CROSSLINKING OF SBR COMPOUNDS FOR TIRE TREAD USING BENZOCYCLOBUTENE CHEMISTRY

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ABSTRACT

This research investigates the potential of benzocyclobutene (BCB) chemistry for crosslinking styrenebutadiene rubber in conjunction with sulfur curatives with the objective of achieving curing at lower temperatures and/or in shorter times compared with entirely sulfur-based cure formulations. The reversible polysulfidic linkages produced in sulfur crosslinking allow self-healing characteristics but suffer from poor heat-aging stability. The C–C crosslinks from BCB chemistry are irreversible and offer higher resistance to aging, but they do not present apparent self-healing properties. The hybrid curative package based on C–C, C–S, and S–S linkages developed is expected to provide reduced crosslinking time and/or temperature, along with higher crack-growth resistance, the ability to selfheal, higher resistance to fatigue-to-failure, reduced hysteresis, and increased abrasion resistance. The crosslinking performance of 1-substituted BCB-based compounds in conjunction with sulfur is specifically investigated. [doi:10.5254/rct.18.81512]

INTRODUCTION

Elastomers are inherently soft plastic materials with low Young's modulus and higher elongation at break. They are not suitable for tire treads until they are compounded with the appropriate ingredients, such as fillers, coupling agents, curatives, accelerators, activators, and processing aids, and are finally cured.^{1–4} The viscoelastic nature of tire tread compounds precludes complete recovery of deformation after the applied stress is removed. The viscous part also leads to appreciable viscous dissipation during the deformation process, thus leading to hysteresis. A significant part of hysteresis, and therefore rolling resistance, originates from the frequent breakup and reformation of filler–filler and filler–polymer networks. A uniform dispersion and distribution of fillers and, hence, strong filler–polymer interactions are two important attributes in achieving lower values of hysteresis at an appropriate extent of cure.^{5–9}

VULCANIZATION USING SULFUR

The sulfur-based curing process itself is energy intensive. Sulfur has a higher activation temperature and is used in rubber compounds at a typical loading of 1-3 phr to obtain curing typically in the range of 140-190 °C.¹⁰ The use of sulfur generates both linear and cyclic crosslinks; the latter are responsible for poor aging properties.¹ The curing time of sulfur can be reduced, and the ultimate properties of the rubber compound can be improved by the use of accelerators. Currently, a wide range of accelerators, including thiurams, dicarbamates, thiazoles, amines, and sulfonamides, are used that influence the curing characteristics and the properties of the compound. The accelerators release radicals at higher temperature and help to improve the aging resistance at elevated temperatures.¹¹⁻¹⁴

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FIG. 1. — Chemical structures of (a) polypentalfluorostyrene substituted with 10 mol% and 20 mol% BCB units (XA 1, PPFS-BCB_n), (b) bisBCB with an ethoxyethoxy spacer (XA2, BCB-EOEO-BCB), and (c) bisBCB with a polybutadience spacer (XA3, BCB-PB-BCB).

SYNERGY OF S-S, C-S, AND C-C CROSSLINKS

Low-temperature curatives, especially those that augment the S–S crosslinks with additional C–C or C–S linkages, are essential for the preparation of low-energy-loss tire tread compounds. The additional C–C bonds also increase the crosslink density and therefore the mechanical properties of the rubber compound. Peroxides are commonly used to introduce C–C crosslinks and to obtain improved high-temperature aging properties.¹⁵ The current work is based on the use of 1-substituted benzocyclobutene (BCB) compounds as crosslinking agents for rubber compounds.^{16,17}

BCB AS A CROSSLINKER

BCB undergoes ring-opening isomerization to an *o*-quinodimethane intermediate at an elevated temperature due to the strained cyclobutene structure. It is stable at ambient temperature but undergoes crosslinking at temperatures greater than 220 °C via Diels Alder and perhaps radical mechanisms. However, this temperature can be reduced by substitution at the 1-position of the cyclobutene ring with an electron-donating or electron-withdrawing group.^{18–21} This reduction in crosslinking temperature coupled with the advantages of the conventionally used sulfur systems may provide energy-efficient tire compounds.

