber coating on the walls of the pill vial, allowing the efficient extraction of the residual curatives and reaction intermediates into isopropyl alcohol. Enough isopropyl alcohol to cover the rubber was added, then the isopropyl alcohol was replaced after 24 h and allowed to extract for a further 24 h. The combined extract was evaporated, and the resid-

ual dissolved for HPLC analysis. In the figures, the concentration of reactants and intermediates are expressed in terms of the initial concentration of reactants.

The samples used in the determination of the freezing point depression of the solvent in the swollen vulcanizate<sup>19</sup> were swollen in cyclohexane for 24 h. The swollen gels were cut to size and

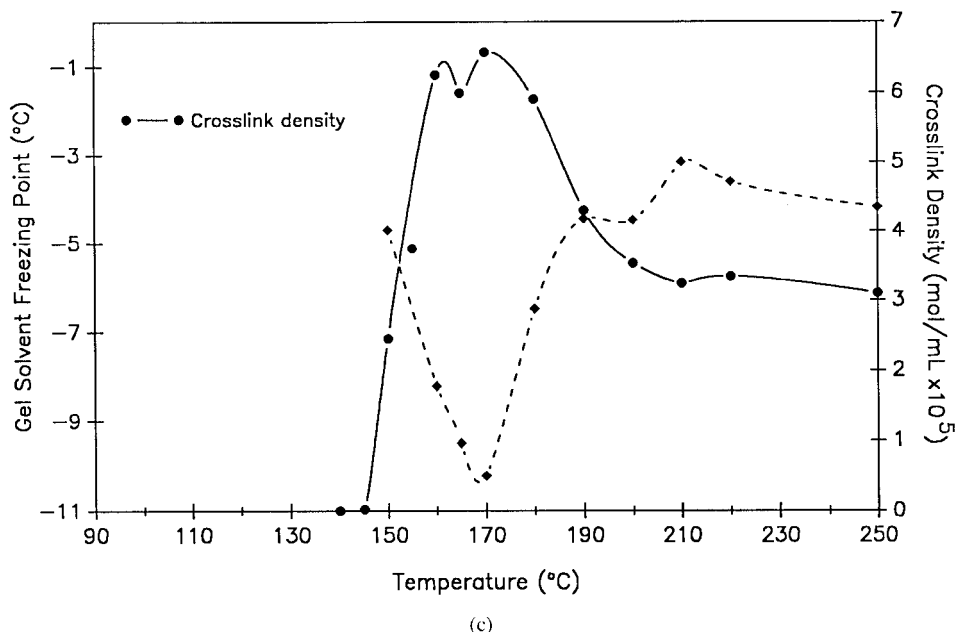


Figure 4 (Continued from the previous page)

encased in DSC pans with excess solvent. The pans were then placed in cyclohexane and left for 24 h. Pans were removed, dried externally, and cooled in the DSC at a rate of 5°C/min. Figure 1 shows a typical curve obtained. Peak 1 is due to freezing of pure solvent surrounding the swollen gel, and peak 2 due to freezing of solvent in the swollen gel. The gel solvent freezing point was taken as the temperature at which peak 2 begins.

The mass percentages of rubbers in the soluble and insoluble fractions of blends, vulcanized to different extents, were determined by thermogravimetry (TG).<sup>20-22</sup> Analysis of a number of standard mixes showed that the percentage of each component rubber could be determined from the derivative of the mass loss curve.

## RESULTS

### Dynamic Heating

#### IR-TMTD/Sulfur

The DSC cure curve obtained on heating an IR-TMTD/sulfur compound at 2.5°C/min is similar to that described by Kruger et al.<sup>7,8</sup> Analysis of the extractable curatives shows that the concentration of tetramethylthiuram polysulfides (TMTP) reaches a maximum before decreasing again prior to crosslinking (Fig. 2). (A range of TMTP of different sulfur rank, as reported earlier, 3, 8 was

observed, and only the total TMTD concentration is shown here.) This decrease, and that of TMTD, are associated with pendent group formation. The crosslink density reaches a maximum at 160°C before rapid reversion at higher temperatures.

#### SBR-TMTD/Sulfur

The DSC cure curve for the SBR-TMTD/sulfur shows similar characteristics to that of the IR compound [Fig. 3(a)]. The endotherm, associated with the rapid evolution of dimethyldithiocarbamic acid at the onset of crosslinking,<sup>5</sup> is soon masked by the much larger vulcanization exotherm, peaking at 198°C. TMTD is more soluble in SBR than IR,<sup>23</sup> and, as in the case of BR compounds,<sup>12</sup> there is no clear endotherm that can be associated with the melting of TMTD. The vulcanization exotherm is similar to that of BR,<sup>12</sup> both starting at 150°C and peaking at 190°C.

Crosslinking is observed at 160°C, some 15 to 20°C higher than in the case of IR. Crosslinking is rapid, and the crosslink density reaches a maximum value of  $6.25 \times 10^{-5}$  mol/mL at 180°C, some 50% higher than the maximum crosslink density obtained in the IR system. Reversion is less marked than in the IR system, as is also found with MBTS-accelerated formulations.<sup>24</sup> When crosslinking begins, most of the TMTD has been bound to the polymer and is not extractable [Fig. 3(b)].

