

Studies on Chemical Interactions Between Chlorosulphonated Polyethylene and Carboxylated Nitrile Rubber

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ABSTRACT: 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, whose reactivity is due to the $-\text{SO}_2\text{Cl}$ groups. When CSM reacts with carboxylated nitrile rubber (XNBR), a chemical reaction takes place between the two rubbers at high temperature. Dynamic mechanical analysis shows that CSM and XNBR form a homogeneous blend. Fourier transform infrared (FTIR) studies support that CSM/XNBR (50/50 w/w) is a thermally induced self-cross-linking blend, when cross-linking takes place through carboxylic groups of XNBR and $-\text{SO}_2\text{Cl}$ groups or *in-situ* generated allyl chloride moieties of CSM. There is a loss of some $-\text{CN}$ groups during cross-linking; this may be due to an attack on the $-\text{CN}$ groups by HCl (produced during heating of CSM) in the presence of inherent moisture in the polymers. Due to cross-linking, an ester or amide type of linkage is formed. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 1761-1768, 1997

Key words: CSM-XNBR chemical interaction; self-cross-linking of CSM/XNBR blend; characterization of CSM/XNBR blend; thermally-induced cross-linking of CSM/XNBR; chemical reactions between CSM and XNBR

INTRODUCTION

Improvements in the properties of conventional polymers can be achieved by chemically modifying them. Functionalization of polymers results in new materials with a wide spectrum of properties not available in the parent polymers. Chemical modification of polymer backbone, grafting onto a polymer chain, interchain reactions, and formation of interpenetrating networks are the subject of a number of reviews.¹⁻⁴ The introduction of chlorine and sulfur dioxide onto the polyethylene molecule destroys the crystallinity, thereby

changing the thermoplastic material into an amorphous polymer, commercially known as chlorosulphonated polyethylene (CSM), which contains 25 to 43% by weight of chlorine and 1 to 1.5% by weight of sulfur as $-\text{SO}_2\text{Cl}$ units. Thus, CSM rubber is highly reactive, and reactivity is due to the $-\text{SO}_2\text{Cl}$ groups.

In recent years, De and associates reported a series of self-cross-linkable 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 epoxidized natural rubber (ENR) and carboxylated nitrile rubber (XNBR),⁵ CSM and ENR,⁶ and CSM and XNBR.⁷

According to Mukhopadhyay et al.,⁷ the sulphonyl chloride groups of CSM combine with the carboxylic structural units in XNBR to give mixed

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anhydride type of linkages between the two elastomers; but the principal objection against this mechanism is obviously the thermal instability of the sulfonyl chloride groups of CSM. Anhydride formation requires a very high reactive temperature at which CSM loses all of its $\text{—SO}_2\text{Cl}$ groups, so the main objective of this work is to study the actual nature of chemical interaction between CSM and XNBR in detail.

EXPERIMENTAL

Materials

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

The XNBR used was Krynac-X7.50, which contained 27% acrylonitrile and 7% carboxylated monomer by weight. It was procured from Polysar, Canada.

The NBR used was Krynac-34.50 (Polysar, Canada), which contained 34 wt % acrylonitrile.

Hydrogenated acrylonitrile-butadiene rubber (HNBR) used was Therban-1707, which contained 34.7 wt % acrylonitrile and 0.5 mol % residual unsaturation.

Solvents, like chloroform, tetrahydrofuran (THF), and toluene used in the present investigation were of analytical grade (E. Merck, India).

CSM/NBR (50/50 w/w), CSM/HNBR (50/50 w/w), and CSM/XNBR (50/50 w/w) were prepared on a laboratory size (14 × 6 in.) 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 170°C for 60 min in a TeflonTM-coated mold. The molded samples were taken out only after cooling them to room temperature under pressure by circulating cold water through the platens of the press. In order to determine the gel content (accurately weighed), all the single rubbers and blends are extracted with boiling THF for 10 h, and residue after extraction was determined by weighing. Gel content for the heat treated (1 h at 170°C) samples were measured in the same manner.

