Crystallization of Vulcanizates. I. Low-Temperature Crystallization as a Function of Extent of Cure for Polyisoprene Vulcanized with Tetramethylthiuram Disulfide/Sulfur and 2-Bisbenzothiazole-2,2′-disulfide/Sulfur

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ABSTRACT: The crystallization of polyisoprene, vulcanized to various degrees of cure with tetramethylthiuram disulfide/sulfur and 2-bisbenzothiazole-2,2′-disulfide (MBTS)/ sulfur formulations, was studied in a density column at $-25°C$. The densities of vulcanizates before crystallization decrease progressively with cure time, which is ascribed to an increase in free volume occasioned by the formation of accelerator-terminated pendent groups on the polymer chain. The induction period before the onset of crystallization increases and both the rate of and the degree of crystallization decrease with extent of cure. This is attributed primarily to the presence of residual pendent groups on the polymer chain and secondly to crosslink formation. The changes are more marked with MBTS formulations where pendent groups are more bulky. MBTS compounds fail to crystallize once vulcanized to the point where a gel has formed. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 2565–2572, 2001

Key words: crystallization; polyisoprene; vulcanization; tetramethylthiuram disulfide; 2-bisbenzothiazole-2,2′-disulfide

INTRODUCTION

Stress-induced crystallization is considered to contribute to the tensile properties of crystallizable vulcanizates.[1–3] With natural rubber (NR) and polyisoprene (IR) a pronounced drop in tensile strength from 10 to 20 MPa to 1–2 MPa occurs over a narrow temperature range (10–20°C) as the temperature increases.[2] Like Thomas and Whittle,[3] Gent et al.[2] attributed this drop to failure of the bulk material to crystallize quickly enough to resist crack propagation. In IR that contains a small amount of *trans* material, the transition from high to low tensile strength occurs at a slightly lower temperature. There have been various studies of the crystallization of NR on cooling[4,5] and on cooling after extension.[2,6–8] The rate of crystallization of NR and IR is a maximum at $-25°C$,[9,10] although crystallization is slower by a factor of 3 for IR with 2.4% *trans* units and by a factor of 1000 with 10% *trans* units.[9] Half-lives for the crystallization of lightly crosslinked NR and IR ($\frac{1}{2}M_c = 5.6 \times 10^{-5}$ mol/mL) at $-25°C$ are 60 and 120 h, respectively.[2] In uncrosslinked IR, crystallization can be detected after 20 h.[11] Shearing forces that operate during compounding lead to the localized orientation of polymer chain segments, which influences the induction period for crystallization on cooling. In carbon black–

filled compounds the induction period decreases with increased carbon black loading,[11,12] whereas in compounds without fillers this orientation relaxes rapidly on heating of the sample and, consequently, it does not noticeably affect the induction periods of vulcanizates.[13]

Industrially, many different formulations are used to prepare vulcanizates and vulcanizates with the same crosslink density may display quite different properties. Different formulations can lead to substantial differences in the extent of main-chain modification in terms of residual pendent groups and cyclic sulfide formation in the final vulcanizate.[14–17] In tetramethylthiuram disulfide (TMTD)[18–22] and 2-bisbenzothiazole-2,2′-disulfide (MBTS)[23–25] accelerated sulfur vulcanization, accelerator polysulfides lead to the formation of accelerator-terminated polysulfidic pendent groups on the polymer chain. Crosslinking is commonly considered to result from chain-pendent group reaction or from disproportionation between pendent groups.[14–18,26,27] However, recent studies[20,25–29] showed disproportionation to occur slowly in the absence of zinc compounds, while pendent group-chain reactions are limited. Instead, crosslinking is suggested to result from the reaction of accelerator pendent groups with thiols, formed on reaction of sulfurated dimethyldithiocarbamic acid (Hdmtc) (in TMTD systems)[30] or sulfurated 2-mercaptobenzothiazole (MBT) (in MBTS systems).[25]

