# Curing Reaction of Elastomers with Triazine Thiols and Sulfen Amides

KUNIO MORI and YOSHIRO NAKAMURA, *Department of Applied Chemistry, Faculty of Engineering, Iwate University, Morioka, 020, Japan*

Synopsis

Curing reaction of elastomers with triazine thiols and sulfen amides in the presence of ZnO and stearic acid was investigated for curing parameters and curing mechanism. The curing parameters such as curing rate, induction period, and curing efficiency were influenced by the pKa of thiol groups in triazine thiols and amines corresponding in sulfen amides, by the steric hindrance of 6-substituted groups in triazine thiols and on amino groups in sulfen amides, by the molar ratio of sulfen amides to triazine thiols, and by the reacting positions and the properties of elastomers. Triazine thiols acted as curing agents. Sulfen amides played two important roles in curing elastomers with triazine thiols. They gave poly(triazinyl disulfide) which is a curing precursor. Curing activators are formed in the reaction of the precursors, sulfen amides, and ZnO. The activators react with elastomers to give crosslinks, pendants and triazine dithiols or triazinyl disulfide oligomers. The pendants react with sulfen amides to give the crosslinks. The triazine thiols or triazinyl disulfide oligomers react with sulfen amides to reproduce the curing precursors. The structure of crosslinks is estimated to be
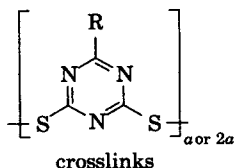
crosslinks

INTRODUCTION

Recently, triazine thiols and their derivatives have been developed as crosslinking agents for halogen-containing elastomers,[1-3] as coupling agents for adhesion between elastomers and metals such as tire cords,[4-6] and between elastomers in fuel hold hoses,[6,7] and as stabilizers for heat aging resistance and sour gasoline.[8,9] At the present, some of these are commercially used in Japan. Triazine thiols have become increasingly importnt as polyfunctional additives to prepare composite materials, since they react easily with various elastomers[10] or with metals and their oxides.[11] Therefore, their reactions should be sufficiently studied to develop various applications. In a previous paper, we reported the curing reaction of unsaturated elastomers with triazine thiols and benzothiazolyl disulfide or peroxides.[10,12]

In this paper, the curing reaction of various unsaturated elastomers with triazine thiols and sulfen amides has been investigated for kinetic parameters, the structure of crosslinks, and the curing mechanism.

EXPERIMENTAL

Materials and Reagents

Unsaturated elastomers were commercially available. The commercial name, the abbreviation name, and the reacting points of the elastomers are shown in Table I. Triazine thiols were purchased from Sankyo Kasei Co., Ltd. (Osaka, Japan). Sulfen amides were purchased from Kawaguchi Chemical Industry Co., Ltd. The abbreviation of triazine thiols and sulfen amides are shown in Table II.

Compounding and Curing

Recipe for elastomer compounds are shown in Table III. Elastomers and additives were mixed on a two-roll mill at 60°C. Curing measurements for the blends were made on an oscillating disk rheometer (Toyoseiki Co. Ltd.,). The degree of curing was expressed in torque and plotted against time of curing. The curing curves obtained were employed to determine the kinetic parameters such as rate constant, induction period, and torque after curing (curing torque, $f_m - f_0$; f_m = maximum torque, f_0 = minimum torque). These parameters show the degree of curing rate, scorch time, and curing efficiency.

Reaction of Trizaine Thiols with Sulfen Amides

Molar Ratio 1/1: Mixture of triazine thiols (0.01 mol) with sulfen amides (0.01 mol) in methylene dichloride (50 mL) containing acetic acid (0.01 mol) was stirred at 30°C for 6 h. The mixture was poured into methanol (200 mL) to give poly(triazinyl disulfide) (PTDS) in good yield; the methanol solution was evaporated to give the cyclohexyl amine of 2-mercaptobenzothiazole (CMBT) in good yield.

Molar Ratio 1/2: Triazine thiols (0.01 mol) were added into the methylene dichloride (50 mL) solution of sulfen amides (0.02 mol) in the presence of acetic acid (0.02 mol) over a period of 30 min at 30°C. The mixture was poured into methanol (200 mL) to give 6-substituted-2,4-bis(benzothiazolyl dithio)1,3,5-triazine (SBBT) for *N*-cyclohexyl 2-benzothiazole sulfen amides or 6-subsituted-2,4-bis(morpholinyltrithio)1,3,5-triazine (SBMT) for dithiomorpholine (DTM), after stirring for 30 min at 30°C. The results are shown in Table IV.

Measurement and Analysis

The network chain density of curing products was determined from the Flory–Rehner equation, measuring equilibrium swelling ratio after allowing cured samples to stand (0.2 g) for 48 h at 20°C in a solvent (20 mL).[13,14] The structure of crosslinks was estimated from the measurement of network chain density before and after the thiophenol reduction of the curing products[15] and of the IR spectra for the sample extracted with solvents. Nitrogen and sulfur contents in triazine thiol derivaties, and the extracted samples were determined by Keldahl and Schoniger methods.