Dynamic mechanical studies were carried out between -100 and $+100^\circ\text{C}$ at 3.5 Hz, under tension mode, using a dynamic viscoelastometer (Rheovibron, model DDV-III-EP, Orientec Corpo-

Table I Gel Content^a

Sample	Gel Content (%)	
	Untreated	Heat treated ^b
CSM	nil	nil
NBR	nil	nil
HNBR	nil	nil
XNBR	nil	nil
CSM/NBR (50/50 w/w)	nil	18
CSM/HNBR (50/50 w/w)	nil	14
CSM/XNBR (50/50 w/w)	nil	40

^a Solvent, boiling THF; extraction time, 10 h.

^b At 170°C for 1 h.

ration, Japan). The strain amplitude used was 0.0025 cm, and the heating rate was 2°C min^{-1} .

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} . For FTIR-ATR measurements, the spectrometer was equipped with a liquid-nitrogen-cooled mercury cadmium telluride (MCT) detector. 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 temperature 100°C (for uncross-linked blend) and 170°C (for cross-linked blend). Melting times were 2 min for uncross-linked blends and 60 min for cross-linked blends.

RESULTS AND DISCUSSION

Gel Formation

The thermally induced self-cross-linking of CSM/XNBR blend can be assessed by the determination of gel content. It has been seen that both CSM and XNBR are completely gel free and also do not develop any cross-linked material (or gel), when heated at 170°C for 60 min (Table I). Thermal treatment on acrylonitrile-butadiene rubber (NBR) and HNBR also fails to produce any gel in the polymers. But in blends with CSM, all the three nitrile-containing polymers (NBR, HNBR, and XNBR) develop significant amounts of gel by thermal treatment, indicating that chemical reaction takes place between the blend components. The highest chemical reactivity of XNBR, and its reac-

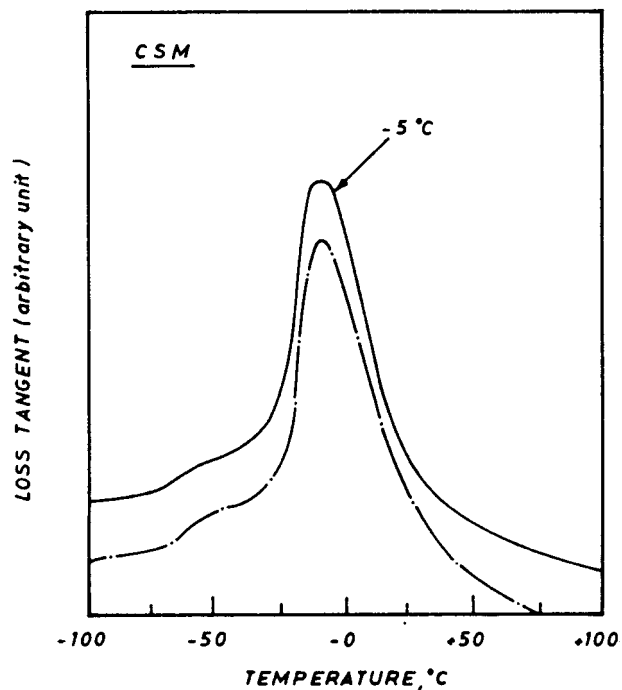


Figure 1 Temperature dependence of loss tangent of CSM (pure); (----), and CSM (heat-treated) (-○-○-).

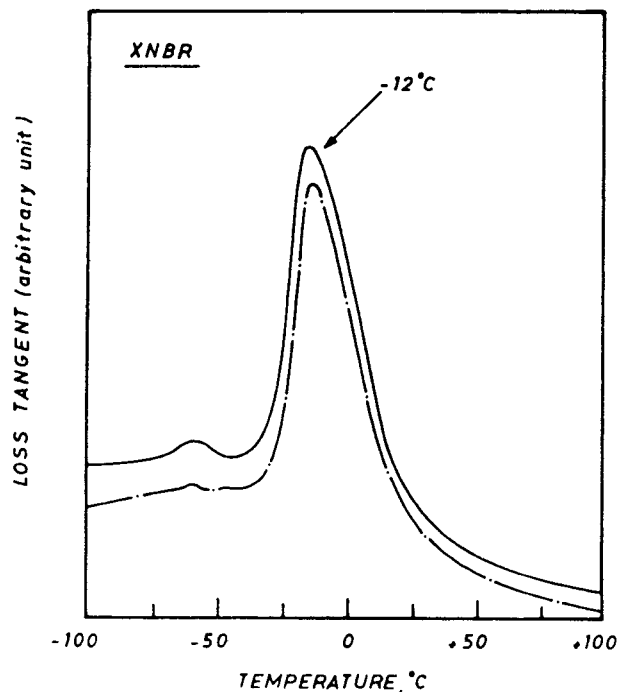


Figure 2 Temperature dependence of loss tangent of XNBR (pure) (----), and XNBR (heat-treated) (-○-○-).

