

Studies on Ethylene-Propylene-Diene Rubber Modification by *N*-Chlorothio-*N*-Butyl-Benzenesulfonamide

H. Zhang,^{1,2} R. Datta,¹ A. Talma,¹ J. W. M. Noordermeer^{1,2}

¹Department of Elastomer Technology and Engineering, Faculty of Engineering Technology, University of Twente, 7500AE, Enschede, The Netherlands

²Dutch Polymer Institute (DPI), 5600 AX Eindhoven, The Netherlands

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ABSTRACT: *N*-Chlorothiosulfonamides have been used to modify ethylene-propylene-diene rubber (EPDM) to enhance the compatibility of EPDM in, e.g., natural rubber (NR)/butadiene rubber (BR)/EPDM blends for ozone resistance. *N*-Chlorothio-*N*-butyl-benzenesulfonamide (CTBBS) was selected as a representative for *N*-chlorothiosulfonamides. In this study, we found that CTBBS behaves differently with various types of EPDM. Three types of EPDM were selected: ethylidene norbornene (ENB)-EPDM, hexadiene (HD)-EPDM, and dicyclopentadiene (DCPD)-EPDM. HD-EPDM showed the greatest effectiveness toward CTBBS-modification. However, this EPDM is not commer-

cially available anymore. On the opposite side, DCPD-EPDM showed the lowest reactivity so that almost no modification could be realized. The result with ENB-EPDM was, that upon application of CTBBS to ENB-EPDM, gelation occurred and, therefore, a low amount of modification was achieved. With the limited modification efficiency for ENB-EPDM, there is no significant improvement when applying the modified ENB-EPDM into NR/BR/EPDM blends. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 1146–1154, 2009

Key words: blends; EPDM modification; chlorothiosulfonamides; tire sidewall

INTRODUCTION

It has long been known that the ozone resistance of high-diene rubbers such as natural rubber (NR), styrene-butadiene rubber (SBR), nitrile-butadiene rubber (NBR), and butadiene rubber (BR) can be greatly improved by the incorporation therein of low-unsaturation rubbers, such as ethylene-propylene-diene rubber (EPDM).¹ However, the vulcanizates of such elastomer blends generally are poor in both static and dynamic mechanical properties, such as ultimate strength-related properties, fatigue resistance, and hysteresis.

The main problems associated with the generally poor properties of EPDM/high-diene blends are the large differences in the chemical reactivity of EPDM and polydiene rubbers. The difference in molar concentrations of double bonds in each of the elastomers results in a difference in polarity and the number of allylic sites for sulfur vulcanization to obtain crosslinks.² Such a difference is reflected in the relative rates of crosslinking during vulcanization, diffusion of curatives toward the faster curing

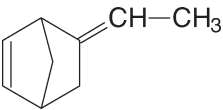
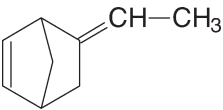
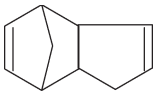

high-diene phase, and a heterogeneous filler distribution between the different rubber phases.^{3–7}

There have been several attempts to improve the properties of EPDM/high-diene blends. Generally, these attempts have sought to increase the cure rate of EPDM, either by using curatives that have an increased reactivity towards EPDM or by means of modifying the EPDM to make it more reactive towards curing.^{8–17} Coran¹⁰ achieved better cure compatibility for EPDM/NR blends by modifying the EPDM with maleic anhydride. Oliveira and Soares¹¹ studied the functionalization of EPDM with mercapto-groups. Baranwal and Son¹² modified EPDM in solution with accelerator species, like the sulfur donor dithiodimorpholine (DTDM), using ultraviolet irradiation in the presence of a photosensitizer. Morrissey¹³ reported that the halogenation of EPDM in solution could result in a marked improvement in its cure compatibility with highly unsaturated rubbers.

Hopper and Roger^{14–17} modified EPDM with *N*-chlorothiosulfonamides in solution and melt to give pendent groups that would act like a retarder to high-diene vulcanization. Blends of the modified EPDM with synthetic polyisoprene (IR) exhibited greater modulus and tensile strength together with lower heat build-up, which was taken as evidence of improved vulcanization of EPDM. Because there are different types of EPDM in existence as ethylidene

Correspondence to: J. W. M. Noordermeer (j.w.m.noordermeer@utwente.nl).

