

Influence of Pendent Groups on the Tensile Properties of Polyisoprene Vulcanizates

M. J. VAN DER MERWE, M. H. S. GRADWELL, W. J. MCGILL

Polymer Chemistry, University of Port Elizabeth, P.O. Box 1600, Port Elizabeth 6000, South Africa

Received 30 April 2000; accepted 29 August 2000

ABSTRACT: Gum compounds of polyisoprene were vulcanized with a number of different curing systems to give networks with crosslink densities in two different ranges. Stress–strain curves were obtained upon rapid (500 mm/min) and slow (0.5 mm/min) extension. In tetramethylthiuram disulfide (TMTD)/sulfur and zinc dimethyldithiocarbamate/sulfur vulcanizates, which crystallize readily, failure occurred at higher tensile values upon rapid than upon slow extension and this is attributed to a greater contribution to tensile strength by a larger amount of stress-induced crystallites. X-ray diffraction showed that 2-benzothiazole-2,2'-disulfide (MBTS)/sulfur vulcanizates did not stress-crystallize and failure occurred at lower tensile values. Furthermore, samples extended rapidly failed at lower tensile values than did slowly extended samples. These differences, compared to TMTD vulcanizates, are attributed to extensive main-chain modifications (pendent groups), causing delays in the movement of sections of the chain, leading to the load being unequally distributed between chains. The fewer load-bearing chains ensure earlier failure. The addition of zinc stearate to TMTD/sulfur and MBTS/sulfur formulations increases the ability of vulcanizates of similar crosslink density to crystallize and enhances tensile properties of vulcanizates with similar crosslink densities, outcomes that are attributed to zinc stearate's promoting crosslinking of pendent groups and reducing impediments to crystallization and chain movement. Dicumyl peroxide-cured networks crystallize readily and exhibit a very rapid upturn in the stress–strain curve. However, failure occurs at lower stress values than apply to accelerated sulfur networks and it is suggested that the distribution of subchain lengths between crosslinks may contribute to their inferior properties. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2587–2596, 2001

Key words: tensile properties; crystallization; networks; dicumyl peroxide; tetramethylthiuram disulfide; 2-bisbenzothiazole-2,2'-disulfide; zinc dimethyldithiocarbamate

INTRODUCTION

It is well known that the tensile strength of vulcanizates is a function of crosslink density, in

which the tensile strength characteristically passes through a maximum as the crosslink density is increased.^{1–5} A number of theories have been developed to explain the effect of crosslinking on tensile failure. Flory⁶ argued that tensile strength depends on the fraction of the polymer that becomes effectively part of the network. Short chains, which develop at high crosslink densities, will induce crystallization at low extensions and, because a large fraction of chains re-

Correspondence to: W. McGill (E-mail: chawjm@upe.ac.za)
Contract grant sponsor: Continental Tire South Africa.
Contract grant sponsor: South African National Research Foundation.

Journal of Applied Polymer Science, Vol. 81, 2587–2596 (2001)
© 2001 John Wiley & Sons, Inc.

main unfavorably orientated for crystallization, tensile strength decreases. The theory fails to explain why the tensile strength of noncrystallizing rubbers also passes through a maximum. In a closely similar theory Taylor and Darin⁷ postulate that the stress in a specimen at rupture will be borne mainly by the chains that are oriented in the direction of extension and nearly at their ultimate elongation. The derived equation robustly fits data for poly(styrene-*co*-butadiene) (SBR) at the crosslink density that corresponds to the maximum tensile strength, but not as robustly at higher crosslink densities. In crystallizing rubbers it is assumed that crystals increase the number of network chains per unit volume oriented at a given angle to the direction of extension. Bueche⁸ suggests that in random crosslinking there will be a wide variety of subchain lengths between crosslinks and, upon deformation, some chains will experience a tension greater than their breaking strength. This in turn transfers the load to other chains that subsequently break.

The ability of rubbers to stress-crystallize is considered an important factor in preventing the propagation of microcracks, thus leading to high tensile strength.^{1,4,9,10} Particulate fillers, notably carbon black, can substantially increase the tensile strength of noncrystallizable rubbers such as SBR, in some cases to values comparable to that of crystallizable rubbers, while exerting little effect in this sense on the latter.¹ Filler particles are considered to act similarly to crystallites in blocking the propagation of cracks that may develop in the network. A minimum crack length is considered necessary for failure.⁴

One of the most controversial questions is the relationship between tensile strength and the crosslink mechanism and crosslink type. Four factors may be considered: bond strength, crosslink distribution, main-chain modification, and relaxed network.

Bond Strength

Greensmith et al.¹ first reported that the tensile properties of vulcanizates decrease in the order conventional > efficient > peroxide > radiation cured for compounds with the same crosslink density. Numerous other authors^{11–13} have since supported the finding. This led Bateman et al.¹³ to propose that, because the bond energy decreases in the order carbon–carbon > monosulfidic > disulfidic > polysulfidic,¹⁴ weaker polysulfidic crosslinks could break under stress and reform.

