

GORDANA MARKOVIĆ¹
MILENA
MARINOVIĆ-CINCOVIĆ²
BLAGA RADOVANOVIĆ³
JAROSLAVA
BUDINSKI-SIMENDIĆ⁴

¹Tigar, Pirot, Serbia and
Montenegro

²Institute of Nuclear Science
VINČA, Belgrade,
Serbia and Montenegro

³Faculty of Science, Niš,
Serbia and Montenegro

⁴Faculty of Technology,
Novi Sad, Serbia and
Montenegro

SCIENTIFIC PAPER

678.4-036.7+542.9+539.196:678.7

STUDIES OF CHEMICAL INTERACTIONS BETWEEN CHLOROSULPHONATED POLYETHYLENE AND NITRILE RUBBER

Highly polar rubbers interact with each other through their active functional groups via condensation or substitution reactions at high temperature. Chlorosulphonated polyethylene (CSM) rubber is a highly reactive rubber, the reactivity of which is due to the $-SO_2Cl$ groups. When CSM reacts with nitrile rubber (NBR), a chemical reaction takes place between the two rubbers at high temperature. Fourier transform infrared (FTIR) studies support that CSM/NBR (50/50 w/w) isothermally induces a self cross-linking blend, when cross-linking takes place via the acrylonitrile groups of NBR and the SO_2Cl groups or the in-situ generated allyl chloride moieties of CSM. There is a loss of some $-CN$ groups during cross-linking. This may be due to an attack on the $-CN$ groups by HCl (produced during the heating of CSM) in the presence of inherent moisture in the polymers. Amid type of linkage is formed due to cross-linking.

Improvements in the properties of conventional polymers can be achieved by chemically modifying them. Functionalization of the polymers results in new materials with a wide spectrum of properties not available in the parent polymers. Chemical modification of the polymer backbone, grafting onto a polymer chain, interchain reactions, and the formation of interpenetrating networks are the subject of a number of reviews [1–4]. The introduction of chlorine and sulfur dioxide into polyethylene reduces the crystallinity, thereby changing the thermoplastic material into an amorphous polymer, commercially known as chlorosulphonated polyethylene (CSM), which contains 25 to 43 wt.% of chlorine and 1 to 1.5 wt.% of sulfur as $-SO_2Cl$ units.

In recent years, De and associates [5] reported a series of self-crosslinkable polymer blends—mixtures of two or more functionally reactive polymers that are capable of undergoing mutual cross-linking via condensation or substitution reactions at high temperatures. Such self-cross-linkable rubber–rubber blends include epoxidised natural rubber (ENR) and carboxylated nitrile rubber (XNBR), CSM and ENR.

According to Mukhopadhyay et al. [6], the sulphonyl chloride groups of CSM combine with the acrylonitrile group in NBR to give linkages between the two elastomers. The principal objection against this mechanism is obviously the thermal instability of the sulfonyl chloride groups of CSM. At very high reactive temperatures CSM loses all of its $-SO_2Cl$ groups. The main objective of this investigation was to study the chemical interaction between CSM and NBR in detail.

*Paper is presented at VI Symposium "Counterporary Technologies and Economic Development", Leskovac, October 21–22, 2005, Serbia and Montenegro

Author address: G. Marković, Tigar, Pirot, Serbia and Montenegro
E-mail: gmarkov@tigar.com

Paper received: September 12, 2005

Paper accepted: October 25, 2005

EXPERIMENTAL

Materials

The CSM used in the present study was Hypalon-40, which contained 35 wt.% chlorine and 1 wt.% sulfur and was obtained from E.I. duPont de Nemours and Co., Inc., U.S.A.

The NBR used was Krynac-3345 (Polysar Canada), which contained 33 wt% acrylonitrile. CSM/NBR blends (50/50 w/w), were prepared on a laboratory size (300x600 mm) two-roll mixing mill. The elastomers were separately milled for about 1 min each, keeping a tight nip gap (0.8 mm), and subsequently blended for 3 min. After mixing, different test pieces for rubber testing were cured under 10 MPa pressure at 160°C for 60 min in a Teflon TM-coated mold. The molded samples were taken out only after cooling them to room temperature under pressure by circulating cold water through the plates of the press.