$$XSSX + S_8 \leftrightharpoons XS_xX \qquad (1a)$$

$$RH + XS_xX \rightarrow RS_{x-1}X + HSX \qquad (1b)$$

$$HSX + S_8 \leftrightharpoons HS_xX \qquad (1c)$$

$$RH + HS_xX \rightarrow RS_{x-1}H + HSX \qquad (1d)$$

$$RS_xH + HSX \rightarrow RS_xX + H_2S \qquad (1e)$$

$$RS_xH + XSSX \leftrightharpoons RS_xX + HSX \qquad (1f)$$

$$RS_xX + RS_xH \rightarrow RS_yR + HSX \qquad (1g)$$
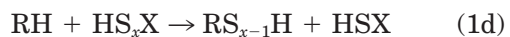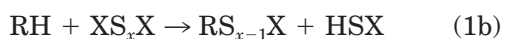
where X = alkyldithiocarbamyl.

Crosslinking decreases the number of pendent groups on the chain, although pendent group positions on the chain are replaced by crosslinks, whereas cyclic sulfides may form during crosslink shortening reactions.[14–17] Thus, as the vulcanization reaction progresses, there is not only an increase in the number of crosslink points but also changes occur in terms of the nature and extent of main-chain modifications, which will affect crystallization. Mallon and McGill[31] suggested that the difference in the tensile strength of IR gum vulcanizates, cured to similar crosslink densities with TMTD- and MBTS-accelerated sulfur formulations, can be attributed to the failure of MBTS vulcanizates to stress-crystallize.

Unlike in model compounds, pendent groups and main-chain modifications such as cyclic sulfides cannot be observed directly in rubber vulcanizates. However, the presence of such modifications in the polymer chain will be reflected in the rate and extent to which vulcanizates crystallize on cooling. This study compares the effect that the extent of cure has on the crystallization at −25°C of IR cured for various times with TMTD/sulfur and MBTS/sulfur formulations. The effect of crystallization on tensile properties will be discussed in a later study.

EXPERIMENTAL

Materials

IR (Afprene IR80) was obtained from Karbochem (Newcastle, South Africa); Orac TMTD (chemical purity 97%) and MBTS (chemical purity 93%) were obtained from Orchem (Sasolburg, South Africa); and sulfur (98% soluble in CS_2) was obtained from AECI (Johannesburg, South Africa).

Compounds were mixed in a Brabender Plasticorder and vulcanized in a press at 150°C as previously described.[32] Curative loadings used are given in parts per hundred rubber (phr; values are indicated within parentheses in the text). To establish how crystallization changed with the extent of cure, the reaction was stopped at points along the cure curve and the mold cooled in water. At each point extractable reaction products and intermediates were analyzed by HPLC[32,33] and crosslink densities determined by swelling.[34] The final vulcanizates comprised samples that had been cured to 95% of their optimum cure as determined by a Monsanto Rheometer (Monsanto, St. Louis, MO).

Crystallization studies were conducted in a density column maintained at −25 ± 0.1°C. The liquids used to set up the column comprised two sodium chloride solutions in water/methanol (50/50 v/v) with densities of 0.87 and 0.95 g/mL.
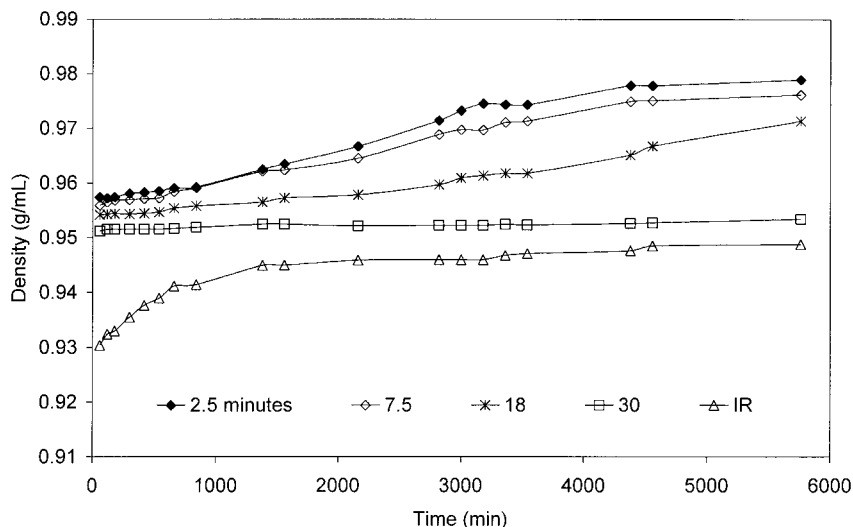
Figure 1 Changes in density with time at $-25.1°C$ for IR and for IR(100)/TMTD(4)/ sulfur(3) vulcanized isothermally at 130°C for various times (min).