The presence of weak links in a compound were considered a prerequisite for good tensile properties. However, Tobolsky and Lyons¹⁵ found no evidence for the mechanical lability of weak crosslinks at room temperature, although these linkages are considered to be highly mobile at vulcanization temperatures. Lal¹⁴ treated networks having a high concentration of polysulfidic crosslinks with triphenyl phosphine, which converts polysulfidic to monosulfidic crosslinks, and found their tensile strength to remain unchanged. This showed that the nature of the crosslinks was unimportant. Baldwin and Ver Strate¹⁶ contended that, although polysulfidic bonds have strengths of 138 kJ/mol, there are other bonds in the vulcanizate that are weaker than S—S bonds in disulfides (290 kJ/mol) [e.g., C—C (250 kJ/mol) and C—S (220 kJ/mol) bonds]. In addition, the ability of natural rubber (NR) to stress-crystallize made it a poor model for the study. Using noncrystallizing NR, Brown et al.¹⁷ found that vulcanizates with polysulfidic crosslinks were superior to those with monosulfidic crosslinks of carbon–carbon. The findings of Lal¹⁴ are different from those of Bristow and Tiller¹¹ and Nasir and Teh,⁵ who recorded a decrease in tensile strength upon converting polysulfidic to monosulfidic crosslinks in NR and SBR vulcanizates. In carbon black–filled poly(ethylene-*co*-propylene-*co*-ethylidene norbornene) (EPDM), where the points at which crosslinks will form are fixed by the location of the ter-monomer, vulcanizates with peroxide/sulfur have significantly higher tensile strengths when some crosslinks were polysulfidic ($S_x > 3$).¹⁶ Both tensile strength and elongation increase with the ratio of polysulfidic crosslinks to other types of crosslinks. The tensile strength of SBR vulcanizates cured with peroxide/sulfur systems were found to be similar,^{2,18} although the reinforcing effect of carbon black may have nullified differences resulting from the network structure.

Crosslink Distribution

The distribution of crosslinks may affect crystallization, in that the distribution is determined by the mechanism of cure. Gehman¹⁹ pointed out that in sulfur vulcanizates there are long chains between crosslink points that may crystallize more readily than randomly crosslinked peroxide vulcanizates, where the probability of short-chain segments is higher.

Graig²⁰ suggested that crosslinking may make adjacent regions of the chain more reactive, lead-

Table I IR Formulations and Crosslink Density of Compounds

Compound	Sulfur (phr)	TMTD (phr)	MBTS (phr)	Zn ₂ (dmtc) ₄ (phr)	Zn Stearate (phr)	DCP (phr)	$\frac{1}{2}M_c \times 10^5$ (mol/mL)
A	2.0			3.0			3.6
B	2.5			3.0			4.5
C	3.0			3.0			5.8
D	3.0	4.0					4.5
E	4.0	6.0					5.6
F	4.0		6.0				4.6
G	6.0		8.0				5.4
H	2.2		3.0		2.0		4.8
I	2.2		3.1		2.0		5.6
J						1.0	5.3

Sulfur compounds contained 1 phr *N*-isopropyl-*N'*-phenyl-*p*-phenylenediamine (IPPD) and dicumyl peroxide (DCP) compounds contained 0.05 phr IPPD.

ing to a nonuniform distribution of crosslinks. Likewise, sulfur, split out from polysulfidic crosslinks, may be very reactive and lead to localized crosslinking. The formation of vicinal crosslinks in polybutadiene (BR) has been demonstrated.^{21,22} Grobler and McGill¹² suggested that in conventional vulcanizates, in which the sulfur-to-accelerator ratio is high, much of the crosslinking will be promoted by the zinc accelerator complex that is regenerated in the process. Because the zinc accelerator is less soluble than disulfidic accelerators, this may lead to localized crosslinking.

Main-Chain Modification

Lal¹⁴ argued that, because different recipes can lead to substantial differences in network structure (other than in the number of sulfur atoms in the crosslink), conclusions that polysulfidic crosslinks ensure superior properties are not unequivocal and that different cure systems may therefore differently affect crystallization in NR. Radiation-cured NR² and polyisoprene (IR)¹² were found to have slightly lower tensile strengths than those of peroxide cures, although both series of vulcanizates contain carbon-carbon crosslinks. The possibility that isomerization upon radiation²³ could affect crystallization must be borne in mind. Radiation also creates trifunctional crosslinks.

Relaxed Network

At room temperature polysulfidic bonds are not mobile, but Tobolsky and Lyons¹⁵ argued that, in

accelerated sulfur vulcanization, a relaxed network will be formed by the high mobility of crosslinks in polysulfidic networks at vulcanization temperatures. The tensile strength of radiation-cured NR² and IR¹² is slightly lower than that of peroxide-cured samples and Pearson and Bohm² suggested that, because radiation cure is carried out at lower temperatures, the network may not be as relaxed as that obtained with peroxide cures. Shorter chains in the randomly crosslinked network would thus more quickly be brought to their critical rupture length.

