Crystallization of Vulcanizates. II. Low-Temperature Crystallization as a Function of Extent of Cure for Polybutadiene Vulcanized with Dicumyl Peroxide, Tetramethylthiuram Disulfide, 2-Bisbenzothiazole-2,2′-disulfide, and Zinc–Accelerator Complexes

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ABSTRACT: Polybutadiene compounds, vulcanized to various degrees of cure, were crystallized in a density column at $-16°C$. The percentage crystallinity of vulcanizates was also determined by differential scanning calorimetry where samples, precooled at a programmed rate, were reheated. Curing with peroxides has little effect on either the rate or the extent of crystallization, except at very high crosslink densities, although the induction period prior to crystallization increases progressively with increased crosslink density. Tetramethylthiuram disulfide (TMTD)/sulfur and 2-bisbenzothiazole-2,2′-disulfide (MBTS)/sulfur vulcanizates, cured for progressively longer periods, were found to have lower densities, a result attributed to an increase in free volume occasioned by the formation of accelerator-terminated pendent groups on the polymer chain. The induction period for crystallization increases and both the rate and the extent of crystallization decrease with extent of cure. These changes are more marked for MBTS vulcanizates that do not crystallize once a gel has formed. Formulations with zinc stearate develop higher crosslink densities and crystallize to a greater extent on cooling, showing the effect of zinc stearate in the crosslinking of pendent groups. The densities of both zinc dimethyldithiocarbamate $[Zn_2(dmtc)_4]$– and zinc mercaptobenzothiazole $[Zn(mbt)_2]$–accelerated sulfur vulcanizates increase with cure time, a result attributed to the formation of ZnS in the compounds. $Zn_2(dmtc)_4$ compounds crystallize extensively on cooling, pointing to limited main-chain modification. It is suggested that main-chain modification in these vulcanizates may comprise cyclic sulfide formation. $Zn(mbt)_2$ compounds crystallize less readily than $Zn_2(dmtc)_4$ compounds, but to a greater extent than MBTS/sulfur compounds. The crystallization of the vulcanizates is discussed in terms of vulcanization reactions that give rise to crosslinking with the different formulations used. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 2573–2586, 2001

Key words: crystallization; polybutadiene; vulcanizates; cooling

INTRODUCTION

The ability of a vulcanizate to crystallize on extension is considered an important factor in determining its tensile properties.[1,2] The nature of the vulcanizate produced is dependent on the formulation used, which determines the network structure and both the nature and the extent of modifications to the polymer chain. These differences should be reflected in the crystallization of the vulcanizates on cooling. Thus, one can use crystallization as a measure of modification in vulcanizates. In the previous study[3] in this series it was shown that, at −25°C, the crystallization of both tetramethylthiuram disulfide (TMTD)– and 2-bisbenzothiazole-2,2′-disulfide (MBTS)–accelerated sulfur vulcanizates of polyisoprene (IR) decrease with increased cure times, although MBTS vulcanizates fail to crystallize once a gel has formed. This was attributed to residual pendent groups in the compound and, in particular, to the bulky benzothiazole pendent groups in MBTS vulcanizates. The density of compounds prior to crystallization decrease with cure time, which was ascribed to an increase in free volume associated with the formation of pendent groups on the polymer chain. With TMTD/sulfur formulations crosslinking does not commence until the concentration of extractable TMTD has fallen to 20 mol %,[4–7] whereas in MBTS/sulfur vulcanizates crosslinking initiates at a slightly higher unbound accelerator concentration.[4,8,9] In compounds that do not contain zinc, accelerator polysulfides react with the chain to form accelerator-terminated polysulfidic pendent groups that, on further reaction, give rise to crosslink formation.[10–15]

Some modification to details of the crosslinking process have recently been proposed.[5,8] The mechanism of vulcanization by zinc–accelerator complexes remains unclear. It is generally accepted that vulcanization involves accelerator-terminated polysulfidic pendent groups, similar to those found in formulations without zinc.[12–14] These pendent groups are considered to form by the interaction of polysulfidic zinc–accelerator complexes with the polymer chain. However, accelerator-terminated pendent groups have not been detected in compounds cured with zinc–accelerator complexes[16–18] and it has been suggested that such groups cannot be detected because their crosslinking is rapidly catalyzed by zinc–accelerator complexes.[16] Another suggestion is that thiol pendent groups form by sulfurated

$Zn_2(dmtc)_4$, which inserts sulfur into the allylic C—H bond, and that the thiols are too rapidly crosslinked by the catalytic action of $Zn_2(dmtc)_4$ for their detection in model compound studies.[17] Bristow and Tiller[19] showed that $Zn_2(dmtc)_4$ vulcanizates failed to crystallize, even at low crosslink densities, and suggested that the low Moore–Trego[20] efficiencies of $Zn_2(dmtc)_4$ vulcanizates pointed to the formation of a large amount of cyclic sulfides.

The crystallization of IR is slow and consequently may not be as sensitive to changes in vulcanizate structures as a more rapidly crystallizing polymer such as polybutadiene (BR). Cassem and McGill[21] showed that the mechanism of TMTD-accelerated sulfur vulcanization of BR was similar to that reported for IR,[22] whereas the work of Mallon and McGill,[7,9] who employed TMTD and MBTS formulations, demonstrated the similarity of vulcanization reactions occurring with IR and poly(styrene-*co*-butadiene) (in which butadiene provides the crosslinking unit). However, compared to IR vulcanization differences do exist (e.g., the formation of vicinal crosslinks in BR vulcanizates).[23,24]

This study examines the extent to which different formulations modify the network, as monitored by the effect that the degree of cure has on both the rate and the extent of crystallization on cooling of different BR formulations. The effect of TMTD/sulfur and MBTS/sulfur formulations on the ability of BR vulcanizates to crystallize on cooling is compared with the crystallization of similar vulcanizates of IR.[3] Zinc stearate has been shown to promote the crosslinking of pendent groups[25] and the effect of its inclusion on the crystallization of vulcanizates is reported. The crystallization study is also extended to vulcanizates cured with zinc–accelerator complexes.

