Polyisoprene, Poly(styrene-cobutadiene) and Their Blends. III. Tensile Properties of Tetramethylthiuram Disulfide/Sulfur and 2-Bisbenzothiazole-2,2'-disulfide/sulfur Compounds

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ABSTRACT: Polyisoprene (IR), poly(styrene-cobutadiene) (SBR) and IR/SBR blends were vulcanized with tetramethylthiuram disulfide (TMTD)/sulfur and 2-bisbenzothiazole-2,2'-disulfide (MBTS)/sulfur formulations and their tensile properties were determined. MBTS vulcanized IR has inferior tensile properties to TMTD vulcanizates. This is attributed in part to main chain modification in MBTS vulcanizates decreasing the ability of chains to crystallize or to align as effective load-bearing chains under stress. A similar discrepancy is not found in SBR compounds that cannot stress-crystallize. Polybutadiene, which readily crystallizes on cooling, is used to demonstrate differences in the effect of MBTS and TMTD on the ability of chains in the vulcanizates to align. These differences are confirmed by X-ray diffraction studies of stressed IR vulcanizates. The addition of zinc stearate reduces main chain modification, promotes crystallization, and improves tensile properties. Blends have inferior properties to IR, and tests involving the pulling apart of laminates and analysis of the tear surfaces are used to illustrate that failure does not occur in adhesion, but within the IR phase close to the interface. It is argued that diffusion of curatives from SBR to the faster curing IR phase, leads to the development of a layer of highly crosslinked material in IR close to the phase boundary. Failure occurs in this layer and may be attributed to a decrease in the number of effective load-bearing chains in this region or to the shorter chains in this layer becoming taut. Less diffusion of the accelerator occurs with MBTS than with TMTD, leading to a less highly crosslinked IR zone close to the interface. Consequently, higher loads are required to initiate failure. Failure in blends is likewise considered to initiate in the highly crosslinked region in the IR phase close to the phase boundary with SBR. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 2143–2149, 1999

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

INTRODUCTION

It is well known that the ultimate tensile strength (UTS) of vulcanizates passes through a maximum with an increase in crosslink density.[1–6] Taylor and Darin[6] suggested that the strength of a compound is related to the number of effectively aligned chains, and the reduction in strength seen at higher crosslink densities is the result of a decrease in the number of effectively aligned chains. The argument is similar to that of Flory[5] who contended that the strength may be attributed to the fraction of the polymer that becomes effectively part of the network.

The physical properties of rubber blends are often inferior to those predicted from the properties of the component rubbers[7,8] and this is generally attributed to the fact that covulcanization is not achieved in the blend.[1,9] Covulcanization may be defined as the formation of equal amounts of crosslinks in both phases as well as at the interface. Blends in which covulcanization is achieved, i.e., blends of rubbers with similar polarity and rate of cure, exhibit additive properties.[10] The influence of various parameters on properties have been studied. Thus, the zone size of phases in the blend does not seem to have an influence on modulus, if well compounded,[11] though where the dispersed phase has a lower modulus than the continuous phase, smaller dispersed zones give greater elongation.[12] Also, in polybutadiene (BR)/ethylene-propylene-diene rubber blends, the harder phase was found to impose restrictions on the movement of the softer phase and this led to the stress-strain response being less sensitive to the blend morphology than expected.[13] It is recognized that the blend ratio has an effect on properties, even for blends of natural rubber and poly(styrene-cobutadiene) (SBR), where the component rubbers have similar properties.[14,15]