**Table I** Mass Percentage IR and SBR in the Insoluble Fraction of Blends Vulcanized to Different Temperatures in the DSC

Blend Temperature (°C)	IR-SBR-TMTD/Sulfur		[IR-TMTD-Sulfur]/SBR		[IR-SBR-TMTD/Sulfur]	
	IR (%)	SBR (%)	IR (%)	SBR (%)	IR (%)	SBR (%)
143.00	80.10	19.90				
144.00	63.70	36.20				
145.00	67.50	32.50	80.20	19.80	76.40	23.60
146.00	61.40	38.60				
147.00	61.20	38.80				
148.00	55.40	44.60				
150.00	43.10	56.90	59.70	40.30	61.20	38.90
155.00	43.60	56.40	51.10	48.90	50.90	49.10
160.00	46.60	53.30	50.10	49.90	51.30	48.70
165.00	50.40	49.60	49.20	50.70	48.90	51.10
170.00	48.90	51.10	47.10	52.90	46.80	53.20
180.00	47.50	52.60				
190.00			49.30	50.70	48.50	51.50
200.00			52.30	47.70	44.90	55.20
220.00			46.50	53.60		
250.00			48.40	51.60	45.50	54.50

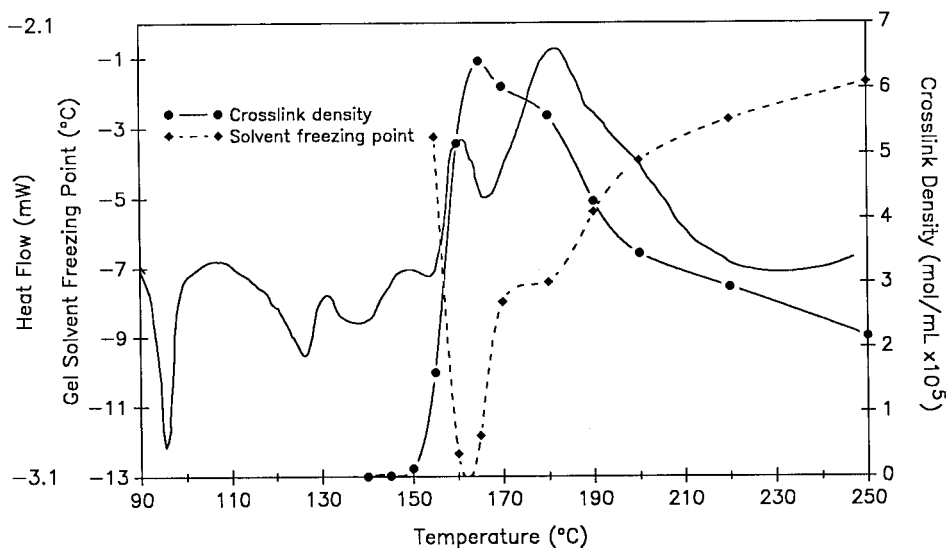
**IR-SBR-TMTD/Sulfur**

The DSC cure curve obtained on heating a IR-SBR-TMTD/sulfur blend at 2.5°C/min is shown in Figure 4(a) and the concentrations of the extractable curatives in Figure 4(b). The maximum crosslink density of  $6.57 \times 10^{-5}$  mol/mL is slightly higher than that found with SBR ( $6.30 \times 10^{-5}$  mol/mL) and occurs at 170°C, a temperature between the IR and SBR crosslink density maxima at 160 and 180°C, respectively.

It is well known<sup>19,25-28</sup> that the freezing point depression of a solvent in a swollen gel increases with an increase in the crosslink density. A number of explanations for this decrease in freezing point have been put forward. It has been contended that in a nonuniformly crosslinked sample, freezing nucleates in the less highly crosslinked zones<sup>19,28,29</sup> Figure 4(c) compares the freezing point of cyclohexane in the swollen vulcanizates with crosslink density calculated from the Flory-Rehner equation. Since the solvent freezing point curve does not exactly mirror the crosslink density curve, as calculated from swelling experiments, it is clear that crosslinking in the two phases did not occur to the same extent at any given time. It can also be surmised that since crosslinking occurs much earlier in IR compared to SBR, the crosslink density will be less in the

SBR phase, at least in the early stages of the vulcanization, and the freezing point will be an indication of the extent of crosslinking in this phase. The maximum in the freezing point depression occurs at the second crosslink density maximum, as calculated from the volume fraction of rubber in the swollen vulcanizate. Although there is a relatively small change in the crosslink density between samples cured to 160 and 170°C, there is a relatively large change in the solvent freezing point of the swollen vulcanizate (approximately 2°C). This may indicate that once crosslinking in the earlier curing IR phase has been completed, crosslinking in the SBR phase continues, although the overall crosslink density of the sample does not increase to the same degree, with swelling being dictated by the continuous IR phase. Nuclear magnetic resonance (NMR) techniques may also be used to differentiate between the crosslink densities of phases in a two-phase system.<sup>30</sup>

To confirm the relative rates of vulcanization of the IR and SBR phases in the blend, samples were vulcanized in the DSC calorimeter to different temperatures and then swollen in benzene. The insoluble gel was removed, dried, and analyzed by TG to determine the percentage composition of each of the rubbers (Table I). Since the



**Figure 5** DSC cure curve, crosslink density, and freezing point of cyclohexane in the swollen vulcanizates for [IR-TMTD/sulfur]-SBR ( $M_D = 14.5598$  mg) heated at  $2.5^\circ\text{C}/\text{min}$ .

molecular weight of each polymer will also influence the amount of material crosslinked, the actual percentages must be read as a qualitative indication of the preferential crosslinking of IR. It can be seen that in the early stages of the vulcanization, IR constitutes the greater amount of the crosslinked phase by mass. As the vulcanization continues, the composition of the crosslinked material becomes closer to that of the composition of the blend.