The column was calibrated with glass beads, the densities of which were determined by flotation. Daily checks revealed that the linear density gradient did not change over the period of 96 h for which the column was used. A new column was set up for each series of experiments. Samples cut from the vulcanized pad were gently lowered into the liquid and stabilized their positions within 30 min. Changes in density were followed over a period of 96 h or longer. Crystallization data are presented as changes in density with time, rather than in terms of Avrami relationships, because the degree of crystallization in samples heated for longer periods decreased substantially and, considering the fraction of crystallization completed at any time, could have been misleading. Furthermore, slower crystallizing compounds did not attain equilibrium after 96 h. There is no definite induction period before the onset of crystallization, as reflected by the change in density of samples in the column (Fig. 1). The literature[2,11] reports induction periods of greater than 20 h for IR at $-25°C$. The reason for this difference in nucleation time is not apparent. IR is not swollen by water or methanol and the liquid medium in the density column and the crystallization in the column of samples of IR immersed in methanol and aqueous NaCl for 2 weeks did not differ from that of freshly cut samples. It is possible that the methanol/water/NaCl solution promotes surface nucleation. In this investigation the relative rates of crystallization of vulcanizates, cured to different extents, are compared and conclusions based

on relative rates will be valid, despite nucleation occurring earlier than previously reported.

As a control, and to establish the degree of crystallization that develops in unmodified IR, a sample of IR cut from the bale was included in all columns. When an IR sample was masticated in the Brabender, samples taken from different points in the mix displayed small differences in initial density and in the induction period prior to rapid crystallization, which can be attributed to variations in localized chain alignment during mixing.[13] These fluctuations were minor compared to changes induced by vulcanization. Orientation in unfilled compounds relaxes rapidly[13] and will have disappeared in vulcanizates cured for 5 min or more.

The density of 100% crystalline IR at $-25°C$ was not known and, to calculate the percentage crystallinity that developed in samples, the unit cell dimensions[35] at room temperature and the difference between the initial and final densities (after 96 h) were used. Overall trends for compounds cured for different times, however, are clear from the curves. Induction periods, shown in tables, were estimated from the intersection of a line drawn through the initial density–time points and a line drawn through points once the density increased more rapidly, using data over the entire 96-h crystallization period. In many instances crystallization was slow and it was difficult to determine induction times with accuracy. The rates of crystallization are expressed in terms of the time at which crystallization is 50% complete ($t_{1/2}$).

Table I   Crosslink Density and Crystallization Data at −25.1°C for IR and for IR(100)/TMTD(4)/Sulfur(3) Cured at 130°C for Various Times

Cure Time (min)	$\frac{1}{2} M_c \times 10^5$ (mol/mL)	Induction Time (min)	Rate $t_{1/2}$ (min)	Crystallinity (%)	Density (g/mL)	
					Initial	At 6000 min
2.5		180	2400	32	0.9574	0.9790
7.5		180	2400	29	0.9559	0.9762
12.5		180	3200	29	0.9557	0.9760
18.0	Gel	300	4500	23	0.9555	0.9670
20.0	1.88	660		1	0.9512	0.9521
25.0	3.28			2	0.9520	0.9541
30.0	5.75			3	0.9512	0.9535
35.0	5.68			4	0.9512	0.9537
IR only			580	27	0.9304	0.9488

RESULTS AND DISCUSSION

IR(100)/TMTD(4)/Sulfur(3)

Figure 1 shows the change in density at −25°C as a function of time for IR and IR compounds vulcanized isothermally for various times at 130°C. Increased cure times lead to samples with lower initial densities. The decrease in initial density is especially marked in the period prior to the development of crosslinks in the sample (Table I). Once crosslinking commences, further changes in the initial densities of samples cured for longer periods are limited. Compounds heated for longer times crystallize more slowly, as indicated by $t_{1/2}$ and the lower slope of the density–time curves, and once samples had been cured to a point where a gel formed, crystallization was essentially suppressed and little or no change in density occurred over a period of 96 h. In many cases it is

difficult to determine precise induction periods prior to the onset of crystallization. Nevertheless, it is evident that samples heated for longer periods display longer induction periods, $t_{1/2}$ is lengthened, and lower degrees of crystallinity develop (Table I).