In the previous articles in this series it was shown that for polyisoprene (IR)/SBR blends, both tetramethylthiuram disulfide (TMTD)-[16] and 2-bisbenzothiazole-2,2′-disulfide (MBTS)-[17] accelerated sulfur formulations led to the more rapid vulcanization of the IR phase than the SBR phase in the initial stages of crosslinking. Diffusion of curatives across the phase boundary resulted in the development of a zone of highly crosslinked material within the IR phase, close to the phase boundary. IR is more susceptible to reversion than SBR,[16,17] and the crosslink density in this highly crosslinked interfacial zone within the IR phase rapidly declines on further heating. Failure in blends is frequently attributed to a lack of crosslinking at the interface between component rubbers,[1,9] but in these IR/SBR blends, at least, a zone of highly crosslinked material has been identified close to the interface between the components. This report shows that failure of these blends under load can be attributed, not to a lack of crosslinks at the interface, but to failure in the highly crosslinked zone. The effect of zinc stearate on the vulcanizate microstructure and on tensile properties is also reported.

EXPERIMENTAL

Materials: 98% *cis*-BR (Neodene, Karbochem, Newcastle, South Africa). Other materials and curatives have been detailed.[16,17]

Compounds (100 parts per hundred (phr) IR, 100 phr SBR, or 50 phr IR/50 phr SBR) were mixed with 4 phr accelerator (TMTD or MBTS) and 3 phr sulfur in a Brabender Plasticorder as described[16] and vulcanized in a press at 150°C (TMTD/sulfur) and 160°C (MBTS/sulfur). Times to optimum cure were determined on a Monsanto oscillating disc rheometer at the appropriate temperature. Crosslink densities were determined by swelling.[16] Crystallization studies of BR vulcanizates were conducted by cooling samples as described below in a Du Pont 910 differential scanning calorimetry (DSC) module connected to a Du Pont 9000 Thermal Analyzer. Tensile tests were conducted on an Instron 441 Tensiometer with an Instron Long Travel Elastomeric Extensiometer attached. A 1-kN load cell and a gauge length of 20 mm were used.

RESULTS AND DISCUSSION

IR and SBR

The UTS of IR and SBR vulcanizates, cured in a press to 60%, 80%, 90%, and 95% of their optimum cure, as determined from rheometer cure curves, are given in Table I. Within the range of crosslink densities achieved, TMTD cured IR has a higher UTS than MBTS cured IR. The UTS of the latter increase with crosslink density, but do not reach similar values to those of TMTD vulcanizates.

In both TMTD- and MBTS-accelerated sulfur vulcanization, accelerator polysulfides react with the polymer chain to form accelerator-terminated polysulfidic pendent groups[18,19] that initiate crosslink formation. The presence of residual pendent groups and the formation of cyclic sulfides during vulcanization, will negatively affect the UTS by inhibiting the ability to crystallize under stress.[5,6]

Main chain modifications will be evident by their effect on the crystallization of the polymer on cooling. Bistow and Tiller[20] showed that the formation of cyclic sulfides greatly increased the resistance of vulcanizates to low-temperature crystallization, while Andrews[21] also showed that small modifications in molecular microstructure influenced the rate of crystallization. The mecha-

Table I   Ultimate Tensile Strength of Vulcanizates

IRTMTD/Sulfur		IR/MBTS/Sulfur		IR/MBTS/Sulfur/ Zn Stearate		SBR/TMTD/ Sulfur		SBR/MBTS/ Sulfur		SBR/MBTS/ Sulfur/Zn Stearate	
½ Mc mol/ mL × 10⁵	UTS MPa	½ Mc mol/ mL × 10⁵	UTS MPa	½ Mc mol/ mL × 10⁵	UTS MPa	½ Mc mol/ mL × 10⁵	UTS MPa	½ Mc mol/ mL × 10⁵	UTS MPa	½ Mc mol/ mL × 10⁵	UTS MPa
2.12	22.7	1.22	6.7	5.44	21.3	2.07	2.9	1.04	2.4	7.9	1.5
4.10	25.4	2.49	12.7	5.63	22.0	7.01	3.0	2.31	2.2		
6.20	25.4	2.84	15.0	5.91	22.9	8.64	2.4	4.53	1.9		
5.80	22.7	3.30	17.7			10.30	1.8	4.45	2.1		