In this work, two types of BCB-based compounds were investigated: (1) the solid powder, polypentafluorostyrene (PPFS), with multiple BCB units attached through an ether link at the 1-position (PPFS-BCB_n; Figure 1a) and (2) liquid bisBCBs connected through ether linkages at the 1-



FIG. 2. — Schematic of the arene-perfluoroarene interactions between CB, PPFS, and SBR.

position (Figure 1b,c). This allowed comparison of the effects of the physical state (e.g., solid vs liquid) and molecular mobility of the curatives on rubber crosslinking via C–C bond formation. For the first type of curative, the PPFS moieties have the added benefit of being able to interact with SBR chains through arene-perfluoroarene interactions (Figure 2).²² Scheme 1 illustrates the known crosslinks formed by BCB units, using PPFS-BCB_n with SBR as an example.



SCHEME 1. — Dibenzocyclooctane crosslinks formed by curing SBR with PPFS-BCB_n; crosslinks formed by oligomerization of the BCB units are not shown.



SCHEME 2. — Synthesis scheme of curative XA1, PPFS-BCB_n.

EXPERIMENTAL

MATERIALS

Solution styrene-butadiene rubber (S-SBR) was donated by Eastman Chemical Company (Akron, OH, USA) with 25 wt% styrene and 42 wt% vinyl content under grade BUNA VSL VP PBR 4041 and was used as received. *N-t*-butyl-2-benzothiazylsulfenamide (TBBS) accelerator, sulfur curing agent (grade Rubber Maker[®]), stearic acid (flakes), and zinc oxide (powder) were obtained from Akrochem Corporation (Akron, OH, USA). Tetrahydrofuran (THF; reagent grade; Aldrich, Milwaukee, WI, USA) was used for solution mixing of the curative in the rubber compound. Tetramethylthiuram disulfide (TMTD) and 2-mercaptobenzothiazole (MBT) obtained from Akrochem and Aldrich, respectively, were also used as accelerators. Hydrocarbon oil (Tudalen 4192, treated distillate aromatic extract [TDAE]) was used as the processing aid, and carbon black (CB; N234, supplied by Eastman) was used as received. Three BCB curatives were used: BCB-substituted PPFS (curative XA1; Figure 1a) and two bisBCBs, one with an ethoxyethoxy spacer (curative XA2, BCB-EOEO-BCB; Figure 1b) and one with a polybutadiene spacer (curative XA3, BCB-PB-BCB; Figure 1c). The syntheses of curatives XA2 and XA3 are presented below.

SYNTHESIS OF PPFS-BCBN (CURATIVE XA1)

The curative XA1 was synthesized using the reaction scheme presented in Scheme 2. Using XA1 with 10 mol% of the repeat units substituted with 1-BCB as an example, a solution of pentafluorostyrene (PFS) (4.0 g, 21 mmol) and benzoylperoxide (BPO) (82 mg, 0.34 mmol) in THF (40 mL) in a Schlenk tube were degassed by five freeze-pump-thaw cycles, and the Schlenk tube was sealed under vacuum with a glass stopper. After stirring at 65 °C for 48 h, the polymerization solution was precipitated in cold methanol (100 mL) to yield 2.6 g (65%) of PPFS as a white powder: $M_n = 7.41 \times 10^3$, D = 1.67.

HO-EthoxyBCB was separately deprotonated by adding NaH (53 mg, 1.3 mmol; 60% in mineral oil) in batches over 2.5 h to a solution of HO-EthoxyBCB (0.22 g, 1.3 mmol) in THF (10 mL) at room temperature under N₂, and the resulting suspension was stirred at room temperature for 10 min. A solution of PPFS (2.6 g, 13 mmol) in THF (10 mL) was added dropwise over 30 min to the suspension of Na⁺, ⁻OEthoxyBCB in THF, and the reaction mixture was stirred at 60 °C for 48 h. The reaction mixture was cooled to room temperature and quenched with methanol (5 mL), and the functionalized polymer was precipitated in cold MeOH (200 mL) to yield 2.5 g (97%) of XA1 as a white powder; $M_n = 8.49 \times 10^3$, D = 1.77. XA1 (2.8 g) with 20 mol% of the repeat units substituted



SCHEME 3. — Synthesis scheme of curative XA2, BCB-EOEO-BCB.

with 1-BCB was prepared in 90% yield starting from a different batch of PPFS ($M_n = 9.35 \times 10^3$, D = 1.62); $M_n = 1.08 \times 10^4$, D = 1.71. Comparison of the ¹⁹F NMR spectra of PPFS-BCB_n and PPFS in Figure 3 confirms the incorporation of BCB.

