Effect of Carboxylic Acids on 2-Bisbenzothiazole-2,2'-Disulfide- and Tetramethylthiuram Disulfide-Accelerated Sulfur Vulcanization. IV. Vulcanization of Polyisoprene Compounds with ZnO

W. J. MCGILL, S. R. SHELVER

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

Received 8 June 1998; accepted 17 August 1998

ABSTRACT: The effect of benzoic and stearic acids on 2-bisbenzothiazole-2,2'-disulfide (MBTS)- and tetramethylthiuram disulfide (TMTD)-accelerated sulfur vulcanization of polyisoprene compounds, containing ZnO, was studied at 150°C. In the presence of ZnO, the acids are rapidly converted to their zinc salts that, unlike the acids, do not attack accelerator polysulfides and, instead, promote vulcanization. The addition of accelerator polysulfides to the chain is not affected by zinc salts, but the rate of crosslinking of pendent groups is facilitated. In MBTS vulcanization, the promotion of crosslinking reactions reduces the number of pendent groups involved in cyclization reactions and higher crosslink densities are attained. In TMTD compounds, crosslink densities are increased on addition of ZnO and of ZnO/carboxylic acids. A mechanism is suggested to account for the promotion of crosslinking by the zinc salts. Bis(2-mercaptobenzothiazolo)zinc(II) and bis(dimethyldithiocarbamato)zinc(II) can act similarly to zinc benzoate or stearate to promote the crosslinking of pendent groups, but are less efficient. With benzoic acid, a limited attack by zinc benzoate on TMTP leads to a slightly lower increase in crosslink density than is achieved with the addition of ZnO alone. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1021-1030, 1999

Key words: vulcanization; polyisoprene; stearic acid; benzoic acid; 2-bisbenzothiazole-2,2'-disulfide; tetramethylthiuram disulfide; ZnO

INTRODUCTION

In accelerated sulfur vulcanization, the addition of ZnO to formulations is recognized as being important for attaining good physical properties in vulcanizates.^{1,2} Stearic acid is commonly added as a coactivator for ZnO. It reacts very rapidly with ZnO above its melting point,³ and during compounding, where shearing forces will prevent the formation of a layer of zinc stearate around ZnO particles, the reaction will readily go to completion.

Zinc stearate decreases the rate and increases the crosslink density of polyisoprene (IR)/2-bisbenzothiazole-2,2'-disulfide (MBTS)/sulfur vulcanizates.^{4,5} Coran⁶ suggested a reaction mechanism in which the Zn^{2+} ion was chelated to the accelerator, increasing its reactivity, while Lorenz and Echte⁷ suggested that zinc stearate increased the number of crosslinking points. With tetramethylthiuram disulfide (TMTD)-accelerated sulfur vulcanization, Coran^{6,8} found a decrease in the rate of reaction if the stearic acid concentration was increased. Palmitic acid has a mild activating effect.⁹

Correspondence to: W. J. McGill.

Contract grant sponsors: South African Foundation of Research; Gentyre Industries.

Journal of Applied Polymer Science, Vol. 72, 1021-1030 (1999)

^{© 1999} John Wiley & Sons, Inc. CCC 0021-8995/99/081021-10



Figure 1 Crosslink density and HPLC analysis of reactants and products in the vulcanization of IR/MBTS/sulfur/ZnO at 150°C: (\blacksquare) crosslink density; (\blacktriangle) MBTS; (\bigcirc) MBTM; (\bigtriangledown) MBTP; (\Box) MBT; (\bullet) sulfur.

In previous articles, we showed that carboxylic acids attacked accelerator polysulfides¹⁰ and decreased the crosslink density of MBTS vulcanizates in particular.¹¹ In the presence of ZnO, no free acid will exist in the compound and it was shown¹² that the zinc salts of carboxylic acids do not attack accelerator polysulfides as readily as do the acids. This article examines the role of carboxylic acids in MBTS- and TMTD-accelerated formulations containing ZnO on the vulcanization process.

