A new method of styrene-butadiene rubber curing using *in situ* generated Lewis acids

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Abstract: Heating of blends composed of styrene-butadiene rubber (SBR) and chlorosulphonated polyethylene (CSM) at $T = 453$ K in the presence of fine powdered Zn leads to curing of the elastomers involving interelastomer reactions of the blend components. Analysis of IR spectra leads to the conclusion that the curing in the studied blends is a result of the interelastomer Friedel-Crafts alkylation of the SBR phenyl rings with the elastomeric polyhalide. This reaction is catalyzed with a Lewis acid ($ZnCl_2$) generated *in situ* by the reaction of CSM with the Zn powder. This new, unconventional method can be used for the curing of the SBR/CSM blends containing selected fillers.

Keywords: interelastomer reactions, styrene-butadiene rubber, chlorosulphonated polyethylene, elastomer blends.

Nowa metoda sieciowania kauczuku butadienowo-styrenowego za pomocą kwasów Lewisa generowanych *in situ*

Streszczenie: Ogrzewanie w $T = 453$ K mieszanin zawierających kauczuk butadienowo-styrenowy (SBR) i chlorosulfonowany polietylen (CSM) w obecności rozdrobnionego Zn prowadzi do usieciowania składników. Na podstawie widm w podczerwieni (IR) stwierdzono, że sieciowanie składników mieszanki jest wynikiem interelastomerowego alkilowania w reakcji Friedela-Craftsa pierścieni fenylowych makrocząsteczek SBR elastomerycznym polihalogenkiem. Reakcje te są katalizowane kwasem Lewisa ($ZnCl_2$) generowanym *in situ* w reakcji CSM ze sproszkowanym Zn. Nowa, niekonwencjonalna metoda może być wykorzystana do sieciowania mieszanin SBR/CSM zawierających wybrane napełniacze.

Słowa kluczowe: reakcje interelastomerowe, kauczuk butadienowo-styrenowy, chlorosulfonowany polietylen, mieszaniny elastomerowe.

In our earlier studies [1—7], it was found that it is possible to cure styrene-butadiene rubber (SBR) without using a conventional crosslinking system composed of sulphur, accelerator(s) and activator(s) [8]. The SBR can be cured in a reaction involving the Friedel-Crafts alkylation of SBR phenyl rings by an elastomeric polyhalide, including chlorobutyl rubber (CIIR) or chlorosulphonated polyethylene (CSM), catalyzed with Lewis acid formed *in situ* from its precursors [1—4, 9, 10]. The precursors of the *in situ* generated Lewis acids ($ZnCl_2$, $FeCl_3$, $SnCl_2$) were CIIR or CSM as chlorine donors and ZnO, Fe_2O_3 or SnO as metal donors. In this work, we present the results of SBR curing using fine powdered metallic zinc and CSM as precursors of a Lewis acid ($ZnCl_2$) and CSM as an alkylation agent in the Friedel-Crafts reaction.

The influence of CSM type, amount incorporated into compounds and the effect of selected reinforcing fillers (carbon black and silica) on crosslinking and properties of the cured SBR/CSM blends were investigated.

EXPERIMENTAL PART

Materials

The elastomers chosen for this study were styrene-butadiene rubber (SBR, KER 1502 brand from Synthos Group) and chlorosulphonated polyethylene (CSM, Hypalon 45, 20, 40 and 30 brands from DuPont, Table 1). Metallic zinc used in our studies was brand STAPA Zinc 8 from Carl Eckart GmbH & Co with a particle size < 30 μm. As a filler, silica brand PERKSIL KS408 from Grace was used.

Sample preparation

Blends were prepared in the conventional way using a standard, laboratory, two roll-mill. Blends were pressed in an electrically heated hydraulic press at 453 K.

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Methods of testing

The vulcametric measurements were determined using rheometer type WG-02 at T = 433 K for 60 minutes according to PN-ISO 3417:1994 standard.

The crosslinking degree was determined on the basis of vulcametric measurements, equilibrium swelling in toluene and hexane (Q_{VTOL}, Q_{VHEX}) and Monney-Rivlin elasticity constants ($2C_1$) determined from Mooney-Rivlin equation [11, 12]. The degree of SBR-CSM bounding (BD_{CSM}) was estimated on the basis of sol-gel analysis, extraction with boiling acetone and determination of bound Cl content (BCC) in cured and extracted samples.