EXPERIMENTAL

Materials

Neodene (98% *cis*-BR) was obtained from Karbochem (Newcastle, South Africa); dicumyl peroxide was obtained from BDH Ltd. (Poole, UK); zinc dimethyldithiocarbamate [$Zn_2(dmtc)_4$, Vulcazit L] and zinc mercaptobenzothiazole [$Zn(mbt)_2$, Vulcazit ZM] were obtained from Bayer (Leverkusen, Germany); zinc stearate was obtained from Associated Additives (Johannesburg, South Africa); and ZnO (active grade, 99.72% purity)

Table I   Crosslink Density and Crystallization Data at −16.0°C for BR and for BR(100)/dicumyl peroxide(*x*) Cured at 150°C for 30 Min

Peroxide (phr)	$\frac{1}{2}M_c \times 10^5$ (mol/mL)	Induction Time (min)	Rate $t_{\frac{1}{2}}$ (min)	Crystallinity (%)	Density (g/mL)	
					Initial	At 3000 min
0.003	Gel	5	28	43	0.9324	0.9611
0.020	0.54	15	31	42	0.9333	0.9614
0.030	3.10	20	52	41	0.9338	0.9606
0.040	4.28	27	60	40	0.9338	0.9601
0.400	16.30	280	1100	30	0.9372	0.9571
BR only		5	22	42	0.9324	0.9599

was obtained from Zinc Process (Cape Town, South Africa).

Compounds were mixed on a Barbender Plasticorder and vulcanized in a press at temperatures indicated in the text.[3,26] Curative loading values used are given in parentheses in the text in parts per hundred rubber (phr). The reaction was stopped at various points along the cure curve and the mold cooled in water to stop the reaction. Small samples were crystallized in a density column described in the previous study.[3] The densities of the aqueous/methanol/NaCl solutions used to prepare the density column for BR samples were 0.89 and 0.98 g/mL. BR crystallizes more rapidly than IR and a number of column temperatures were investigated to determine a suitable temperature at which samples could be differentiated in terms of crystallization rates.

A column temperature of −16°C was found to be most suitable for the study. The density of 100% crystalline BR at −16°C is not known and, as in the IR study,[3] the percentage crystallinity that developed was calculated from the unit cell dimensions[27] of BR at room temperature and the difference between the initial and final (96 h) densities of samples in the column.

Samples that crystallize slowly stabilize their positions in the column within 30 min and the induction period prior to crystallization was determined 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. In most figures only the initial portion of the density versus time curves are shown, although data for the whole 96-h (or longer) crystallization period were used to estimate the induction period prior to the onset of crystallization. Many BR samples crystallized rapidly and, before their positions in the column had stabilized, the rate of change of their positions accelerated. In these cases the induction period was estimated as the time at which the change in position of samples accelerated.

The rate of crystallization recorded in the tables is expressed in terms of the time at which crystallization is 50% complete ($t_{1/2}$). Samples were also crystallized by cooling at 5°C/min to −50°C in a DSC, holding samples at −50°C for 30 min, and then reheating at 5°C/min. A standard differential scanning calorimeter DSC10 cell connected to a Thermal Analyst 2000 (TA Instruments) was used. Samples that crystallized rapidly showed an exotherm on cooling, in which the onset temperature gave an indication of the ease of crystallization.[28] The area under the melting endotherm, obtained on reheating, was used to calculate the percentage crystallization.

The value for the enthalpy of melting (170.57 J/g) used in the calculations was obtained by assuming that a BR sample crystallized in the column and a sample crystallized in the DSC developed similar crystallinities. HPLC analysis of residual curatives extracted from vulcanizates at various stages of cure was previously described[29] and crosslink densities were determined by swelling.[30]

RESULTS AND DISCUSSION

BR(100)/Dicumyl Peroxide(0.003–0.4)

Different crosslink densities were obtained by curing compounds with different dicumyl peroxide loadings at 150°C for 30 min (Table I). Samples were crystallized in the column and the initial portions of the density versus time curves are shown in Figure 1. It is clear that, except at very
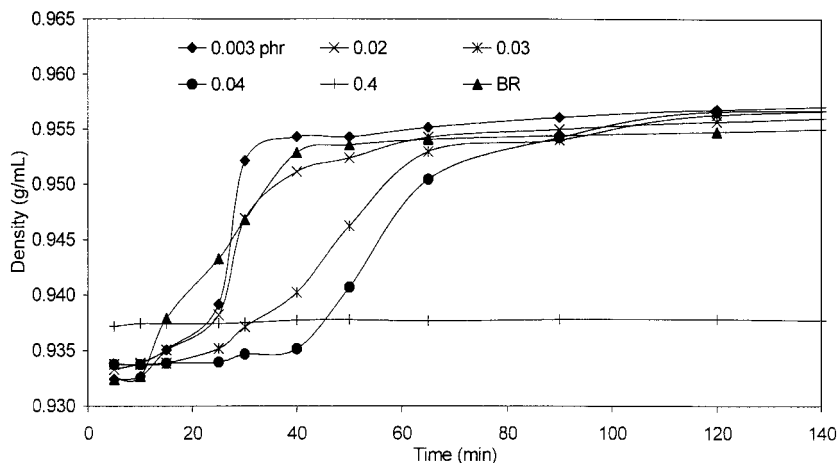
Figure 1 Changes in density with time at $-16°C$ for BR(100)/peroxide(x) cured isothermally at 150°C for 30 min.

high crosslink densities, crosslinks per se do not have a marked effect on the rates of crystallization or on the percentage crystallinity (Fig. 1 and Table I). Slight increases in the induction times are evident, as seen in the samples with crosslink densities of 3.10×10^{-5} and 4.28×10^{-5} mol/mL. In very highly crosslinked samples (16.3×10^{-5} mol/mL) there is a considerable increase in induction time and the rate of crystallization is greatly reduced.