EXPERIMENTAL

The materials used were detailed in an earlier article in this series.¹¹ Compounds were prepared in a Brabender Plasticorder as described earlier^{11,13,14} and vulcanized in sealed pans in a DSC, either isothermally at 150°C or at a programmed heating rate of 2.5° C/min.^{13,14} Residual curatives and soluble intermediates were extracted from the rubber at various stages of the reaction and analyzed by HPLC.^{13,14} Curative loadings of compounds in parts per hundred rubber are shown in parentheses in the text. In the figures, concentrations of the reactants, intermediates, and products are expressed in terms of the initial mol concentration of the reactant. Crosslink densities were determined by swelling.¹⁴

RESULTS AND DISCUSSION

IR(100)/MBTS(12.27)/Sulfur(9.49)/ZnO(5.0)

In the absence of IR, an MBTS/sulfur mix will yield an equilibrium concentration of 40 mol %

2-bisbenzothiazole-2,2'-polysulfides (MBTP) after 3 min,¹⁰ and the low MBTP concentration obtained with IR (Fig. 1) points to their rapid reaction with the polymer chain. After 3 min, 40 mol % of MBTS had reacted, yet a negligible amount of MBTP was extractable from the rubber. The maximum crosslink density of 10.5×10^{-5} mol/mL is similar to that achieved in the absence of ZnO,¹¹ although the rate of crosslinking is faster (Fig. 2). As discussed in the previous article, MBTS does not react with ZnO at vulcanization temperatures 12,15,16 and its addition is not expected to influence the reaction. 2-Mercaptobenzothiazole (MBT) is liberated during crosslinking and its reaction with ZnO also is limited. This is attributed to the formation of a layer of insoluble bis(2-mercaptobenzothiazolo)zinc(II) $[Zn(mbt)_{2}]$ at the ZnO particle interface, preventing the reaction from going to completion. (On mixing MBT into a compound containing ZnO, a complete reaction does occur as shearing forces expose fresh ZnO.^{17,18}) The more rapid reaction in the presence of ZnO cannot be attributed to the small amount of Zn(mbt)₂ formed acting as an accelerator since Zn(mbt)₂-accelerated sulfur vulcanization is slow (Fig. 3) compared to the MBTS/ ZnO-accelerated reaction.

IR(100)/MBTS(12.27)/Sulfur(9.49)/ZnO(5.0)/Benzoic Acid(4.51)

Zinc salts, unlike the carboxylic acids, do not readily lead to 2-benzoylthiobenzothiazole (BzM)¹² and no detrimental effect on crosslinking is expected. On the contrary, zinc benzoate has a sub-



Figure 2 Crosslink densities of (\Box) IR/MBTS/sulfur and (\bullet) IR/MBTS/sulfur/ZnO vulcanized at 150°C.

stantial beneficial effect on crosslinking reactions as indicated by the faster rate and higher crosslink density compared to compounds without ZnO/benzoic acid (cf. Figs. 1 and 4).

The rate of MBTP consumption in the formation of pendent groups attached to the rubber chain is relatively fast in both systems (indicated by the low concentrations of extractable MBTP), and zinc benzoate must play a role, not in pendent group formation, but in promoting the crosslinking of pendent groups. From Figure 4, it is observed that by 10 min at 150°C the crosslink density has reached its maximum value with the formation of 72 mol % MBT, whereas by 10 min in the absence of zinc benzoate, only half the maximum crosslink density is reached with the production of 78 mol % MBT (Fig. 1). Similar amounts of MBT are produced, but the crosslinking efficiency is higher with zinc benzoate. The maximum crosslink density, which is achieved



Figure 3 Crosslink density of IR/Znmbt₂/sulfur vulcanized at 150°C.

only after 15 min, is considerably lower than in the presence of zinc benzoate (1/2Mc = 10.8 $\times 10^{-5}$ versus 15×10^{-5} mol/mL). Thus, a higher rate of crosslinking and an overall higher concentration of crosslinks per mol of MBT formed is inherent upon the addition of benzoic acid to a compound containing ZnO.

Gradwell and McGill¹⁸ suggested that benzothiazole-terminated pendent groups crosslinked by the highly electronegative nitrogen atom of the benzothiazole group abstract hydrogen from a neighboring chain, forming a crosslink and MBT. MBT evolution coincided with crosslink formation. Abstraction from the same chain would lead to a cyclic sulfide. It is proposed that zinc benzoate alters the crosslinking mechanism as presented in Scheme 1. Zinc benzoate, with its highly positive charge on the zinc atom, attracts the lone pair of electrons on the nitrogen in the aromatic structure of the benzothiazole group, facilitating its removal. The carboxylic oxygens of the benzoate molecule may facilitate abstraction of an allylic hydrogen from an IR chain. With the involvement of the zinc stearate, molecular steric factors could favor the promotion of crosslinking between different IR chains, rather than the formation of cyclic sulfides. Both the formation of cyclic sulfides and crosslinking would result in the liberation of MBT, and the higher concentration of crosslinks per mol of MBT produced in the presence of zinc benzoate points to zinc benzoate promoting the intermolecular reaction. ZnO, too, may promote the reaction of benzothiazole pendent groups via a mechanism analogous to that in Scheme 1, accounting for the faster rate of reaction observed on addition of ZnO to IR/MBTS/ sulfur (Fig. 2). As the catalyst in this case is a