This study compares the stress-strain curves of IR gum vulcanizates, cured with dicumyl peroxide and with a number of accelerated sulfur formulations, with the ability of these vulcanizates to crystallize upon cooling and under stress. Low-temperature crystallization studies of these vulcanizates were reported in earlier investigations in the series.^{24,25}

EXPERIMENTAL

The IR and curatives used were described in an earlier study.^{24,25} Compounds (Table I) were mixed in a Brabender Plasticorder as previously described²⁶ and cured at 150°C in a press to 95% of the optimum cure times as determined from rheometer cure curves. Two formulations were used with each curative system, resulting in two sets of samples with crosslink densities in two different ranges. Tensile samples were cut from the vulcanized pads using a dumbbell die (type D), conforming to ASTM D412, and tensile tests were performed on an Instron 4411 Tensiometer

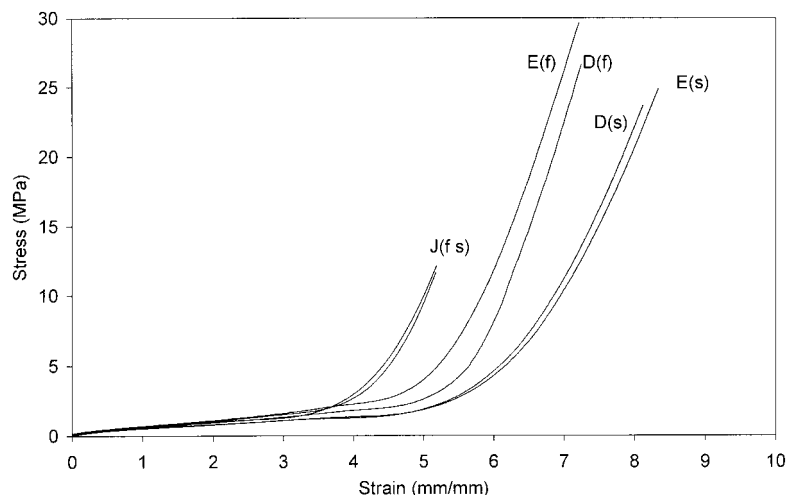


Figure 1 Stress-strain curves for IR/TMTD/sulfur vulcanizates in Table I extended at 500 mm/min (f) and 0.5 mm/min (s).

with an Instron Long Travel Elastomeric Extensometer attached. A 1-kN load cell and a gauge length of 20 mm were used. Six samples were cut from each pad, three of which were extended rapidly (500 mm/min) and three slowly (0.5 mm/min), and are represented in figures by the letters f (fast) and s (slow), respectively. Stress-strain curves for each set were closely similar and the figures represent average values for the curves obtained. Antioxidant *N*-isopropyl-*N'*-phenyl-*p*-phenylenediamine (IPPD) was included in the formulation because, when it was omitted, slowly extended samples broke at low extensions, presumably as a result of oxidative degradation. Peroxide vulcanization is impeded by antioxidants. An IPPD loading of 0.05 phr was used in this study and rheometer cure curves showed that, at this level, it did not seriously alter the cure curve, in which the rheometer torque increased from the outset. Crosslink densities in Table I were determined by swelling.²⁷

Stress-induced crystallization of the more highly crosslinked set of samples was observed at 600% extension, using a Philips PW generator (40 kV, 30 mA) with a PW 1050 diffractometer (α K radiation, 1.531 Å). The large diffraction peak at $2\theta = 21^\circ$ was recorded at room temperature immediately after elongation (0 h) and again after 24 h, and was used as an indication of stress-induced crystallization.²⁸

RESULTS AND DISCUSSION

IR/Tetramethylthiuram disulfide (TMTD)/Sulfur

Figure 1 shows that the stress-strain curves of

rapidly extended sulfur vulcanizates always lie above those for slow extension, the divergence of which is greater in the more heavily crosslinked samples (E). Samples extended slowly elongated to a greater extent before failure but broke at lower stress values. The upturn in the stress-strain curves is less steep upon slow extension. Peroxide-cured compounds (J) failed at slow extensions and stress-strain curves showed no difference in terms of rate of extension.

IR/2-Bisbenzothiazole-2,2'-disulfide (MBTS)/Sulfur

The upturn in the stress-strain curves (Fig. 2) is more gradual than that with TMTD vulcanizates of comparable crosslink density (Fig. 1). Rapidly extended vulcanizates failed at lower tensile values than did slowly extended samples, whereas vulcanizates with higher crosslink densities (G in Fig. 2) failed at lower tensile values than those with lower crosslink density (F), unlike that found with all other vulcanizates discussed in this study. The divergence between the stress-strain curves obtained upon fast and slow extension was less marked than with TMTD systems and the extent of the divergence decreased with increased crosslink density (divergence in F > G).

IR/Zinc dimethyldithiocarbamate [Zn₂(dmtc)₄]/Sulfur

The behavior of the system is similar to that of the TMTD vulcanizates, in that the divergence between the fast and slow extended samples increases with crosslink density and failure occurs at higher stress values upon rapid extension (Fig. 3).