tion with CSM, possibly explain the maximum gel formation in CSM/XNBR (50/50 w/w) blend.

Blend Homogeneity by DMA

Loss tangent versus temperature plots for CSM, XNBR, and CSM/XNBR (50/50 w/w) have been reported in Figures 1–3. Single rubbers and blends all have single maximum in loss tangent, associated with the glass transition. But a single glass transition of the CSM/XNBR blend is not an attestation of blend homogeneity because of T_g s of the component polymers (-5 and -12°C) are very close. Nevertheless, it is noteworthy that the thermal treatment (i.e., heating at 170°C for 1 h) on individual polymers, and the blend as well, cannot produce any change in T_g ; only the peak maxima decrease. This means that self-cross-linking of blend is not accompanied by a large number of undesired side reactions. In fact, polymer/polymer reaction in the absence of any side reaction contributes to blend homogeneity by generating graft, block, and cross-linked polymers.

Chemical Interaction Studies by Infrared Spectra

Figures 4(a) and (b) represent the FTIR-ATR spectra of XNBR and CSM, respectively. The assignments of the principal bands are presented in

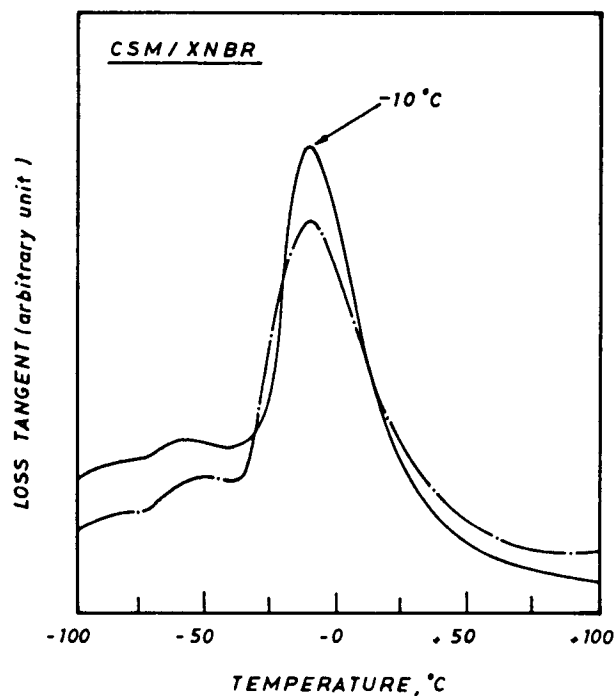


Figure 3 Temperature dependence of loss tangent of 50/50 (w/w) CSM/XNBR (untreated) (---) and 50/50 (w/w) CSM/XNBR (heat treated) (-○-○-).