nism of BR vulcanization is similar to that of IR, with both rubbers forming polysulfidic accelerator-terminated pendent groups and these lead to crosslinking.[22] Qualitatively, the effect of pendent groups on the crystallization of BR would therefore be similar to their effect on IR. IR crystallizes very slowly on cooling[23] but the crystallization of BR can readily be studied by DSC. BR/TMTD/sulfur and BR/MBTS/sulfur samples, vulcanized for various times, were cooled in a DSC at 5°C/min to −50°C, held there for 15 min, and reheated at 5°C/min to obtain a crystalline melting endotherm. Figure 1 shows the area per unit mass under the melting endotherms and Figure 2 shows the onset temperature for the melting of the samples. The areas of the melting endotherms are a measure of the degree of crystallization that developed in the sample during cooling and clearly show that, although crosslinking decreased crystallization of IR/TMTD/sulfur vulcanizates, crystallization is still possible, even for high crosslink densities. In contrast, the crystallization of IR/MBTS/sulfur vulcanizates rapidly

drops to zero, even at very low crosslink densities. This is an indication of a large amount of main chain modification. A decrease in the crystalline melting point is indicative of the formation of smaller crystallites,[24] and the results in Figure 2 are consistent with the decrease in crystallization in Figure 1.

IR/TMTD/sulfur and IR/MBTS/sulfur compounds with similar crosslink densities (2.12 $\times 10^{-5}$ and 2.49 $\times 10^{-5}$ mol/mL) were stretched to 700% elongation and subjected to low-angle X-ray diffraction. Figure 3 shows that TMTD compounds crystallized immediately on stretching, with further crystal growth occurring on holding the sample for 12 h. MBTS compounds failed to crystallize, even after 24 h under stress. The lower UTS of IR/MBTS/sulfur compounds can be attributed, at least in part, to their inability to crystallize under load.

SBR vulcanizates have inferior properties to IR vulcanizates cured with the same formulations (Table I). The bulky styrene groups prevent crystallization of SBR and will reduce the degree of
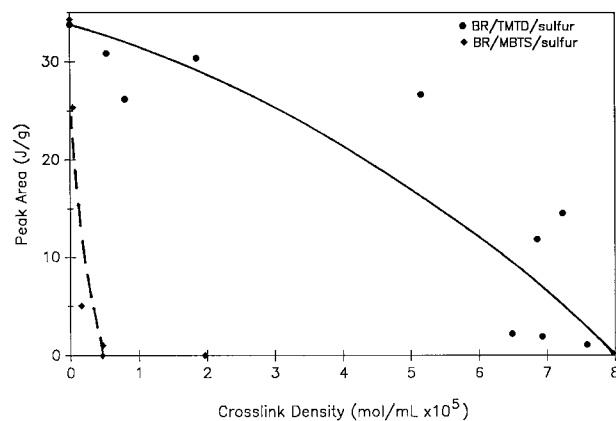
Figure 1   Area under the crystalline melting endotherm vs. crosslink density for BR/TMTD/sulfur and BR/MBTS/sulfur vulcanizates.
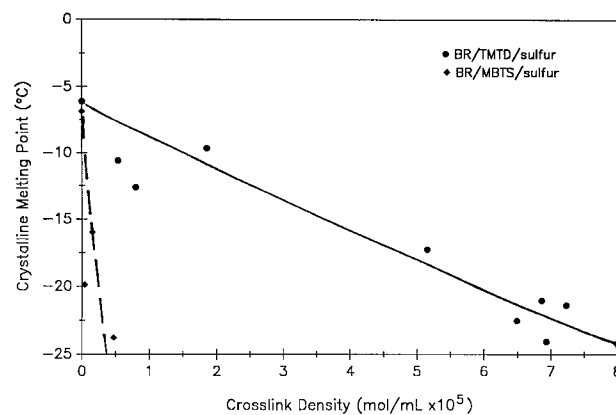
Figure 2   Crystalline melting point vs. crosslink density for BR/TMTD/sulfur and BR/MBTS/sulfur vulcanizates.
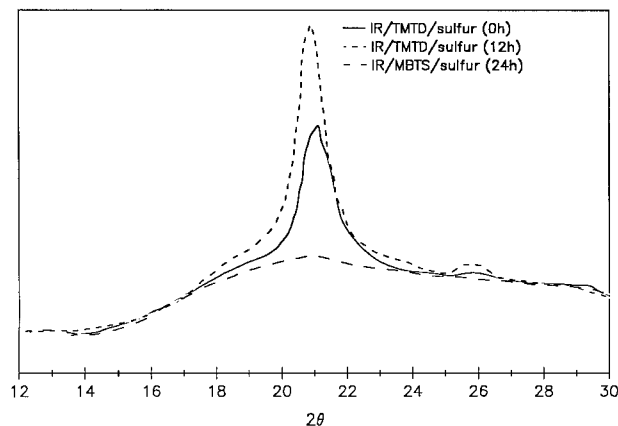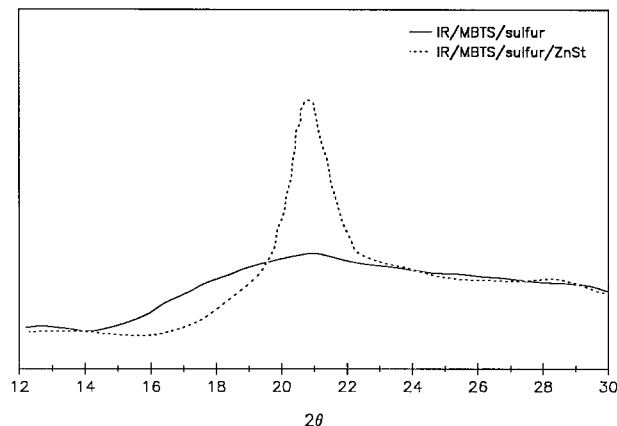
Figure 3 X-ray diffraction peaks at 2θ for samples at 700% elongation.

