

# Polyisoprene, Poly(styrene-cobutadiene), and Their Blends. Part II. Vulcanization Reactions with 2-Bisbenzothiazole-2,2'-Disulfide/Sulfur

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**ABSTRACT:** Polyisoprene (IR), poly(styrene-cobutadiene) (SBR), and IR-SBR blends were vulcanized with 2-bisbenzothiazole-2,2'-disulfide (MBTS) and sulfur in a differential scanning calorimeter (DSC) at a programmed heating rate and isothermally in a press at 150°C. The reaction was stopped at various stages, crosslink densities were measured, and residual curatives and extractable reaction intermediates were analyzed by high-pressure liquid chromatography (HPLC). The reactivities of IR and SBR towards MBTS was found to be more similar than that of the rubbers towards tetramethylthiuram disulfide. In blends, the slightly greater reactivity of IR led to its earlier crosslinking, as shown by thermogravimetric analysis (TGA) of the insoluble material present at various cure times. The depletion of curatives in the IR phase led to their diffusing 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: 1264–1270, 1999

**Key words:** polyisoprene; poly(styrene-cobutadiene); blends; 2-bisbenzothiazole-2,2'-disulfide; covulcanization

## INTRODUCTION

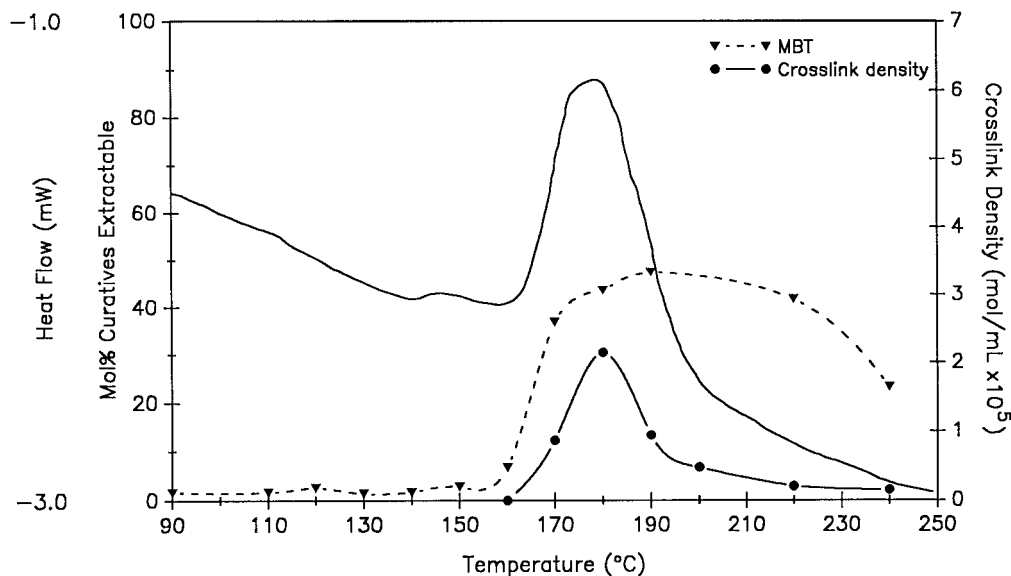
The 2-bisbenzothiazole-2,2'-disulfide-(MBTS)-accelerated sulfur vulcanization of natural rubber and polyisoprene (IR) has been the subject of many studies, while MBTS vulcanization of poly(styrene-cobutadiene) (SBR) and of IR-SBR blends has not been reported in similar detail. As with tetramethylthiuram-disulfide-(TMTD)-accelerated sulfur vulcanization,<sup>1</sup> accelerator polysulfides, formed by the interaction of sulfur

with the accelerator, are considered to lead to the formation of accelerator-terminated polysulfidic pendent groups.<sup>2–8</sup> Many authors<sup>2–6</sup> report 2-mercaptobenzothiazole (MBT) liberation during pendent group formation, while in the absence of ZnO others<sup>7,8</sup> found MBT to be released only on crosslinking. Crosslinking of pendent groups via a radical process<sup>4,9–11</sup> has been suggested, though other authors<sup>8</sup> favor a concerted reaction between a pendent group and a rubber chain.