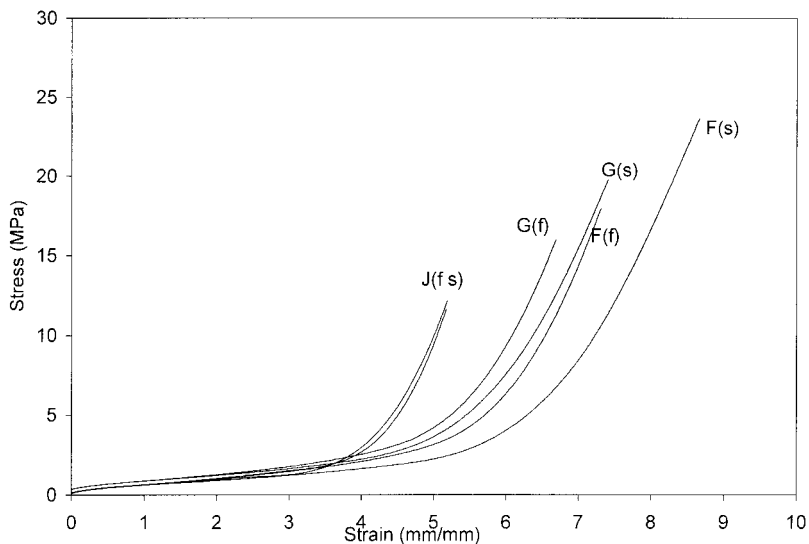


Figure 2 Stress-strain curves for IR/MBTS/sulfur vulcanizates in Table I extended at 500 mm/min (f) and 0.5 mm/min (s).

IR/MBTS/Sulfur/Zinc stearate

Unlike the MBTS system without zinc stearate, the rapidly extended samples broke at greater extensions than those extended slowly and the upturn in the stress-strain curves is steeper for samples containing zinc stearate (Fig. 4). Note that in the presence of zinc stearate (Table I, compounds H and I) a much smaller addition in accelerator loading is required to produce the same increase in crosslink density as in its absence (compounds F and G). This confirms the efficiency of zinc stearate in promoting the crosslinking of pendent groups.²⁹ It was previously demonstrated²⁵ that vulcanizates containing zinc stearate crystallize readily upon cooling, pointing to the absence of residual pendent groups on the chain, whereas in the absence of zinc stearate, MBTS-accelerated compounds developed very low crystallinities, once crosslinked to the point where a gel had formed.

Stress-Induced Crystallization

X-ray diffraction showed that peroxide-cured samples stress-crystallized upon extension, with no change in the diffraction pattern upon maintaining the sample at 600% extension for 24 h (Fig. 5). Vulcanizates cured with TMTD/sulfur and $Zn_2(dmtc)_4$ /sulfur crystallized readily upon extension, in that the diffraction peaks showed some further crystal growth over a 24-h period (Fig. 5). The MBTS/sulfur vulcanizate showed es-

entially no crystallization upon extension, and no change occurred in the diffraction pattern over a 24-h period (Fig. 6). The addition of zinc stearate to MBTS formulations produced vulcanizates that stress-crystallize.

Peroxide Vulcanizates

It is suggested that the rapid upturn in the stress-strain curve for peroxide-cured IR emphasizes the importance of stress-induced crystallization (Fig. 1). The upturn occurs at low extensions and this is attributed to the ease of crystallization and the high degree of crystallinity that develops in peroxide cures, as demonstrated previously for

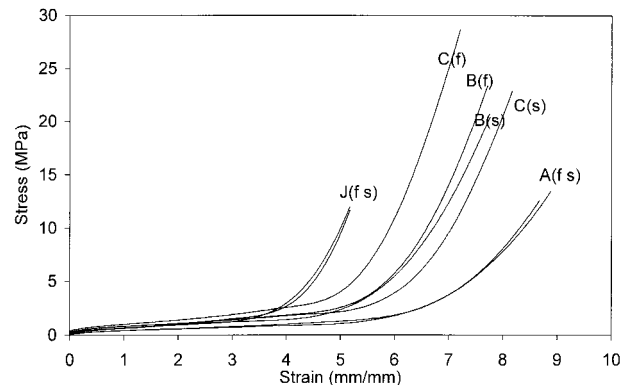


Figure 3 Stress-strain curves for IR/ $Zn_2(dmtc)_4$ /sulfur vulcanizates in Table I extended at 500 mm/min (f) and 0.5 mm/min (s).