TABLE I
The Commercial Name, Abbreviation, and Reacting Points of Unsaturated Elastomers

Elastomers	Commercial Name	Abbreviation	reacting point	μ^a
Polyisoprene	Nipol IR 2200	IR	$\begin{array}{c} CH_3 \\ | \\ \end{array}$	0.39 (toluene)
Polyisobutylene	JSR Butyl 420	IIR	$-CH_2C=CHCH_2-$	—
Polybutadiene	Nipol BR 1200	BR		0.39 (benzene)
Styrene–butadiene copolymer	Nipol SBR 1500	SBR	$-CH_2CH=CHCH_2-$	—
Acrylonitrile–butadiene copolymer	JSR N230S	NBR		—
Ethylene–propylene terpolymer	JSR EP-24	EPDM	$\begin{array}{c} -CH-CH- \\ | \quad CH_2 \\ CH \quad CH \\ | \quad | \\ CH-C=CHCH_3 \end{array}$	0.44 (n-heptane)
Acryl polymer	JSR AR 420	AR		—
Propylene oxide–allylglycidyl ether copolymer	Parel 58	Parel	$-CH_2CH=CH_2$	—

^{a} Flory–Huggins constant; ( ) = Solvent

TABLE II
The Abbreviation of Triazine Thiols or Sulfen Amides and Their pKa

Triazine thiols or sulfen amides	Abbreviation	pKa[a]
1,3,5-Triazine-2,4,6-trithiol	TT	6.5
6-Anilino-1,3,5-triazine-2,4-dithiol	AF	5.5
6-Dibutylamino-1,3,5-triazine-2,4-dithiol	DB	4.1
N-Cyclohexyl-2-benzothiazole sulfen amide	CBS	10.6
t-Butyl-2-benzothiazole sulfen amide	BBS	10.4
N-Oxydiethylene-2-benzothiazole sulfen amide	OBS	8.4
N-Dicyclohexyl-2-benzothiazole sulfen amide	DCBS	11.1
Dithiodimorpholine	DTM	8.4

[a] pKa of thiol group in triazine thiols or corresponding amines in sulfen amides.

RESULTS AND DISCUSSION

Essential Component for Curing Reaction

In general, the curing reaction of elastomers is well known to occur by the synergistic effects of various additives such as curing agents, accelerators, metal activators, retarders, and high aliphatic acids. So the curing of SBR or EPDM with triazine thiols and sulfen amides was first investigated to elucidate the essential components as shown in Figure 1. The four types of additives such as triazine thiols, sulfen amides, ZnO, and stearic acid were necessary to cure sufficiently. The curing is remarkably retarded even in the absence of one of the four components. Such a tendency is observed regardless of the type of elastomers for the curing of unsaturated elastomers with triazine thiols and sulfen amides. The curing was also influenced by the concentration of components in the blends. The curing parameters changed with concentration of ZnO up to 3 phr and stearic acid up to 1 phr, but reached constant values over the concentrations. The influence of concentration of triazine thiols and sulfenamides is described below.

Effect of Sulfen Amides

Curing parameters such as curing rates, scorch time, and curing torques are influenced by the structure and the chemical properties of sulfen amides as shown in Figure 2. The curing rates and torques increased with increasing pKa of amines (Table II), which are formed from sulfen amides during curing, whereas scorch time decreased with increasing pKa. The steric
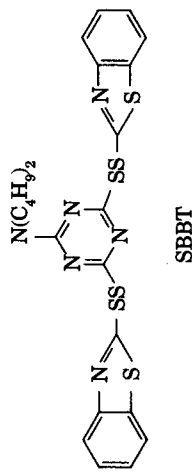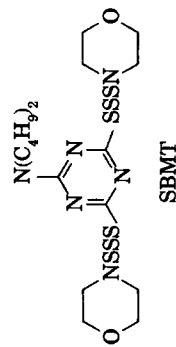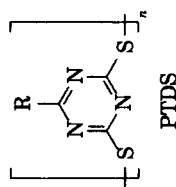
TABLE III
Recipe for Elastomer Compounds

Elastomer	100 parts
Triazine thiol	Variable
Sulfen amide	Variable
ZnO	5 phr
Stearic acid	2 phr

TABLE IV
Reaction Products of Triazine Thiols with Sulfen Amides

Triazine thiols	Sulfen amides	Molar[a] ratio	Products[b]	mp (°C)	Elemental analysis			
					N	(%)	S	(%)
TT	CBS	1	PTDS	250	19.6	(19.83)	51.1	(51.80)
AF	CBS	1	PTDS	250	23.8	(23.93)	27.0	(27.40)
DB	CBS	1	PTDS	77–86	1919	(20.74)	23.6	(23.14)
DB	DTM	1	SBMT	99–100	14.6	(14.74)	33.0	(33.68)
DB	CBS	2	SBBT	149–150	13.6	(13.95)	31.7	(31.92)
DB	DTS	2	SBMT	99–100	14.5	(14.74)	33.6	(33.68)