SYNTHESIS OF ETHOXYETHOXY-LINKED BISBCB (CURATIVE XA2)

The curative XA2 was synthesized using the reaction scheme presented in Scheme 3. Isoamyl nitrite (11 g, 95 mmol) was added dropwise over 10 min to an ice-cooled solution of anthranilic acid (10 g, 73 mmol) and trichloroacetic acid (0.13 g, 0.79 mmol) in THF (100 mL) in an open beaker. The resulting yellow solution was stirred at 0 °C for 30 min. The beaker was removed from the ice bath, and the solution was stirred at room temperature for 2.5 h, during which time a light-yellow solid precipitated from the orange solution. The precipitate was collected in a fritted glass funnel and washed with CH₂Cl₂ to replace the THF, being careful to keep the solid moist with solvent at all times. (Note of caution: benzenediazonium-2-carboxylate is explosive when dry.) The slurry was transferred to a Parr reactor containing di(ethylene glycol) divinyl ether (3.8 g, 24 mmol). The reaction mixture was heated to 100 °C over 30 min and then stirred at approximately 95 °C for 2 h. The maximum pressure reached was 110 psi. The reaction mixture was cooled to room temperature and exposed to the atmosphere, and the solution was concentrated by atmospheric evaporation. The concentrated dark-colored solution was added batchwise to a beaker containing silica gel (12 g) in hexanes (100 mL) at 50 °C. After filtering off the silica gel in a fritted glass filter, solvent was removed from the transparent orange filtrate by rotary evaporation. The crude product (3.7 g, 49%) was purified by column chromatography using silica gel as the stationary phase and hexanes/diethyl ether (70:30) as the eluant to yield 2.2 g (22%) of BCB-EOEO-BCB as a brown oil. The ¹H NMR spectrum of XA3 is presented in Figure 4.

SYNTHESIS OF PB-LINKED BISBCB (CURATIVE XA3)

The curative XA3 was synthesized using the reaction scheme presented in Scheme 4. NaH (0.43 g, 18 mmol) was added over 30 min to a solution of bishydroxypolybutadiene (9.6 g, 8.0 mmol HO-PB-OH) in dimethylformamide (DMF) (100 mL) at room temperature under a N_2 atmosphere. After stirring the resulting solution at room temperature for 30 min, 1-BrBCB (1.8 g,



FIG. 3. — Comparison of the ¹⁹F NMR spectra of PPFS and PPFS-BCB_n; the F resonances are identified ortho, meta, and para relative to the polymer backbone.



SCHEME 4. — Synthesis scheme of curative XA3, BCB-PB-BCB.

9.8 mmol) was added all at once, and the solution was stirred at 90 °C for 15 h. The reaction mixture was cooled to room temperature, and additional NaH (0.50 g, 21 mmol) was added over 30 min, followed by stirring for 30 min. Additional 1-BrBCB (1.8 g, 9.8 mmol) was then added all at once. After stirring at 90 °C for 48 h, methanol (5 mL) was added to quench the excess NaH, and the solution was poured into water (250 mL). The aqueous mixture was extracted four times with Et_2O (150 mL each), and the combined extracts were dried over MgSO₄. After filtration, the solvent was removed by rotary evaporation to yield 9.9 g (88%) BCB-PB-BCB as a dark-brown viscous oil. The ¹H NMR spectrum of XA3 is presented in Figure 5.