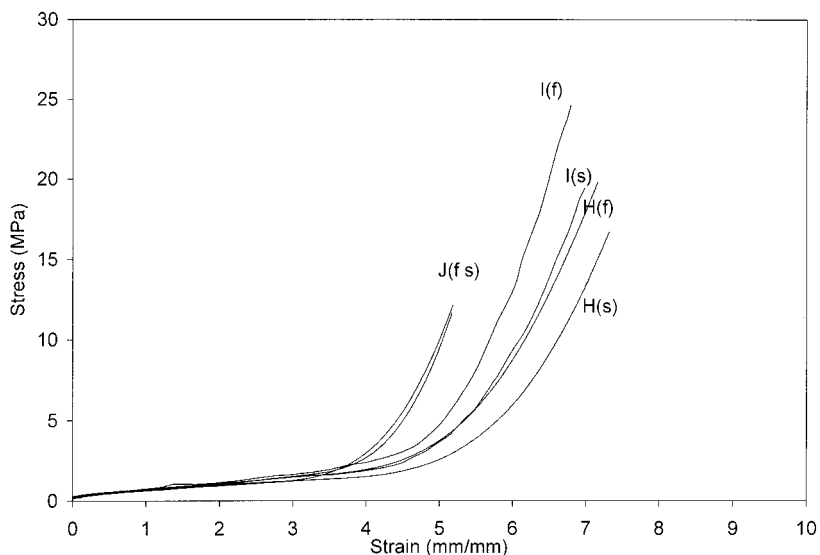


Figure 4 Stress-strain curves for IR/MBTS/sulfur/zinc stearate vulcanizates in Table I extended at 500 mm/min (f) and 0.5 mm/min (s).

BR compounds.²⁵ However, despite extensive crystallization, which should enhance tensile strength, failure occurs at a relatively low tensile strength compared to that of accelerated sulfur cures (Figs. 1–4).

Gehman¹⁹ considered the probability of finding long- and short-chain sequences in crosslinking reactions and concluded that the occurrence of short-chain sequences will be more frequent in randomly crosslinked systems, such as in perox-

ide cures. Flory⁶ suggested that short chains may induce crystallization at low extensions, resulting in a larger fraction of chains remaining unfavorably oriented to contribute to bearing of the load. Crystallization reduces the volume fraction of chains that can undergo extension and, at any given extension, the effective extension of chains in the amorphous regions is greater than that in a compound that develops a lower degree of crystallization. Thus, if in contrast to Flory's proposal,

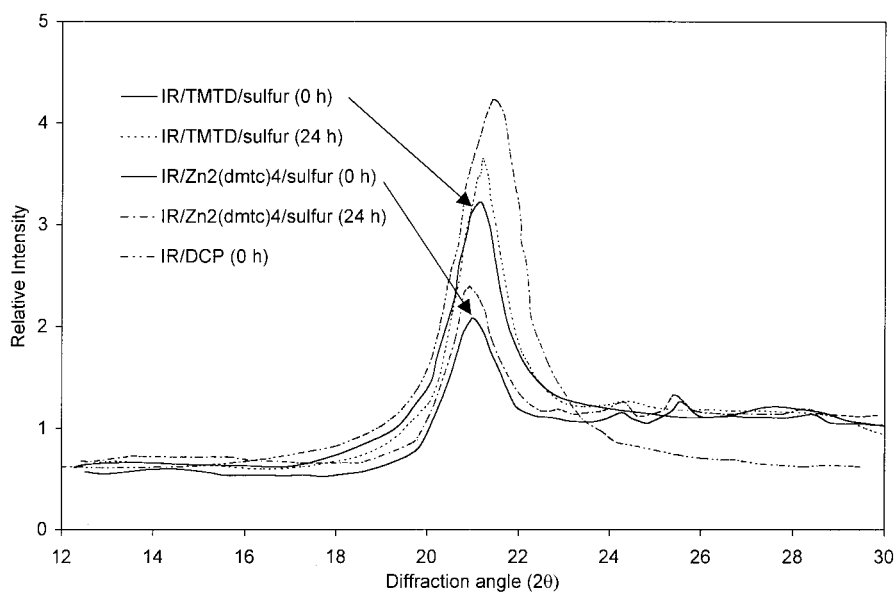


Figure 5 X-ray diffraction intensity versus 2θ for vulcanizates at 600% elongation.

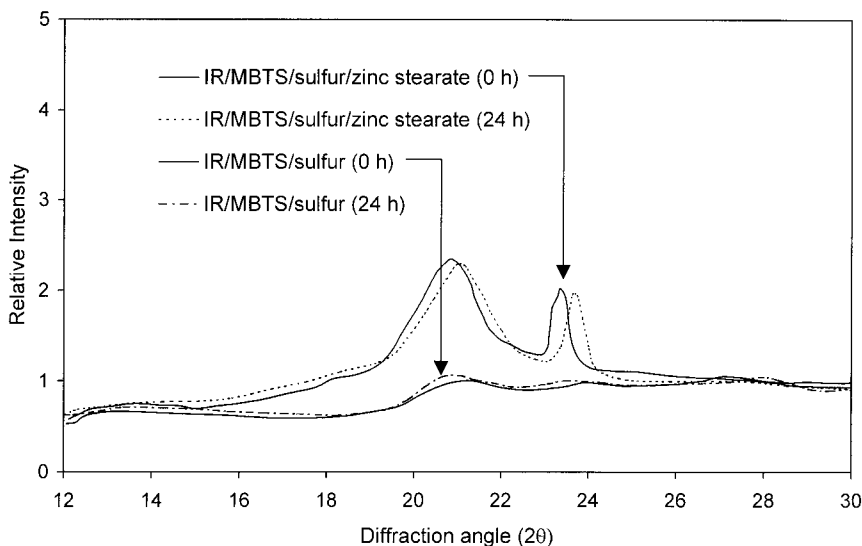


Figure 6 X-ray diffraction intensity versus 2θ for vulcanizates at 600% elongation.