Residual curatives were extracted from samples and, after drying, samples were loaded into the column. The initial densities of extracted samples vary randomly (Table II) and the progressive decrease in the initial density of samples cured for longer periods, seen in Table I, is no longer evident. Rates of crystallization ($t_{1/2}$) are slower than those before extraction. Induction times prior to crystallization, although difficult to measure accurately, are also lengthened (Table II).

Extracted samples were reheated to establish the effect of crosslinking residual pendent groups that may be present on the polymer chain. How-

Table II   Crosslink Density and Crystallization at −25.2°C After Extraction and Drying of IR and IR(100)/TMTD(4)/Sulfur(3) Cured at 130°C for Various Times

Cure Time (min)	$\frac{1}{2} M_c \times 10^5$ (mol/mL)	Induction Time (min)	Rate $t_{1/2}$ (min)	Crystallinity (%)	Density (g/mL)	
					Initial	At 6000 min
2.5		180	1750	21	0.9358	0.9495
7.5		210	4300	29	0.9297	0.9495
12.5		520	3300	27	0.9326	0.9508
18.0	Gel	605	4800	23	0.9398	0.9557
20.0	1.88	660	4600	1	0.9369	0.9380
25.0	3.28	4320		0	0.9413	0.9415
30.0	5.75			1	0.9405	0.9406
35.0	5.68			0	0.9471	0.9474
IR only			1500	28	0.9334	0.9524

Table III Crosslink Density and Crystallization at −25.2°C After Extraction, Drying, and Reheating of IR and IR(100)/TMTD(4)/Sulfur(3) Cured at 130°C for Various Times

Cure Time (min)	$\frac{1}{2} M_c \times 10^5$ (mol/mL)	Induction Time (min)	Rate $t_{1/2}$ (min)	Crystallinity (%)	Density (g/mL) Initial	Density (g/mL) At 6000 min
2.5		180	1200	29	0.9257	0.9460
7.5		210	3000	36	0.9295	0.9545
12.5		300	2700	32	0.9257	0.9467
18.0	Gel	580	3700	20	0.9351	0.9488
20.0	1.16		3700	5	0.9388	0.9422
25.0	3.76			1	0.94439	0.9447
30.0	5.73			1	0.9461	0.9465
35.0	5.41			0	0.9541	0.9548
IR only			700	25	0.9320	0.9488

ever, no significant change in crosslink density was observed (Table III). Rates of crystallization were slightly faster than those in extracted samples and induction times were marginally shorter (compare Tables II and III).
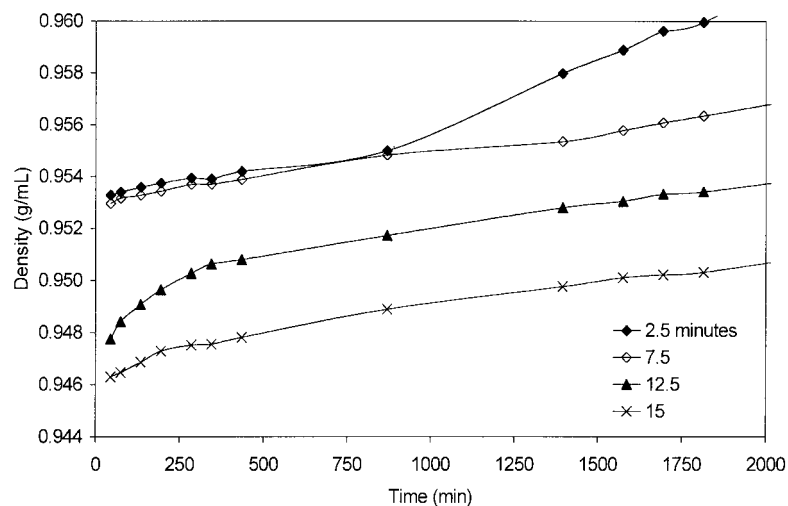
IR(100)/MBTS(4)/Sulfur(3)