#### [IR-TMTD/Sulfur]-SBR

This system was prepared by first mixing all the curatives into IR and then mixing the IR master batch with SBR. This was done in an attempt to achieve a higher concentration of curatives in the IR phase prior to vulcanization, though it is recognized that redispersion of the curative would occur during the mixing process of the IR master batch with the SBR. TMTD and sulfur are more soluble in SBR than in IR.<sup>23</sup>

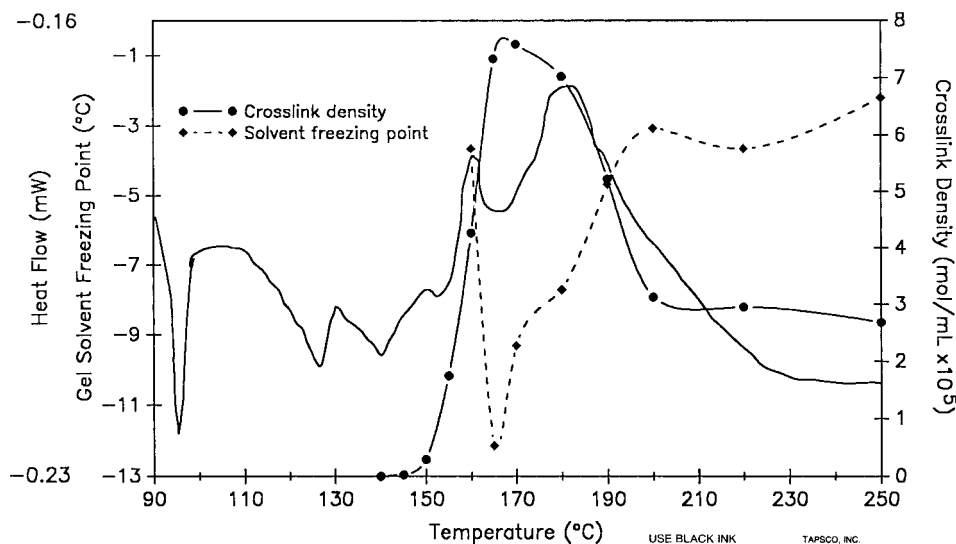
The DSC cure curve (Fig. 5) is similar to that for the IR-SBR-TMTD/sulfur system, although the exotherm, which begins at  $170^\circ\text{C}$ , is slightly larger and broader. The maximum crosslink density achieved is the same. The maximum depression of the freezing point of the cyclohexane in the swollen vulcanizate occurs in compounds cured to just below  $165^\circ\text{C}$ , while the maximum in the crosslink density, as calculated from swelling data, occurs in samples cured to  $165^\circ\text{C}$ . There is

an increase in the overall crosslink density of about  $1.26 \times 10^{-5}$  mol/mL between the samples cured to 160 and  $165^\circ\text{C}$ , while the solvent freezing point depression in the swollen gel remains essentially the same. Since all curatives were mixed into the IR, which is the faster curing phase, it can be expected to be the most heavily crosslinked and, therefore, to restrict the swelling of the dispersed SBR phase. The solvent freezing point is very low ( $-12.5^\circ\text{C}$ ), and further restriction on swelling, occasioned by the increase in overall crosslink density, may not markedly affect the solvent freezing point.

Table I shows the percentage of each of the two rubbers in the insoluble fraction of the vulcanizates cured to different temperatures. As was the case in the IR-SBR-TMTD/sulfur system, IR constitutes the major portion of the insoluble fraction in the early stages of the vulcanization.

#### IR-[SBR-TMTD/Sulfur]

The compound was prepared by mixing all of the curatives into the SBR and then blending the SBR master batch with IR. The DSC cure curve (Fig. 6) is similar to those of the other IR-SBR blends. The second exotherm, starting at  $165^\circ\text{C}$ , is larger and broader than in the IR-SBR-TMTD/sulfur compound, as was the case in the [IR-TMTD/sulfur]-SBR compound. Crosslinking begins at  $150^\circ\text{C}$  and increases rapidly to a value of



**Figure 6** DSC cure curve, crosslink density, and freezing point of cyclohexane in the swollen vulcanizates for IR-[SBR-TMTD/sulfur] ( $M_D = 16.0957$  mg) heated at  $2.5^\circ\text{C}/\text{min}$ .

$7.58 \times 10^{-5}$  mol/mL at  $170^\circ\text{C}$ , a slightly higher value than in the other two blends.

Initially, there is a decrease in the freezing point of the cyclohexane in the swollen vulcanizate as the crosslink density increases. Between samples cured to 165 and  $170^\circ\text{C}$ , there is a slight increase in the overall crosslink density; but there is a large decrease in the solvent freezing point depression, indicating a decrease in the crosslink density (reversion) of the less heavily crosslinked region. Reversion in IR would be rapid at these temperatures. Since all curatives were mixed into the SBR, further extensive crosslinking in SBR may restrict the swelling of IR adjacent to the SBR zones, thereby decreasing the overall swelling. However, the recorded solvent freezing point may be dictated by reversion in IR regions remote from the interface.