PREPARATION OF SBR RUBBER COMPOUNDS

Compounds with and without the curatives were prepared using a two-step process in a Brabender Plasticorder internal mixer of internal volume 85 cm³. Tables I and II list the recipe of the compounds prepared using sulfur and BCB-based compounds. In the first stage, the desired amounts of rubber, zinc oxide, and stearic acid were mixed for 5 min at 80 °C and 60 rpm. In the second stage, predetermined amounts of sulfur and accelerators were mixed with the compounds obtained in the first stage for 3 min at 50 °C and 40 rpm to avoid premature crosslinking of rubber. The compounds were cured in a mold of dimension 15 cm \times 15 cm \times 2 mm using a Wabash compression molding press at 160 and 180 °C under pressure that was raised from 25 to 65 MPa during the process. The temperatures chosen are in the range of 160–190 °C, in which the differential scanning calorimetry exotherm peaks for conventional accelerated sulfur curing systems are observed. In each case, 10% excess material was used to ensure complete filling of the mold. The materials were cured for a time (t₉₅) for the torque to reach 95% of the maximum value. The value of t₉₅ was determined using moving die rheometer (MDR) cure curves.



FIG. 4. — ¹H NMR (300 MHz) spectrum of BCB-EOEO-BCB (XA2).



FIG. 5. — ¹H NMR (300 MHz) spectrum of BCB-PB-BCB (XA3).

INFLUENCE OF CB

CB is a conventionally used filler for tire tread compounds. In view of this, the effects of CB on the cure characteristics and crosslink density were investigated. The typical formulations used in conjunction with curatives XA1, XA2, and XA3 and with CB loading of 30 phr are presented in Tables III and IV. The compounds containing CB as the filler were mixed in two stages to prepare both the master batch and the final batch. In the first stage, the compounds were mixed in a Brabender mixer set at 65 rpm and 80 °C. The volume of the mixer was 80 cm³, and a fill factor of 0.7 was used. The rubber was masticated for 1 min, after which half of the amount of CB filler was added. After a mixing time of 3 min, the rest of the CB along with TDAE was introduced in the mixer. At 5 min, the activators, ZnO and stearic acid, were added, and the mixing was continued for an additional 2 min. In the second stage of mixing, a two-roll mill was used in which the master batch containing rubber, CB, and activators was heated for 1 min and subsequently sulfur, curatives, and accelerators were added and mixed to prepare the final batch. For this purpose, the two-roll mill was heated to 50 °C, and the speed of the rollers was set at 11 rpm. The milled sheet was folded and rolled 20 times, to ensure effective mixing. The compounds were later cured in the compression molding press at 160 and 180 °C under pressure raised from 25 to 65 MPa during the process.

TABLE I FORMULATION OF RUBBER COMPOUNDS CONTAINING XA1 (PPFS-BCBN)			
	Control	PPFS-BCB (XA1)	
SBR, phr	100	100	
Zinc oxide, phr	2.5	2.5	
Stearic acid, phr	2	2	
Sulfur, phr	1.3	1.3	
TBBS, phr	3	3	
PPFS-BCB, phr	0	3	

	Control	bisBCB-based molecules (XA2 and XA3)	
SBR, phr	100	100	
Zinc oxide, phr	2.5	2.5	
Stearic acid, phr	2	2	
Sulfur, phr	1.5	1.5	
2-mercaptobenzothiazole, phr	0.4	0.4	
Tetramethylthiuram disulfide, phr	0.75	0.75	
BCB-based curative, phr	0	3	

TABLE II FORMULATION OF RUBBER COMPOUNDS CONTAINING BISBCB-BASED MOLECULES XA2 (BCB-EOEO-BCB) AND XA3 (BCB-PB-BCB)

CHARACTERIZATION

CHARACTERIZATION OF CURE

An MDR was used at 7% strain and 1.67 Hz frequency to determine the cure characteristic of rubber compounds. For this purpose, approximately 5 g of rubber compound was placed between two plates and cured at 160 and 180 °C. The cure times, t₁₀, t₉₀, and t₉₅, corresponding to 10, 90, and 95% of the maximum torque values, respectively; the scorch times (t_{s1}, t_{s2}) ; and rheometer torques (ML, MH) were obtained. The scorch times t_{s1} and t_{s2} represent, respectively, the prevulcanization time in which the rubber can still be processed; torque values ML and MH represent, respectively, the minimum and maximum values of torque. The torque at 95% curing (S_{95}) was calculated from Eq. 1.

$$(MH - ML) \times 0.95 + ML = S_{95} \tag{1}$$

CROSSLINK DENSITY

In this work, both C–C and C–S crosslinks were formed in the compounds. The crosslinks per unit volume were determined using the Flory-Rehner equation, presented in Eq. 2.^{23–25} For this purpose, specimens of known weight were immersed in toluene, which is a good solvent for SBR,