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

Changes in density as a function of time for compounds vulcanized at 130°C are shown in Figure 2. The progressive decrease in the initial density

of samples cured for longer times, seen in IR compounds,[3] is also evident here (Table II). Rates of crystallization decrease with increased cure times and the induction period before crystallization increases.

Crystallization in the density column of IR samples after extraction of residual curatives appeared to be influenced by traces of solvent retained on drying.[3] A similar series of experiments was conducted on extracted BR compounds, using DSC techniques, instead of the density column. The presence of trace amounts of solvent should not contribute to the BR melting endotherm. Four sets of data comprising the crystallization in (1) vulcanized samples; (2) vulcanized extracted
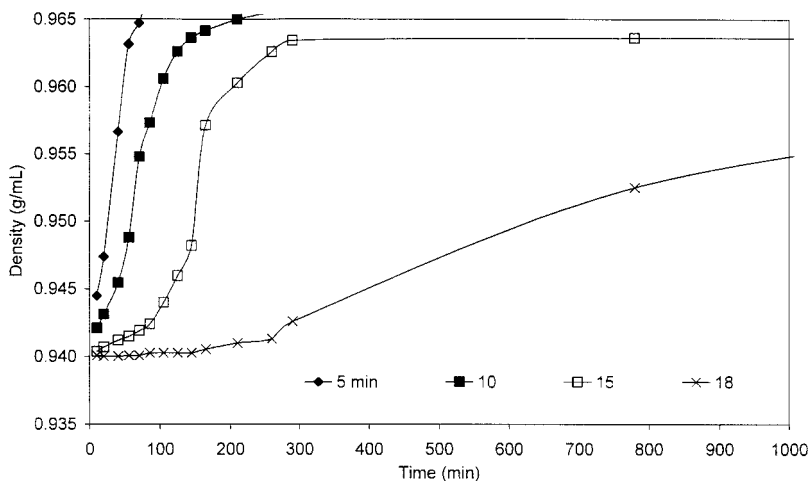
Figure 2 Changes in density with time at $-16°C$ for BR(100)/TMTD(4)/sulfur(3) cured isothermally at 130°C for various times (min).

Table II   Crosslink Density and Crystallization Data at −16.1°C for BR and for BR(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 $t_{\frac{1}{2}}$ (min)	Crystallinity (%)	Density (g/mL)	
					Initial	At 3000 min
5		10	45	45	0.9445	0.9742
10		15	80	42	0.9421	0.9699
15	Gel	130	150	37	0.9404	0.9646
18	0.64	260	670	31	0.9401	0.9603
21	3.02	970	3900	15	0.9387	0.9487
24	4.17	1070	2100	8	0.9396	0.9445
27	6.43	1450	5700	6	0.9388	0.9429
30	8.66	1460		5	0.9392	0.9424
BR only		5	22	37	0.9346	0.9587

samples; (3) extracted, reheated samples; and (4) extracted samples, reheated for 10 min at 130°C after swelling in a solution of zinc stearate and drying are presented in Table III. Values of onset of crystallization are dependent on the development of nuclei on cooling and on the growth of these nuclei being sufficiently rapid for the latent heat evolved to be recorded as the onset of an exotherm. It can be regarded as a measure of the ease with which crystallization occurred. It is evident from Table III that the ease of crystallization decreased and the percentage crystallinity decreased slightly with increased cure times. After extraction of residual curatives some samples, cured for longer times, showed increased degrees of crystallinity compared to their crystallinity values before extraction, with the onset of crystallization showing no definite trend.

On reheating of extracted samples for 10 min at 130°C an increase in crosslink density was obtained, showing some crosslinking of residual pendent groups present in the compounds. However, this did not result in any significant change in the onset of crystallization nor in the degree of crystallization developed. The efficiency of zinc stearate in crosslinking residual pendent groups was previously demonstrated.[5,15] Reheating (for 10 min at 130°C) of extracted samples after swelling in a solution of zinc stearate and subsequent drying led to drastic increases in crosslink density, yet no significant change in either the onset or the degree of crystallization was observed.

BR(100)/MBTS(4)/Sulfur(3)

The initial densities of compounds cured at 150°C show a progressive decrease with increased cure time (Fig. 3 and Table IV). As in IR these decreases are greater in MBTS than those in TMTD vulcanizates.[3] Compared to TMTD-accelerated systems, induction times increase substantially prior to the onset of crosslinking. The 12-min sample, although only a gel, has an induction time of 100 h (Table IV). The percentage crystallinity is substantially lower than that for TMTD samples of similar crosslink density and samples cured for longer times do not crystallize within the time frame of the experiments (111 h).

As with the TMTD system, the DSC study of MBTS vulcanizates shows the same trends that are observed in the density column for vulcanizates cured for longer periods (Table V). The percentage crystallinity decreased with increased cure time and no onset of crystallization or melt was detected in samples cured for 19 min and longer.

Reheating (for 10 min at 150°C) of extracted samples after swelling in a solution of zinc stearate and subsequent drying led to a marked increase in crosslink density, particularly in samples cured for shorter periods where a large number of unreacted pendent groups would be present. Despite the crosslinking of these pendent groups, no crystallization was observed in samples cured for longer than 19 min.