Figure 4 X-ray diffraction peaks at 2θ for samples at 700% elongation. For IR/MBTS/sulfur, 1/2 Mc = 2.49 $\times$ 10^{-5} mol/mL and for IR/MBTS/sulfur/zinc stearate 1/2 Mc = 5.44 $\times$ 10^{-5} mol/mL.

alignment that can develop under load. TMTD and MBTS compounds have similar UTS and main chain modification in MBTS vulcanizates does not noticeably influence the number of chains that can be effectively aligned to become load bearing.

Effect of Zinc Stearate

It is well known that the addition of zinc stearic increases the crosslink density of compounds and it has been shown[25] that zinc stearate promotes the crosslinking of accelerator-terminated polysulfidic pendent groups. Cyclic sulfide formation and the number of residual pendent groups in the compound are reduced by the increase in crosslinking efficiency. Table I shows that the addition of 2 phr zinc stearate to MBTS compounds leads to an increase in crosslink density and UTS of IR vulcanizates. The crosslink density of SBR compounds also is increased, but without a corresponding effect on UTS (Table I). X-ray diffraction shows that stress-induced crystallization of IR compounds containing zinc stearate readily occurs (Fig. 4). Zinc stearate has a similar effect in enhancing the crystallization of BR/MBTS/sulfur vulcanizates, the area under the crystallization melting endotherm for a compound of crosslink density 2.87 $\times$ 10^{-5} mol/mL is 33.73 J/g (cf. Fig. 1) and the crystalline melting point is $-11.9°C$ (cf. Fig. 2).