Fourier transform infrared spectra (FTIR) were recorded on a Bruker IFS-66 spectrometer with an attenuated total reflection (ATR) attachment. A minimum of 500 scans was signal-averaged at a resolution of 4 cm^{-1} . The spectrometer was equipped with a liquid-nitrogen-cooled mercury cadmium telluride (MCT) detector for FTIR-ATR measurements. The internal reflection element (IRE) chosen was a 45 degree KRS-5. Samples for FTIR-ATR measurements were approximately 0.3 mm thick sheets, prepared by compression molding between two teflon films at 100°C (for the uncross-linked blend). The melting times were 2 min for cross-linked blends.

RESULTS AND DISCUSSION

Chemical Interaction Studies by Infrared Spectroscopy

Figure 1 shows the chemical reaction between in-situ generated primary amides and allyl chlorides.

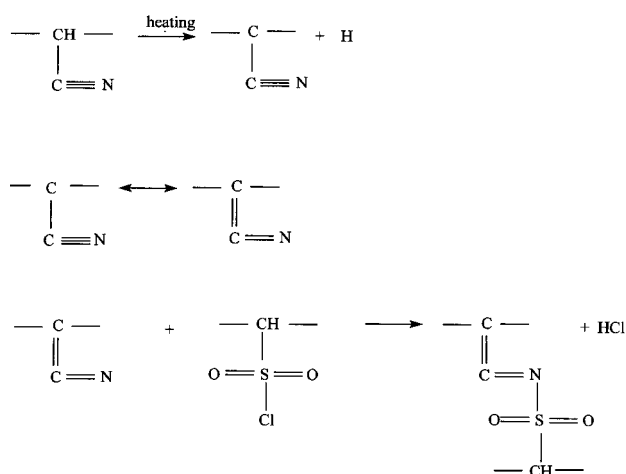


Figure 1. Chemical reaction between *in-situ* generated primary amides and allyl chlorides

Figures 2(a) and (b) represent the FTIR-ATR spectra of NBR and CSM, respectively. The assignment of the principal bands are presented in Tables 1 and 2.

Figure 2(c) represents the FTIR-ATR spectra of a NBR/CSM blend. The two characteristic bands of CSM (the absorption bands at 1100 and 1292 cm^{-1}) completely disappear in the spectrum of the self-cross-linked material.

Table 1. Assignment of the infrared bands of acrylonitrile-butadiene rubber

Wave number (cm^{-1})	Group	Assignment
2932	CH_3 , $-\text{CH}_2$, $>\text{CH}-$	ν ($-\text{C}-\text{H}$)
2860	CH_3 , $-\text{CH}_2$, $>\text{CH}-$	ν ($-\text{C}-\text{H}$)
2238	$-\text{CN}$	ν ($-\text{C}=\text{N}$)
1647	$-\text{CH}=\text{CH}-$	ν ($-\text{C}=\text{C}$)
1440	$-\text{CH}_2-$	δ ($\text{C}-\text{H}$)
1287	$-\text{CH}_2-$	γ (CH_2)
969	Trans $-\text{CH}=\text{CH}-$	δ ($=\text{C}-\text{H}$)
967	$\text{CH}_2=\text{CH}-$	δ (CH_2)

ν – valence deformation; δ – in plain deformation; γ – out-of-plane deformation.

Table 2. Assignment of the infrared bands of chlorosulfonated polyethylene

Wave number (cm^{-1})	Group	Assignment
2935	CH_3 , $-\text{CH}_2$, $>\text{CH}-$	ν ($-\text{C}-\text{H}$)
2862	CH_3 , $-\text{CH}_2$, $>\text{CH}-$	ν ($-\text{C}-\text{H}$)
1435	$-\text{CH}_2-$	δ ($\text{C}-\text{H}$)
1292	$-\text{SO}_2\text{Cl}$	ν (SO_2) asym.
1192	$-\text{CH}_2-$	ν (CH_2)
1100	$-\text{SO}_2\text{Cl}$	ν (SO_2) sym.
815	$-\text{CH}_2-$	γ (CH_2)