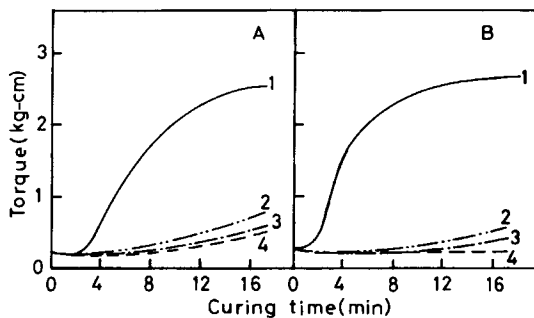[a] Molar ratio of sulfen amides to triazine thiols.
[b]

PTDS

SBMT

SBBT

Fig. 1. Essential components in the curing of EPDM(A) or SBR(B) with triazine thiols and sulfen amides at 160°C: (A): (1) TT 3,CBS 3, ZnO 5, and stearic acid 2 phr; (2) TT 3, CBS 3, and ZnO 5 phr; (3) TT 3,CBS 3, and stearic acid 2 phr; (4) TT 3 and CBS 3 phr. (B): (1) AF 2.4,DTM 2.5,ZnO 5, and stearic acid 2 phr; (2) AF 2.4,DTM 2.5, and ZnO 5 phr; (3) AF 2.4,DTM 2.5, and stearic acid 2 phr; (4) AF 2.4 and DTM 2.5 phr.

hindrance of the substituents on the sulfen amide has a significant effect on the curing parameters. Sulfen amides with bulky alkyl groups retard the curing reaction and lower the curing torques. As a result, curing reactivity increases in the order of DTM < OBS < BBS < DCBS < CBS for sulfen amides, and the curing torques do in the order of DTM < DCBS < OBS < BBS < CBS, respectively. A similar tendency was also observed regardless of the type of triazine thiols and elastomers.
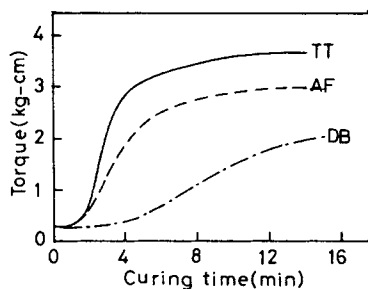
Effect of Triazine Thiols

In the present curing system, the kinds of triazine thiols have an important effect on the curing reaction and torques. Figures 3 and 4 show the effect of triazine thiols on the curing of unsaturated elastomers (EPDM or SBR) with triazine thiols and sulfen amides (CBS or DTM). The effect of
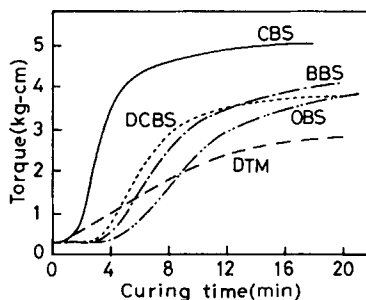
| Sulfen amides	CBS	BBS	OBS	DCBS	DTM
Torque (kg · cm)	5.0	4.3	4.0	3.8	2.5
k (min^{-1})	0.62	0.22	0.15	0.38	0.11
t_0 (min)	2.0	3.9	5.4	3.5	2.0

Fig. 2. Effect of sulfen amides on the curing of EPDM with triazine thiols (3 phr) and sulfen amides (34 mmol) in the presence of ZnO (5 phr) and stearic acid (2 phr) at 160°C.

Triazine thiols	TT	AF	DB
Torque (kg · cm)	3.6	2.8	
k (min^{-1})	0.26	0.50	0.17
t_0 (min)	2.1	2.3	4.8

Fig. 3. Effect of triazine thiols on the curing of EPDM with triazine thiols (15 mmol) and CBS (7.9 phr) in the presence of ZnO (5 phr) and stearic acid (2 phr) at 160°C.

triazine thiols on the curing reaction differed from the kinds of sulfen amides, regardless of elastomers. For the curing of EPDM in the combination of triazine thiols and CBS, the curing efficiency increased in the order of DB < AF < TT, and the curing rate increased in the order of DB < TT < AF. This is due to the reason that their parameters are influenced by the pKa of triazine thiols and the steric hinderance of 2-substituted groups. While the substituted group in TT has the smallest steric hinderance in the triazine thiols, the curing efficiency of TT is the highest. As AF compensates for pKa and stearic hinderance, it gives the highest curing rate. The similar tendency is observed for sulfen amides except for DTM. On the other hand, the curing efficiency and rate increased in the order of TT < DB < AF for triazine thiols when DTM was used as a sulfen amide. This occurs because the parameters depend upon the compensation of the
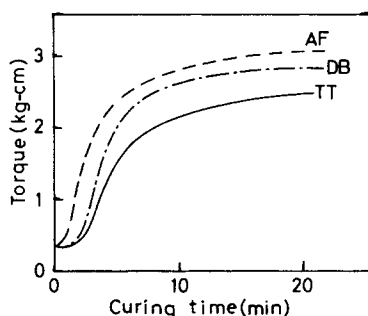
Triazine thiols	TT	AF	DB
Torque (kg · cm)	2.0	2.6	2.3
k (min^{-1})	0.27	0.39	0.34
t_0 (min)	2.3	1.0	2.2

Fig. 4. Effect of triazine thiols on the curing of EPDM with triazine thiols (10 mmol) and DTM (2.5 phr) in the presence of ZnO (5 phr) and stearic acid (2 phr) at 160°C.

pKa and the steric hinderance of triazine thiols since the steric hinderance of sulfen amide group in DTM is very small.