Mechanical properties: tensile strength (TS_b) and elongation at break (E_b) were measured using a Zwick tester according to the PN-ISO 37:2007 standard.

IR spectra were recorded using a Bio-Rad 175 spectrometer. The SBR/CSM blends were analyzed as films of thickness less than 40—50 μm. The spectra were taken before and after crosslinking.

RESULTS AND DISCUSSION

Preliminary studies showed that heating at 453 K of the SBR/CSM blend (85/15 by wt) without any metal donor does not lead to crosslinking of the elastomers. This follows from the lack of growth of the vulcametric torque (ΔM) and complete solubility in toluene of the heated samples. At first, we studied the influence of CSM type, differing in total bound Cl content (24—43 wt %) and in Cl content in ~SO_2Cl groups (Table 1). On the basis of our earlier studies [8, 9], a curing temperature T = 453 K and addition of 3 g Zn/100 g CSM in the SBR/CSM blends (85/15 by wt) were chosen for further experiments.

T a b l e 1. The characteristics of used CSM

CSM type	Symbol	Bound chlorine content, wt %	
		total	in ~SO_2Cl groups
Hypalon 45	CSM24	24	1.10
Hypalon 20	CSM29	29	1.55
Hypalon 40	CSM35	35	1.10
Hypalon 30	CSM43	43	1.20

The observed increase of vulcametric torque after 25 minutes heating (ΔM_{25}) and equilibrium swelling in toluene or hexane (Q_{VTOL}, Q_{VHEX}, respectively) of cured samples indicate that the highest curing degree was reached in SBR/CSM29 blends (85/15 by weight) (Figs. 1 and 2), *i.e.* in blends containing CSM characterized by the largest amount of Cl bound in ~SO_2-Cl groups, the greatest concentration of chlorosulphonic groups.

The obtained curing degree of the blends containing CSM of lower concentration of chlorosulphonic groups was lower. This signifies that the chlorosulphonic groups

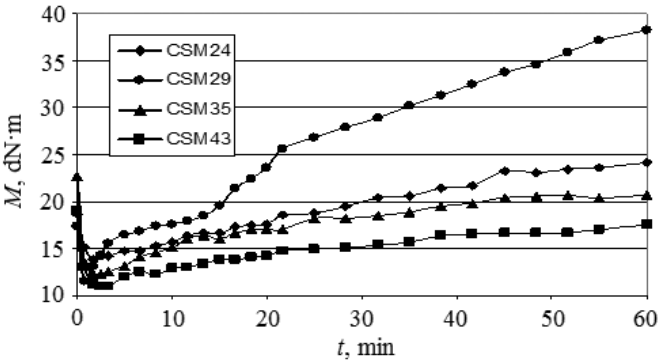


Fig. 1. The effect of CSM type on vulcametric torque (M) of the SBR/CSM blends (85/15 by wt) heated at T = 453 K in the presence of 3 phr Zn/CSM

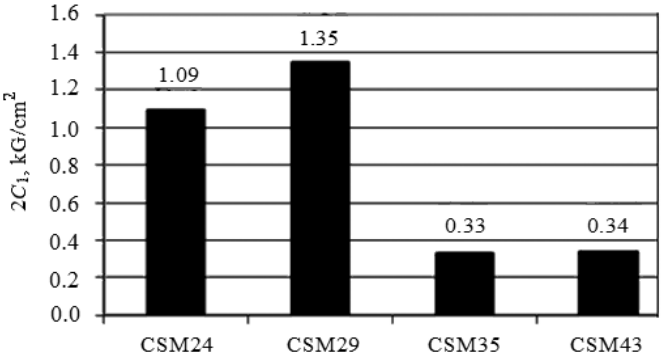


Fig. 2. The effect of CSM type on Mooney-Rivlin elasticity constants ($2C_1$) of the SBR/CSM blends (85/15 by wt) cured at T = 453 K for 40 min in the presence of 3 phr Zn/CSM

take part in the curing reaction of the studied system. This correlates with the determined values of the elasticity constants $2C_1$ (Fig. 2) and the interelastomer bonding degree of CSM on SBR, estimated on the basis of extraction in boiling acetone and bound Cl content determinations in cured and extracted, purified compounds (Table 2).