TABLE I
Types of EPDM Rubber Used

Material	Structure of the third monomer	Composition	Supplier
Keltan 5508 (LENB-EPDM)		4.5 wt % ethylidene-norbornene (ENB) 70 wt % ethylene	DSM Elastomers B.V., The Netherlands
Keltan 4703 (HENB-EPDM)		9 wt % ethylidene-norbornene (ENB) 48 wt % ethylene	
Keltan 520 (DCPD-EPDM)		4.5 wt % Dicyclopentadiene (DCPD) 58 wt % ethylene	
Nordel 1070 (HD-EPDM)		4 wt % Hexadiene (HD) 54 wt % ethylene	Dupont, Wilmington, DE

norbornene (ENB)-EPDM, hexadiene (HD)-EPDM, and dicyclopentadiene (DCPD)-EPDM, a study on the selectivity of *N*-chlorothiosulfonamides toward these various EPDMs is of great interest. The objective of this work was therefore to study the reactivity of *N*-chlorothiosulfonamides toward these various EPDMs and their influence on vulcanization behavior in blends with highly unsaturated rubbers.

EXPERIMENTAL

Materials

N-Chlorothio-*N'*-butyl-benzenesulfonamide (CTBBS) was prepared by the use of *n*-butylamine (99.5%, Sigma-Aldrich, Munich, Germany), triethylamine (99.5%, Sigma-Aldrich), dichloromethane (99.9%, Biosolve, Westford, MA), benzenesulfonyl chloride (99.0%, Sigma-Aldrich), sulfurdichloride (98%, Fluka/Sigma-Aldrich), and diethyl ether (99.8%, Fluka).

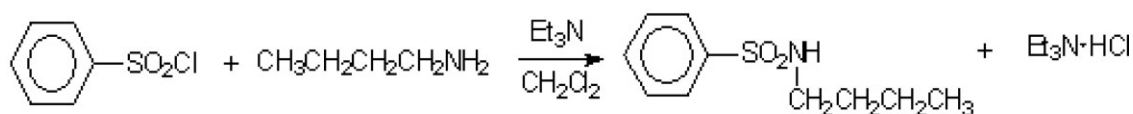
The elastomers selected for the blend were natural rubber (SIR20, Standard Indonesian Rubber), butadiene rubber (Kosyn KBR01, Kumho Petrochemical, Seoul, Korea) and four types of EPDM rubber, as listed in Table I. The other compounding ingredients

used were extra pure grade zinc oxide (Merck, Darmstadt, Germany), finely divided sulfur (Merck), 95% pure stearic acid (Sigma-Aldrich), poly(2,2,4-trimethyl-1,2-dihydroquinoline) or TMQ (Flexsys B.V., Deventer, The Netherlands) and *N*-cyclohexyl-2-benzothiazolesulfenamide (CBS) or Santocure[®] (Flexsys B.V.).

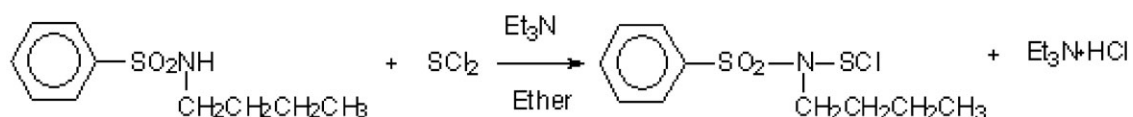
Synthesis of CTBBS

CTBBS was prepared by two steps as shown in Scheme 1. In the first step, 7.3 g of *n*-butylamine and 10.1 g of triethylamine were dissolved in 200 mL of dichloromethane. The solution was then cooled to 0°C in an ice bath. Afterwards, a solution of 17.6 g of benzenesulfonyl chloride in 50 mL of dichloromethane was slowly added. The reaction mixture was stirred at room temperature for 2 h and refluxed for 1 h to complete the reaction. The reaction mixture was then washed several times with a diluted hydrochloric acid solution and pure water in a separation funnel to remove unreacted triethylamine and triethylamine hydrochloride. The organic layer was dried by Magnesium sulfate, filtered, and evaporated. The remaining material was *N*-butyl-benzenesulfonamide, which was characterized by NMR:

Step 1:



Step 2:



Scheme 1 Synthesis of CTBBS.

TABLE II
CTBBS-Amounts Added for the Different Types of EPDM

EPDMs	Third monomer (mmol/100 g EPDM)	CTBBS amounts relative to available unsaturation (mmol)					
		10%	20%	30%	40%	50%	60%
LENB-EPDM	11.3	1.13	2.26	–	–	–	–
HENB-EPDM	22.5	2.25	–	–	–	–	–
HD-EPDM	14.6	1.46	2.92	4.38	5.84	7.30	8.76
DCPD-EPDM	10.2	1.02	2.04	3.06	4.08	5.10	6.12

7.88–7.50 ppm, 7.59–7.49 ppm, 4.60 ppm, 2.99–2.95 ppm (quartet), 1.50–1.20 ppm, 0.88–0.82 ppm.