TABLE III FORMULATION OF RUBBER COMPOUNDS CONTAINING XA1 (PPFS-BCBN) AND CB FILLER			
	Control	XA1	
SBR, phr	100	100	
Zinc oxide, phr	2.5	2.5	
Stearic acid, phr	2	2	
Sulfur, phr	1.3	1.3	
TBBS, phr	3	3	
PPFS-BCB, phr	0	3	
Carbon black N234, phr	30	30	
TDAE	15	15	

TABLE III
FORMULATION OF RUBBER COMPOUNDS CONTAINING XA1 (PPFS-BCBN
AND CB FILLER

	Control	XA2/XA3
SBR, phr	100	100
Zinc oxide, phr	2.5	2.5
Stearic acid, phr	2	2
Sulfur, phr	1.5	1.5
2-mercaptobenzothiazole, phr	0.4	0.4
Tetramethylthiuram disulfide, phr	0.75	0.75
BCB-based curative, phr	0	3
Carbon black N234, phr	30	30
TDAE	15	15

TABLE IV FORMULATION OF RUBBER COMPOUNDS CONTAINING XA2 (BCB-EOEO-BCB) OR XA3 (BCB-PB-BCB) AND CB FILLER

for nearly 72 h. The solvent was changed every 24 h, thus ensuring removal of all uncrosslinked rubber materials. The residue was weighed after 72 h, and the crosslink density (V_e) was determined using Eq. 2.

$$V_e = -\frac{\ln(1 - V_r) + V_r + \chi V_r^2}{V_1 \left(V_r^{1/3} - \frac{1}{2}V_r\right)}$$
(2)

In Eq. 2, V_1 is the molar volume of toluene, V_r is the rubber volume fraction, and $\chi = 0.446$ represents the rubber–solvent interaction parameter.

RESULTS AND DISCUSSION

CURE CHARACTERISTICS

The BCB–sulfur hybrid curative system was anticipated to produce curing of rubber at lower temperatures due to lower cure activation temperature of the 1-substituted BCB moieties. However, the results indicated a lower curing time compared with the conventional sulfur-cured systems when both systems were cured at 160 and 180 °C. Note that reduction of the curing time is preferred in rubber industries over reduction of the curing temperature. The cure characteristics of specific cure systems are discussed in the following sections.

CURING USING XA1

The system containing mixed curative sulfur-XA1 showed a 10-15% reduction in the curing time, as is evident from the MDR curves presented in Figure 6. In this case, the MDR torque was monitored over a period of 60 min when the samples were cured at 180 °C.

The data presented in Table V and Figure 6 show the following trends. First, the values of both ML and MH were higher than the control when XA1 was used as the curing agent. Note that a higher torque indicates a higher degree of cure and higher crosslink density. The materials with XA1 curatives also reduced the value of t_{95} by almost 2 min, from 14.33 min of the control material to 12.34 min for the XA1 curative with 20% substitution. The scorch time (t_{s1} and t_{s2}) also showed reduction by 6%, and the torque at 95% cure time showed about a 9% increase compared with the control materials. The data listed in Table V indicate that the 10% versus 20% substitution in XA1 structure had no significant effect on the cure characteristics. The additional C–C linkages produced



FIG. 6. — Characteristic cure curves with XA1 (PPFS-BCB_n) with 10%, 20% substitution cured at 180 °C.

by XA1 curatives in conjunction with the C–S linkages from sulfur curing produced materials with almost 10% increase in the value of crosslink density, as shown in Figure 7.

CURING USING BISBCB-BASED MOLECULES

BCB-EO-BCB (XA2). — The cure characteristic curve of compounds cured with XA2 is presented in Figure 8, and the corresponding relevant data are listed in Table VI. It appears that the curative XA2 did not perform well and that the compound *MH* value and S_{95} values were about 17% lower than the control. Although the t_{10} and t_{90} values were lower, the t_{95} value was slightly greater than that of the control materials. However, the scorch time values t_{s1} and t_{s2} show a large reduction (27 and 23%, respectively) compared with the control materials.