On the other hand, the obtained curing degree of blends containing CSM of the same ~SO_2Cl groups concentration (CSM24, CSM35 and CSM43, see Table 1) decreases with an increased amount of total bound Cl in the incorporated CSM. This can be explained by the different miscibilities of the elastomeric components in the SBR/CSM system connected with increasing CSM polarity, which in turn leads to an increased thermodynamic dissimilarity between SBR and CSM. This follows from the comparison of the cohesion parameters (δ) of the blends component: δ_{SBR} = 18.9; δ_{CSM24} = 18.2; δ_{CSM29} = 18.6; δ_{CSM35} = 19.2 and δ_{CSM43} = 19.6 MPa^{-1}, respectively [13].

On the basis of the results obtained, the influence of different amounts of the chosen CSM29 (15—25 phr; phr — parts per hundred parts of rubbers) in the blend on curing, and selected properties of cured CSM29/SBR blends, was investigated. It was found that there is no need to use more than 25 phr CSM29 in blends with SBR

because this amount is sufficient for the formation of an adequate amount of *in situ* generated Lewis acids ($ZnCl_2$) necessary to catalyze the Friedel-Crafts alkylation reaction and support the interpolymer CSM bonding with SBR.

T a b l e 2. The effect of the CSM type on the selected properties of SBR/CSM blends (85/15 by wt) cured at T = 453 K for 40 min; Zn content: 3 phr/CSM

Property	CSM24	CSM29	CSM35	CSM43
S_{100}, MPa	0.86 ± 0.06	1.05 ± 0.07	0.56 ± 0.02	0.52 ± 0.02
S_{200}, MPa	1.18 ± 0.10	1.95 ± 0.20	0.70 ± 0.02	0.67 ± 0.05
S_{300}, MPa	1.53 ± 0.14	-	0.80 ± 0.02	0.80 ± 0.07
TS_b, MPa	2.00 ± 0.12	2.34 ± 0.10	2.27 ± 0.04	2.17 ± 0.05
E_b, %	402 ± 23	211 ± 16	926 ± 36	942 ± 49
Q_{VTOL}, cm^3/cm^3	5.69 ± 0.15	3.83 ± 0.15	14.6 ± 0.3	19.0 ± 0.4
Q_{VHEX}, cm^3/cm^3	1.17 ± 0.05	1.21 ± 0.11	1.05 ± 0.01	1.06 ± 0.01
$E_{theor.}$, wt/wt	0.201	0.201	0.201	0.201
$E_{exp.}$, wt/wt	0.064 ± 0.005	0.055 ± 0.005	0.070 ± 0.005	0.071 ± 0.005
$BCC_{theor.}$, wt %	3.60	4.35	5.25	6.45
$BCC_{exp.}$, wt %	2.86	3.65	5.12	4.91
BD_{CSM}, wt %	79	84	98	76

$S_{100,200,300}$ — stress at elongation of 100, 200, 300 %, respectively; TS_b — tensile strength at break; E_b — elongation at break; Q_{VTOL}, Q_{VHEX} — equilibrium swelling in toluene, hexane; $E_{theor.}$, $E_{exp.}$ — theoretical, experimental content of the fraction soluble in acetone, $E_{theor.} = U_{SBR}E_{SBR} + U_{CSM}E_{CSM}$ where: U_{SBR}, U_{CSM} — weight fraction of SBR or CSM in the blend, E_{SBR} = 0.060 (determined content of non-rubber constituent extracted from SBR with acetone), E_{CSM} = 1 (theoretical content of CSM fraction soluble in acetone, if no CSM curing or bonding during heating occurs); $BCC_{theor.}$ — calculated bound Cl content in CSM used (*e.g.* in CSM24 total bound Cl content 24 % · 0.15 = 3.60 % in SBR/CSM blend = 85/15 by wt); $BCC_{exp.}$ — estimated bound Cl content in blends extracted with acetone after curing; BD_{CSM} — CSM bonding degree, CSM bounded with SBR calculated as 100 ($BCC_{exp.}/BCC_{theor.}$).