In the second step, 10.7 g of *N*-butyl-benzenesulfonamide and 5.1 g of triethylamine were dissolved in 200 mL of diethyl ether and cooled to 0°C. Then a solution of 5.2 g of sulfur dichloride in 50 mL of ether was added slowly while maintaining the temperature at 0°C. During the reaction, a precipitate of triethylamine hydrochloride was formed and filtered afterwards. After evaporation of the ether, the residue was characterized by NMR as *N*-chlorothio-*N'*-butyl-benzenesulfonamide: 8.00–7.96 ppm, 7.71–7.65 ppm, 2.99–2.95 ppm (triplet), 1.50–1.20 ppm, and 0.97–0.92 ppm.

Modification of EPDM by CTBBS

In solution

To begin, 5 g of EPDM was first dissolved in 200 mL of hexane and flushed with nitrogen. For the ENB-type EPDM, a suspension of calcium stearate in dichloromethane was added to the polymer solution before reaction to act as acid acceptor for the reaction.¹⁷ The amount of calcium stearate was equal on a molar basis to the amount of CTBBS to be added next. For HD-EPDM and DCPD-EPDM, this was omitted. Then, a CTBBS-solution in dichloromethane was added slowly into the EPDM solution. The CTBBS-amounts added were varied, to correspond to relative ratios (%) with respect to the total amount of third monomer available for reaction: Table II.

After stirring for several hours at ambient temperature, the final rubber sample was isolated by coagulation and washing with acetone, followed by drying in a vacuum oven. The time needed for the reaction to be completed and the highest CTBBS amount which can be added before gelation was different for the various types of EPDM, as shown in Table III.

In internal mixer

Modification of ENB-EPDM by CTBBS also was tried in a Brabender PL2000 with a chamber volume of 50 cm³ with the use of a rotor speed of 80 rpm, a fill factor of 0.8, and an initial temperature varied

between 100 and 140°C. The EPDM was first masticated for 1 min, and then calcium stearate in molar equivalents to CTBBS was added. After another 3 min of mixing, CTBBS was added and the mixing was continued for another 6 min. The final compound temperature before dumping from the mixer was in the range of 140°C ± 10°C. A sample for analysis was purified by dissolving in chloroform, coagulated and washed with acetone, then dried in a vacuum oven.

Characterization of the modified EPDMs

IR

The infrared spectra of the modified EPDM-samples were recorded by using the attenuated total reflectance infrared technique (ATR/IR) with a spectrometer FTS-60 (Bio-Rad Laboratories B.V., The Netherlands). The infrared spectra were recorded with 512 scans at a resolution of 8 cm⁻¹ in the range of 4000–600 cm⁻¹.

NMR

The ¹H-NMR spectra of the modified EPDM-samples were recorded with a Varian Unity 300 MHz system at 25°C with CDCl₃ as the solvent.

Preparation of blends, vulcanization, and tensile test

NR/BR/EPDM blends were prepared in a Schwabenthan two-roll mill. The recipes are shown in Table IV. NR was first masticated for 1 min, then BR and EPDM (or modified EPDM) were added and mixed for another 2 min. Subsequently, ZnO and

TABLE III
Reaction Times and Highest CTBBS Amounts that Can Be Added Before Gelation for Different Types of EPDM

EPDM types	Reaction time	Highest CTBBS amount
LENB-EPDM	4 h	20%
HENB-EPDM	4 h	10%
HD-EPDM	48 h	60%
DCPD-EPDM	No reaction	No reaction

TABLE IV
Formulation of NR/BR/EPDM Compounds

Ingredient	Content (phr)
NR	35
BR	35
EPDM (grafted EPDM)	30–32.5
Stearic acid	2
Zinc oxide	4
TMQ	1
CBS	1.98
Sulfur	2.5

TMQ were added. After 2 min of mixing, CBS and sulfur were added, and the mixing was continued for another 2 min. The final compound was sheeted out.

The optimum cure time ($t_{c,90}$) of the fully compounded gum blends was determined as the time needed to reach 90% of the maximum torque in a RPA 2000 (Alpha Technologies) at 150°C, 0.833 Hz, and 0.2° strain. The blends were then vulcanized into 2-mm-thick plates for the optimum cure time $t_{c,90}$ in a Wickert WLP 1600 laboratory compression press at 150°C and 100 bar pressure. Tensile tests were conducted according to ISO 37, with a Zwick tensile tester Model Z 1.0/TH1S at a constant cross-head speed of 500 mm/min.

RESULTS AND DISCUSSION

Modification of different types of EPDM by CTBBS in solution

Modification of EPDM by CTBBS was first tried by the solution technique. The reacted EPDM was then characterized by ATR and NMR to check whether modification occurred.

ENB-EPDM

Figure 1 shows the ATR infrared spectra of CTBBS-modified ENB-EPDM in comparison with virgin EPDM. CTBBS-modified EPDM clearly shows some additional peaks. As the samples were washed with acetone before the ATR-measurement, the presence of absorption peaks indicates that CTBBS-fragments were indeed grafted onto ENB-EPDM. These peaks and their assigned functional groups are listed in Table V.