In the previous article,<sup>12</sup> we showed that differences in the reactivity of TMTD towards IR and SBR led to the IR phase in the blends crosslinking more extensively than the SBR phase, and that a zone of high crosslink density developed in the IR phase close to the interface. At vulcanization temperatures, the solubility of

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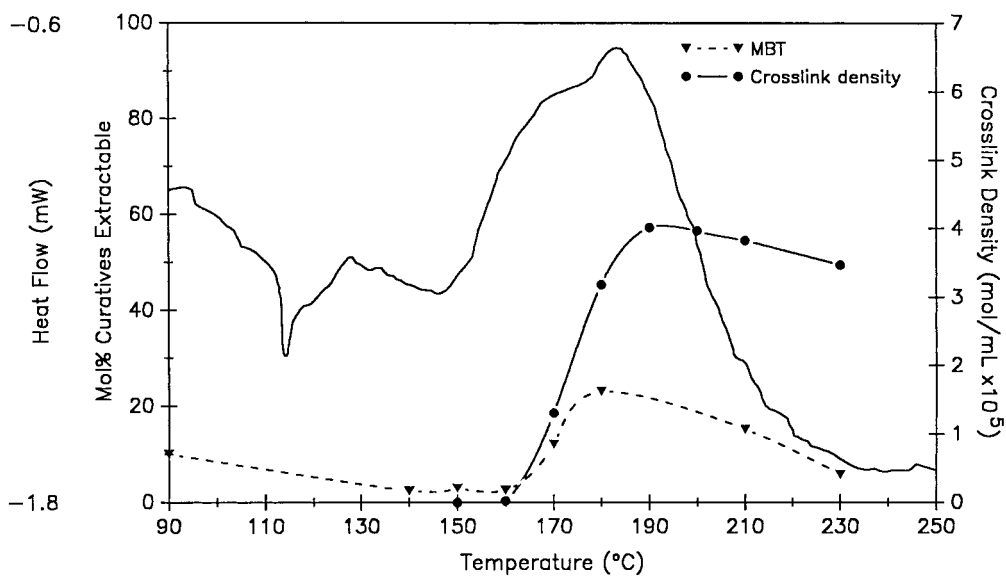
**Figure 1** DSC cure curve, crosslink density and MBT evolution for IR/MBTS/sulfur heated at 2.5°C/min.

TMTD in SBR is very much higher than in natural rubber, while the solubility of MBTS in SBR is only about twice that in natural rubber.<sup>13</sup> This would affect the extent of curative migration between phases in the blend. This article very briefly reports on aspects of a similar study with MBTS as the accelerator for the vulcanization of IR, SBR, and IR-SBR blends.

## EXPERIMENTAL

### Materials

MBTS was supplied by Orchem, Sasolburg, South Africa. The other materials used were listed previously.<sup>12</sup> Compounds (4-phr MBTS and 3-phr sulfur) were prepared on a Brabender Plastimeter and vulcanized in a differential scanning



**Figure 2** DSC cure curve, crosslink density, and MBT evolution for SBR-MBTS/sulfur heated at 2.5°C/min.

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

Temperature	IR-SBR-MBTS/Sulfur		[IR-MBTS/Sulfur]SBR		IR-[SBR-MBTS/Sulfur]	
	IR (%)	SBR (%)	IR (%)	SBR (%)	IR (%)	SBR (%)
160	79.6	20.4	77.5	22.5	72.9	27.1
165	59.3	40.7	64.6	35.4	79.9	20.1
170	52.2	47.6	59.4	40.6	58.8	41.2
175			52.4	47.6	49.6	50.4
180			50.4	49.6	49.8	50.2
190			49.1	50.9	46.6	53.4
200	40.1	59.9	49.5	50.5	43.9	56.1
220			47.1	52.9	42.2	57.8
250	40.8	59.2	42.3	57.7	42.2	57.8