The vulcametric measurements (Fig. 3) indicate that the curing degree of the compounds, to a limited extent, only depends on the CSM29 content (15—25 phr) in blends but the degree of CSM interpolymer bonding with SBR and the tensile strength of cured products increases with the CSM29 amount in blends (Figs. 4 and 5).

In earlier papers [1—3] we proposed a mechanism of curing and interelastomer reactions in SBR/CSM blends containing ZnO. The same mechanism should be valid in the SBR/CSM blends containing powdered Zn. For this reason, IR spectra of the SBR/CSM/Zn blends (75/25 and 85/15 by wt, Zn content: 3 phr/CSM) were made before and after their curing (Figs. 6 and 7, Table 3) and analyzed.

The relative absorption intensity at 1667 cm^{-1} (>C=C<$_{cis}$ in 1,4-*cis*-butadiene monomer units) decreases during

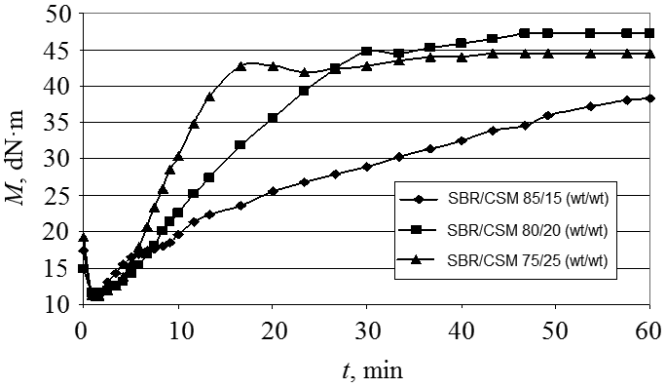


Fig. 3. The effect of CSM29 amount on vulcametric torque (M) of the SBR/CSM29 blends heated at T = 453 K in the presence of 3 phr Zn/CSM

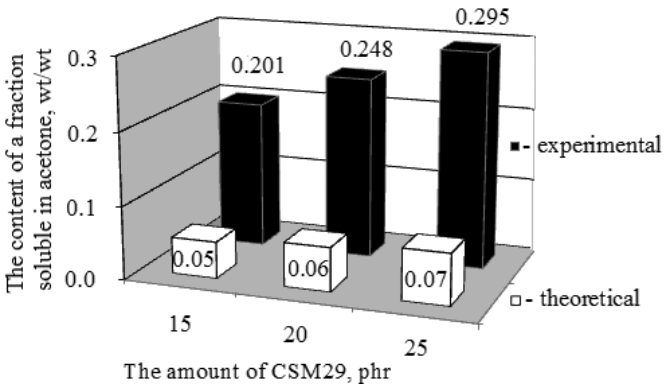


Fig. 4. The effect of CSM29 amount on the theoretical and determined content of a fraction soluble in acetone of the SBR/CSM29 blends cured at T = 453 K for 40 min in the presence of 3 phr Zn/CSM

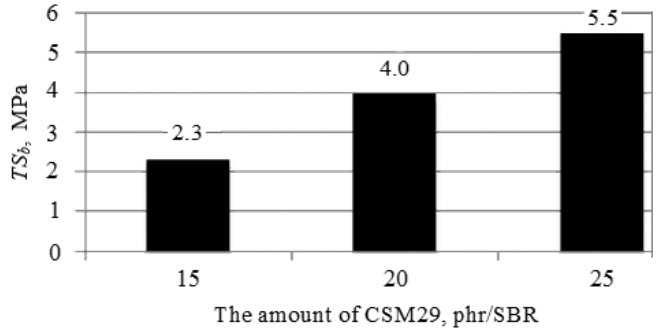


Fig. 5. The effect of CSM29 amount on the tensile strength (TS_b) of the SBR/CSM29 blends cured at T = 453 K for 40 min in the presence of 3 phr Zn/CSM

heating of SBR/CSM blends. The same trend is observed for the relative intensities of absorption bands of vinyl side groups at 1639 cm^{-1} (>C=C< in 1,2-butadiene monomer units). However, the relative intensities of the absorption bands at 967 cm^{-1} (>C=C<$_{trans}$ in 1,4-*trans*-butadiene monomer units) increase during heating of the SBR/CSM blends. This leads to the conclusion that both