BR(100)/TMTD(4)/Sulfur(3)/Zinc Stearate(1)

Compounds were cured at 130°C. A comparison of data in Table VI with data in the first set of columns in Table III shows that the addition of zinc stearate to formulations substantially increased both the rate and the extent of crosslink formation. The percentage crystallinity decreased

Table III Crosslink Densities and DSC Data of BR(100)/TMTD(4)/Sulfur(3) Cured for Different Times

Cure Time (min)	Original Vulcanizate			Extracted			Extracted, Reheated 10 min at 130°C			Extracted, Swollen in Zn Stearate, Heated 10 min at 130°C		
	$\frac{1}{2}M_c \times 10^5$ (mol/mL)	Crystallinity (%)	Onset of Crystallinity (°C)	$\frac{1}{2}M_c \times 10^5$ (mol/mL)	Crystallinity (%)	Onset of Crystallinity (°C)	$\frac{1}{2}M_c \times 10^5$ (mol/mL)	Crystallinity (%)	Onset of Crystallinity (°C)	$\frac{1}{2}M_c \times 10^5$ (mol/mL)	Crystallinity (%)	Onset of Crystallinity (°C)
0		40	−14.6									
5		38	−21.5									
10		35	−23.6									
15		35	−26.7		39	−26.3	0.31	35	−28.5			
18	0.46	35	−28.7	0.46	40	−22.8	0.51	32	−29.4	5.35	36	−28.9
21	0.89	34	−29.2	0.89	42	−23.2	2.27	36	−33.2	5.93	37	−30.8
24	1.71	32	−29.7	1.71	39	−30.6	5.82	32	−31.9	8.39	35	−31.3
27	2.11	28	−30.4	2.11	38	−34.3	3.62	32	−37.4	10.20	34	−37.3
30	6.12	26	−34.4	6.12	37	−33.6	4.88	35	−35.7	7.13	35	−32.4

progressively with longer cure times, but even heavily crosslinked samples crystallized.

BR(100)/MBTS(4)/Sulfur(3)/Zinc Stearate(1)

Compounds were vulcanized at 150°C. A comparison of data in Tables V and VII shows that zinc stearate did not shorten the induction period before the detection of crosslinking, but that once crosslinking did commence, the reaction was faster and higher crosslink densities were achieved than in the absence of zinc stearate. The effect of zinc stearate on crystallization was less than that in the case of TMTD vulcanizates. The onset of crystallization on cooling in the DSC was not observed in samples once crosslinked to the point where a gel formed, although on holding samples at −50°C crystallization did occur, as evidenced by the melting endotherm on reheating. Even highly crosslinked samples crystallized, unlike samples cured without zinc stearate. The percentage crystallinity that developed was lower than that in TMTD vulcanizates of similar crosslink density.
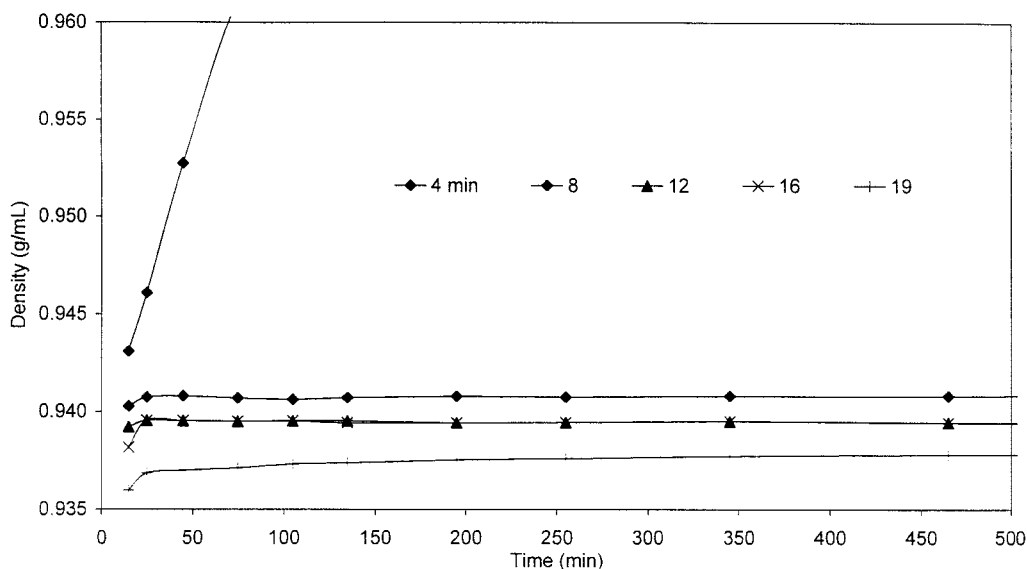
BR(100)/MBTS(4)/Sulfur(3)/ZnO(5)

Compounds containing ZnO, cured at 150°C, developed slightly higher degrees of crystallinity on cooling than those of vulcanizates without ZnO (compare Tables V and VIII). Compounds cured for 19 min had similar crosslink densities (0.41 × 10^{-5} versus 0.43 × 10^{-5} mol/mL), yet the ZnO-containing vulcanizate developed 18% crystallinity compared to none in the absence of ZnO.

BR(100)/Zn(mbt)$_2$(4)/Sulfur(3)

Figure 4 shows changes in density of compounds vulcanized at 150°C for various times. Increased cure times led to vulcanizates with increased initial densities (Table IX), in direct contrast to vulcanizates cured with TMTD (Table II) and MBTS (Table IV) systems. Rates of crystallization decreased with increased cure times (Table IX). Induction times increased with increased cure times, such that crystallization in the sample cured for 140 min was recorded only after 48 h, yet even this sample developed 20% crystallinity, unlike MBTS vulcanizates, where less than 10% crystalline material was recorded in crosslinked samples (Table IV).