Once again, it can be seen that in the early stages of the vulcanization, IR constitutes the major portion of the crosslinked gel (Table I).

### Isothermal Vulcanization

The vulcanization of the compounds was studied isothermally at  $130^\circ\text{C}$  in a press. For isothermal reaction, the separation of the two crosslinking processes would be greater than for a dynamic study and differences could be further enhanced by decreasing the temperature to  $130^\circ\text{C}$ . The IR/[SBR/TMTD/sulfur] blend was studied in detail because, by mixing all the curatives in the SBR

phase, the diffusion effects of curatives would be maximized.

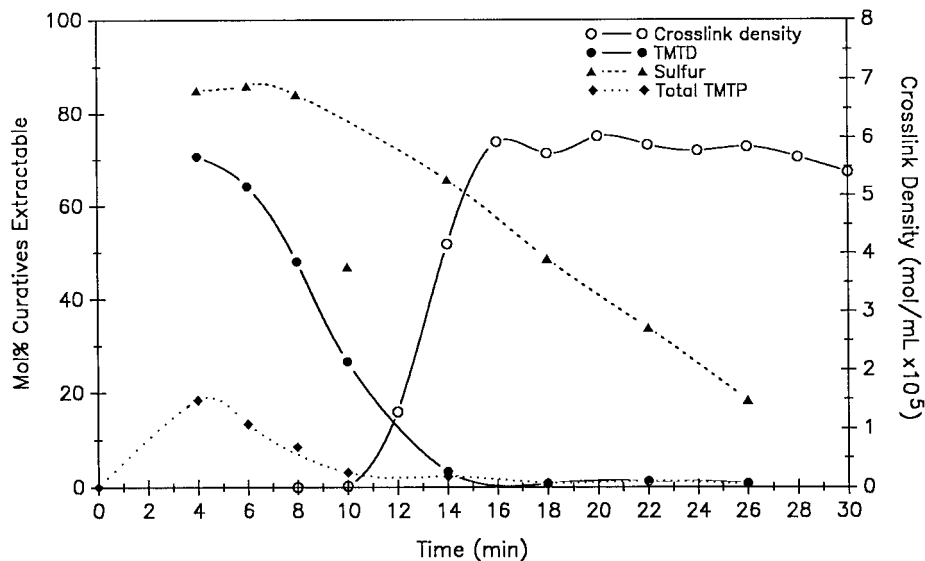
### IR-TMTD-Sulfur

At  $130^\circ\text{C}$ , crosslinking in the sample begins at about 10 min (Fig. 7) and increases rapidly to a value of  $5.5 \times 10^{-5}$  mol/mL, after which it remains constant. TMTP formation is rapid and decreases again prior to crosslinking as pendent group formation takes place. The sulfur concentration decreases as crosslinking begins and continues to decrease, despite no further increase in the crosslink density being recorded after 16 min. This would imply that the rate of reversion approximates the rate of new crosslink forming reactions.

### SBR-TMTD/Sulfur

At  $130^\circ\text{C}$ , crosslinking is observed at 18 min, but the crosslink density remains very low until 22 min, when it increases from  $1.75 \times 10^{-7}$  mol/mL at 18 min to  $3.66 \times 10^{-7}$  mol/mL at 20 min (Fig. 8). Crosslinking is observed about 8 min later than in IR, but the rapid increase in the crosslinking density occurs about 12 min later than in IR. The TMTP concentration decreases at a slower rate than in IR and may indicate that the delay in crosslinking in the SBR system is due to the slower formation of pendent groups, which are the crosslink precursors. A similar, though less marked,





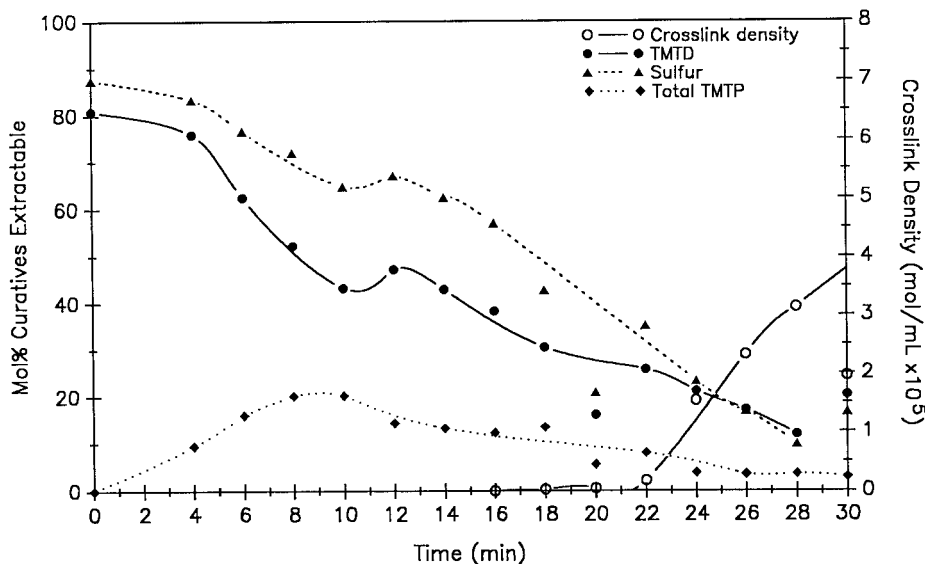
**Figure 7** Crosslink density and HPLC analysis of extractable curatives for isothermal vulcanization of IR-TMTD/sulfur at 130°C.

difference in the rate of TMTP reaction was evident in the dynamic study [cf. Figs. 2 and 3(b)].