As the relevant peaks partly overlap with peaks of EPDM, they are not suited for a quantification of the modification. Therefore, an attempt was made to obtain more information from the H^1 -NMR spectrum of the samples. The NMR spectra of CTBBS-modified and virgin ENB-EPDM are shown in Figure 2. Compared with virgin EPDM, the modified EPDM shows additional peaks in the range from 7.4

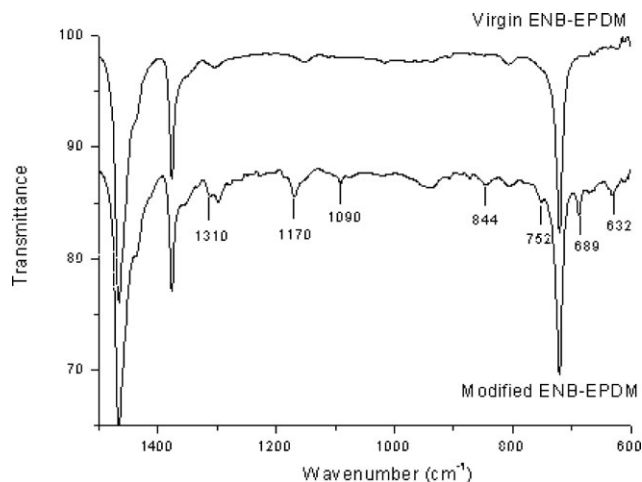


Figure 1 ATR-spectra of CTBBS-modified ENB-EPDM in comparison with virgin ENB-EPDM.

to 8 ppm, which can be attributed to the aromatic protons from CTBBS. Two peaks at 5.0 and 5.22 ppm are caused by the olefinic vinyl hydrogen of the ENB group with two different configurations.¹⁷ The peak at 0.8 ppm is from large amount of methyl groups in EPDM. Because the amount of methyl groups will not have changed after the modification reaction, this peak at 0.8 ppm was defined as reference peak. Then, the integration area of the peaks of vinyl hydrogen from the ENB group can be quantified, remaining after the modification with CTBBS.

After CTBBS modification, the peak area of residual olefinic protons decreases. By changing the CTBBS/EPDM ratio, a calibration curve of olefinic proton peak area versus CTBBS-amount could be obtained, as in Figure 3. For LENB-EPDM, when the CTBBS-amount increased to 30%, the viscosity of the polymer solution increased significantly and the solution became completely gelled 15 min after the

TABLE V
Infrared Absorption Peaks and Their Assignments

Infrared absorption peak (cm^{-1})	Functional group
1310, 1090	
1170	
844, 752, 690	
632	C-Cl

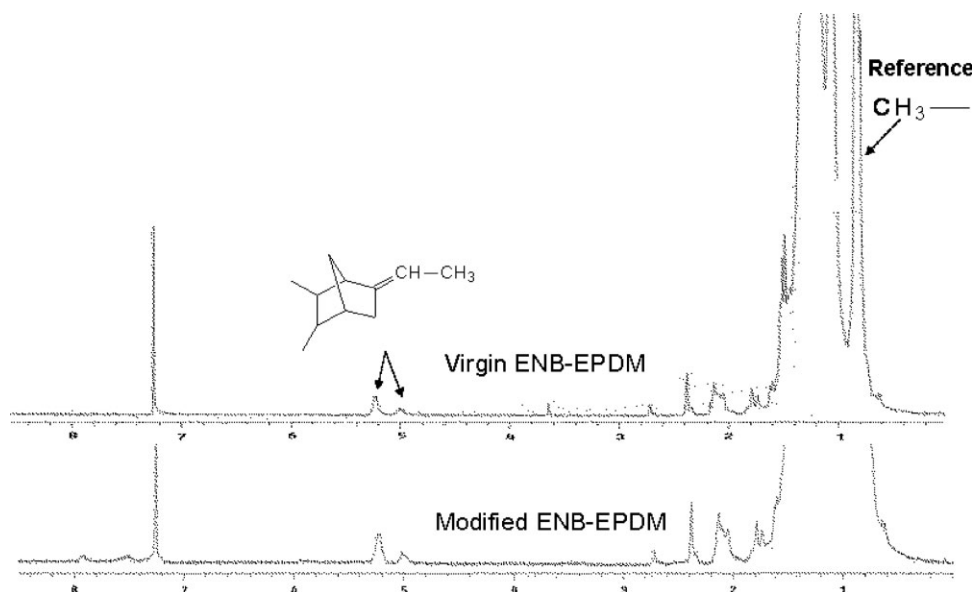


Figure 2 NMR-spectra of CTBBS-modified ENB-EPDM in comparison with virgin EPDM.

addition of CTBBS. As HENB-EPDM contains a twice higher amount of ENB, it is even more sensitive to become gelled. For HENB-EPDM, the highest dosing of CTBBS before gelation is only 10%. In principle, one CTBBS molecule can only consume one olefinic proton. Therefore, theoretical curves can be drawn as shown in Figure 3. Compared with the theoretical curves, the experimental curves deviate significantly. The ENB-double bond conversion is greater than might have been expected on the basis

of stoichiometry, which means many more olefinic protons are consumed than expected. This indicates the fact that side reactions take place during modification.