The Moore and Trego[26] efficiency parameter E gives an indication of the sulfur utilization. At optimum cure in IR/TMTD/sulfur compounds E = 14 and in IR/MBTS/sulfur, E = 26. This further illustrates the greater extent of main chain modification in MBTS compounds. On addition of zinc

stearate, E decreases to 15 in MBTS systems. For SBR compounds, higher efficiencies are obtained (with TMTD, E = 8.2 and with MBTS, E = 19), indicating lower degrees of cyclization. This is consistent with the lower MBT/crosslink ratio for SBR/MBTS/sulfur (1.5) than for IR/MBTS/sulfur (5) reported previously,[17] pointing to less cyclization in SBR than in IR. MBT is released coincident with crosslinking[17,19,27] and results from reaction of a pendent group with a neighboring chain, or from reaction with the same chain, in which case cyclization occurs.[19]

IR/SBR/TMTD/sulfur blends achieved higher crosslink densities than IR/SBR/MBTS/sulfur blends though in all cases the UTS of blends were inferior to that of IR compounds (cf. Tables I and II).

Laminates

A series of experiments were devised in an attempt to determine whether failure in blends initiated at the interface between component rub-

Table II   Ultimate Tensile Strength of Blends

IR/SBR/TMTD/Sulfur		IR/SBR/MBTS/Sulfur	
½ Mc mol/mL $\times$ 10^5	UTS MPa	½ Mc mol/mL $\times$ 10^5	UTS MPa
4.99	19.8	1.81	5.9
9.56	20.0	2.91	5.2
8.43	11.0	3.72	6.1
11.65	3.0	4.03	2.6

Table III   Adhesive Strength and Infrared Analysis of Break Surfaces

Laminate Composition[a]	TMTD/Sulfur			MBTS/Sulfur		
	Force to Break (N)	IR Layer	SBR Layer	Force to Break (N)	IR Layer	SBR Layer
IR-(XL)IR	14			56		
SBR-(XL)SBR	18			33		
IR-(XL)SBR	2	IR	SBR	8	IR	SBR
SBR-(XL)IR	11	IR	IR	41	IR	IR
IR-SBR	15	IR	IR	45	IR/SBR	IR/SBR

[a] (XL) indicates prevulcanization of the layer.

bers. Accordingly, a study was conducted on laminates to determine the locus of failure and the relative force required to tear apart two vulcanized compounds. One layer of the laminate was prevulcanized and an uncured pad of rubber, containing curatives, was placed on top of the cured layer and the whole assembly was reheated. A reinforcing fabric was incorporated into each layer to prevent extension of the samples when tested. The tear strength (Table III) is expressed in Newton and is the force required to pull apart a test piece 15 mm in width at a test speed of 50 mm/min. The values indicated are averages of the force required. The break surfaces were examined by Total Reflection Infrared spectroscopy to determine where the break had occurred (Table III) and three situations can be identified. Case 1: In the IR-(XL)SBR laminates, where XL indicates that the SBR layer had been precured, partition occurred readily and the locus of failure appeared close to the interface; no traces of IR were detected on the surface of the SBR, and vice versa. Little interfacial crosslinking had occurred. Case 2: When the IR layer was precured (a SBR-(XL)IR laminate) failure occurred in the IR layer. In TMTD/sulfur cured IR/SBR laminates, in which neither layer was precured, failure also occurred in the IR phase. Case 3: The only instance in which the locus of failure repeatedly traversed the interface, giving rise to very uneven break surfaces, occurred with MBTS/sulfur cured laminates where neither layer had been precured. In no case did failure occur in the SBR phase only.

These experiments provide further evidence for the formation of a highly crosslinked zone within the IR phase. Failure occurs when the shorter chains in this region become taut, or because of a decrease in the number of chains that can be aligned effectively to bear the load.[6] Except in case 1, for the IR-(XL)SBR laminate (Table III),

where rapid reaction in the IR phase essentially prevents diffusion of curatives across the interface, crosslinking at the interface is sufficient to prevent interfacial failure. Instead, failure occurs inside the IR phase. In the MBTS/sulfur cured IR-SBR laminate (case 3) also, the locus of failure traverses the interface; the interface itself is not a weak point. The force required to cause fracture in MBTS cured systems is greater than in TMTD. The reactivities of the two rubbers toward MBTS are more similar,[17] and this will reduce the crosslink density differential between the bulk IR and the more highly crosslinked layer resulting from curative diffusion across the interface. The deformation of a wider region of material in the interfacial zone, before chains become taut, will be reflected in a greater tearing force (Table III). With TMTD compounds, failure occurs more readily as the interfacial zone is narrower and more highly crosslinked, comprised of shorter subchains that become taut at lower elongations.