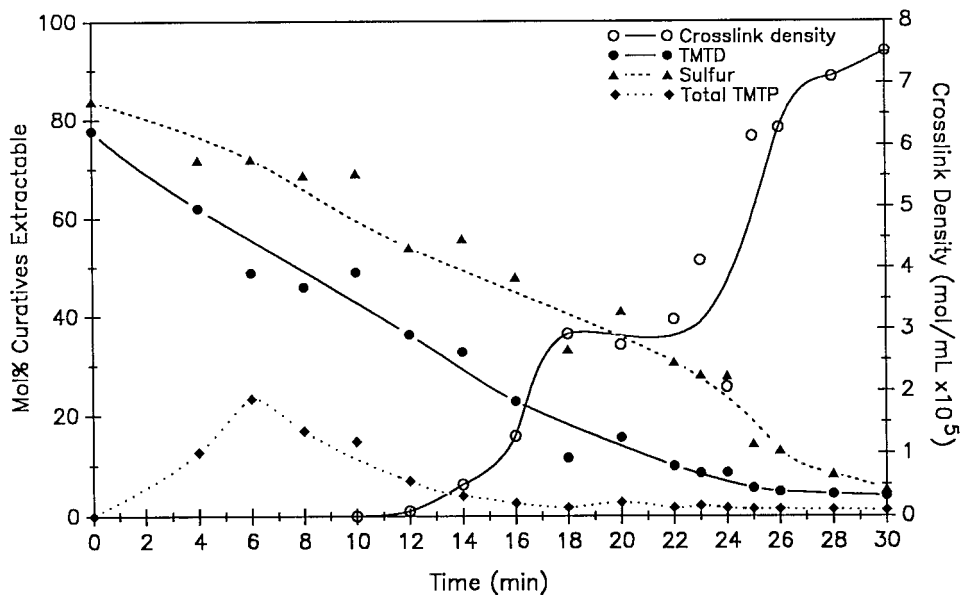
**IR-[SBR-TMTD/Sulfur]**

Crosslinking begins at 12 min (Fig. 9), which is slightly later than in the IR system, but about 6 min prior to crosslinking in the SBR system. There is an increase in the average crosslink density of the vulcanizates up to 18 min, after which

there is a levelling off, or a dip in the crosslink density, before it again increases after 24 min. This dip in the crosslink density was obtained in several experiments and was more pronounced in some than in other experiments. This will be discussed in more detail later. The second increase in the crosslink density corresponds to the time when the increase in the crosslink density occurs in the SBR system.



**Figure 8** Crosslink density and HPLC analysis of extractable curatives for isothermal vulcanization of SBR-TMTD/sulfur at 130°C.

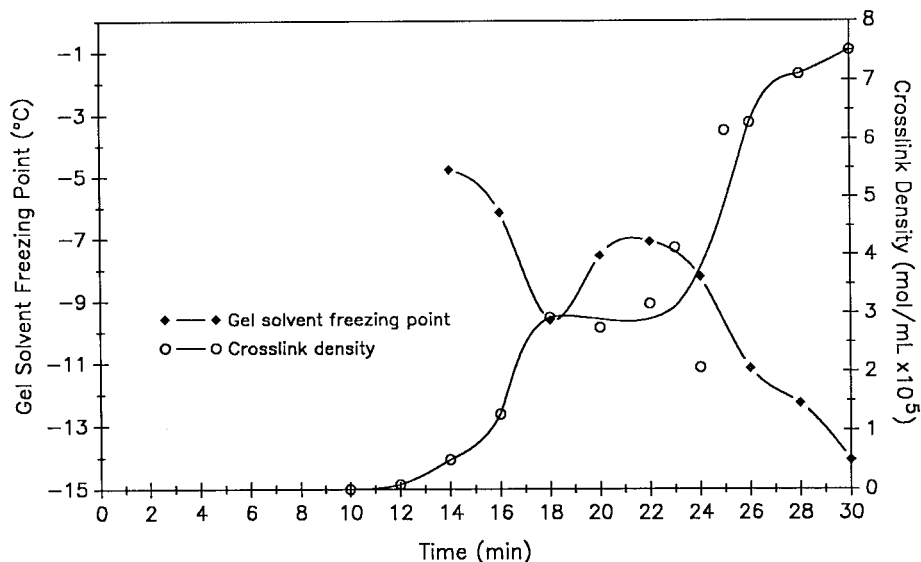


**Figure 9** Crosslink density and HPLC analysis of extractable curatives for isothermal vulcanization of IR-[SBR-TMTD/sulfur] at 130°C.