Density changes in the column of samples vulcanized for short times yielded higher values for the percentage crystallinity (Table IX) than the

Figure 3 Changes in density with time at $-16°C$ for BR(100)/MBTS(4)/sulfur(3) cured isothermally at 150°C for various times (min).

value of 40% found for the crystallization of pure BR. A number of these vulcanizates were therefore also crystallized by cooling in the DSC. Again, all samples were shown to crystallize, but the percentage crystallinity calculated from DSC data was comparable (40% or less) with that found for other curing systems (compare Table X with Tables III–VIII). This apparent anomaly is discussed below.

BR(100)/Zn$_2$(dmtc)$_4$(4)/Sulfur(3)

Figure 5 shows the change in density for compounds vulcanized at 130°C. As in the Zn(mbt)$_2$ system, increased curing times led to samples

with increasing initial densities (Table XI). Rates of crystallization were of the same order of magnitude as those for Zn(mbt)$_2$ vulcanizates (compare Tables XI and IX), although induction times were considerably shorter for vulcanizates with similar crosslink densities.

Nucleation and Growth

Nucleation requires the formation of a crystallite larger than the critical nuclear size that can grow spontaneously with a decrease in free energy.[31] Chain segments at or close to a crosslink cannot be incorporated into the crystal lattice and thus, in a crosslinked polymer, nucleation is confined to

Table IV   Crosslink Density and Crystallization Data at $-16.2°C$ for BR and for BR(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 $t_{\frac{1}{2}}$ (min)	Crystallinity (%)	Density (g/mL)	
					Initial	At 6700 min
4		5	60	39	0.9431	0.9689
8		140	3100	16	0.9403	0.9509
12	Gel	600	6400	26	0.9392	0.9564
16	0.50			8	0.9382	0.9387
19	0.85			3	0.9360	0.9379
22	1.65			0	0.9397	0.9385
25	1.76			1	0.9340	0.9393
30	7.66			1	0.9403	0.9407
BR only		5	24	40	0.9332	0.9588

Table V   Crosslink Densities and DSC Crystallization Data for BR(100)/MBTS(4)/Sulfur(3) Vulcanized at 150°C for Various Times

Cure Time (min)	BR(100)/MBTS(4)/Sulfur(3)			After Extraction, Swelling in Zn Stearate, and Reheating at 150°C for 10 min		
	$\frac{1}{2} M_c \times 10^5$ (mol/mL)	Crystallinity (%)	Onset of Crystallinity (°C)	$\frac{1}{2} M_c \times 10^5$ (mol/mL)	Crystallinity (%)	Onset of Crystallinity (°C)
0		41	−20.7			
4		35	−21.1			
8		20	−29.5			
12		28	−36.4			
16	0.26	8	No onset	5.33	8	No onset
19	0.41	No melt		5.98	No melt	
22	0.61			6.89		
25	1.15			6.10		
30	4.50			10.20		
35	8.18			10.40		
BR only		40	−20.2			

areas away from crosslinks. If one imagines a distribution of crosslinks within the polymer, it is suggested that nucleation can be envisaged to occur in a volume of chain segments that are away from crosslinked points, where the points of crosslinking constitute the boundary of the volume or cage containing polymer that can nucleate, as shown schematically in Figure 6. At or just below the crystallization temperature the probability of nucleation, or the time taken before a nucleation event occurs, will depend on the volume of the material in which nucleation can occur; the larger the volume, the greater the probability that the necessary number of chains will align to form a nucleus of critical size. Thus, in the density column, the induction period will be lengthened in networks where nucleation is more difficult. The induction period will increase with increased crosslink density as the volume of unmodified chain sequences contained within the cage, depicted in Figure 6, is decreased. When using DSC, a delay in nucleation resulting from modification of the polymer is reflected by a change in the onset temperature of crystallization, such that crystallization is detected only at lower temperatures. The critical nuclear size (r^*) decreases with increased supercooling (ΔT).[31]

Table VI   Crosslink Density and DSC Crystallization Data for BR(100)/TMTD(4)/Sulfur(3)/Zinc Stearate(1) Cured at 130°C for Various Times

Cure Time (min)	$\frac{1}{2} M_c \times 10^5$ (mol/mL)	Crystallinity (%)	Onset of Crystallinity (°C)
0		40	−21.4
5	3.6	34	No onset
10	16.5	32	
15	19.5	24	
18	18.5	23	
21	19.0	18	
24	17.5	14	
27	17.9	5	

Table VII   Crosslink Density and DSC Crystallization Data for BR(100)/MBTS(4)/Sulfur(3)/Zinc Stearate(1) Cured at 150°C for Various Times

Cure Time (min)	$\frac{1}{2} M_c \times 10^5$ (mol/mL)	Crystallinity (%)	Onset of Crystallinity (°C)
0		40	−21.4
4		39	−22.4
8		38	−25.7
12		36	−33.3
16		32	−33.4
19	Gel	25	No onset
22	3.06	18	
25	7.22	17	
30	10.30	17	
35	12.40	21	

Table VIII   Crosslink Density and DSC Crystallization Data for BR(100)/MBTS(4)/Sulfur(3)/ZnO(5) Cured at 150°C for Various Times

| Cure Time (min)	$\frac{1}{2} M_c \times 10^5$ (mol/mL)	Crystallinity (%)	Onset of Crystallinity (°C)
0		40	−21.4
4		36	−38.6
8		29	−42.5
12	Gel	27	No onset
16	0.47	16	
19	0.43	18	
22	1.51	1	
25	1.69		
30	6.04		

$$r^* = (-4\gamma T_m/\Delta H)\Delta T$$

where γ is the strain free energy per unit interfacial surface area between crystal and melt, T_m is the crystalline melting point, and ΔH is the latent heat of crystallization.