Scheme 2 shows potential reactions of CTBBS with ENB-EPDM. At the first stage of modification, a simple addition reaction happens between CTBBS and ENB-EPDM. Because of steric resistance effects, the sulfonamidothio-radical covalently bonds to the exocyclic olefinic carbon atom and the chloride radical

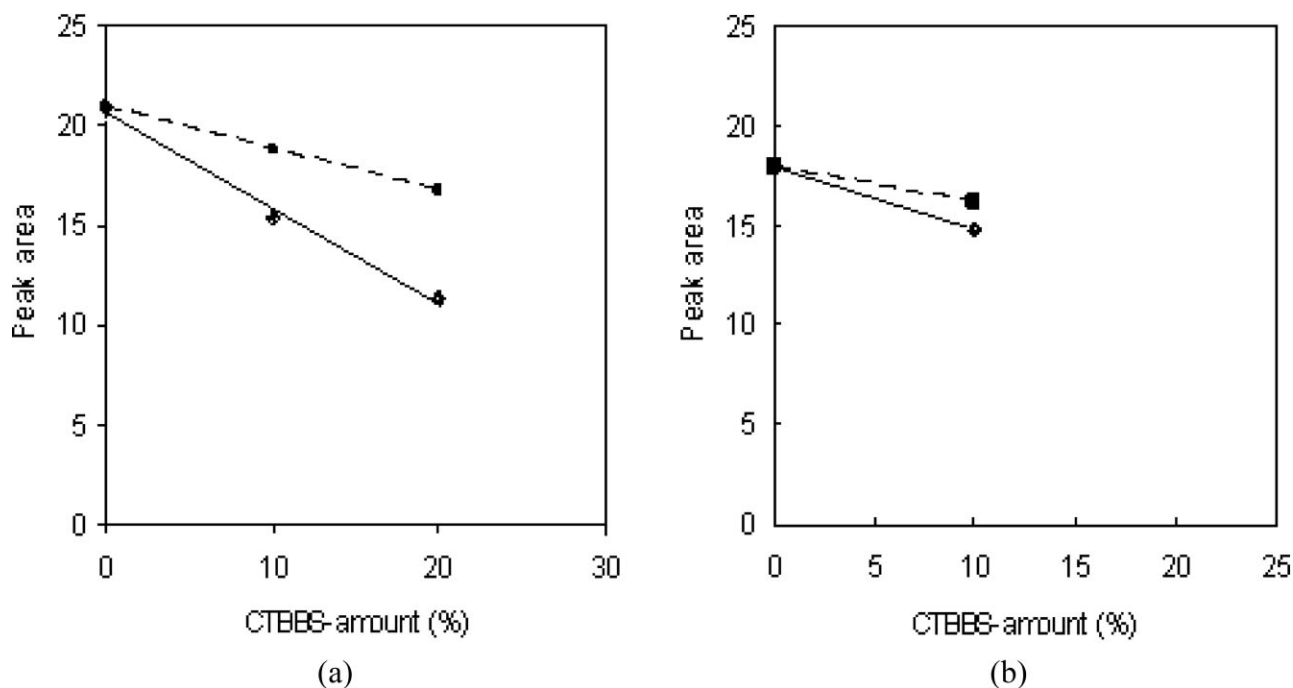
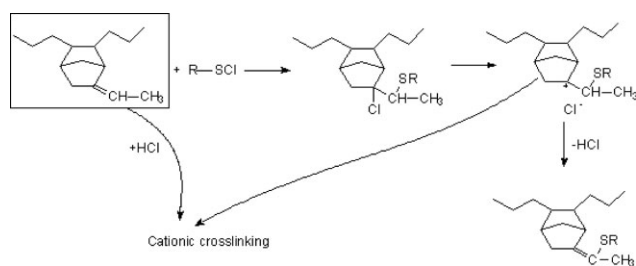


Figure 3 Calibration curves of olefinic proton peak areas versus CTBBS-amount added for ENB-EPDM: (◆—◆) experimental; (■---■) theoretical; (a) LENB-EPDM; (b) HENB-EPDM.



Scheme 2 Reactions during CTBBS-modification onto ENB-EPDM.

to the olefinic carbon atom in the ring of ENB. However, this reaction product is not stable and will react further. A chloride ion can be eliminated easily because of the high stability of the carbon cation being formed. Thereafter, the double bond is reformed and hydrochloric acid is released. Because the ENB group is very sensitive to cationic reactions, the presence of hydrochloric acid promotes the gelation of ENB-EPDM via crosslinking. Calcium stearate has been added to scavenge acidity and limit cationic side reactions, but with limited success. Other acid acceptors like amines and ZnO have also been tried without improvement.