Figure 4 Crosslink density and HPLC analysis of reactants and products in the vulcanization of IR/MBTS/sulfur/ZnO/benzoic acid at 150°C: (\blacksquare) crosslink density; (\blacktriangle) MBTS; (\bigcirc) MBTM; (\bigtriangledown) MBTP; (\Box) MBT; (\blacklozenge) sulfur.

solid particle, cyclization reactions may be promoted to a similar extent, resulting in an increase in the reaction rate but not in the overall crosslink density.

In the absence of ZnO, MBT formation coincides with crosslinking.^{11,18} In Figure 1, it can be seen that some MBT is liberated prior to the detection of a gel when ZnO is present. However, the amount of MBT formed in the early stages is too little to suggest that MBT is released on pen-





dent group formation via a substitution reaction, as occurs with TMTD.^{19–21} ZnO-promoted cyclization reactions would yield MBT.

IR(100)/MBTS(12.27)/Sulfur(9.49)/ZnO(5.0)/Stearic Acid(10.49)

Figure 5 shows that the effect of stearic acid on the vulcanization process is similar to that of benzoic acid. As noted earlier, stearic acid and ZnO react well below vulcanization temperatures, and removal of free acid from the system prevents the formation of stearic thiobenzothiazole (StM) which would partially destroy the accelerator.¹⁰ Zinc stearate, as in the case of zinc benzoate, increases the rate of crosslinking and stimulates the formation of a higher crosslink density. Furthermore, a higher ratio of crosslinks per mole of MBT produced $(1/2Mc = 10.8 \times 10^{-5} \text{ mol/mL})$ crosslinks with the production of 80 mol % MBT versus 14.2×10^{-5} mol/mL crosslinks with the production of 68 mol % MBT) indicates that a more efficient crosslinking mechanism prevails in the presence of zinc stearate, with cyclization being reduced. The reaction mechanism depicted in Scheme 1 would apply. The low MBTP concentration, observed throughout the vulcanization sequence in the presence and absence of the acid, indicates that the rate of pendent group formation is rapid in both compounds and that it is not this step in the reaction sequence that is enhanced by zinc stearate.



Figure 5 Crosslink density and HPLC analysis of reactants and products in the vulcanization of IR/MBTS/sulfur/ZnO/stearic acid at 150°C: (\blacksquare) crosslink density; (\blacktriangle) MBTS; (\bigcirc) MBTM; (\bigtriangledown) MBTP; (\square) MBT; (\bullet) sulfur.

IR(100)/MBTS(12.27)/Sulfur(9.49)/Zinc Stearate(23.32)

Figure 6 shows that, of the compounds studied, this system produces the highest crosslink density. It has twice the zinc stearate concentration present in the ZnO/stearic acid compound, and this will increase the number of pendent group abstraction reactions and lead to an increased rate and higher crosslink density.

IR(100)/MBTS(12.27)/Sulfur(9.49)/ZnO(5.0)/ Zn(mbt)₂(14.61)

To check whether $Zn(mbt)_2$ may have a similar effect to zinc stearate in facilitating the crosslink-

ing of pendent groups, it was added to an IR/ MBTS/sulfur/ZnO system. Figure 7 shows that it reduced the induction period prior to crosslinking and led to a faster reaction, but had little effect on the maximum crosslink density obtained. The solubility of zinc stearate in rubber may increase its availability for reaction with pendent groups, compared to Zn(mbt)₂, which is insoluble.

IR(100)/TMTD(8.86)/Sulfur(9.49)/ZnO(5.0)

On vulcanization at 150°C, the induction period prior to crosslinking is shortened from 4.5 min (ref. 11) to 1 min (Fig. 8) on addition of ZnO to an IR/TMTD/sulfur compound, and higher crosslink



Figure 6 Crosslink density and HPLC analysis of reactants and products in the vulcanization of IR/MBTS/sulfur/zinc stearate at 150°C: (\blacksquare) crosslink density; (\blacktriangle) MBTS; (\bigcirc) MBTH; (\bigtriangledown) MBTP; (\square) MBT; (\bullet) sulfur.