Effect of Molar Ratio of Sulfen Amide to Triazine Thiols

To estimate the synergism of sulfen amides and triazine thiols, the effect of molar ratios has been investigated. Figure 5 shows the effect of molar ratio of CBS to TT on the curing parameters in the curing of EPDM at 160°C. The curing rate increased with an increase in molar ratio, and the induction period decreased. That is, the curing reaction is accelerated with an increase in the concentration of CBS. The curing efficiency increased up to the molar ratio of 2, and reached a constant value over the molar ratio. Figure 6 shows the relation between the network chain density and the molar ratio. The network chain density also increased up to the molar ratio of 2. These results suggest that 2 mol of CBS are necessary to form 1 mol of crosslinks, using 1 mol of triazine thiols.

Effect of Kinds of Elastomers

· The kinds of elastomers have a significant influence on the curing reaction. This is because the chemical and physical properties such as the reacting points and polarity of elastomers and the solubility of additives differ with specific elastomer. Figures 7 and 8 show the curing curves and the obtained curing parameters in the curing of elastomers with TT and CBS or with AF and DTM. The curing rate increased in the order of IIR < AR < EPDM < Parel < BR < IR < NBR for the TT–CBS curing system and of IIR < AR < EPDM < Parel < BR < NBR < SBR < IR for the AF–DTM curing system. The reacting points are generally active in the order of ethylidene norbornene < $-CH_2CH=CH_2$ < $-CH_2C(CH_3)=CHCH_2-$ < $-CH_2CH=CHCH_2-$ for the present curing systems. The concentration of reacting points and the porality of elastomers appear to be independent of the curing rate. The difference in the two curing systems above is due to the fact that in a curing precursor and the curing mechanism, the former curing system gives triazinyl crosslinks, but the latter gives both sulfur and triazinyl crosslinks.
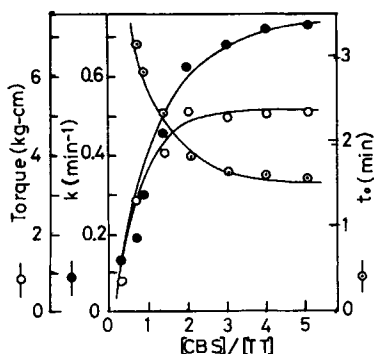

Fig. 5. Effect of molar ratio of CBS to TT ([CBS]/[TT]) on the curing parameters in the curing of EPDM with TT (3 phr) and CBS (variable) in the ZnO (5 phr) and stearic acid (2 phr) at 160°C.
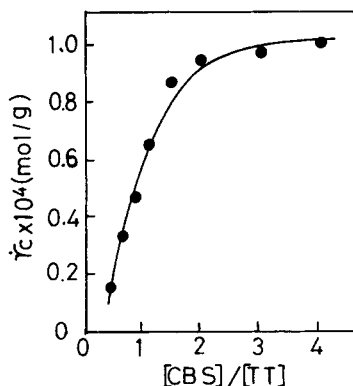
Fig. 6. Relation between crosslinking density (γ) and molar ratio ([CBS]/[TT]) in the vulcanizates of EPDM with TT (3 phr),CBS (variable),ZnO (5 phr), and stearic acid (2 phr) after curing at 160°C for 30 min.

On the other hand, the curing efficiency increased in the order of IIR < AR < Parel < IR < NBR < SBR < EPDM < BR for the TT–CBS curing system, and of AR < IIR < Parel < IR < BR < SBR < NBR < EPDM for the AF–DTM curing system. In general, nonpolar elastomers tended to give high curing efficiency for the former curing system, although the order is not applied in the latter curing system which has a complex curing mechanism. For the diene elastomers, the concentration and steric hinderance of reacting points have an influence on the curing efficiency; the curing efficiency increased in the order of NBR < SBR < BR for the former, and of IR < BR for the latter. EPDM vulcanizates have much higher curing efficiency than other elastomers with ethylidene norbornene units as reacting points. This is probably due to the difference in the polarity of elastomer and solubility of additives in elastomers.
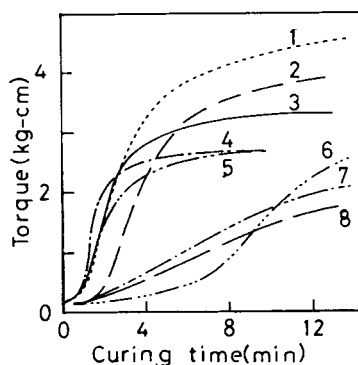
|	1	2	3	4	5	6	7	8
Elastomer	BR	EPDM	SBR	NBR	IR	Parel	AR	IIR
Torque (kg · cm)	4.2	3.7	3.0	2.4	2.4	2.3	2.0	1.8
k (min^{-1})	0.49	0.45	0.77	1.05	0.73	0.53	0.11	0.08
t_0 (min)	1.2	2.2	1.0	0.7	0.9	7.5	2.8	1.8