The lower cure torque (MH) in compounds containing BCB indicates that there are interactions between BCB molecules and sulfur. These interactions can be investigated through NMR studies for a model compound containing BCB and sulfur and will be reported elsewhere. The data in Figure 9 indicate a 15% reduction of crosslink density values for compounds with XA2 curing agent commensurate with what was observed from the values of MH.

TABLE V CURE CHARACTERISTIC VALUES FOR XA1 (PPFS-BCBN) AT 180 °C			
	Control	XA1 (10% BCB)	XA1 (20% BCB)
ML, dNm	0.47	0.49	0.52
MH, dNm	6.77	6.89	7.37
<i>MH – ML</i> , dNm	6.3	6.4	6.85
t _{s1} , min	5.38	5.37	5.07
t _{s2} , min	6.57	6.6	6.19
t ₁₀ , min	4.36	4.34	4.36
t ₉₀ , min	11.87	10.72	10.47
S ₉₅ , dNm	6.46	6.57	7.03
t ₉₅ , dNm	14.33	12.44	12.34



FIG. 7. — Crosslink density values for compounds containing PPFS-BCB_n (XA1).



FIG. 8. — Cure characteristic curve for sample containing XA2 (BCB-EOEO-BCB) cured at 180 $^\circ$ C.

CURE CHARACTERISTIC VALUES FOR XA2 (BCB-EOEO-BCB) AT 180 °C			
	Control	BCB-EOEO-BCB (XA2)	
<i>ML</i> , dNm	0.67	0.76	
MH, dNm	8.24	7.3	
MH – ML, dNm	7.57	6.54	
t _{s1} , min	2.24	1.37	
t _{s2} , min	2.73	1.81	
t ₁₀ , min	2.1	1.24	
t ₉₀ , min	11.09	11.79	
<i>S</i> ₉₅ , dNm	7.86	6.97	
t95, dNm	14.86	18.73	

TABLE VI CURE CHARACTERISTIC VALUES FOR XA2 (BCB-EOEO-BCB) at 180 $^\circ\mathrm{C}$



FIG. 9. — Crosslink density values for compounds containing BCB-EOEO-BCB (XA9).

BCB-PB-BCB(XA3). — The cure characteristic curve for compounds cured using the bisBCB with a polybutadiene spacer, XA3, is shown in Figure 10. In this case, the compounds were cured using the MDR at 160 °C for 60 min.

The data listed in Table VII show a 10% reduction in torque (*MH*) and S_{95} values and a 15% reduction in crosslink density values compared with the control materials (Figure 11). The t_{95} data show a reduction of almost 30% for XA3. However, considering the large reduction in crosslink density, such a reduction in curing time may not be useful for this compound system.

INFLUENCE OF CB ON CURE CHARACTERISTICS OF TIRE TREAD COMPOUNDS

Curing Using PPFS-BCB (XA1) in the Presence of CB Filler. — In this case, the MDR torque was monitored over a period of 60 min when the samples were cured at 180 °C. It was confirmed



FIG. 10. — Cure characteristic curve for sample containing XA3 (BCB-PB-BCB) at 160 °C.

TABLE VII CURE CHARACTERISTIC VALUES FOR XA3 (BCB-PB-BCB)			
	Control	BCB-PB-BCB (XA3)	
<i>ML</i> , dNm	0.69	0.74	
MH, dNm	8.17	7.39	
MH – ML, dNm	7.48	6.65	
t _{s1} , min	2.24	2.33	
t _{s2} , min	2.71	2.84	
t_{10} , min	2.09	2.15	
t ₉₀ , min	11.47	7.55	
<i>S</i> ₉₅ , dNm	7.8	7.06	
t ₉₅ , dNm	15.4	10.11	

earlier that the cure characteristics are independent of the BCB substitution in the XA1 curative. In view of this, PPFS–BCB with 20% BCB substitution was used in the curing study.