Figure 7 Crosslink densities of (\Box) IR/MBTS/sulfur and (\blacksquare) IR/MBTS/sulfur/Znmbt₂ vulcanized at 150°C.

densities are obtained [1/2Mc = 18×10^{-5} versus 6.5×10^{-5} mol/mL (ref. 11)]. As in the absence of ZnO, the reaction is initiated by tetramethylthiuram polysulfides (TMTP) that react with the polymer chain to form polysulfidic thiuram-terminated pendent groups and dimethyldithiocarbamic acid (Hdmtc).^{19–21} The reaction between TMTD and ZnO is slow^{12,22,23} and bis(dimethyldithiocarbamato)zinc(II) [Zn₂(dmtc)₄] is formed largely by the interaction of Hdmtc with ZnO. DSC and TG curves for IR/TMTD/sulfur/ZnO were similar to those reported by Kruger and McGill²² where the formation of Zn₂(dmtc)₄ and crosslinking coincided with a sharp exotherm at 133°C.

Crosslinking commences well before the complete consumption of TMTD, indicating that the $Zn_2(dmtc)_4$ formed plays an active role in the crosslinking process. However, in agreement with Kruger and McGill,²⁴ higher crosslink densities are achieved with IR/TMTD/sulfur/ZnO than with IR/sulfur/Zn₂(dmtc)₄ (cf. Figs. 8 and 9). This points to the importance of the thiuram pendent groups formed from TMTP in the early stages of the reaction. Such pendent groups are not formed in $Zn_2(dmtc)_4$ -accelerated systems.²⁵ Geyser and



Figure 8 Crosslink density and HPLC analysis of reactants and products in the vulcanization of IR/TMTD/sulfur/ZnO at 150°C: (\blacksquare) crosslink density; (\blacktriangle) TMTD; (\bigtriangledown) TMTP; (\Box) Zn₂dmtc₄; (\bullet) sulfur.



Figure 9 Crosslink density of IR/Zn₂dmtc₄/sulfur vulcanized at 150°C.

 $McGill^{20}$ found that when $Zn_2(dmtc)_4$ was added to a 2.3-dimethyl-2-butene/TMTD/sulfur mixture just prior to crosslinking crosslinking proceeded rapidly and was accompanied by a rapid decrease in the concentration of pendent groups. $Zn_2(dmtc)_4$ was attributed a catalytic role in the process. A reaction analogous to that in Scheme 1 is envisaged. The ability of $Zn_2(dmtc)_4$ to promote the crosslinking of thiuram pendent groups was further illustrated in the following experiment: A thin film of IR/TMTD/sulfur was heated for 10 min at 150°C under a vacuum to extract the Hdmtc produced during pendent group formation. Residual curatives were extracted with methanol (48 h). Half of this film was reheated for 10 min at 150°C and when placed in benzene was found to have formed a lightly crosslinked gel. In the absence of thiols on the polymer chain, formed from Hdmtc polysulfides, the crosslinking of pendent groups is slow, crosslinking involving a reaction between thiols and thiuram pendent groups.²⁶ Zn₂(dmtc)₄ was added to the other half of the sample, and on reheating for 10 min at 150°C, a crosslink density of 2 \times 10⁻⁵ mol/mL was obtained.

 $Zn_2(dmtc)_4$ is an accelerator in its own right but the mechanism of $Zn_2(dmtc)_4$ -accelerated sulfur vulcanization remains unclear. The formation of polysulfidic $Zn_2(dmtc)_4$ complexes is most frequently proposed,²¹ while Geyser and McGill²⁵ suggested that crosslinking may occur without the formation of a true intermediate, pendent groups being removed immediately by the catalytic action of $Zn_2(dmtc)_4$. As noted, the lower crosslink densities obtained with $Zn_2(dmtc)_4$ -accelerated systems show that formation of this accelerator is not responsible for the higher crosslink density of ZnO-containing systems.