Fig. 7. Effect of elastomers on curing with TT (2 phr) and CBS (6 phr) in the presence of ZnO (5 phr) and stearic acid (2 phr) at 160°C.
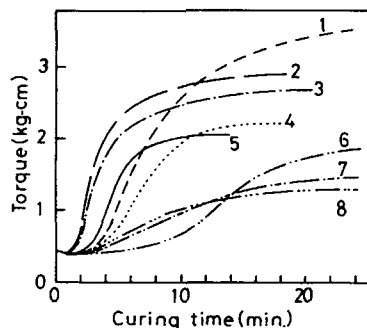
Elastomer	1	2	3	4	5	6	7	8
	EPD-M	NBR	SBR	BR	IR	Parel	IIR	AR
Torque (kg · cm)	3.5	2.3	2.0	1.8	1.6	1.4	1.2	1.1
k (min^{-1})	0.14	0.46	0.48	0.33	0.68	0.20	0.08	0.14
t_0 (min)	3.5	1.0	1.4	2.8	2.0	8.4	2.6	2.4

Fig. 8. Effect of elastomers on curing with AF (2.4 phr) and DTM (2.5 phr) in the presence of ZnO (5 phr) and stearic acid (2 phr).

The structure of crosslinks should be first determined to elucidate the curing mechanism. Table V shows the elemental analysis data and the network chain density of the vulcanizates. The elemental analysis was determined for the samples extracted with organic solvents; the used additives and their reaction products which do not link with elastomers are all excluded from the samples by extraction treatment. The cured film showed the absorption bands at 1470, 1230, 830, and 790 cm^{-1}, which are assigned to N=C and N—C stretching vibration in triazine ring, respectively. Further, the atomic ratio of S content to N content in the samples exactly agreed with that of triazinyl disulfide (TDS) units:

R

N N

— S   N   S —
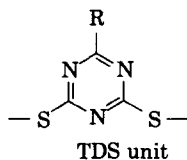
TDS unit

The results suggest that the crosslinks contain TDS units. The conversion shown (Table V) is calculated from the S content of the cured products. The ratios ($\dot{\gamma}_c/\dot{\gamma}$) in the table show the ratios of network chain density calculated from the conversion to the experimentally obtained density. The ratio means the number of TDS units in the crosslinks. The units differed by the kind of elastomers, triazine thiols and sulfen amides. In general, their compounds with steric hindrance in a reacting position tended to give the larger number of TDS units. The results are of importance in understanding the curing mechanism. The ratio ($\dot{\gamma}_c/\dot{\gamma}$) of the network chain density after

TABLE V
Elemental Data and Crosslinking Density ($\dot{\gamma}$) of Vulcanizates and Their pKa

	1	2	3	4	5	6	7
Elastomer[a]	EPDM	EPDM	EPDM	BR	IR	EPDM[b]	EPDM[b]
Triazine thiol	TT	AF	DB	TT	TT	PTT[b]	PTT[b]
Accelerator	CBS	CBS	CBS	CBS	CBS	CBS	CMBT
S (%)	0.94	0.90	0.81	1.14	0.60	1.20	1.09
N (%)	0.41	0.40	0.32	0.48	0.27	0.54	0.49
Conversion (%)[c]	61	83	81	74	39	74	67
$\dot{\gamma} \times 10^4$ (mol/g)[d]	0.81	0.71	0.42	0.98	0.28	1.07	0.70
$\dot{\gamma}_c \times 10^4$ (mol/g)[e]	0.98	1.41	1.27	1.10	0.63	1.25	1.14
$\dot{\gamma}_r \times 10^4$ (mol/g)[f]	0.55	0.30	0.08	0.70	0.05	0.70	0.10
$\dot{\gamma}_c/\dot{\gamma}$	1.22	2.00	3.02	1.12	2.25	2.20	1.63
$\dot{\gamma}_r/\dot{\gamma} \times 100$(%)	68	42	19	71	21	65	14

[a] Elastomer compound: elastomer 100 parts, triazine thiol 1.7 mmol, accelerator 3.4 mmol ZnO 5 phr, stearic acid 2 phr, 160° C × 30 min hot press.
[b] Oxidized TT polymer.
[c] ((32 × 3 or 32 × 2)/0.017) × 100.
[d] Crosslinking density of vulcanizates.
[e] Crosslinking density calculated from the conversion.
[f] Crosslinking density after reducing with thiophenol.