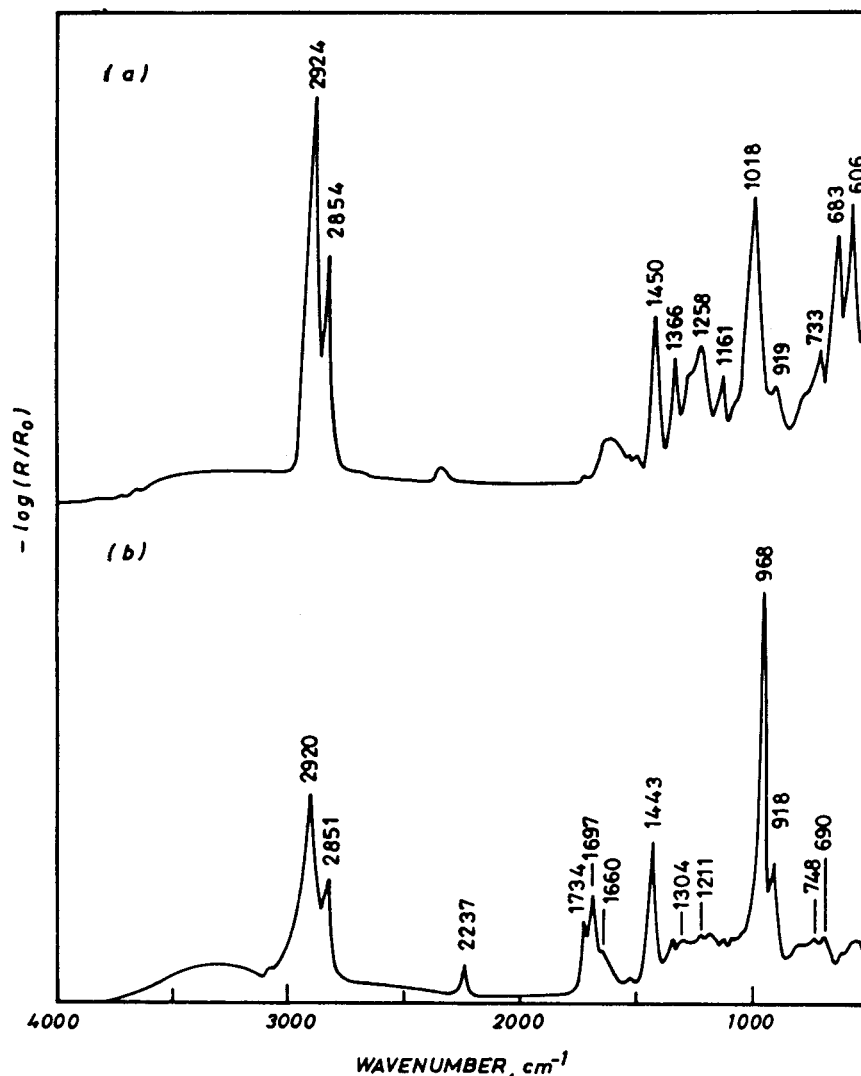
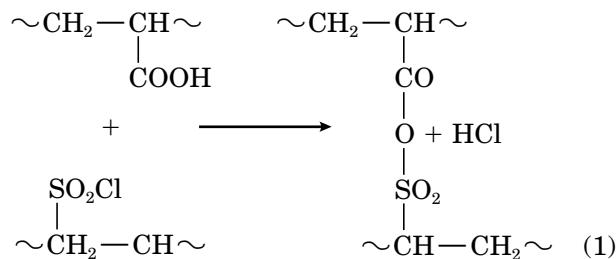


Figure 4 (a) FTIR-ATR spectrum of XNBR; (b) FTIR-ATR spectrum of CSM.

Tables II and III. Figure 5 represents the FTIR-ATR spectra of CSM/XNBR blend before (spectrum a) and after (spectrum b) thermally induced self-cross-linking. Spectrum c in Figure 5 is the difference spectra of the cross-linked and uncross-linked CSM/XNBR blends. The absorption bands at 1161 and 1366 cm^{-1} in the uncross-linked blend are assigned, respectively, to the symmetric and asymmetric stretching modes of SO_2 of $-\text{SO}_2\text{Cl}$ groups.⁸ These two characteristic bands of CSM totally vanish in the spectrum of self-cross-linked material. The difference spectrum (spectrum c) also illustrates the loss of $-\text{SO}_2\text{Cl}$ groups (negative absorption bands centered at 1162 and 1366 cm^{-1}). However, there are two new absorptions at 1171 and 1375 cm^{-1} in spectrum b (Fig. 5). In view of poor thermal stability of $-\text{SO}_2\text{Cl}$ groups, it does not seem justified to relate these two bands

to any sulfonylchloride derivative. That is why the mechanism [eq. (1)] suggested by Mukhopadhyay et al.⁷ cannot be accepted.