Blends

An IR/[SBR/TMTD/sulfur] compound was prepared by mixing an SBR master batch with IR.[16] Figure 5 shows the UTS and elongation at break obtained on curing for various times. These cure times correspond to those used in a previous article[16] in which crosslink densities and the freezing point of cyclohexane imbibed into the blend were measured, as depicted in Figure 5.

It has been shown[16] that the reactivities of IR and SBR differ greatly for a TMTD/sulfur curing system. Rapid reaction in IR, and the diffusion of curatives from the SBR phase, result in the formation of a more highly crosslinked zone within the IR phase in areas surrounding the dispersed SBR phase. The initial increase in tensile strength can be associated with crosslinking of
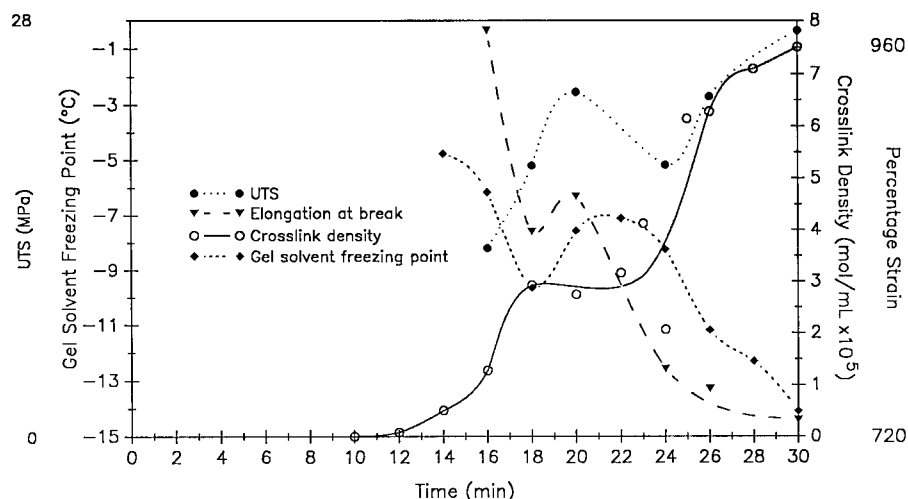
Figure 5   Ultimate tensile strength, elongation at break, crosslink density, and solvent freezing point for an IR/[SBR/TMTD/sulfur] compound vulcanized at 130°C for various times.

the continuous IR phase in the blend.[16] The elongation at break decreases, but increases for samples cured for between 18 and 20 min. The increase is coincident with the rise in the freezing point of solvent imbibed into the blend (Fig. 5). As suggested previously,[16] the leveling off or decrease in crosslink density, and the rise in the freezing point of the imbibed solvent, occur when the very restrictive, more highly crosslinked zone of IR surrounding the SBR undergoes partial reversion. Limited reversion will allow samples to undergo a greater elongation before chains in the highly crosslinked IR "skin" region become taut and failure occurs. Lowering of the crosslink density in the small, heavily crosslinked IR "skin" allows the load to be shared more uniformly with neighboring regions. The number of load-bearing chains is increased and an increase in UTS accompanies the increase in elongation. At longer vulcanization times, the SBR phase crosslinks, leading to an increase in UTS and a decrease in elongation at break. It is not evident why the UTS at 24 min decreases (Fig. 5).

It is suggested above that in the blend, failure initiates in the more highly crosslinked IR zone surrounding the SBR phase, at least in the early stages of vulcanization. When the sample is extended, the polymer chains in this region will become taut first and this will initiate failure. Figure 6 is a schematic representation of the proposed processes. The following series of experiments were conducted in support of the above contention.