Thus, when the alignment of a smaller number of chain sequences is sufficient to generate a nucleus, as applies at lower temperatures where r^* is smaller, the probability of nucleation is correspondingly increased. This situation is akin to the freezing on cooling of a solvent in a swollen polymer network, where the solvent freezing point, which depends on the formation of a nucleus, decreases with an increase in crosslink density of the swollen network.[32,33] The higher the crosslink density, the smaller are the pockets of solvent contained between polymer chains in which nucleation can occur (Fig. 6). Thus, although the extent to which dicumyl peroxide–cured networks crystallized was not markedly affected by crosslinking (other than at high crosslink densities), nucleation was delayed because the volume of material in which the nucleation event could occur was reduced by reducing the volume of the cage between crosslinks (Table I).

Crosslinks will impede nucleation, but if sequences between crosslinks are unmodified, these can eventually be incorporated into the crystal lattice without seriously reducing the degree of crystallization that develops (except at very high crosslink densities). The formation of pendent groups or main-chain modifications in accelerated sulfur vulcanization will further impede the nucleation process as modified chain sequences also constitute chain segments that cannot participate in nucleation. Such pendent groups and main-chain modifications will also seriously exert an impact on the degree of crystallinity that develops because more and more parts of the chain sequences between crosslinks can no longer be incorporated into the crystal. Thus, a delay in the onset of crystallization, without a major change in the degree of crystallinity, points to a crosslinking process that does not involve the formation of pendent groups, or to a process in which, if pendent groups do form, they are rapidly removed in further reactions and no or few residual pendent groups remain, nor do major main-chain modifi-
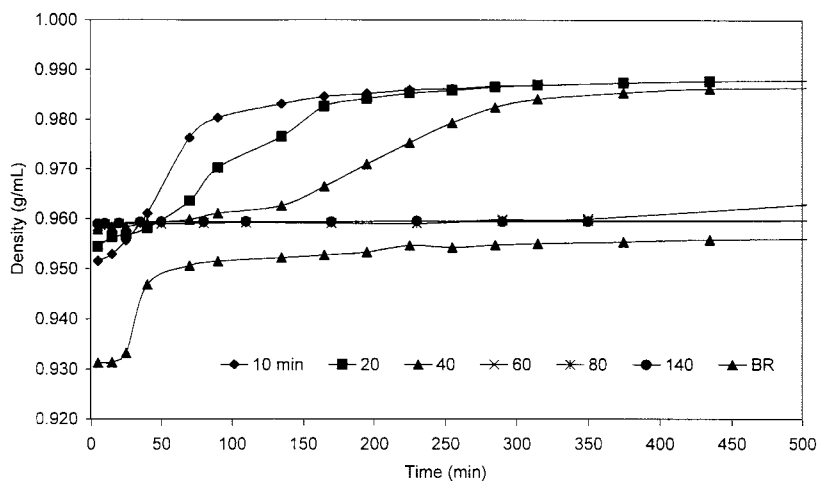
Figure 4   Changes in density with time at −16°C for BR(100)/Zn(mbt)$_2$(4)/sulfur(3) cured isothermally at 150°C for various times (min).

Table IX   Crosslink Density and Crystallization Data at −16.1°C for BR and for BR(100)/Zn(mtb)₂(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 $t_{\frac{1}{2}}$ (min)	Crystallinity (%)	Density (g/mL)	
					Initial	At 7000 min
10		5	60	60	0.9515	0.9916
20		10	110	57	0.9544	0.9919
40	Gel	140	220	50	0.93578	0.9912
60	0.40	350	1000	42	0.9585	0.9858
80	0.71	1100	2400	32	0.9586	0.9296
140	1.31	2900	3700	20	0.9589	0.9724
BR only		5	30	43	0.9313	0.9594

cations result. A change in the degree of crystallization indicates main-chain modification (pendent group of cyclic sulfide formation) or a very high crosslink density.

Density Column versus DSC Crystallization

Crystallization data obtained in the density column show similar trends to data obtained on crystallization in the DSC. Thus, Tables II and III show that in samples cured for longer times, nucleation was more difficult, as reflected in the increased induction periods (density column) and by the lower temperatures to which samples cooled before the onset of crystallization was detected (DSC). For the more highly crosslinked samples, higher percentages of crystallinity developed in DSC samples than in samples crystallized in the column. This implies that crystal growth at −50°C was faster than that at −16°C, and higher percentages of crystallinity can be expected if samples were held in the column for periods beyond 96 h. Samples that crystallized

Table X   Crosslink Density and DSC Crystallization Data for BR(100)/Zn(mbt)₂(4)/Sulfur(3) Cured at 150°C for Various Times

Cure Time (min)	$\frac{1}{2}M_c \times 10^5$ (mol/mL)	Crystallinity (%)	Onset of Crystallinity (°C)
0		38	−25.2
10		38	−28.6
60	Gel	26	−30.1
100	0.40	25	−38.9
1120	0.71	25	−42.7
140	1.31	25	−42.9

rapidly developed similar crystallinities, irrespective of the experimental technique used.

Peroxide Formulations

The slight increase in the initial density of peroxide samples (Table I) may be attributed to the inclusion in the compounds of progressively larger amounts of curatives of higher density than that of the rubber. The crosslink efficiency of dicumyl peroxide in BR[34] is 12, which is indicative of a chain reaction. Clusters, comprising a number of closely positioned crosslinks, may develop. Despite this, crosslink densities of up to 5 × 10⁻⁵ mol/mL have a negligible effect on both the rate and the percentage crystallinity (Fig. 1 and Table I) and only a slight increase in induction period was observed.