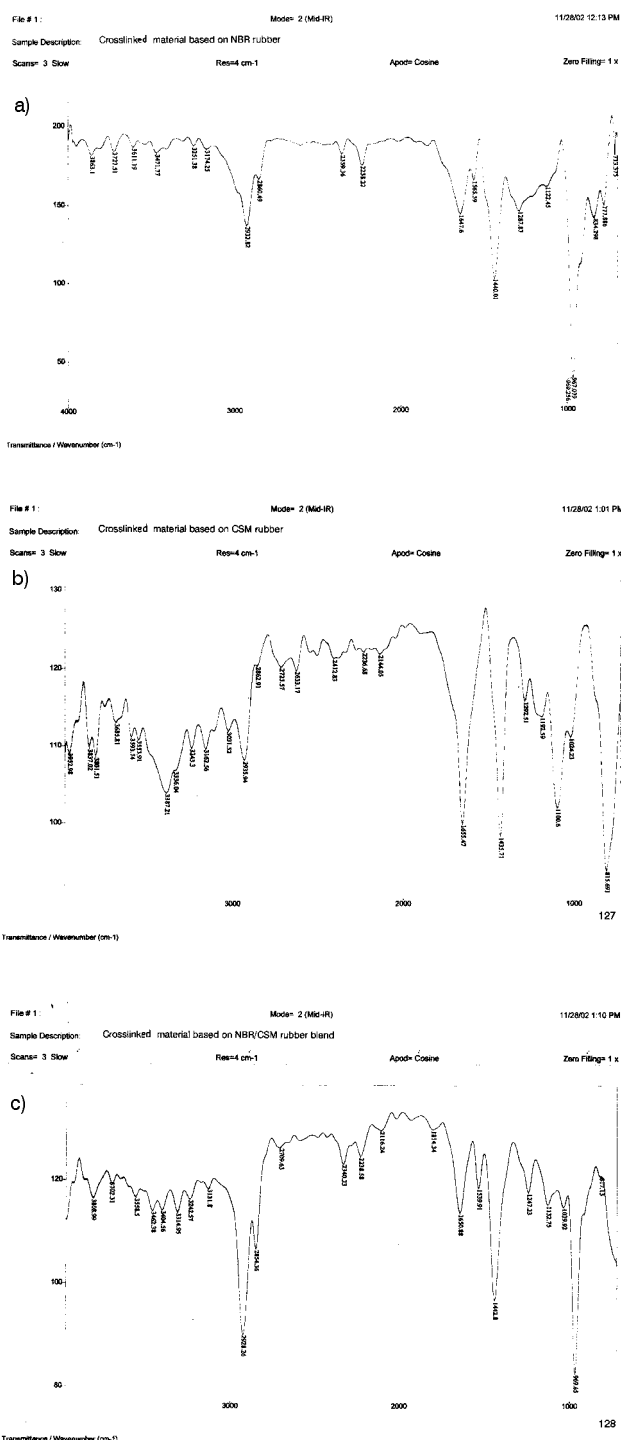


Figure 2. FTIR-ATR spectrum of NBR (a); FTIR-ATR spectrum of CSM (b); FTIR-ATR spectrum of NBR/CSM (c)

The absorption band at 2238 cm^{-1} , attributed to the $\text{C}=\text{N}$ stretching mode [5–7], is strongly attenuated by self-cross-linking of the blend. This indicates a significant loss or conversion of cyanide groups, which may be due to the cyanide/cyanide reaction [8] or even to the hydrolysis of cyanide groups. Hence, it is logical to infer that CSM/NBR does not contain any side products due to the cyanide/cyanide reactions. The decrease of

the –CN concentration in the blends is therefore attributed to the partial hydrolysis of cyanide groups by the action of HCl gas evolved from CSM during high-temperature heating in the presence of inherent moisture in the polymers.

Similar observations were made by Manoj et al. with reference to the thermally induced self-cross-linking of PVC/NBR [9–10], as well as PVC/HNBR [20] blends. The controlled liberation of HCl from PVC favors self-cross-linking by causing the hydrolysis of cyanide groups to amides and acids. In-situ generated amides and carboxylic acids are capable of reacting with the allylic sites of the degraded PVC [10,11].

The absorption bands at 1100 and 1292 cm^{-1} in the CSM rubber were assigned to the symmetric and asymmetric stretching modes of SO_2 of $-\text{SO}_2\text{Cl}$ groups, respectively. These two characteristic bands of CSM completely disappear in the spectrum of the self-cross-linked material. The difference spectrum (spectrum c, Fig. 2) also illustrates the loss of $-\text{SO}_2\text{Cl}$ groups.