some shorter chain sequences are unable to enter the crystalline regions, their extension, in the already reduced volume of deformable material, may lead to their more rapidly becoming taut and initiating failure, in accord with the mechanism proposed by Bueche.⁸ Thus, the high degree of crystallinity, which improves tensile strength by blocking crack propagation, may exacerbate the negative effect of crosslink distribution. Gent et al.³⁰ showed that at a sufficiently high temperature, when crystallization upon extension is no longer possible, the tensile strength of NR falls to a very low value of 1–2 MPa. We suggest that this also demonstrates that, when the beneficial effect of stress-induced crystallization is removed, the negative effect of shorter chain sequences that become taut in a network containing a higher probability of short subchains, dominates. Interestingly, Kok and Yee³ reported similarly low tensile strength values for unfilled peroxide-cured SBR, whereas SBR compounds cured with a number of different accelerated sulfur formulations, in which shorter sequences between crosslinks will be less frequent, had considerably higher tensile strengths.

Tobolsky and Lyons¹⁵ note that, in peroxide cures, crosslinks are formed in an irreversible manner, which may result in built-in stresses or strains, whereas in vulcanization systems that produce polysulfidic bonds, crosslinks break and are reformed, providing a network that is free from stress. Thus differences in tensile strength at room temperature may arise from a difference

in the network structure. However, the authors see no apparent reason why the lability of sulfidic crosslinks at vulcanization temperatures is needed to create a relaxed network, unless the material is partially oriented at the onset of crosslinking. Shearing forces that operate in compounding lead to the partial alignment of polymer chains in randomly localized regions of the compound, as demonstrated by the more rapid onset of crystallization in both IR³¹ and BR^{32,33} after compounding, in which the localized partially oriented regions promote nucleation. Upon heating, this partial orientation is destroyed, a random chain distribution develops, and the onset of crystallization is delayed accordingly.³³ Giuliani and McGill³³ noted that relaxation of oriented regions occurred readily upon heating to 150°C, in that the bulk of the changes took place during the first 10 min of annealing. It may be argued that, in accelerated sulfur vulcanization, there is an induction period prior to crosslink formation, during which time chain orientation that developed upon mixing can relax. In peroxide cures crosslinking commences immediately upon heating and compounding stresses may become built into the network. However, Giuliani and McGill³³ found that stress-strain curves were identical for peroxide cures in which the samples had been relaxed at 80°C for various periods (0 to 60 min) before crosslinking at 150°C. It is concluded that the lower tensile strength of unfilled peroxide, compared to that of sulfur cures, cannot reside in peroxides forming a nonrelaxed network as de-

finer by Tobolsky and Lyons,¹⁵ and it appears more likely that the random distribution of crosslinks contributes¹⁹ to the inferior tensile properties of peroxide cures.

TMTD Vulcanizates

TMTD-accelerated vulcanizates of IR²⁴ and BR²⁵ crystallize upon cooling as well as upon extension (Fig. 5). However, the induction period is longer and the rate and extent of crystallization are less than that in peroxide cures of comparable crosslink density.²⁵ The upturn in the stress-strain curve of vulcanizates subjected to a load can, in part, be attributed to crystallization and, accordingly, the upturn in the stress-strain curve for TMTD-accelerated sulfur vulcanizates occurs at a higher extension than that for peroxide cures (Fig. 1), that is, crystallization occurs more slowly and to a lesser degree. The early upturn in the stress-strain curves for peroxide cures shows the rapid growth of nuclei formed upon extension and there is no observable difference between the curves for rapid and slow extension. In TMTD-accelerated sulfur vulcanizates the upturn upon slow extension is delayed compared to the upturn upon rapid extension, in that the difference increases with increased crosslink density of the vulcanizate (Fig. 1). This delay is interpreted as a delay in stress-induced crystallization, as discussed below.

Crystallization involves two processes, nucleation and growth. Stress induces deformation of the material by the alignment of chain sequences in the direction of the load. At some point a favorable alignment of chain sequences will give rise to a crystal nucleus to which further addition can occur. The addition of further chain sequences to the nucleus (crystal growth) relies on the mobility of chains, in that the entropy of the chains was already decreased by strain, permitting their crystallization at room temperature or higher. At room temperature IR is about 100°C above its glass-transition temperature, which permits ready rotation about carbon-carbon bonds in the chain, and rapid crystal growth is possible. Pendent groups on the chain will increase the potential energy required for rotation about adjacent carbon-carbon bonds, whereas the movement of chain segments containing cyclic sulfides will also be restricted. Main-chain segments containing modifications will be excluded from crystal areas. The bulk of the polymer chain will be unmodified, but the reduced mobility of modified sectors along

the chain will impede the overall movement of chain sequences. Hence, the rate of addition of chain sequences to the growing crystal will be reduced, even prior to crosslink formation, as found^{24,25} for the crystallization of TMTD (and other) vulcanizates. Thus a result of slower crystal growth is that many stress-induced nuclei will melt and disappear, rather than grow. Hence, as shown earlier^{24,25} and reflected here by the upturn in the stress-strain curve, crystallization is less rapid for TMTD-accelerated sulfur vulcanizates than it is for peroxide cures. Furthermore, high-energy barriers to the rotation about carbon-carbon bonds in some modified sectors of the polymer chain will necessarily induce a greater degree of deformation, and therefore the more complete alignment of the unmodified sequences, if the same rate of strain is enforced.