TMTD and MBTS Formulations

The difference in the initial density between compounds heated for 5 and 18 min is 4.4×10^{-3} g/mL in the TMTD system (Table II) and in MBTS samples heated for 4 and 19 min the difference is 7.1×10^{-3} g/mL (Table IV). As discussed in the previous study[3] on IR, it is suggested that these decreases reflect increases in free volume in the polymer occasioned by the attachment of accelerator fragments to the polymer chain as pendent groups. HPLC analysis shows that the change in the extractable MBTS between the 4- and 19-min samples corresponds to the formation of 9.2×10^{-5} mol of benzothiazole pendent groups per mL of rubber. The corresponding change in the TMTD system represents the formation of 20.3×10^{-5} mol of thiuram pendent groups per mL of rubber, or 10.1×10^{-5} mol/mL of pendent groups if it is assumed that half the thiuram groups are

Figure 5   Changes in density with time at $-16°C$ for BR(100)/Zn$_2$(dmtc)$_4$(4)/sulfur(3) cured isothermally at 130°C for various times (min).

lost as dimethyldithiocarbamic acid.[5,8,10–15] The difference between the initial densities of the two MBTS vulcanizates is twice that of the corresponding TMTD samples. This clearly indicates the effect of the larger benzothiazole groups on the free volume of vulcanizates.

The onset of crystallization and the percentage crystallinity that developed were also more severely impeded in MBTS than in TMTD vulcanizates. At higher crosslink densities the induction period in TMTD systems was considerably lengthened (Table II) but in MBTS systems it was essentially infinite once a gel has formed (Table IV). In the time span of the experiments

(96 h) TMTD vulcanizates with a crosslink density as high as 8.66×10^{-5} mol/mL developed measurable crystallinities, whereas the MBTS vulcanizate with a crosslink density of 0.5×10^{-5} mol/mL developed only 8% crystallinity. Crystallinity will be impeded by pendent groups. Furthermore, the Moore–Trego[20] efficiency E, which relates to the number of sulfur atoms combined per crosslink formed, was much higher in MBTS than in TMTD vulcanizates of similar crosslink density (MBTS: $E = 12.2$ for $\frac{1}{2}M_c$ of 6.77×10^{-5} mol/mL; TMTD: $E = 5.3$ for $\frac{1}{2}M_c$ of 7.08×10^{-5} mol/mL). Bristow and Tiller[19] showed that the formation of cyclic sulfides greatly

Table XI   Crosslink Density and Crystallization Data at $-16.1°C$ for BR and for BR(100)/Zn$_2$(dmtc)$_4$(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 3500 min
5		5	35	50	0.9514	0.9843
15		10	45	47	0.9550	0.9855
20	0.27	15	40	46	0.96018	0.9903
25	0.28	290	830	32	0.9623	0.9832
30	2.88	380	600	30	0.9641	0.9832
35	3.70	680	1000	17	0.9657	0.9770
40	5.72			0	0.9672	0.9674
BR only		5	35	40	0.9335	0.9591
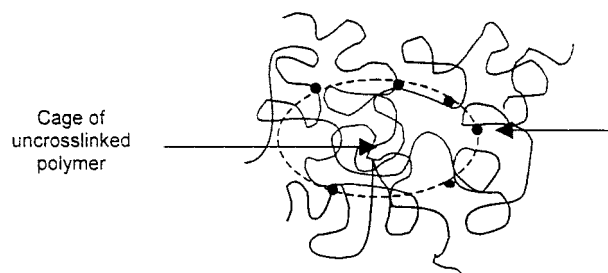
Figure 6 Schematic showing volume of polymer between crosslinks in which crystallization may nucleate. Crosslinked points represent the boundary of the cage containing unmodified polymer.

increased the resistance of rubbers to crystallization at low temperatures.

MBTS systems showed a small increase in density soon after introduction to the column (Fig. 3) and this may relate to unreacted MBTS in the compound coming out from solution in the rubber and crystallizing.

Where cooling conditions are different from those in the density column, the DSC study allows one to draw the same above-noted conclusions as those reached for crystallization in the density column. All TMTD vulcanizates crystallized, although the onset of crystallization occurred at progressively lower temperatures as the crosslink density increased (Table III). No crystallization was detected in MBTS vulcanizates with crosslink densities higher than 0.03×10^{-5} mol/mL (Table V).

Extracted Formulations

It is not clear why extracted TMTD samples showed a small increase in percentage crystallinity (Table III). Reheated, extracted samples showed an increase in crosslink density, whileereas samples reheated after swelling in zinc stearate showed a considerable increase in crosslink density, indicating the presence of pendent groups in the preheated compounds. It also shows the effectiveness of zinc stearate in crosslinking pendent groups.[5,25] The increased percentage crystallinity that develops in the latter samples, despite the increased crosslink density, points to the removal of pendent groups that impeded crystallization in the original samples and confirms the contention, stated earlier, that pendent groups more seriously impede crystallization than do crosslinks.

Reheating MBTS compounds after swelling in zinc stearate also led to an increase in crosslink density (Table V), although samples still failed to crystallize. This may indicate the formation in the original vulcanizate of cyclic sulfides and monosulfidic benzothiazole pendent groups, as shown by Gregg et al.[23]

Zinc Stearate–Containing Formulations

The addition of zinc stearate to the TMTD formulation resulted in crosslink densities increasing by as much as 20-fold (compare Tables III and VI). Crosslinking also started earlier (5 versus 18 min). The high percentage crystallinity that developed is interpreted as indicative of only a small amount of pendent groups being present in the vulcanizates. A peroxide-cured BR sample, with a crosslink density of 16.3×10^{-5} mol/mL, developed 30% crystallinity (Table I), whereas 32% crystallinity was achieved in a BR/TMTD/sulfur/zinc stearate compound with a crosslink density of 16.5×10^{-5} mol/mL (Table VI). As demonstrated with peroxide-cured samples where pendent groups are absent, the percentage crystallinity was unaffected by crosslink density, up to high crosslink densities. However, nucleation is affected by the presence of crosslinks, and the failure to detect the onset of crystallization in zinc stearate compounds on cooling in the DSC must be ascribed to the higher crosslink density in these samples; pendent groups would have a major effect on crystallinity and 32% crystallization would not be achievable.