An inspection of spectrum c (Figure 2) reveals a new absorption band centered at 1539 cm^{-1} . The new absorption could be assigned to the amide II band, which is due to a motion combining both the N–H bending and C–N stretching vibrations of $-\text{CONH}$ groups [11]. The amide I band, which is ascribed to the C=O stretching mode of the amide group, generally occurs in region the 1680–1630 cm^{-1} [12]. In the present system, the amide I band cannot be detected because of the interference from C=C stretching in the same region. It is also noteworthy that the amide present in the NBR/CSM self-cross-linked blend is likely to be a secondary amide because the amide II band of the primary amide (in

the condensed phase) occurs at 1650–1620 cm^{-1} , while the corresponding absorption due to a secondary amide (solid) appears at 1570–1515 cm^{-1} . This indicates a chemical reaction between in-situ generated primary amides and allyl chlorides.

CONCLUSIONS

Infrared studies show that cross-linking takes places via the allyl chloride and amide produced by hydrolysis of the $-\text{C}=\text{N}$ group.

REFERENCES

- [1] M.A. Smook, I.D. Roche, W.B. Clark, *Ind. Rubb. World*, **128** (1953) 54
- [2] J.T. Maynard and P.R. Johnson, *Rubb. Chem. Technol.*, **36** (1963) 963
- [3] D.A. Smith, *J. Polym. Sci.*, **B2** (1964) 665
- [4] M.A. Dudley and D.A. Smith, *Rubb. Chem. Tech.* **40** (1967) 445
- [5] R. Alex, P.P. De, and S.K. De, *Polym. Commun.*, **31** (1990) 118
- [6] S. Mukhopadhyay and S.K. De, *Polymer*, **32** (1991) 1223
- [7] S. Mukhopadhyay, P.P. De, and S.K. De, *J. Appl. Sci.*, **43** (1991) 347
- [8] B. Bikson, J. Jagur-Grodzinski, and D. Vofsi, *Polymer*, **32** (1981) 640
- [9] S. Bhattacharjee, PhD Thesis, Indian Institute of Technology, Kharagpur, 1992
- [10] P. Ramesh and S.K. De, *Rubb. Chem. Technol.*, **65** (1992) 24
- [11] P. Ramesh and S.K. De, *Polym. Commun.*, **31** (1990) 466
- [12] G. Socrates in *Infrared Characteristic Group Frequencies*, J. Wiley-Interscience, Chichester, 1980

IZVOD

PROUČAVANJE HEMIJSKE INTERAKCIJE HLOSULFONOVANOG POLIETILENA I NITRILNOG KAUČUKA

(Naučni rad)

Gordana Marković¹, Milena Marinović-Cincović², Blaga Radovanović³, Jaroslava Budinski-Simendić⁴

¹Tigar, Piroć, Srbija i Crna Gora, ²Institut VINCA, Beograd, Srbija i Crna Gora,

³Tehnički fakultet, Niš, Srbija i Crna Gora, ⁴Technološki fakultet, Novi Sad, Srbija i Crna Gora

Visokopolarni kaučuci reaguju međusobno aktivnim funkcionalnim grupama kondenzacionim ili supstitucionim reakcijama na visokim temperaturama. Hlorosulfonovani polietilenski kaučuk (CSM) je visokoreaktivni kaučuk, zahvaljujući $-\text{SO}_2\text{Cl}$ grupi. Reakcija CSM kaučuka sa nitrilnim kaučukom (NBR) odvija se na visokim temperaturama. Fourier Transform infracrvena spektroskopija (FTIR), pokazuje da su CSM/NBR (50:50) blende samoumrežavajuće, pri čemu se umreženje odvija putem akrilonitrilne grupe iz NBR i $-\text{SO}_2\text{Cl}$ grupe iz CSM kaučuka. U toku umrežavanja $-\text{CN}$ grupa reaguje sa HCl iz CSM-a i obrazuje amid.

Ključne reči: CSM–NBR hemijska interakcija • Samoumrežavanje CSM/NBR blendi kaučuka • Karakterizacija •

Key words: CSM–NBR chemical interaction • Self-cross-linking of CSM/NBR blend • Characterization of CSM/NBR blend • Chemical reactions between CSM and NBR •