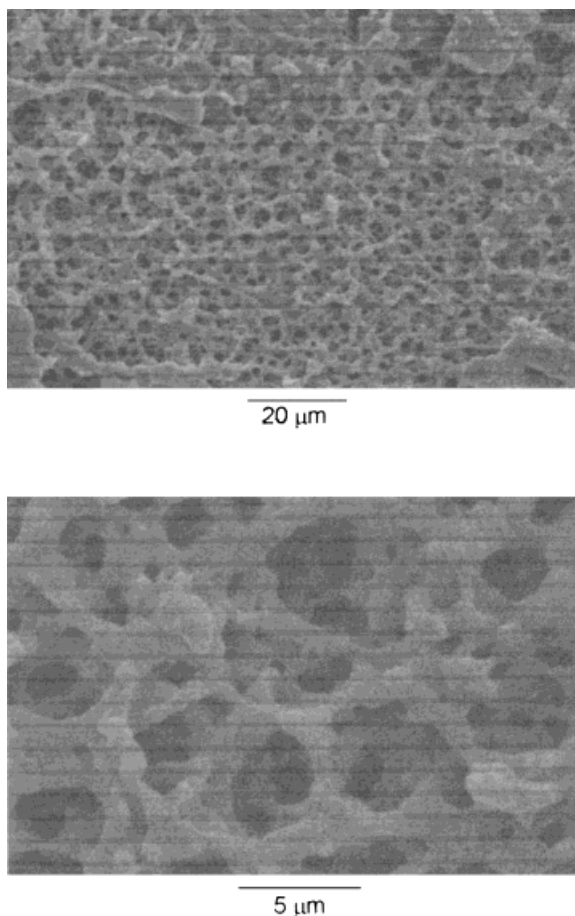
A plot of the cyclohexane freezing point in the swollen vulcanizates for the IR-[SBR-TMTD/sulfur] blend (Fig. 10) shows that as the reaction progresses, there is a decrease initially in the freezing point; but at 20 min, there is an increase and then a decrease once again at 24 min. The increase and subsequent decrease in the solvent freezing point reflects the trend in the overall crosslink density. This result is consistent with

the results obtained in the dynamic study, in which, in the blend systems, there were increases in the freezing point of the solvent in the swollen vulcanizate while the crosslink density increased or changed by very little. Reasons for this will be discussed below.

The crosslinking in the IR/[SBR/TMTD/sulfur] system occurs at similar times to the reactions in IR/SBR/TMTD/sulfur at 130°C (Table 2). From



**Figure 10** Crosslink density and freezing point of the cyclohexane in the swollen vulcanizates for IR-[SBR-TMTD/sulfur] vulcanized isothermally at 130°C.



**Figure 11** SEM micrograph of cryofracture surface of IR-[SBR-TMTD-sulfur] vulcanized for 14 min at 130°C, at various magnifications.

Table 2 it can be seen that in the early stages of the crosslinking, IR constitutes the major portion of the insoluble phase, while SBR constitutes the major portion of the soluble phase. It must be remembered that in a 50/50 blend of IR and SBR, IR is the continuous phase<sup>31-33</sup> and, as it crosslinks, it becomes more difficult to extract the uncrosslinked SBR from the swollen IR gel network. Some crosslinking at the interface may also prevent the extraction of SBR.

### Scanning Electron Microscopy

Figure 11 shows the SEM micrographs, at two magnifications of the cryofracture surface of a IR/[SBR/TMTD/sulfur] sample vulcanized isothermally at 130°C for 14 min. The samples were prepared in the manner described by Grobler and McGill.<sup>34</sup> The crosslinked sample was swollen in a mixture of petroleum ethers with different boil-