and before reducing with thiophenol is also indicated to estimate the structure of crosslinks. When the ratio is 1, the crosslinking chain is comprised of only one TDS unit. When the ratio is larger than 1, the crosslinks contain more TDS chains than one unit. In this case, the crosslinks contain triazinyl disulfide oligomer (TDSO) units; they are reduced by thiophenol:

TDSO
crosslinking chain
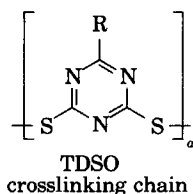
On the other hand, the molar ratio of sulfen amides to triazine thiols had a significant effect on the curing reaction. This suggests that triazine thiols react with sulfen amides in the blends during curing. The reaction was experimentally confirmed as shown in Table IV. That is, the reaction of triazine thiols with CBS give PTDS or SBBT, cyclohexyl amine (CHA), and 2-mercaptobenzothiazole (MBT) as follows:

$$(1)$$

$$(2)$$
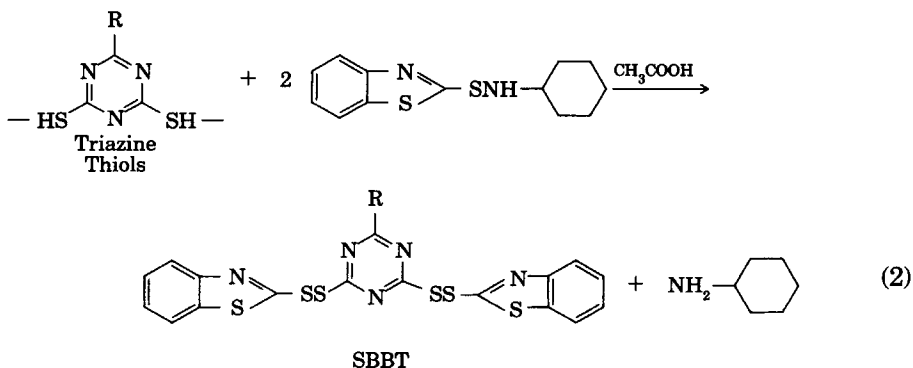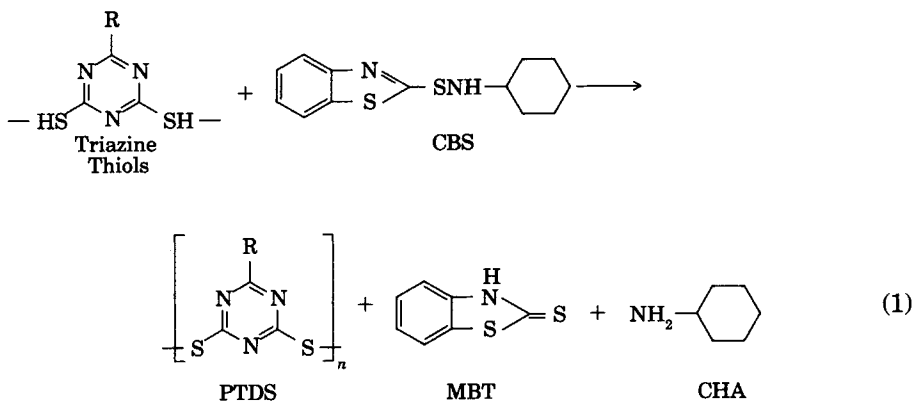
We reported that PTDS and SBBT respectively are curing precursors in the curing of SBR with triazine thiols and benzothiazolyl disulfide.[10] In the curing of elastomers with triazine thiols and CBS, the curing precursor is mainly PTDS as estimated from the structure of the crosslinks described above, but is not SBBT. However, in the curing of elastomers with triazine thiols and DTM, the curing precursor would be SBMT because no triazinyl polysulfide polymer was obtained by a model reaction. Sulfen amides have a significant function: to induce the formation of the curing precursor, by reacting with triazine thiols.

Figure 9 shows the effect of accelerators on the curing of EPDM with PTDS at 160°C. PTDS itself reacts with elastomers and needs the help of accelerators in order to functionn as a curing agent. However, the accelerators such as ZnO, stearic acid, MBT, or CBS itself were not effective for the curing reaction of elastomers with PTDS. The combination of stearic acid and ZnO, or of stearic acid, ZnO, and MBT were also ineffective as accelerating systems. However, the combination of sulfen amides, MBT, or amines and ZnO accelerated the curing reaction of elastomers with PTDS. Here, stearic acid is hardly needed in the curing reaction of EPDM with PTDS. Stearic acid plays an important role in inducing the precursor-forming reactions as shown [eqs. (1) and (2)]. In the curing reaction of elastomers with PTDS, the increase of concentration of CMBT and CHA over 2 phr did not induce the increase of curing torques, although it induced that of curing rate. Therefore, the other important function of sulfen amides is to generate the accelerators such as MBT and CHA during curing. However, the curing rate and torques in the curing reaction increased with an increase in the concentration of CBS. The result is of importance in discussing the curing mechanism.