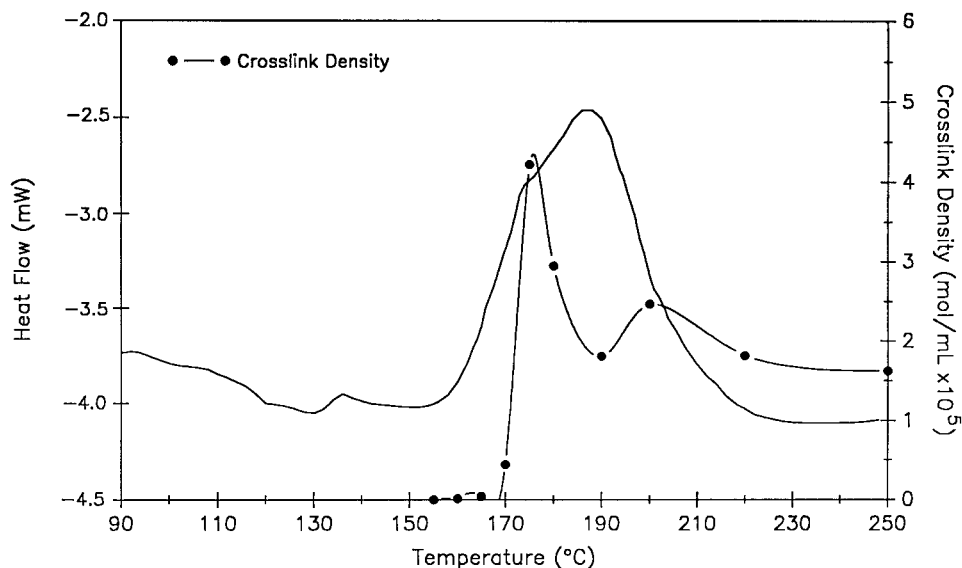
calorimeter (DSC) at a programmed rate of 2.5°C/min, or isothermally in a Monsanto Rheometer at 160°C and in a press at 150°C, as described earlier.<sup>12</sup> HPLC analysis of extractable curatives, Thermogravimetric analysis (TGA) of the insoluble portion of vulcanizates, crosslink density measurements by swelling, and the measurement of the freezing point of cyclohexane imbibed into the rubbers after vulcanization have been described.<sup>12</sup>

## RESULTS

On heating in a DSC at 2.5°C/min, IR-MBTS/sulfur crosslinks above 160°C, with rapid rever-

sion setting in at higher temperatures (Fig. 1). The maximum crosslink density recorded before rapid reversion ( $2.14 \times 10^{-5}$  mol/mL at 180°C) is considerably less than in a similar TMTD system ( $4.3 \times 10^{-5}$  mol/mL at 160°C).<sup>12</sup> As reported,<sup>7,8,14</sup> MBT liberation in the absence of ZnO coincides with crosslinking (Fig. 1). Changes in the concentrations of other curatives are similar to these reported earlier.<sup>8,14</sup>

The DSC cure curve of SBR-MBTS/sulfur is slightly broader than that of IR-MBTS/sulfur (Fig. 2) and shows an endotherm due to the melting of sulfur at 114°C. Crosslinking begins at 160°C. A higher crosslink density ( $4 \times 10^{-5}$  mol/mL) is reached at 190°C; and unlike with IR, there is little reversion. MBT formation coincides



**Figure 3** DSC cure curve and crosslink density for IR-[SBR-MBTS/sulfur] heated at 2.5°C/min.

with crosslinking, though the amounts of MBT liberated are considerably less than with IR (cf. Figs. 1 and 2). At the maximum crosslink density, the MBT-to-crosslink density ratio is much lower (1.5 versus 5). The formation of 2-benzothiazole-2,2'-polysulfides (MBTP) and the reaction of MBTS and sulfur are essentially similar in IR and SBR and follow the trends reported<sup>8,14</sup> for IR. (Note that curative loadings used in the present study are much lower than those in the earlier articles<sup>8,14</sup> referred to.)