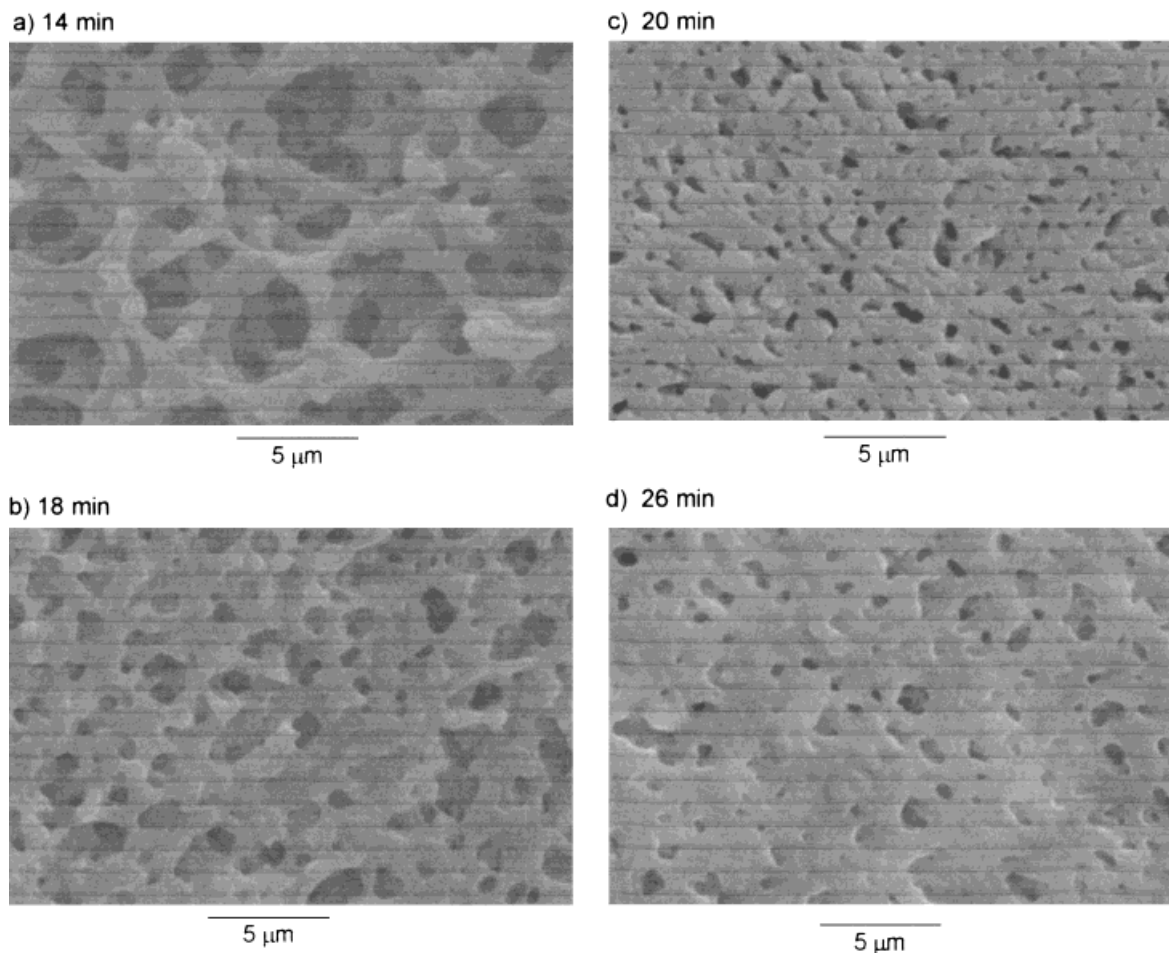
ing ranges (this is done to minimize the crystallization of the solvent when it is cooled). The swollen gel was then placed in liquid nitrogen for several minutes, removed, and fractured. The fractured samples were dried in air and then under high vacuum, and the surface was examined by scanning electron microscopy (SEM).

Figure 11 clearly shows a honeycomb-type structure. It is suggested that the structure remaining is largely that of the IR phase of the blend. If after 14 min at 130°C, the IR phase had crosslinked to a large extent and the SBR phase has not yet begun to crosslink, then the uncrosslinked SBR phase would dissolve from the vulcanized IR network, resulting in the honeycomb-type structure. Some SBR would crosslink to IR at the interface. Since the curatives were initially mixed into the SBR phase, it appears that diffusion must have occurred to allow IR to crosslink. Much of the crosslinking would take place close to the interface as curatives enter the IR phase, and some of the IR phase may remain soluble in this sample. In 50/50 blends of IR and SBR, dispersed zones of SBR between 0.7 and 2.0  $\mu\text{m}$  have been reported for intimately mixed compounds.<sup>22,33,34</sup> The voids in this sample are approximately 5  $\mu\text{m}$  in diameter and would be consistent with SBR phase in a less intimately mixed compound.

Figure 12 shows the electron micrographs of cryofractured, deswollen surfaces for IR-[SBR-TMTD/sulfur] samples vulcanized for various times at 130°C. The sample vulcanized for 14 min shows a coarse honeycomb-type structure; but in the samples vulcanized for a longer time, the voids become smaller, and at 26 min, few voids are evident. At 14 min, the SBR has not yet begun to crosslink; at 18 min, the SBR phase begins to crosslink; and after 26 min, the SBR phase is substantially crosslinked.

## DISCUSSION

The results of both the isothermal and vulcanization studies at a programmed heating rate show that for the TMTD/sulfur vulcanization system, IR crosslinks more readily than SBR. On heating at 2.5°C/min, IR crosslinks 20°C earlier than SBR [cf. Figs. 2 and 3(a)]. The maximum crosslink density reached, however, is higher in SBR than IR, and there is considerably less reversion in the SBR vulcanizates compared to IR. In the isother-



**Figure 12** SEM micrograph of cryofracture surface of IR-[SBR-TMTD-sulfur] vulcanized for various times.

mal study, at 130°C, SBR begins to crosslink about 8 to 12 min later than IR, (cf. Figs. 7 and 8).

The slower decrease in TMTP concentration in SBR suggests that the delay in the crosslinking reaction in SBR is due to the slower formation of the rubber bound pendent groups, which are the crosslink precursors. On heating the IR system (Fig. 2), there is a rapid decrease in the concentration of TMTP after 130°C, which may be taken as an indication of pendent group formation. In the SBR system, there is a more gradual decrease in the TMTP concentration, and it occurs later than in the case of IR [Fig 3(b)]. At 150°C, the total TMTP concentration has decreased to 2% in IR; while in SBR, the concentration is reduced to about 14%. In the isothermal study, the TMTP concentration in IR dropped rapidly after 10 min (Fig. 7), while in SBR, there is only a gradual decrease in the TMTP concentration after 10 min (Fig. 8). There is a lesser degree of unsaturation

in the SBR than IR, as well as the lower reactivity of the ethylenic compared to the methylenic allylic hydrogen atoms.