Figure 2 shows changes in density during the initial stages of crystallization of samples cured isothermally at 150°C for various times. The progressive decrease in the initial density of samples during the induction period (Table IV), seen in TMTD-cured systems (Table I), is also evident here. Rates of crystallization are slower than those for TMTD vulcanizates (compare Tables I and IV) and induction periods before the onset of

crystallization are longer, even for samples in which no gel had formed. All samples showed a slow increase in density prior to the more rapid density change associated with crystallization (Fig. 2). A similar drift was not seen in TMTD vulcanizates.

Initial Densities

The higher density of compounds, compared to that of pure IR, is attributed to the inclusion of curatives of higher density than that of the rubber. Both accelerators interact with sulfur to form accelerator polysulfides (TMTP[15,21,36–38] and MBTP[23,39,40]) that interact with the polymer chain to form accelerator-terminated polysulfidic pendent groups [eqs. (1a) and (1b)].[15,16,19–24,39] In

Figure 2 Changes in density with time at −25.2°C for IR(100)/MBTS(4)/sulfur(3) vulcanized isothermally at 150°C for various times (min).

Table IV   Crosslink Density and Crystallization at −25.2°C for IR and IR(100)/MBTS(4)/Sulfur(3) Cured at 150°C for Various Times

Cure Time (min)	$\frac{1}{2} M_c \times 10^5$ (mol/mL)	Induction Time (min)	Rate $t_{1/2}$ (min)	Crystallinity (%)	Density (g/mL)	
					Initial	At 6000 min
2.5		870	2900	41	0.9533	0.9812
7.5		1400	2700	15	0.9530	0.9637
12.5		2900	5000	39	0.9478	0.9746
15.0	Gel		8300	35	0.9463	0.9706
20.0	0.15	6400	8100	1	0.9530	0.9613
25.0	1.05			5	0.9512	0.9546
30.0	4.93			1	0.9532	0.9540
35.0	5.12			1	0.9528	0.9533
IR only			800	28	0.9183	0.9383

TMTD/sulfur systems, pendent group formation is a substitutive reaction with the evolution of Hdmtc, that may escape from the system,[14–17,41] although more recent studies[30,42] have shown it to actively participate in the crosslinking process by forming thiol pendent groups [eqs. (1c) and (1d)]. Volatiles, in the form of H_2S from the exchange between Hdmtc and thiol pendent groups [eq. (1e)], together with some Hdmtc, would be lost from the compound, as demonstrated by the small endotherm just prior to the vulcanization exotherm in DSC cure curves.[41] It may therefore be suggested that the decrease in the density of samples cured for progressively longer times (Table I) is attributed to the loss of volatiles of greater density than that of the rubber (Hdmtc and/or H_2S). However, a similar decrease in density with cure time is seen for MBTS/sulfur systems (Table IV). The reaction that leads to pendent group formation in MBTS compounds is not clear, although substitutive[16] and additive[23,24] reactions have been suggested. However, no volatiles are released, either on pendent group formation or on crosslinking.

It is suggested that these decreases in density of samples cured for longer times (Tables I and IV) reflect increases in the free volume of the polymer, occasioned by the attachment of accelerator fragments to the polymer chain as pendent groups. Benzothiazole groups are more bulky than thiuram groups and lead to a greater increase in free volume. HPLC analysis shows that the extractable MBTS drops from 77 to 65 mol % between samples heated for 2.5 and 12.5 min, respectively, corresponding to the formation of 2.88×10^{-5} mol of benzothiazole pendent groups per mL of rubber. The sample density change is