NMR-spectra were recorded at different reaction times. After 4 h of reaction, the olefinic proton peak area was stabilized. For ENB-EPDM, 4 h is sufficient for the reaction to reach completion.

HD-EPDM

Figure 4 shows the ATR/IR-spectra of CTBBS-modified HD-EPDM in comparison with virgin HD-EPDM. The same additional peaks can be seen as for

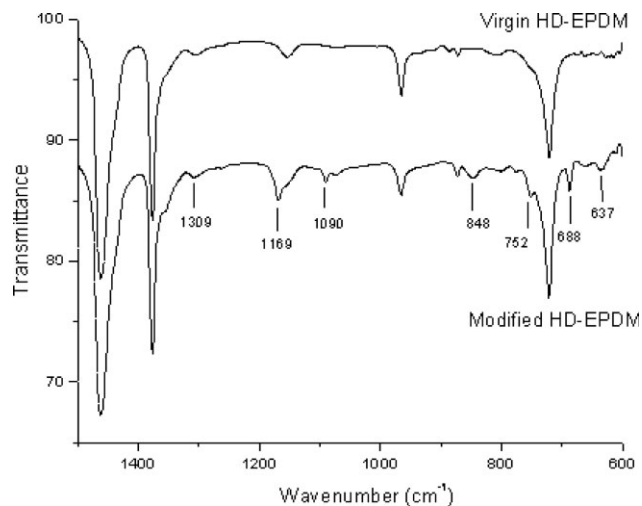


Figure 4 ATR-spectra of CTBBS-modified HD-EPDM in comparison with virgin HD-EPDM.

modified ENB-EPDM. These peaks and their associated functional groups are listed in Table V. The presence of above absorption peaks again indicates that CTBBS-fragments are grafted onto HD-EPDM.

The NMR-spectra of CTBBS-modified HD-EPDM and virgin HD-EPDM are shown in Figure 5. There are three groups of additional peaks. Those at 7.4–8 ppm can be attributed to the aromatic group of CTBBS, the same as for modified ENB-EPDM. The peak at 5.4 ppm is due to olefinic protons of the hexadiene group. As soon as modification occurs, the amount of the olefinic protons decreases. Calibration curves for the area of this peak are shown in Figure 6.

For HD-EPDM, the accessible CTBBS-amount before gelation occurs is 60%, which is substantially greater than for ENB-EPDM. Furthermore, the slope

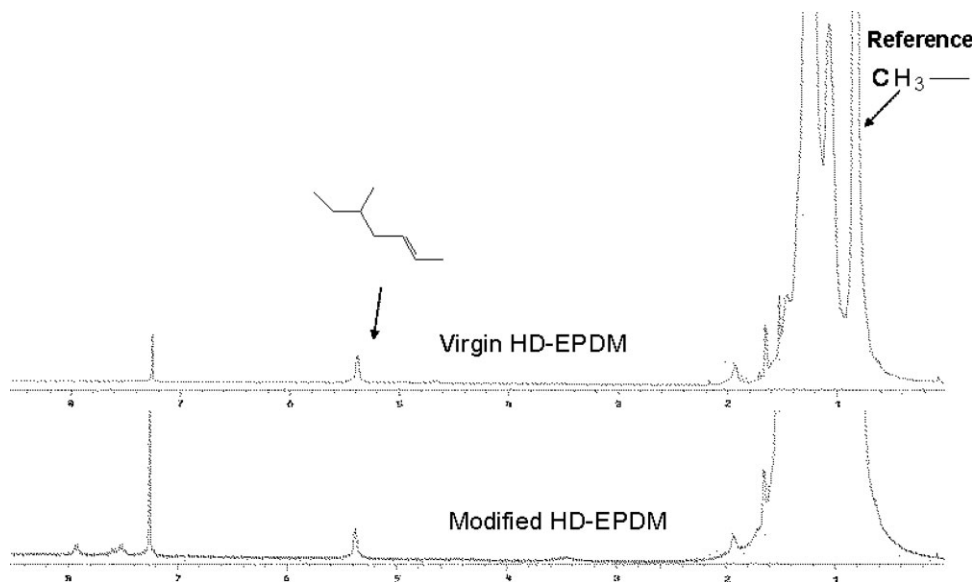


Figure 5 NMR-spectra of CTBBS-modified HD-EPDM in comparison with virgin HD-EPDM.