IR(100)/TMTD(8.86)/Sulfur(9.49)/ZnO(5.0)/Benzoic Acid(4.51)

Benzoic acid will be consumed in zinc benzoate formation below vulcanization temperatures. Zinc benzoate decomposes TMTD and TMTP above 130°C with the liberation of sulfur¹² and a very rapid decrease in TMTD is evident in Figure 10. Partial destruction of TMTP may account for the lower crosslink density obtained with the benzoic acid/ZnO system (1/2Mc = 12.1×10^{-5} versus 18×10^{-5} mol/mL). The rate of crosslinking is also considerably reduced. 2-Benzoyldimethyldithiocarbamate (BzT), which may result from the attack of ZnO/benzoic acid on TMTD, is not an accelerator.¹¹

 $Zn_2(dmtc)_4$ is formed rapidly and its consumption during crosslinking is greater than in the absence of benzoic acid (cf. Figs. 8 and 10). When $Zn_2(dmtc)_4$ acts as an accelerator, its concentration decreases, while when it participates in the crosslinking of thiuram pendent groups originating from TMTP, its role is purely catalytic.^{25,27} This would imply that Zn₂(dmtc)₄ plays an important role as an accelerator in the presence of ZnO/benzoic acid, while its catalytic role is more important in the absence of acid where the higher concentration of TMTP ensures the formation of more thiruam pendent groups. Indeed, with ZnO/ benzoic acid, the crosslink density equates to that obtained with the IR/sulfur/Zn₂(dmtc)₄ system (Fig. 9).



Figure 10 Crosslink density and HPLC analysis of reactants products in the vulcanization of IR/TMTD/sulfur/ZnO/benzoic acid at 150°C: (\blacksquare) crosslink density; (\blacktriangle) TMTD; (\bigcirc) TMTM; (\bigtriangledown) TMTP; (\square) Zn₂dmtc₄; (\bullet) sulfur.

IR(100)/TMTD(8.86)/Sulfur(9.49)/ZnO(5.0)/Stearic Acid(10.49)

The rate of crosslinking and the maximum crosslink density obtained with this system is nearly identical to that for IR/TMTD/sulfur/ZnO (cf. Figs. 8 and 11). Zinc stearate reacts much less readily with TMTP than with MBTP and interaction is not seen until 145°C, while isothermal studies showed only a very slow decomposition of TMTP at 150°C.¹² In the presence of ZnO, stearic acid is, therefore, not expected to detrimentally affect the crosslinking process. Instead, zinc

stearate and/or $Zn_2(dmtc)_4$ promote the crosslinking of pendent groups in reactions analogous to those depicted in Scheme 1. It was shown earlier²⁶ that on heating an IR/TMTD/sulfur film under a vacuum at 150°C for 10 min a crosslink density of 11×10^{-5} mol/mL was obtained on reheating for a further 10 min after the addition of zinc stearate.

The increased rate and extent of crosslinking observed on addition of ZnO/stearic acid is in agreement with the findings of Lorenz and Echte⁷ on natural rubber compounds cured with MBTS/



Figure 11 Crosslink density and HPLC analysis of reactants and products in the vulcanization of IR/TMTD/sulfur/ZnO/stearic acid at 150°C: (\blacksquare) crosslink density; (\blacktriangle) TMTD; (\bigcirc) TMTM; (\bigtriangledown) TMTP; (\square) Zn₂dmtc₄; (\bullet) sulfur.



Figure 12 Crosslink density and HPLC analysis of reactants and products in the vulcanization of IR/TMTD/sulfur/zinc stearate at 150°C: (\blacksquare) crosslink density; (\blacktriangle) TMTD; (\bigcirc) TMTM; (\bigtriangledown) TMTP; (\Box) Zn₂dmtc₄; (\bullet) sulfur.

sulfur. Coran⁴ and Campbell and Wise⁵ suggested a decrease in the rate of crosslinking but an increase in the overall crosslink density.

IR(100)/TMTD(8.86)/Sulfur(9.49)/Zinc Stearate(23.32)

The rate of crosslinking and the maximum crosslink density of this system (Fig. 12) is similar to that recorded for IR/TMTD/sulfur/ZnO with and without stearic acid. This is to be expected as in ZnO/stearic acid systems the acid is converted to zinc stearate during the compounding and the destruction of TMTP is prevented. However, zinc stearate is not an accelerator, and when comparing the rate and crosslink density with that of an IR/TMTD/sulfur system¹¹ (and not with IR/ TMTD/sulfur/ZnO), a considerable shortening of the induction period (1 versus 4.5 min) and increase in the crosslink density (1/2Mc = 16.5)imes 10⁻⁵ versus 6.5 imes 10⁻⁵ mol/mL) is noted. This can be explained in terms of the ability of zinc stearate to facilitate the crosslinking of thiuram pendent groups as depicted in Scheme 1 and demonstrated earlier,²⁶ as mentioned above.