Crosslinked points are even less mobile because their displacement requires the cooperative movement of segments in four subchains. At higher rates of strain these impediments to deformation will increase the probability of nucleation and will introduce a disparity between the stress-strain curves obtained upon rapid and slow extension. The greater the number of crosslinks, the greater will be the difference between crystallization upon rapid and slow extension, in that slow extension permits modified chain segments either to overcome energy barriers or to escape their temporary entrapment and to move again, without extending or aligning sufficiently to generate nuclei for crystallization. (It can be expected that at still higher crosslink densities the curves would again merge.) The tensile strength is higher upon rapid extension, possibly because such systems contain a larger percentage of crystals that can impede crack growth.

MBTS Vulcanizates

Upon cooling very little crystallization occurs in MBTS-accelerated vulcanizates of either IR²⁴ or BR²⁵ and upon extension no stress-induced crystallization is observed (Fig. 6). As discussed previously^{24,25} this can be attributed to extensive main-chain modification rather than to crosslink formation. In the absence of crystallites, which limit extension, the extension at any given tensile value is higher and the upturn in the stress-strain curve is more gradual than that for the TMTD system where crystallization is observed (compare Figs. 2 and 1). It is suggested that failure occurs at lower tensile strength values upon

rapid extension because delays in the movement of some chain segments, occasioned by pendent groups, more readily lead to other chain segments becoming increasingly extended to the point of rupture; impediments to the movement of some chain segments lead to the loads becoming unequally distributed, with fewer chains making their full contribution to carrying the load. This is the only formulation in the series studied where the more highly crosslinked vulcanizate (G in Fig. 2) has a lower tensile strength than that of the less highly crosslinked sample (F), which is consistent with the preceding argument that bulky pendent groups impede chain movement. The higher MBTS loading in the compound would ensure that the more heavily crosslinked sample would also contain more pendent groups, leading more rapidly to entrapped chain segments becoming taut and rupturing, that is, the unequal distribution of the load within the network is increased. It is suggested that with bulky benzothiazole pendent groups, disentanglement of chain segments is slow and that the rate of extension has little effect on the degree to which disentanglement occurs. Hence, the disparity between the stress–strain curves upon slow and rapid extension is small (Fig. 2) and the difference decreases even further with increased curative loading (crosslink density). In peroxide cures stress-induced crystallization is extremely rapid and, under the experimental conditions that apply here, the rate of extension does not influence the shape of the stress–strain curve.

Despite the absence of crystallization the tensile strength of MBTS-accelerated sulfur vulcanizates is higher than that of peroxide cures. This is consistent with the literature and may relate to a lower number of short-chain segments in peroxide compared to that of MBTS vulcanizates.

$Zn_2(dmtc)_4$ Vulcanizates

$Zn_2(dmtc)_4$ vulcanizates crystallize upon cooling²⁵ as well as upon extension (Fig. 5) and their stress–strain behavior (Fig. 3) is analogous to that of TMTD systems, in that rapidly extended samples fail at higher tensile values and the disparity between rapid and slow extensions increases with crosslink density. Pendent groups have not been detected in $Zn_2(dmtc)_4$ vulcanizates and impediments to chain movement must be ascribed to cyclic sulfide formation.¹¹ The Moore–Trego efficiency parameter³⁴ for the vulcanizates studied by Bristow and Tiller¹¹ was of the order of

20, whereas that of vulcanizates used in this study was lower (5 to 7), which may explain why our vulcanizates crystallized more readily than those described by Bristow and Tiller.

Effect of Zinc Stearate

The addition of zinc stearate, which promotes the crosslinking of pendent groups,²⁹ leads to MBTS vulcanizates that crystallize, both at low temperatures²⁵ and upon extension (Fig. 6). Consequently, the upturn in the stress–strain curves (Fig. 4) is more rapid and higher tensile strength values are achieved than in the absence of zinc stearate (Fig. 2). Consistent with the interpretation presented for the TMTD system, rapid extension leads to a greater degree of crystallization, as indicated by the steeper rise in the stress–strain curve, and gives rise to failure at higher tensile strength values than that at slow extension.

CONCLUSIONS

The vulcanization mechanism affects the crystallizability of vulcanizates that, in turn, is one of the factors affecting tensile behavior. Formulations that limit main-chain modification and pendent group formation promote crystallization of vulcanizates and lead to compounds with superior properties. Upon rapid extension vulcanizates that crystallize readily display higher tensile strengths than those upon slow extension, when, it is proposed, slower extension permits time for the melting of many potential crystal nuclei, in preference to their growth. The rate of crystal growth in TMTD, in contrast to that in peroxide vulcanizates, is partially impeded by slower chain movement resulting from main-chain modifications.