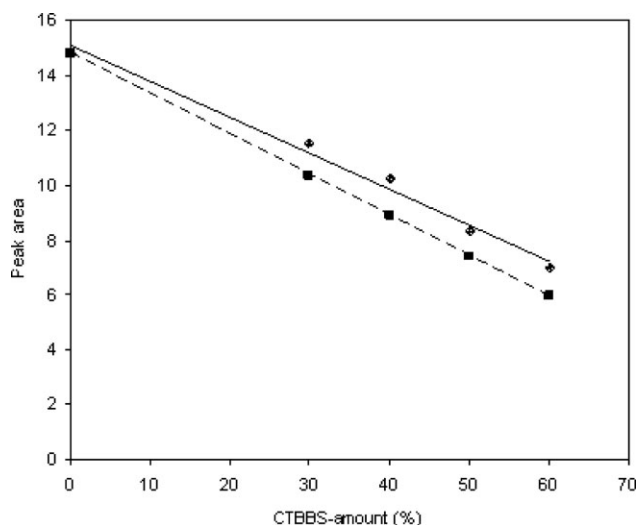


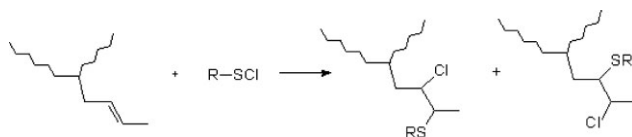
Figure 6 Calibration curves of olefinic proton peak areas versus CTBBS-amount added for HD-EPDM: (◆—◆) experimental; (■---■) theoretical.

of the experimental curve is lower than that of the theoretical one, which means the double bond conversion is less than theoretically expected. It indicates that there are less side reactions taking place compared to ENB-EPDM. By calculation, the double bond conversion of HD-EPDM after CTBBS modification is 85% of the theoretical value. Apparently, a different reaction scheme must be proposed to explain the difference between HD-EPDM and ENB-EPDM.

As shown in Scheme 3, a simple 1,2-addition reaction will occur between CTBBS and HD-EPDM. The sulfonamidothio-radical covalently bonds to one olefinic carbon atom and the chloride radical bonds to the other. This product is much more stable than that of ENB-EPDM. The elimination of chloride is much more difficult and less hydrochloric acid is formed to initiate cationic crosslinking. Therefore, the CTBBS amount before gelation for HD-EPDM is much greater than that for ENB-EPDM. Moreover, for HD-EPDM, 48 h are needed for the reaction to be complete, which also is much longer than for ENB-EPDM.

DCPD-EPDM

Despite the fact that the solution of DCPD-EPDM and CTBBS was stirred for longer time and at



Scheme 3 Modification reaction of CTBBS onto HD-EPDM.

greater temperature (80°C) than ENB-EPDM and HD-EPDM, the ATR/IR-spectrum shows no evidence of CTBBS-modification. This is also confirmed by NMR, since the peak area of the olefinic protons remains unchanged.

Comparison of the various EPDMs

It is remarkable that modification happens for ENB-EPDM and HD-EPDM but not for DCPD-EPDM. The different reactivity of the double bond in their structure is the reason for the different behaviors of those three EPDMs during CTBBS modification. Considering the difference in reaction speed, the reactivity of the three EPDMs toward modification varies in the order ENB-EPDM > HD-EPDM > DCPD-EPDM. Unfortunately, the CTBBS modification in the case of ENB-EPDM is accompanied by a strong tendency toward gelation as the result of cationic side reactions. This substantially limits the attainable conversion. Although HD-EPDM has the greatest conversion with CTBBS, it is no longer commercially available. ENB-EPDM has a too low efficiency, which is not a viable alternative.

Modification of LENB-EPDM in an internal mixer

Modification of LENB-EPDM with CTBBS also was performed in an internal mixer with different CTBBS amounts and at different temperatures in order to minimize gelation. Figure 7 shows the torque and temperature curves during mixing for the blend with 20% equivalent CTBBS. After the addition of CTBBS, the torque first decreases and then rises immediately to its previous value and even a little higher. With temperature increasing continuously, the torque value stays more or less at a constant value, indicating a steady increase in viscosity of the compound. When the CTBBS amount was increased

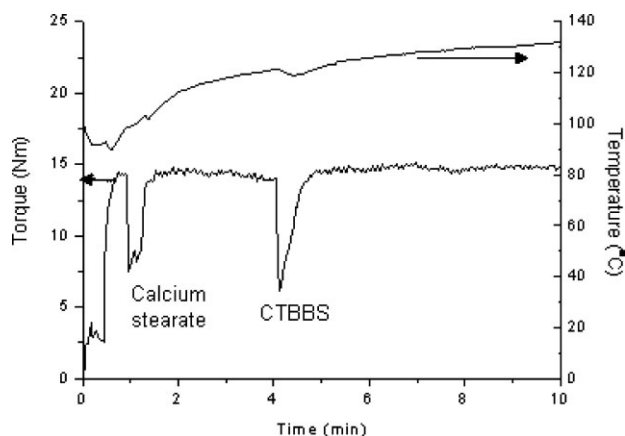


Figure 7 Torque and temperature curves during mixing of LENB-EPDM with 20% CTBBS at 100°C.