CONCLUSIONS

Benzoic and stearic acids readily react with ZnO to form zinc salts. This removes the free acids from the system and attack on the accelerator and its polysulfides is limited. Hence, no negative influence on the crosslinking process is observed.

Zinc salts have a positive effect on crosslinking, reducing the induction period and greatly enhancing the maximum crosslink density. The ratio of crosslinks to the MBT released is increased. A mechanism is proposed whereby the zinc salts facilitate removal of benzothiazole pendent groups, enhancing crosslinking at the expense of cyclic sulfide formation.

MBTS does not react with ZnO, but MBT, released on crosslink formation (or cyclization), forms a limited amount of $Zn(mbt)_2$, the reaction being restricted to the surface of ZnO particles. $Zn(mbt)_2$, too, facilitates the abstraction of pendent groups and reduces the induction period although its efficiency is less than that of zinc stearate, probably due to its low solubility in rubber. Its effect on the overall crosslink density is limited, even when added to the compound in excess.

In TMTD compounds containing benzoic acid, slightly lower crosslink densities are obtained due to the partial destruction of TMTP by zinc benzoate. Reaction between zinc stearate and TMTP is much slower and the addition of stearic acid to compounds with ZnO does not have a detrimental effect on the crosslinking process. Instead, the addition of ZnO or zinc stearate leads to the more rapid crosslinking in TMTD/sulfur systems and higher crosslink densities are achieved due to ZnO and zinc stearate facilitating the crosslinking of thiuram pendent groups. $Zn_2(dmtc)_4$ forms early in the reaction sequence as a result of Hdmtc–ZnO interaction and the $Zn_2(dmtc)_4$ formed may likewise catalyze pendent group crosslinking.

The authors wish to thank the South African Foundation of Research Development and Gentyre Industries for financial support.

REFERENCES

- 1. Dogdakin, B. A.; Shershnev, V. A. Rubb Chem Technol 1960, 33, 401.
- Craig, D.; Davidson, W. L.; Juve, A. E. Rubb Chem Technol 1950, 5, 709.
- Kruger, F. W. H.; McGill, W. J. J Appl Polym Sci 1992, 42, 2643.
- Coran, A. Y. Science and Technology of Rubber; Eirich, F. R., Ed.; Academic: Orlando, FL, 1978; Chapter 7.
- Campbell, R. H.; Wise, R. W. Rubb Chem Technol 1964, 37, 635.
- 6. Coran, A. Y. Rubb Chem Technol 1965, 38, 1.
- 7. Lorenz, O.; Echte, E. Rubb Chem Technol 1958, 31, 117.
- 8. Coran, A. Y. Rubb Chem Technol 1964, 37, 679.
- Craig, D.; Davidson, W. L.; Juve, A. E. J Polym Sci 1951, 6, 177.
- McGill, W. J.; Shelver, S. R. J Appl Polym Sci 1999, 72, 999.
- McGill, W. J.; Shelver, S. R. J Appl Polym Sci 1999, 72, 1007.

- McGill, W. J.; Shelver, S. R. J Appl Polym Sci 1999, 72, 1013.
- 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.
- Kruger, F. W. H.; McGill, W. J. J Appl Polym Sci 1991, 42, 2651.
- Gradwell, M. H. S.; McGill, W. J. J Appl Polym Sci 1994, 51, 169.
- Gradwell, M. H. S.; McGill, W. J. J Appl Polym Sci 1995, 58, 2193.
- Gradwell, M. H. S.; McGill, W. J. J Appl Polym Sci 1996, 61, 1131.
- Kruger, F. W. H.; McGill, W. J. J Appl Polym Sci 1992, 45, 563.
- Geyser, M.; McGill, W. J. J Appl Polym Sci 1996, 60, 431.
- Nieuwenhuizen, P. J.; Reedijk, J.; van Duin, M.; McGill, W. J. Rubb Chem Technol 1997, 70, 368.
- Kruger, F. W. H.; McGill, W. J. J Appl Polym Sci 1992, 45, 1545.
- Geyser, M.; McGill, W. J. J Appl Polym Sci 1996, 60, 425.
- Kruger, F. W. H.; McGill, W. J. J Appl Polym Sci 1992, 45, 755.
- Geyser, M.; McGill, W. J. J Appl Polym Sci 1996, 60, 439.
- Gradwell, M. H. S.; McGill, W. J.; Shelver, S. R.; Shumane, M. J Appl Polym Sci, in press.
- Geyser, M.; McGill, W. J. J Appl Polym Sci 1996, 60, 449.