However, it is suggested that formulations that result in a large number of residual pendent groups on the polymer chain not only develop lower degrees of stress-induced crystallization, which adversely affects tensile properties, but that such pendent groups reduce the rate at which chains disentangle upon extension under load. An important consequence is that the load is not equally distributed between chains and locally entrapped chains may become taut and rupture. In MBTS vulcanizates main-chain modification is extensive and completely inhibits crystallization. These vulcanizates perform better at low rates of extension. Slower extension allows more

time for chain segmental movement to free chain segments entrapped locally by the interaction of pendent groups. This reduces the probability of chain segments between entrapped positions from becoming taut and failing because of the unequal distribution of the load between chains.

The importance of zinc stearate in reducing main-chain modification by promoting crosslinking of pendent groups, and thereby increasing tensile properties, is demonstrated. The crosslink distribution (short-chain segments) in peroxide versus accelerated sulfur cures may contribute to the tensile strength of peroxide cures being inferior to that of accelerated sulfur vulcanizates.

The authors thank Continental Tire South Africa and the South African National Research Foundation for financial assistance.

REFERENCES

- Greensmith, H. W.; Mullins, L.; Thomas, A. G. in *The Chemistry and Physics of Rubber-like Substances*; Bateman, L., Ed.; Maclaren: London, 1963; p. 249.
- Pearson, D. S.; Bohm, G. C. A. *Rubber Chem Technol* 1972, 45, 193.
- Kok, C. M.; Yee, V. H. *Eur Polym J* 1986, 22, 341.
- Hamed, G. R. *Rubber Chem Technol* 1983, 56, 244.
- Nasir, M.; Teh, G. K. *Eur Polym J* 1988, 24, 733.
- Flory, P. J. in *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1975; Chapter 11.
- Taylor, G. R.; Darin, S. R. *J Polym Sci* 1955, 17, 551.
- Bueche, F. *J Polym Sci* 1957, 24, 189.
- Thomas, A. G.; Whittle, J. M. *Rubber Chem Technol* 1970, 43, 222.
- Hamed, G. R.; Kim, H. J.; Gent, A. N. *Rubber Chem Technol* 1996, 69, 807.
- Bristow, G. M.; Tiller, R. F. *Kautsch Gummi Kunstst* 1970, 23, 55.
- Grobler, J. G. H.; McGill, W. J. *J Polym Sci Part B Polym Phys* 1994, 32, 287.
- Bateman, L.; Cunneen, J. J.; Moore, C. G.; Mullins, L.; Thomas, A. G. in *The Chemistry and Physics of Rubber-like Substances*; Bateman, L., Ed.; Maclaren: London, 1963; p. 715.
- Lal, J. *Rubber Chem Technol* 1970, 43, 664.
- Tobolsky, A. V.; Lyons, P. F. *J Polym Sci* 1968, A2/6, 1561.
- Baldwin, F. P.; ver Strate, G. *Rubber Chem Technol* 1972, 45, 709.
- Brown, P. S.; Porter, M.; Thomas, A. G. *Kautsch Gummi Kunstst* 1987, 40, 17.
- Fedors, R. F.; Landel, R. F. *Trans Soc Rheol* 1965, 9, 195.
- Gehman, S. D. *Rubber Chem Technol* 1969, 42, 659.
- Graig, D. *Rubber Chem Technol* 1957, 30, 1291.
- Gregg, E. C.; Katrenick, S. E. *Rubber Chem Technol* 1970, 43, 549.
- Skinner, T. D. *Rubber Chem Technol* 1972, 45, 182.
- Turner, D. *Macromolecules* 1971, 4, 377.
- van der Merwe, M. J.; Gradwell, M. H. S.; McGill, W. J. *J Appl Polym Sci* 2001, 81, 2565.
- van der Merwe, M. J.; Gradwell, M. H. S.; McGill, W. J. *J Appl Polym Sci* 2001, 81, 2573.
- Gradwell, M. H. S.; McGill, W. J. *J Appl Polym Sci* 1995, 58, 2185.
- Kruger, F. W. H.; McGill, W. J. *J Appl Polym Sci* 1992, 44, 581.
- Mitchell, G. R. *Polymer* 1984, 25, 1562.
- McGill, W. J.; Shelver, S. R. *J Appl Polym Sci* 1999, 72, 1021.
- Gent, A. G.; Kawakara, S.; Zhao, J. *Rubber Chem Technol* 1998, 71, 668.
- Cameron, A.; McGill, W. J. *J Polym Sci Polym Chem Ed* 1989, 27, 1071.
- Fouche, P. M.; McGill, W. J. *Plast Rubber Compos Process Appl* 1989, 12, 227.
- Giuliani, B. V. M. K.; McGill, W. J. *Plast Rubber Compos Process Appl* 1993, 19, 305.
- Moore, C. G.; Mullins, L.; McL.Swift, P. *J Appl Polym Sci* 1961, 5, 293.