IR pads were vulcanized and residual curatives were extracted. Uncured IR pads, containing varying amounts of curatives, were placed on top of the cured pads and the assembly was reheated at 150°C for a short period. Tensile test pieces were cut from the layered product and subjected to normal tensile tests. A blank was prepared by reheating an extracted pad for the same time as the assembly was reheated. Assemblies in which the upper layer contained larger amounts of curatives, would have higher crosslink densities and such test pieces required higher stress levels to attain the same elongation (Fig. 7). However, in all cases the lower, prevulcanized layer had a higher crosslink density than the upper layers and would bear most of the load on extension. Diffusion of curatives would lead to a region of high crosslink density close to the interface
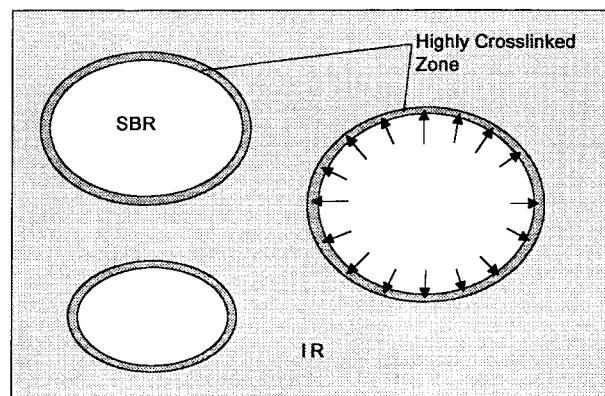
Figure 6   Schematic showing diffusion of curatives from the dispersed SBR phase in the blend and the development of a zone of high crosslink density in IR close to the phase boundary.
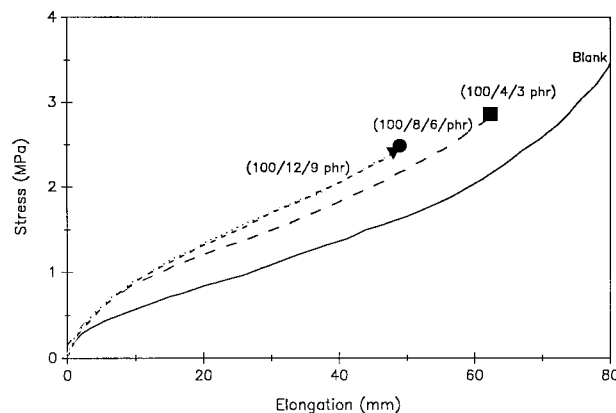
Figure 7 Stress-strain curves for IR/TMTD/sulfur laminates in which the lower layers were precured and the upper layers contained different amounts of curatives that would diffuse into the lower layer during subsequent heating. The formulations of the upper layer are given in the Figure.

within the precured layer and, in terms of the above arguments, failure should initiate when chains in this layer become taut. Figure 7 shows that failure occurred at progressively lower extensions (and lower UTS) for laminates in which the upper pad contained larger amounts of curatives that could diffuse across the interface. This is consistent with the earlier contention that failure in blends initiates, not at the interface between the components, but in the highly crosslinked zones close to the polymer interface. The layered test pieces all broke at right angles to the test piece; separation between layers did not occur.

CONCLUSIONS

IR/MBTS/sulfur vulcanizates have inferior tensile properties to IR/TMTD/sulfur vulcanizates as main chain modification reduces the number of effectively aligned load-bearing chains, and prevents stress-induced crystallization from occurring in the former. The addition of zinc stearate to the formulation promotes crosslinking of pendent groups, reducing main chain modification, permitting stress-induced crystallization and leading to higher UTS. In blends and laminates, diffusion of curatives across the interface from SBR to IR leads to the development of a highly crosslinked layer within the IR phase. Under load, failure initiates in this layer and not at the interface.

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