Three blends containing equal amounts of IR and SBR were studied. In the first, curatives were added directly to an IR-SBR mix; in the second, curatives were added to an IR master batch that was then blended with SBR; and in the third, curatives were added to a SBR master batch that was blended with IR. Though curatives will migrate between phases during compounding and vulcanization, these mixtures were prepared in an attempt to vary the amounts of curatives in each of the phases of the blend at the onset of reaction. In the text, master batches are indicated by square brackets.

In both the individual rubbers, crosslinking starts at 160°C, though TGA<sup>12</sup> of the insoluble portion of the blends shows that in the early stages of reaction, IR crosslinks more rapidly (Table I). This applies to all three blends. (The percentage of IR in the insoluble fraction will also depend on the relative molecular weights of IR and SBR.) Crosslinking in the blend prepared from the SBR master batch is very slightly delayed (Fig. 3) compared to the individual rubbers. Reversion is noticed at higher temperatures and occurs mainly in the IR phase, as indicated by the lower percentage of IR in the insoluble portion of the vulcanizate after the crosslink maximum (Table I). Reversion in the IR phase, as reflected by TG data, is more dramatic with MBTS than TMTD vulcanizates.<sup>12</sup> The influence of this reversion on the ultimate tensile strength of blends will be discussed in a future article.

As in the case of TMTD vulcanizates, the dissimilarity in the degree of crosslinking in the two phases is also shown by the freezing point of cyclohexane in swollen blends. Freezing of the imbibed solvent is nucleated in the less densely crosslinked areas of the network.<sup>15,16</sup> Figure 4(a)-(c) show that the freezing point does not exactly mirror the overall crosslink density, as determined from swelling data. In the IR-SBR-MBTS/sulfur and [IR-MBTS/sulfur]-SBR blends, there is a considerable increase in the freezing point

once reversion dominates, while swelling experiments indicate only a slight decrease in the overall crosslink density (cf. highest crosslink density and next point). In the IR-[SBR-MBTS/sulfur] blend, reversion, as measured by swelling, is initially accompanied by a further decrease in the solvent freezing point [Fig. 4(c)]. These differences support TG data that indicate that the two phases of the blend do not crosslink to the same degree at any given time and that IR can revert while SBR is still being crosslinked.