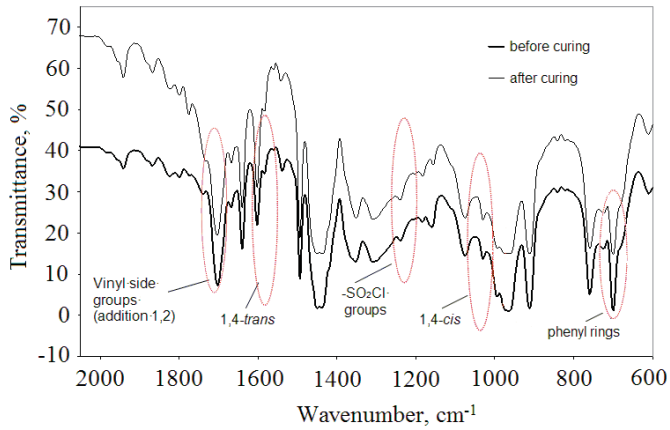


Fig. 6. IR spectra of SBR/CSM/Zn (85/15/0.45 by wt) blend before and after curing at 453 K for 40 min

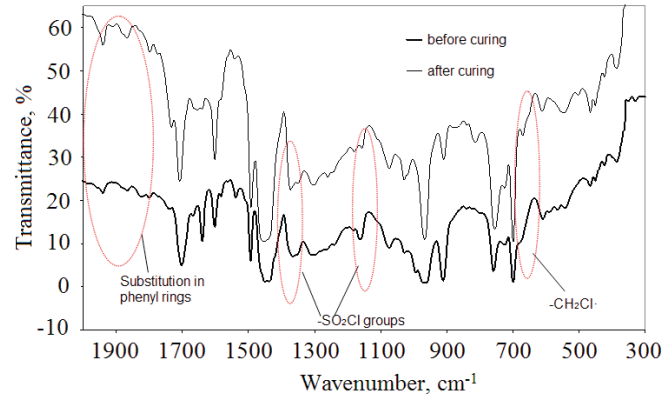


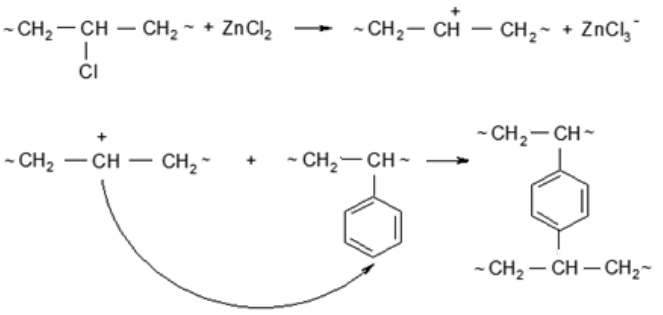
Fig. 7. IR spectra of SBR/CSM/Zn (75/25/0.75 by wt) blend before and after curing at 453 K for 40 min

the vinyl side group and 1,4-*cis*-butadiene units take part in the curing reaction. The observed increase of 1,4-*trans*-butadiene units content is caused by the known *cis-trans* isomerisation catalyzed with *in situ* generated $ZnCl_2$ acting as a Lewis acid. The observed decrease of absorption intensity at 608 cm^{-1} (C-Cl bonds in CSM chains) confirms this conclusion (Table 3).

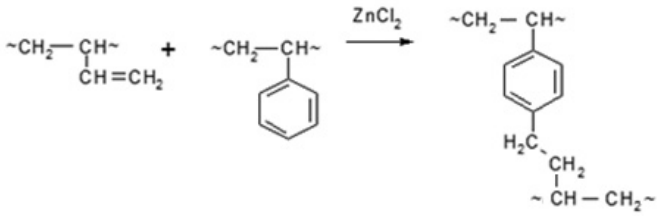
T a b l e 3. Relative intensities of absorption bands in IR spectra of SBR/CSM blend before and after curing at 453 K for 40 min; reference band at 700 cm^{-1} (C-H bond in phenyl ring)