From the above results, the curing mechanism is presented as follows: First, PTDS is formed in the blends by the reaction of triazine thiols with sulfen amides such as CBS. Next, PTDS functions as a curing activator, undergoing the accelerating effect of CMBT or CBS and ZnO as follows:
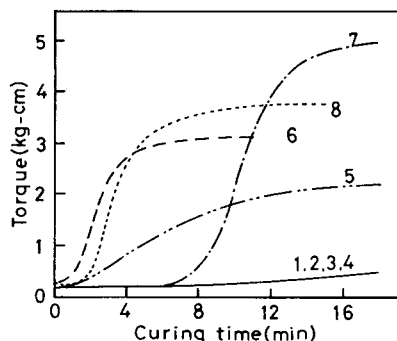
Fig. 9.   Effect of accelerators on the curing of EPDM with oxidized TT polymer (3 phr, nos. 1–7) or TT (3 phr, no. 8) at 160°C. Accelerators: (1) nil, (2) ZnO 5 phr; (3) ZnO 5 and stearic acid 2 phr; (4) MBT 5.7, ZnO 5, and stearic acid 2 phr; (5) CHA 3.3, ZnO 5, and stearic acid 2 phr; (6) CMBT 9 and ZnO 5 phr; (7) CBS 9 and ZnO 5 phr; (8) CBS 9,ZnO 5, and stearic acid 2 phr.

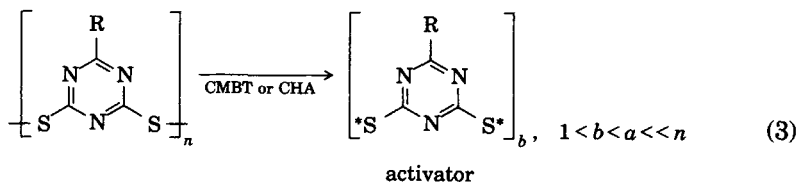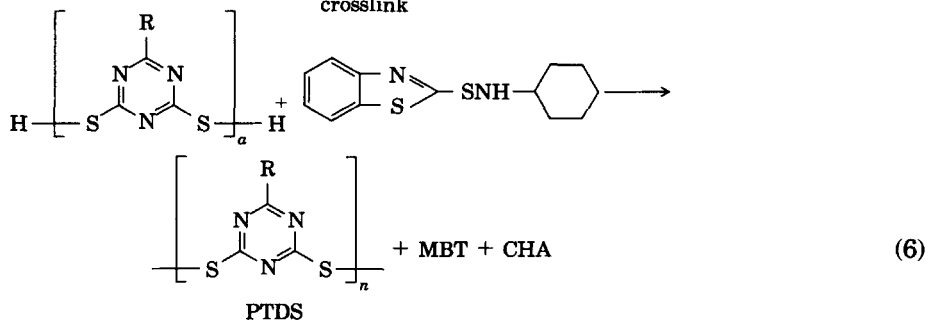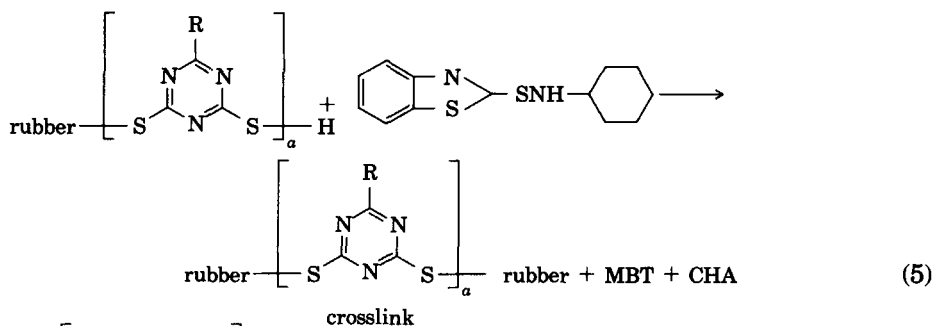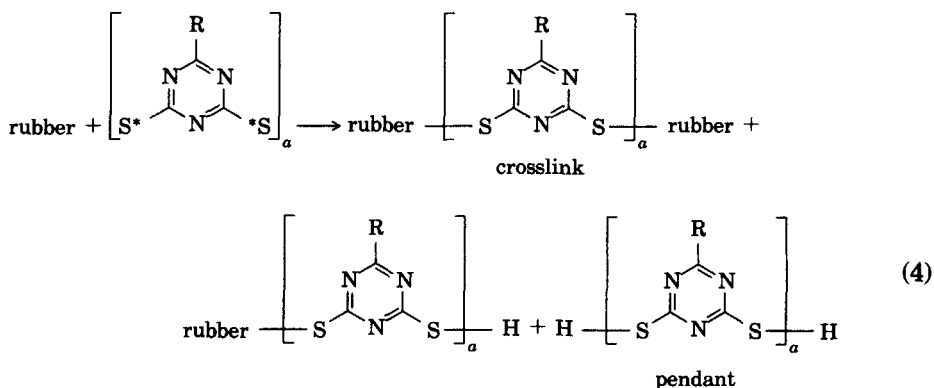$$\left[\begin{array}{c} R \\ \diagdown \text{N} \diagup \\ \text{S} \diagup \text{N} \diagdown \text{S} \end{array}\right]_n \xrightarrow[\text{CMBT or CHA}]{} \left[\begin{array}{c} R \\ \diagdown \text{N} \diagup \\ {}^*\text{S} \diagup \text{N} \diagdown \text{S}^* \end{array}\right]_b, \quad 1<b<a<<n \qquad (3)$$
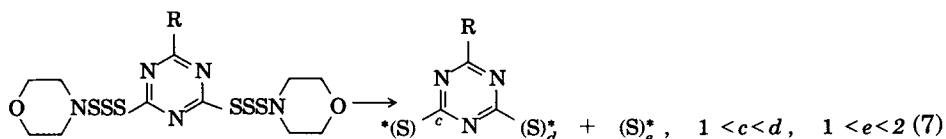
$$\text{activator}$$