The spectral changes in the absorption range of the C=O stretching of $-\text{COOH}$ groups are also noteworthy. The IR spectrum of the uncross-linked blend (spectrum a in Fig. 5) contains two absorption bands due to C=O stretching. The

Table II Assignment of Infrared Bands of Carboxylated Acrylonitrile-Butadiene Rubber

Wave Number (cm ⁻¹)	Group	Assignment ^a
2920	CH ₃ —, —CH ₂ —, $\left. \begin{array}{l} \diagup \\ \diagdown \end{array} \right\} \text{CH—}$	ν (—C—H)
2851	CH ₃ —, —CH ₂ —, $\left. \begin{array}{l} \diagup \\ \diagdown \end{array} \right\} \text{CH—}$	ν (—C—H)
2237	—CN	ν (—C=N)
1736	free —COOH	ν (C=O)
1697	H-bonded —COOH	ν (C=O)
1670–1640	—CH=CH—	ν (C=C)
1443	—CH ₂ —	δ (C—H)
1351	—COOH	ν (C—O) + δ (O—H)
1304	—CH ₂ —	γ (CH ₂)
1211	—COOH	ω (C—O)
968	<i>trans</i> —CH=CH—	δ (=C—H) _{op}
918	CH ₂ =CH—	δ (CH ₂) _{op}
748	<i>cis</i> —CH=CH—	δ (=C—H) _{op}
	—CH ₂ —	γ_{γ} (CH ₂)

^a Abbreviation:^{9,12,13} ν , stretch; δ , bend; γ , twist, wag; γ_{γ} , rock; op, out-of-plane.

band at 1699 cm⁻¹ is attributed to a normal mode involving out-of-plane C=O stretching for the —COOH units associated by hydrogen bonding and band at 1734 cm⁻¹ is due to C=O stretching for the units where the carboxyl groups are not hydrogen-bonded.⁹ In the cross-linked blend, a new absorption band at 1740 cm⁻¹ develops at the expense of the absorptions at 1699 and 1734 cm⁻¹. The negative absorption peaks at 1734 and 1697 cm⁻¹ in the difference spectra further confirm the

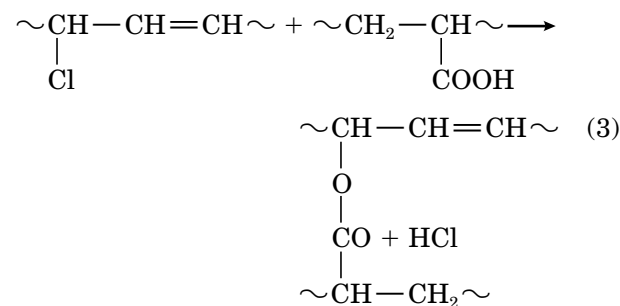
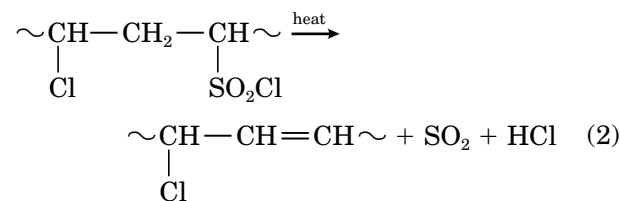
Table III Assignment of Infrared Bands of Chlorosulfonated Polyethylene

Wave Number (cm ⁻¹)	Group	Assignment ^a
2924	CH ₃ —, —CH ₂ —, $\left. \begin{array}{l} \diagup \\ \diagdown \end{array} \right\} \text{CH—}$	ν (C—H)
2854	CH ₃ —, —CH ₂ —, $\left. \begin{array}{l} \diagup \\ \diagdown \end{array} \right\} \text{CH—}$	ν (C—H)
1450	—CH ₂ —	δ (C—H)
1366	—SO ₂ Cl	ν (SO ₂) _{asym} ^b
1258	—CH ₂ —	γ (CH ₂)
1161	—SO ₂ Cl	ν (SO ₂) _{sym}
1018	Unknown	Unknown
740–720	—CH ₂ —	γ_{γ} (CH ₂)
683	—CHCl—	ν (C—Cl)
606	—CHCl—	ν (C—Cl)

^a From Bikson et al.⁸ and Socrates.¹²

^b CH₃ deformational modes at 1378 cm⁻¹ and CH₂ wagging modes at 1368 and 1355 cm⁻¹ contribute to this band absorption.