The data presented in Table VIII and Figure 12 show the following trends. The value of *MH* is lower compared with the control compound when CB was added. This contradicts what was observed when the formulation had no CB filler (Table V). *MH* is reduced by almost 10%, and the scorch times (t_{s1} and t_{s2}) show an increase of 20%. Even though the t_{90} values are lower for the compound containing PPFS-BCB_n, such a reduction is not significant, as the *MH* values are lower. The reduction in torque could be explained by interference of the CB in the crosslinking mechanism. The curative PPFS-BCB could have possible arene-perfluoroarene interactions with the CB, thus hindering the curing process (Figure 1). The reduction in *MH* can be supported by a reduced crosslink density value, as shown in Figure 13.

Curing Using XA2. — The cure characteristics for compounds containing CB with and without BCB-EOEO-BCB (XA2) were monitored using an MDR at 160 °C for 60 min. The reduction in



FIG. 11. — Crosslink density values for compounds containing XA3 (BCB-PB-BCB).

SUBSTITUTION AND CB AT 180 C			
	Control	PPFS – BCB (20%)	
<i>ML</i> , dNm	0.63	0.65	
MH, dNm	12.97	11.81	
<i>MH – ML</i> , dNm	12.34	11.16	
t _{s1} , min	2.17	2.6	
t _{s2} , min	2.94	3.22	
t ₁₀ , min	2.42	2.7	
t ₉₀ , min	11.14	7.8	
S ₉₅ , dNm	12.353	11.252	
t ₉₅ (dNm)	15.1	9.96	

TABLE VIII CURE CHARACTERISTIC VALUES FOR XA1 (PPFS-BCBN) WITH 20% SUBSTITUTION AND CB AT 180 °C

maximum torque (*MH* value) is evident from the data presented in Figure 14. The reduction in torque can be explained in terms of interactions between BCB moieties and sulfur. These interactions can be studied with the help of NMR spectroscopy, which is beyond the scope of the present work. The values of *ML*, *MH*, and scorch times t_{10} and t_{90} are presented in Table IX.

The reduction in *MH* for compounds containing XA2 is nearly 11% for compounds without CB (Table VI). However, this reduction increases to 15% for compounds containing CB. The addition of CB further reduces the maximum torque value, which is indicative of lower crosslink density and can be further explained using NMR spectroscopy. It is evident from Table IX that the t_{10} value for the compound containing XA2 is lower than the control compound, but the t_{90} and t_{95} values are higher than that of the control compound. The reduction in crosslink density values for the compounds containing XA2 is presented in Figure 15.



FIG. 12. — Characteristic cure curves for systems containing XA1 (PPFS-BCBn, 20%) and CB at 180 °C.



FIG. 13. — Crosslink density values for compounds containing PPFS-BCB_n (XA1, 20% BCB) in the presence of CB.

Curing Using XA3. — The cure characteristics of the compounds with and without XA3 were studied at 160 °C in an MDR, as shown in Figure 16.

In recipes without CB, the reduction in the value of MH was nearly 10%. However, with the addition of CB filler, this reduction in torque for BCB-PB-BCB–containing molecules reduced to only 2%, which can be considered insignificant. Thus, the addition of CB filler reduces the difference between MH values for compounds with and without BCB-PB-BCB molecules. NMR spectroscopy of these compounds may aid in further understanding of this trend. The crosslink density values of the compounds with and without XA3 are compared in Figure 17.



FIG. 14. — Cure characteristics for compounds containing XA2 (BCB-EOEO-BCB) and CB cured at 160 °C.

CURED AT 160 °C			
Control	XA2		
0.96	0.94		
12.84	10.9		
11.88	9.96		
1.72	1.47		
2.01	1.83		
1.78	1.47		
9.44	12.02		
12.25	10.4		
12.52	19.39		
	Control 0.96 12.84 11.88 1.72 2.01 1.78 9.44 12.25 12.52		

TABLE IX CURE CHARACTERISTIC VALUES FOR XA2 (BCB-EOEO-BCB) WITH CB CURED AT 160 °C

Although the present study elucidated only the reduction of curing times, some follow-up work is due on evaluation of the effects of C–C crosslinks on mechanical properties of the cured compounds, especially on crack propagation and tear properties.²⁶

CONCLUSION AND FUTURE WORK

It can be concluded from the data presented in this article that the curative XA1 (PPFS–BCB_n) used along with sulfur helped reduce the curing time by almost 15% when cured at 180 °C. This reduction is considerable and beneficial for reduction of processing time. The extent of BCB substitution (10–20%) in these compounds did not exert noticeable effects on cure properties. The compounds containing bisBCB (XA2 and XA3) showed a decrease in t_{90} , although the *MH* values



FIG. 15. — Crosslink density values for compounds containing BCB-EOEO-BCB (XA2) in the presence of CB.