The types of the formed curing activators would be thyl anions, cations, or radicals. The curing activators react at the curing position of elastomers to give crosslinks, pendants and triazine thiols or TDS olygomer units as shown in eq (4). The pendants react with CBS to give crosslinks as shown in eq. (5).

$$\text{rubber} + \left[{}^*\text{S} \diagup \text{N} \diagdown {}^*\text{S}\right]_a \longrightarrow \text{rubber} \left[\text{S} \diagup \text{N} \diagdown \text{S}\right]_a \text{rubber} +$$

$$\text{crosslink}$$

$$\text{rubber} \left[\text{S} \diagup \text{N} \diagdown \text{S}\right]_a \text{H} + \text{H} \left[\text{S} \diagup \text{N} \diagdown \text{S}\right]_a \text{H} \qquad (4)$$

$$\text{pendant}$$

$$\text{rubber} \left[\text{S} \diagup \text{N} \diagdown \text{S}\right]_a \text{H} + \text{benzothiazole-SNH-cyclohexyl} \longrightarrow$$

$$\text{rubber} \left[\text{S} \diagup \text{N} \diagdown \text{S}\right]_a \text{rubber} + \text{MBT} + \text{CHA} \qquad (5)$$

$$\text{crosslink}$$

$$\text{H} \left[\text{S} \diagup \text{N} \diagdown \text{S}\right]_a \text{H} + \text{benzothiazole-SNH-cyclohexyl} \longrightarrow$$

$$\left[\text{S} \diagup \text{N} \diagdown \text{S}\right]_n + \text{MBT} + \text{CHA} \qquad (6)$$

$$\text{PTDS}$$

The triazine thiols and TDS oligomers formed here react with CBS to give PTDS as shown in eq. (6) and then PTDS forms the curing activators by the accelerating effect of CMBT or CHA and ZnO. In the present curing,

sulfen amides have an ability to reproduce PTDS by reacting with triazine thiols

$$1 < c < d, \quad 1 < e < 2 \quad (7)$$

and TDS oligomers. As a result, sulfen amides increase the curing torques. On the other hand, in the curing of elastomers with triazine thiols and DTS, the curing activators [eq. (7)] form during blending.

References

1. Y. Nakamura, K. Mori, and S. Oka, *Nippon Gomu Kyokaishi*, **46**, 514 (1973).
2. Y. Nakamura, K. Mori, and T. Nakamura, *Rubber Chem. Technol.*, **49**, 1031 (1976).
3. K. Mori and Y. Nakamura, *J. Polym. Sci.*, **16**, 1981 (1978).
4. Y. Nakamura and K. Mori, *Kobunshi Ronbunshu*, **36**, 41, (1978).
5. Y. Nakamura, M. Saito, and K. Mori, *Kobunshi Ronbunshu*, **37**, 389 (1980).
6. K. Mori and Y. Nakamura, *J. Adhesion Soc.*, Jpn., **19**, 382 (1983).
7. K. Mori and Y. Nakamura, *Plastic, Rubber Processing Appl.*, **3**, 7 (1983).
8. K. Mori and Y. Nakamura, *J. Appl. Polym. Sci.*, **27**, 1067 (1982).
9. K. Mori and Y. Nakamura, *J. Appl. Polym. Sci.*, **28**, 691 (1983).
10. K. Mori and Y. Nakamura, *Nippon Gomu Kyokaishi*, **53**, 680 (1980).
11. K. Mori and Y. Nakamura, *Nippon Kagakukaishi*, **144** (1979).
12. Y. Nakamura, K. Mori, and F. Akaishi, *Rubber Chem. Technol.*, **50**, 660 (1977).
13. N. Ashikari and T. Kawashima, *Rubber Chem. Technol.* **42**, 1245 (1969).
14. S. Watanabe, *Nippon Gomu Kyokaishi*, **34**, 787 (1961).
15. F. P. Baldwin, P. Borzel, C. A. Cohen, and H. S. Makowski, *Rubber Chem. Technol.*, **43**, 522 (1970).