5.2×10^{-3} g/mL (Table IV). Similarly, in the TMTD formulation, the extractable TMTD drops from 87 to 58 mol % between 2.5 and 12.5 min, corresponding to the formation of 9.66×10^{-5} mol/mL of thiuram pendent groups per mL of rubber. If half of the accelerator were lost as Hdmtc, the pendent group concentration would be 4.83×10^{-5} mol/mL rubber. The difference in the initial densities of the 2.5- and 12.5-min samples is 1.7×10^{-3} g/mL (Table I). Despite the similar (4.83×10^{-5} versus 5.19×10^{-5} mol/mL) or higher (9.66×10^{-5} versus 5.19×10^{-5} mol/mL, if Hdmtc is not evolved) change in the concentration of thiuram than benzothiazole pendent groups formed on the chain between 2.5 and 12.5 min, the initial density change between samples is 3.5-fold greater with MBTS formulations. Thus it is proposed that the progressive decrease in initial density of compounds, heated for longer periods, results from an increase in free volume in compounds occasioned by the formation of pendent groups on the polymer chain. HPLC data confirm earlier findings[30,42] that 80% of the TMTD is attached to the chain by the time crosslinking commences.

Rates of Crystallization

Crosslinks will limit chain segmental movement and, if of sufficient number, will restrict and eventually inhibit crystallization. However, the crystallization process is affected well before gelation and this must be ascribed to pendent groups formed on the polymer chain. Chain segments containing pendent groups will be excluded from crystalline regions and an increase in the number of pendent groups will

lead to longer induction periods prior to crosslinking, slower crystallization, and lower crystallization values, as observed for the TMTD and MBTS systems (Tables I and IV).

Extraction of Residual Curatives

Because curatives not bound to the rubber were removed on extraction, extracted samples had lower initial densities compared to those of unextracted samples. It was anticipated that extraction of residual curatives would permit the effect of bound curatives, in particular pendent groups, on the crystallization process to be studied. However, initial densities of different samples no longer showed a consistent trend with cure time (Table II). This is ascribed to the retention of small amounts of solvent of lower density than that of the rubber, despite samples being dried for 48 h. Induction periods prior to the onset of crystallization are longer and rates of crystallization slower than in that in unextracted samples, although these still show a progressive change with cure time (Table II). These differences can also be ascribed to residual solvent in the rubber.

Crosslink density measurements show that no crosslinking of residual pendent groups occurred on reheating (compare Tables II and III). After reheating of extracted samples the initial densities were again different (Table III) and may indicate the loss of some solvent trapped in extracted samples. Induction periods were somewhat shorter and rates of crystallization faster, which would be consistent with the removal of traces of solvent from the samples (compare Tables II and III).

Crystallization of Curatives in Rubber

At room temperature the solubility of sulfur and accelerators in rubbers is very low (<1 phr) but increases rapidly with temperature, for which a log–log relationship was observed.[43] It is suggested that in MBTS vulcanizates the small slow increase in density with time, prior to the more rapid change attributed to the crystallization of the rubber, is the result of the separation of residual curatives in the compound and their crystallization on cooling (Fig. 2). The densities of compounds were calculated based on additive volumes of components, using the density of rubber as determined in the column at $-25°C$ (0.9280 g/mL) and the lattice dimensions of curatives. (Literature values for the densities of curatives differ markedly, possibly as a result of their having different purities.) The calculated initial density of the MBTS compound is 4.3×10^{-3} g/mL lower (0.45%) and that of the TMTD compound 1.8×10^{-3} g/mL higher (0.19%) than the experimental value. The latter value implies a decrease in free volume of the rubber-curative system on mixing, which indicates stronger interaction between rubber and curatives than in the case of the MBTS compound. This may explain why a drift in density prior to crystallization of IR was not observed with TMTD compounds (compare Figs. 1 and 2).

CONCLUSIONS

The decrease in the density, prior to their crystallization, of compounds cured for progressively longer times is attributed to the formation of accelerator-terminated pendent groups on the polymer chain. The induction period prior to crystallization increases and both the rate and the extent of crystallization decrease with increased cure times. This is attributed largely to residual pendent groups on the chain and, to a lesser extent, to crosslink formation. These effects are more marked with MBTS vulcanizates that fail to crystallize once crosslinked to the point where a gel forms.

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