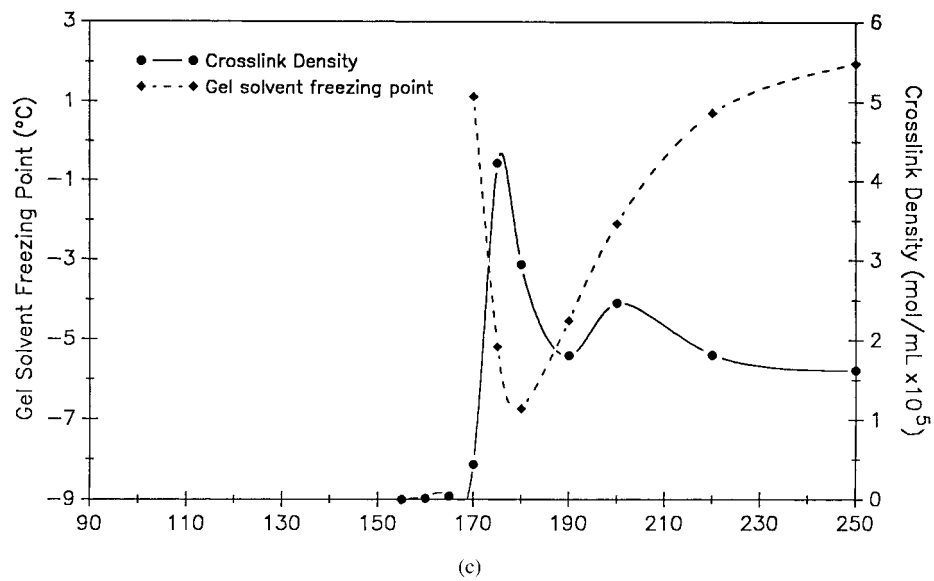
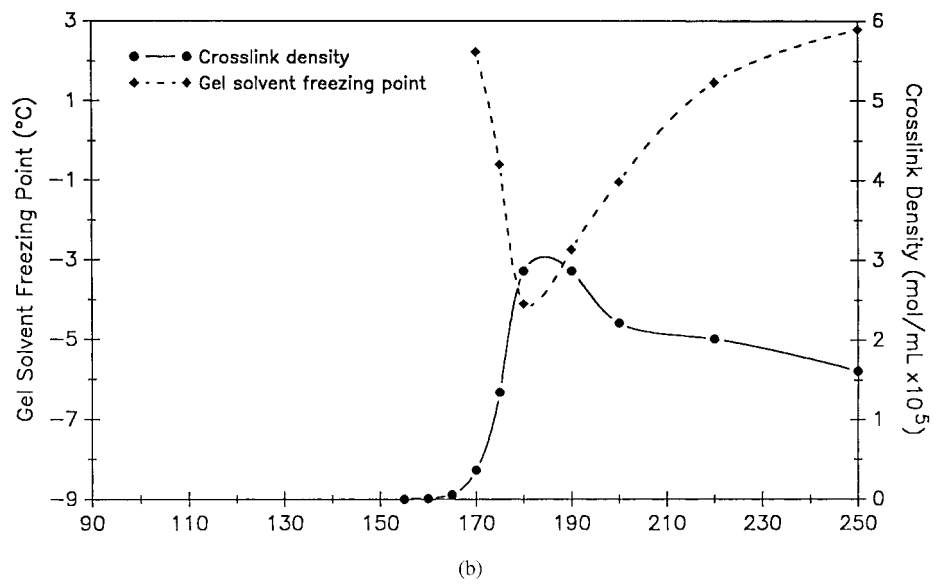
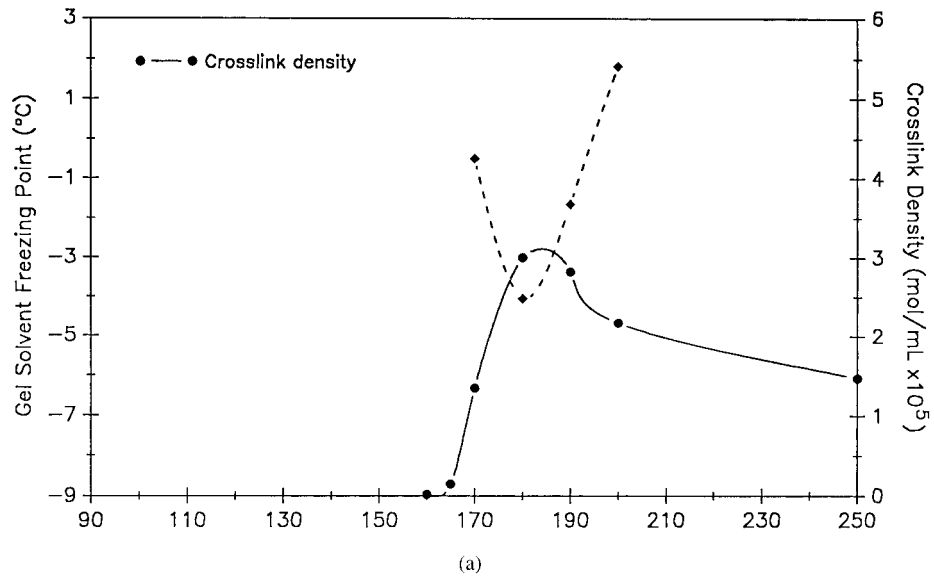
Rheometer cure curves at 160°C show that the reaction in SBR is slower than in IR, with both the initiation of crosslinking and the attainment of the maximum torque occurring at longer times (Table II). TGA of the unextractable portion of samples cured in a press at 150°C confirms that IR crosslinks more rapidly than SBR (Table III).