TABLE VI
Integration Area of Olefinic Hydrogen with 20% CTBBS

LENB-EPDMs	Integration area of olefinic hydrogens
Pure LENB-EPDM	20.9
Internal mixer 100°C (10 min)	11.6
Internal mixer 100°C (15 min)	11.6
Internal mixer 120°C (10 min)	11.9
Solution method	11.3

to 30%, the torque value decreased after CTBBS addition, and did not rise anymore. The EPDM became grainy, which indicates that gelation happened again.

The integration of the area of olefinic protons from NMR-spectrum for the 20% CTBBS-modified EPDM is shown in Table VI. The value by the internal mixer method is almost the same as by the solution method. 100°C and 10 min are sufficient for the reaction to reach saturation, because there is no change with longer mixing time or higher temperature. Apparently, modification in the internal mixer gives similar results as in solution. The problem of gelation still exists.

Properties of mixer CTBBS-modified LENB-EPDM in vulcanized blends with NR/BR

Figure 8 shows the curing curves of NR/BR/EPDM blends according to Table IV with different CTBBS-amounts modified LENB-EPDM. Compared with the unmodified EPDM, blends with modified EPDM have a longer scorch time due to the amine-effect from CTBBS.^{18,19} Modified EPDM also shows greater torque values than pure EPDM, whereas with different CTBBS amounts, there is little difference.

Properties for those blends are reported in Table VII. Blends with CTBBS-modified LENB-EPDM show greater moduli than blends with pure LENB-EPDM, which is consistent with the torque values from the curing curves. Tensile strength and elongation at break show limited improvement by applying modified EPDM into the blends. For different CTBBS-amounts from 10 to 25%, the differences are

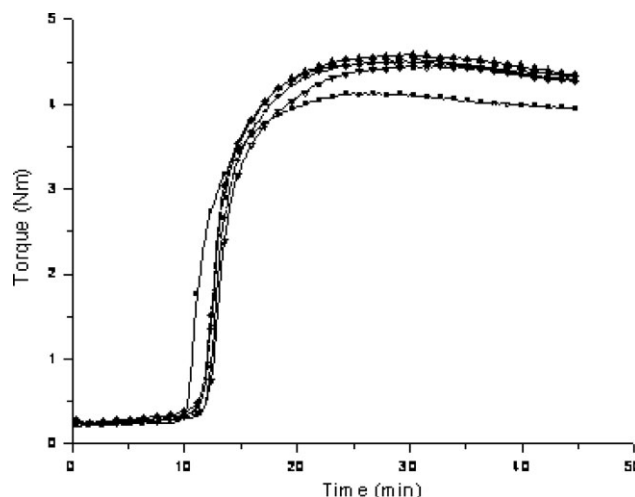


Figure 8 RPA curing curve of NR/BR/EPDM blends with different CTBBS amounts modified LENB-EPDM: (■) 0%; (●) 10%; (▲) 15%; (▼) 20%; and (◆) 25%.

limited as well. As for 25% CTBBS, the EPDM was already partly gelled, higher CTBBS-amounts will not help to get better mechanical properties.

In Hopper's¹⁴ work, wherein 30 phr *N*-chlorothio-*N*-methyl-*p*-toluenesulfonamide modified HD-EPDM was blended with 70 phr NR, tensile properties improved significantly compared with unmodified HD-EPDM/NR blends. Unfortunately, restricted availability of HD-EPDM does not allow to perform comparison work in the current study.

CONCLUSIONS

CTBBS has a different behavior with respect to modification on various EPDM types. The greatest modification efficiency can be reached for HD-EPDM. No modification is observed for DCPD-EPDM. ENB-EPDM has the highest reactivity, however gelation is observed even at low conversions. The highest modification level achievable for LENB-EPDM is 20% relative to the available unsaturation, and for HENB-EPDM, even less.

Both a solution method and an internal mixer method have been tried for the CTBBS modification

TABLE VII
Mechanical Properties of NR/BR/EPDM Blends with Different CTBBS-Amounts Grafted onto EPDM

Tensile properties	CTBBS amounts added to LENB-EPDM relative to available unsaturation				
	0%	10%	15%	20%	25%
100% modulus (MPa)	1.43	1.48	1.54	1.52	1.53
200% modulus (MPa)	2.21	2.38	2.44	2.40	2.42
300% modulus (MPa)	3.10	3.72	3.87	3.80	3.85
Tensile strength (MPa)	4.3	5.0	4.8	4.9	4.7
Elongation at break (%)	300	340	310	320	310

reaction onto ENB-EPDM and show almost the same results. From tensile measurements on vulcanized blends with NR/BR, it must be concluded that ENB-EPDM modified with 25% of CTBBS is insufficient to provide significantly improved mechanical properties of the blends compared to historic data on basis of HD-EPDM.

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