FIG. 16. — Characteristic cure curves with XA3 (BCB-PB-BCB) at 160 °C.

also decreased by 10%. A reduction in *MH* is not desired, as it further affects the mechanical properties and the performance of the tires. These trends indicate strong interactions between BCB moieties and sulfur while producing crosslinked networks.

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FIG. 17. — Crosslink density values for compounds containing BCB-PB-BCB (XA3).

REFERENCES

- ¹M. Morton, *Rubber Technology*, Springer Science & Business Media, Berlin, 2013.
- ²J. E. Mark, B. Erman, and M. Roland, *The Science and Technology of Rubber*, 4th ed., Academic Press, San Diego, CA, 2013.
- ³K. C. Baranwal and H. L. Stephens, *Basic Elastomer Technology*, Rubber Division of the American Chemical Society, Washington, DC, 2001.
- ⁴J. L. Leblanc, Prog. Polym. Sci. 27, 627 (2002).
- ⁵M. J. Wang, RUBBER CHEM. TECHNOL. **71**, 520 (1998).
- ⁶B. B. Boonstra, *Polymer* **20**, 691 (1979).
- ⁷G. Heinrich, M. Kluppel, and T. A. Vilgis, Curr. Opin. Solid State Mater. Sci. 6, 195 (2002).
- ⁸A. Scurati and C. J. Lin, RUBBER CHEM. TECHNOL. 79, 170 (2006).
- ⁹K. W. Stöckelhuber, A. S. Svistkov, A. G. Pelevin, and G. Heinrich, *Macromolecules* 44, 4366 (2011).
- ¹⁰H. M. da Costa, V. D. Ramos, C. B. da Costa, and M. C. de Andrade, J. Therm Anal. Calorimetry 129, 755 (2017).
- ¹¹P. J. Nieuwenhuizen, J. Reedijk, M. Van Duin, and W. J. McGill, RUBBER CHEM. TECHNOL. 70, 368 (1997).
- ¹²M. R. Krejsa and J. L. Koenig, RUBBER CHEM. TECHNOL. 66, 376 (1993).
- ¹³R. P. Dinsmore and W. W. Vogt, RUBBER CHEM. TECHNOL. 1, 410 (1928).
- ¹⁴J.-K. Yang, W. Park, C. Ryu, S. J. Kim, D. Kim, G. Seo, J. H. Kim, and C. B. Chung, RUBBER CHEM. TECHNOL. **91**, 595 (2018).
- ¹⁵J. Kruželák, R. Sýkora, and I. Hudec, RUBBER CHEM. TECHNOL. **90**, 60 (2017).
- ¹⁶T. L. Fishback and M. F. Farona, J. Polym. Sci. A Polym. Chem. 31, 2747 (1993).
- ¹⁷T. L. Fishback and M. F. Farona, *Polym. Bull.* 33, 385 (1994).
- ¹⁸F. R. Jensen, W. E. Coleman, and A. J. Berlin, *Tetrahedron Lett.* 3, 15 (1962).
- ¹⁹J. L. Segura and N. Martín, Chem. Rev. 99, 3199 (1999).
- ²⁰C. Pugh and A. R. Amrutkar, U.S. Patent 20160096932 A1, October 1, 2015.
- ²¹C. Pugh, J. S. Baker, and W. K. Storms, SynLett 25, 147 (2014).
- ²²K. Bahl, N. Swanson, C. Pugh, and S. C. Jana, *Polymer* **55**, 6754 (2014).
- ²³A. J. Marzocca, A. R. Garraza, and M. A. Mansilla, Polym. Test. 29, 119 (2010).
- ²⁴A. J. Marzocca, Eur. Polym. J. 43, 2682 (2007).
- ²⁵P. J. Flory and J. Rehner Jr, J. Chem. Physics 11, 512 (1943).
- ²⁶G. Rong, G. R. Hamed, and J. Jiang, RUBBER CHEM. TECHNOL. **89**, 631 (2016).

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