Groups	Wave-number cm^{-1}	Relative absorption intensities			
		before curing		after curing	
		15*	25*	15*	25*
$–CH_2–Cl$	608	0.48	0.34	0.34	0.22
$>C=C<_{trans}$	967	0.78	0.76	0.80	0.93
$–SO_2Cl$	1178	0.47	0.41	0.32	0.18
$–SO_2Cl$	1309	0.38	0.21	0.33	0.18
$–SO_2Cl$	1352	–	0.76	–	0.47
$CH_2=CH–$	1639	0.97	–	0.73	–
$>C=C<_{cis}$	1667	1.05	1.11	0.45	0.62

* — CSM29 amount in the blend with SBR, phr.



Scheme A



Scheme B

Thus, the crosslinking in SBR/CSM/Zn blends is a result of the alkylation of the SBR phenyl rings with CSM chains (Scheme A) and an autoalkylation of SBR phenyl rings with SBR moieties containing most reactive vinyl side groups (CH_2=CH-; 1,2-butadiene monomer unit) and the moieties containing 1,4-*cis*-butadiene monomer units of weaker reactivity (Scheme B). These reactions are catalyzed with $ZnCl_2$.

T a b l e 4. The composition (phr) and selected properties SBR/CSM29/Zn blends filled with carbon black or silica and cured at T = 453 K for 40 min

SBR	85	85	85
CSM29	15	15	15
Zn	0.45	0.45	0.45
Stearic acid	1	1	1
Carbon black HAF N-330	-	30	-
Silica PERKSIL KS408	-	-	20
Ethylene glycol	-	-	1
ΔM_{40}, dNm	21	20.5	14.8
$Q_{V\,TOL}$, cm^3/cm^3	3.83 ± 0.15	3.53 ± 0.04	7.1 ± 0.1
Q_{VHEX}, cm^3/cm^3	1.21 ± 0.11	1.53 ± 0.04	1.53 ± 0.04
S_{100}, MPa	1.05 ± 0.07	2.31 ± 0.05	0.89 ± 0.03
S_{200}, MPa	1.95 ± 0.20	4.18 ± 0.09	1.30 ± 0.04
S_{300}, MPa	-	6.03 ± 0.08	1.79 ± 0.05
TS_b, MPa	2.34 ± 0.09	6.06 ± 0.07	4.81 ± 0.22
E_b, %	210 ± 16	310 ± 16	768 ± 17

ΔM_{40} — vulcametric torque after 40 min heating at T = 453 K.

We have analyzed the influence of active fillers (silica and carbon black) on the crosslinking and properties of

cured SBR/CSM29 blends (Table 4). From vulcametric measurements, equilibrium swelling and others determinations it follows that the elaborated method can be used for crosslinking of the filled SBR/CSM blends without any negative influence on the properties of the cured materials. The incorporation of carbon black or silica as fillers into SBR/CSM compounds leads to higher tensile strengths of cured SBR/CSM29 blend and silica improves the elongation at break.

CONCLUSIONS

The mechanical properties of products from a new method of curing styrene-butadiene rubber blends using *in situ* generated Lewis acids were studied. The curing rate and extent of curing depend on the kind and amount of CSM incorporated into the blends. From the determined increase of the vulcametric torque ΔM, solubility and equilibrium swelling Q measurements, determinations of the stress-strain properties and Mooney-Rivlin elasticity constants, as well as the bound Cl content in the blends extracted after curing with a suitable solvent, it follows that the best results were obtained for the blends containing 15—25 wt % CSM29 and 3 phr Zn/CSM. The analysis of IR spectra leads to the conclusion that the curing in the investigated blends is a result of the interelastomer Friedel-Crafts alkylation of the SBR phenyl rings with CSM chains and the autoalkylation of SBR phenyl rings with SBR moieties containing vinyl side groups and the moieties containing butadiene monomer units of the 1,4-*cis* addition as well. These reactions are catalyzed with Lewis acids ($ZnCl_2$) generated *in situ* in the reaction of CSM with the zinc powder. The new, unconventional method can be used for the curing of the SBR/CSM blends containing selected fillers.

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