## DISCUSSION

The difference in reactivity of the two rubbers towards MBTS/sulfur is much less marked than in the case of TMTD-sulfur compounds.<sup>12</sup> At vulcanization temperatures, the solubility of both MBTS and sulfur are higher in SBR.<sup>13</sup> Despite this, IR initially crosslinks more rapidly than SBR. Rapid depletion of curatives in IR, and their replenishment by diffusion from the SBR phase, will lead to a zone of high crosslink density in the IR phase close to the interface, as described earlier<sup>12</sup> for the TMTD system. This will restrict swelling of the lower crosslinked, dispersed<sup>12</sup> SBR phase and will lead to a decrease in the freezing point of the imbibed solvent.<sup>15,16</sup> The solvent freezing point for IR-[SBR-MBTS/sulfur] is much lower than for the other blends. Thus, the development of a zone or "skin" of highly crosslinked material close to the interface is more pronounced where a greater degree of diffusion to the IR phase occurs. Note that it is the higher reactivity of IR that depletes curatives and leads to their diffusion from SBR, their rapid reaction

**Table II Rheometer Data at 160°C: Onset of Cure ( $t_5$ ) and Time to 95% Optimum Cure ( $t_{95}$ )**

Compound	$t_5$ (min)	$t_{95}$ (min)
IR-MBTS/Sulfur	5.37	14.00
SBR-MBTS/Sulfur	7.00	35.00
IR-SBR-MBTS/Sulfur	5.25	21.12



**Table III** Mass Percentage of Rubbers in the Soluble and Insoluble Fractions of IR-SBR-MBTS/Sulfur Compounds Vulcanized at 150°C

Time (min)	Soluble IR (%)	Fraction SBR (%)	Insoluble IR (%)	Fraction SBR (%)	$\frac{1}{2}M_c$ mol/mL $\times 10^5$	Insoluble Percentage
12	49.1	50.9	53.4	46.6	gel	18.8
14			54.4	45.6	gel	39.2
16	44.2	55.8	53.6	46.4	gel	47.9
18	37.2	67.3	63.5	36.5	0.10	61.1
20			50.1	49.9	0.34	100

on entering the IR phase giving rise to a highly crosslinked zone. A similar result was found for blends vulcanized with TMTD.<sup>12</sup> SBR shows little reversion; but, at elevated temperatures, rapid reversion in the highly crosslinked IR zone, close to the interface with SBR, will be reflected by an increase in the freezing point of the imbibed solvent and a decrease in crosslink density calculated from swelling experiments [Figs. 4(a)–(c)]. The change in solvent freezing point is more gradual than in TMTD vulcanized blends, in which an initial, very rapid increase in solvent freezing point was followed by a slower change.<sup>12</sup> The difference reflects the higher crosslink density attained in the IR “skin” in TMTD vulcanizates; the restriction on SBR swelling is thus greater, and the effect of reversion is consequently more dramatic in the TMTD case. The overall behavior of the blends is similar to that obtained with TMTD vulcanizates;<sup>12</sup> though, as the reactivities of the rubbers towards MBTS are more similar, the restriction on the swelling of the dispersed phase by the zone of highly crosslinked IR that develops close to the interface, is less marked.

Gradwell and McGill<sup>8</sup> suggested that higher MBT-to-crosslink ratios implied that, in the absence of ZnO, pendent groups underwent cyclization reactions more readily than those crosslinked with neighboring chains. The lower MBT-to-crosslink ratio in SBR than in IR (1.5 versus 5) would imply less cyclization and could account for the higher crosslink density obtained with SBR. In the presence of ZnO, cyclization is considerably less.<sup>8</sup>

## CONCLUSION

As in the case with TMTD-accelerated systems, IR crosslinks more rapidly than SBR, leading to a nonuniform distribution of crosslinks in blends of IR and SBR. Diffusion of curatives to IR ensures a high crosslink density in IR adjacent to the interface and restricts swelling in solvents of the lower crosslinked, dispersed SBR phase. This effect is less marked than in the case of TMTD vulcanizates. IR is more susceptible to reversion than SBR, and the zone of high crosslink density in IR close to the IR-SBR interface is broken down rapidly at higher temperatures.

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**Figure 4** Crosslink density and the gel solvent freezing point for (a) IR-SBR-MBTS/sulfur, (b) [IR-MBTS/sulfur]-SBR, and (c) IR-[SBR-MBTS/sulfur] heated at 2.5°C/min.

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