Addition of zinc stearate to MBTS formulations, even more clearly than the TMTD system, demonstrated the effect of pendent groups on crystallization and their removal by zinc stearate. All samples crystallized, whereas the MBTS system with no zinc stearate showed no measurable crystallization once gel formation had occurred (compare Tables V and VII). The degree of crystallization that developed was still less than that in TMTD/zinc stearate compounds and may indicate the formation in BR of monosulfidic benzothiazole pendent groups and cyclic sulfides.[23] In the MBTS vulcanizate, cured for 30 min, the Moore–Trego efficiency improved from 12.2 to 3.8 on addition of zinc stearate. Thus, a reduction in cyclic sulfide formation will complement the reduction in pendent groups in promoting crystallization in zinc stearate formulations.

The addition of ZnO to MBTS formulations led to vulcanizates that crystallized to a greater extent (compare the 19-min samples in Tables V and VIII). MBTS does not react with ZnO at vul-

canization temperatures[35–37] and little $Zn(mbt)_2$ forms in MBTS/sulfur/ZnO vulcanizates,[25,38] although the formation of a layer of $Zn(mbt)_2$ at the surface of ZnO particles cannot be excluded. The increased crystallinity obtained with ZnO compounds implies that ZnO and/or $Zn(mbt)_2$ can also facilitate crosslinking of pendent groups, although it is not as efficient in this regard as is zinc stearate (Table VII). This is in agreement with the results of McGill and Shelver,[25] who showed that ZnO and $Zn(mbt)_2$ promoted crosslinking, but neither as effectively as zinc stearate.

$Zn(mbt)_2$ and $Zn_2(dmtc)_4$ Formulations

On vulcanization $Zn(mbt)_2$ is converted to ZnS and MBT[39] and it is suggested that the increase in the initial density of compounds vulcanized for longer times (Table IX) can be ascribed to the reaction by-products having a higher density than that of the curatives from which they derived. The calculated density of a BR(100)/sulfur(3)/$Zn(mbt)_2$(4) compound, based on additive volumes of the components, is 0.0340 g/mL lower than that of a compound in which all of the $Zn(mbt)_2$ has converted to ZnS and MBT. The density difference observed between samples heated for 10 and 140 min was 0.0074 g/mL. Not all of the $Zn(mbt)_2$ will be decomposed to ZnS during reaction, and volume changes associated with rubber–curative interactions must also be taken into account; nevertheless, it is evident that the observed increase in density of vulcanizates during curing can be attributed to shrinkage occasioned by the formation of ZnS, which has a high density. ZnS may remain distributed at the molecular level in the rubber or it may crystallize in the column with time.

It can be seen in Tables III to VIII that the maximum percentage crystallinity that developed in BR and BR compounds was about 40%, and it is suggested that the higher crystallinities recorded in $Zn(mbt)_2$ systems (Table IX) at low cure times in the density column can be ascribed to volume changes accompanying the slow precipitation from solution of $Zn(mbt)_2$ in the rubber and its crystallization on cooling; that is, density changes used to calculate the crystallinity data in Table IX reflect changes attributed to the crystallization of BR as well as the crystallization or $Zn(mbt)_2$. This contention is supported by the DSC study (Table X). Because $Zn(mbt)_2$ does not melt or redissolve in BR at the temperatures at which BR crystals melt, its presence would not contribute to the DSC endotherm. Hence, crystallinities of around 40% were recorded in the DSC.

The same arguments as those presented earlier can be used to explain the increased initial density of $Zn_2(dmtc)_4$ compounds on curing for longer times (Table XI), as well as the compounds apparently having higher crystallinities than that of uncompounded BR.

A comparison of the induction times and rates of crystallization of peroxide, TMTD, $Zn(mbt)_2$, and $Zn_2(dmtc)_4$ systems with similar crosslink densities makes it clear that the behavior of the $Zn_2(dmtc)_4$ system falls in between that of the peroxide and TMTD systems. This suggests that $Zn_2(dmtc)_4$ vulcanizates contain fewer pendent groups than those found in TMTD vulcanizates. The $Zn(mbt)_2$ system has longer induction times and slower rates of crystallization than those of any of the other above-noted systems, yet it crystallizes more readily and more extensively than MBTS systems with zinc stearate (compare Tables VII and X). This also points to limited main-chain modification and the absence of pendent groups obtained with zinc–accelerator complexes. The mechanism of crosslink formation in sulfur vulcanization accelerated by zinc–accelerator complexes remains unclear, although there have been numerous suggestions as to the reaction mechanism.[12–18] Pendent groups were not previously detected in model compound studies[16–18] and Bristow and Tiller[19] suggested that the formation of cyclic sulfides prevented crystallization of these vulcanizates on cooling. The crystallization behavior of $Zn_2(dmtc)_4$ and $Zn(mbt)_2$ vulcanizates shows that they contain some main-chain modifications, although the nature of these modifications cannot be fully defined at this stage.

CONCLUSIONS

It is suggested that the main effect of crosslink formation is to increase the induction period prior to the onset of crystallization. Pendent group formation, as occurs extensively with TMTD and MBTS vulcanizates, increases the induction period and decreases both the rate and the extent of crystallization. MBTS vulcanizates that contain bulky pendent groups do not crystallize once crosslinked to the point where a gel has formed. Zinc stearate promotes the crosslinking of pendent groups and leads to higher crosslink densities in compounds. Even highly crosslinked vulcanizates, produced with formulations containing zinc stearate, crystallize readily on cooling, thus showing its effectiveness in crosslinking of pen-

dent groups. Pendent groups have not been detected in vulcanizates produced with zinc–accelerator complexes and it is suggested that the limited decrease in both the rate and the extent of crystallization of these vulcanizates may be attributed to cyclic sulfide formation.

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