In blends, the higher reactivity of IR will lead to crosslinking in the IR phase before crosslinking has begun in the SBR phase. In the dynamic study, crosslinking begins at 150°C for all the blend systems, the same temperature at which IR begins to crosslink on its own (cf. Figs. 2 and 3(a)). In the isothermal study of the IR-[SBR-TMTD/sulfur] blend, crosslinking began at 12 min, which is a slight delay compared to IR on its own, but it is 6 min earlier than SBR crosslinking (cf. Figs 7-9).

The fact that the IR phase begins to crosslink before the SBR does is clearly shown in the TG analysis of the insoluble fractions of the blend vulcanizates for both the programmed heating and isothermal studies (Tables I and II). It is also clearly evident from the SEM micrograph of the

**Table II** Mass Percentage of IR and SBR in the Soluble and Insoluble Fractions of IR-TMTD/Sulfur Vulcanized Isothermally at 130°C for Various Times

Time (min)	Soluble Fraction		Insoluble Fraction		$\frac{1}{2}$ Mc mol/ mL $\times 10^5$	Rubber Insoluble (%)
	IR (%)	SBR (%)	IR (%)	SBR (%)		
8.00	45.60	54.40	57.20	42.80	gel	4.01
10.00	40.90	59.10	48.30	51.70	gel	23.60
12.00	36.50	63.50	53.90	46.10	0.12	48.40
14.00	36.20	63.80	—	—	0.28	85.50
16.00	—	—	—	—	0.94	100.00
20.00	—	—	—	—	1.20	100.00

cryofracture surface of the IR-[SBR-TMTD/sulfur]. After 14 min, IR has crosslinked, but the SBR phase has not yet begun to crosslink (Fig. 11) and can be dissolved out of the vulcanizate, leaving a honeycomb-type structure.

According to the theory for the freezing point depression of a solvent in a swollen vulcanizate, the freezing point observed is that for solvent in the least crosslinked phase of the blend.<sup>19,27,28</sup> For the TMTD/sulfur vulcanization of an IR-SBR blend, the freezing point would therefore be an indication of the degree of crosslinking in the SBR phase, at least in the initial stages of the vulcanization. In the programmed heating study, there is a decrease in the freezing point depression but an increase, or very small change, in the average crosslink density of the samples, as measured by the volume fraction rubber in the swollen vulcanizate, between samples cured for 160 and 165°C in the case of the [IR-TMTD/sulfur]-SBR (Fig. 5) and 165 and 170°C in the case of the IR-[SBR-TMTD/sulfur] (Fig. 6). A simplistic interpretation would be to suggest that the decrease in the freezing point depression indicates a decrease in the crosslink density (reversion) of the less crosslinked phase, in this case, SBR. A decrease of the crosslink density of the SBR phase at these temperatures is unlikely, as this is the temperature at which SBR begins to crosslink. Instead, it is suggested that this decrease in the freezing point depression is caused by a decrease in the restriction on the swelling of the SBR by the more heavily crosslinked IR phase. In 50/50 blends of IR and SBR, IR constitutes the continuous phase.<sup>31-33</sup> In the initial stages, the crosslinked IR phase will restrict the swelling of the less crosslinked SBR phase, and the initial increase in the freezing point depression is largely due to the restriction the increasingly crosslinked IR places

on the swelling of the less crosslinked SBR. At a point, reversion in IR results in the restriction on the swelling being decreased, with a corresponding drop in the freezing point depression as the SBR is allowed to swell to a greater extent. Continued reversion in IR, at elevated temperatures, will lead to the decrease in the overall crosslink density and the increase in solvent freezing point, as observed. At some stage, the solvent freezing point is clearly determined by IR.

In the isothermal study of the IR-[SBR-TMTD/sulfur] blend at 130°C, there was also a large decrease in the freezing point depression with very little change in the crosslink density between 18 and 20 min (Fig. 10). Once again, it is suggested that this decrease is due to the reduction of the restriction of the swelling of the SBR by the more crosslinked IR phase, rather than a decrease in the crosslink density of the SBR phase.

In the IR-[SBR-TMTD/sulfur] blend, where all the curatives are mixed in the SBR phase, diffusion of the curatives will have to occur for the IR to crosslink. Rapid reaction occurs once curatives enter the more reactive IR phase, and this will result in the formation of a highly crosslinked zone or "skin" of IR around the SBR phase. It is this "skin" which restricts the swelling of the SBR phase. Because of differing reactivities and differing solubilities of the curatives in the rubbers, diffusion would occur in all blends, though the "skin" effect would be less marked in the IR-SBR-TMTD/sulfur blend, in which a large amount of the curatives would already be present in the IR phase. The effect of this highly crosslinked interfacial zone on properties will be discussed in a later article in the series.

## CONCLUSIONS

SBR cures more slowly than IR, and this can be attributed to the slower formation of accelerator-terminated polysulfidic pendent groups by TMTP. Higher crosslink densities are achieved with SBR, and reversion is less severe. Despite the higher solubility of TMTD and sulfur in SBR, the more rapid reaction in IR depletes the curatives in the IR phase in the blend and leads to the diffusion of curatives from SBR to the IR phase. This diffusion of the curatives from the SBR to the IR phase results in a highly crosslinked IR zone being formed near to the interface.

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