strong attenuation of the absorption of —COOH groups due to self-cross-linking. A new absorption band at 1747 cm⁻¹ in the difference spectra possibly suggests that a new species is being formed by the chemical reaction between CSM and XNBR. The total elimination of —SO₂Cl group and a concomitant loss of carboxyl groups are consistent with the following mechanisms [eqs. (2) and (3)]:



In-situ generation of allyl chloride moieties from thermal degradation of chlorine-containing polymers and their chemical reactions with carboxylated polymers are not uncommon in literature. Ramesh and De¹⁰ observed that allyl chloride/carboxyl reaction leads to a thermally induced self-

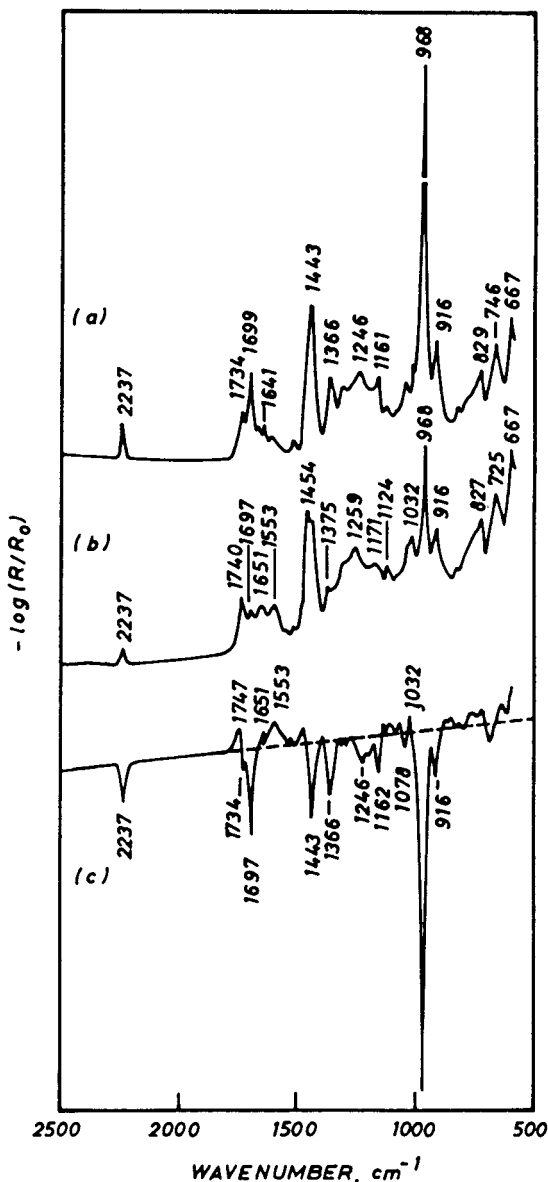


Figure 5 FTIR-ATR spectrum of (a) uncrosslinked 50/50 (w/w) CSM/XNBR blend, (b) self-crosslinked 50/50 (w/w) CSM/XNBR blend, and (c) $b-a$ difference spectrum.

cross-linking in the blends of chlorinated natural rubber (CIR) and XNBR. PVC/XNBR blends are also self-cross-linkable because of the presence of allyl chloride moieties in PVC.¹¹

The ester formation as a result of self-cross-linking is substantiated by IR bands. The absorption at 1740 cm^{-1} in the cross-linked sample is likely to correspond to the C=O stretching of ester linkages.¹² The band at 1124 and 1171 cm^{-1} may be ascribed to the C—O—C asymmetric stretching vibration of an aliphatic ether, but formation of the ester is much stronger because the

band at [mechanism in eq. (3)] $1100\text{--}1200\text{ cm}^{-1}$ can also be attributed to C—O—C stretching vibration of aliphatic ester.

The absorption at 1375 cm^{-1} in spectrum b (Fig. 5) is of little significance. The band is ascribed to the CH_3 deformational modes.⁸ In the uncross-linked blend, a much stronger absorption is due to SO_2 asymmetric stretch because 1366 cm^{-1} conceals this weak absorption.

The absorption band at 2237 cm^{-1} , which is attributed to C=N stretching mode,^{9,13} 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 cyanide/cyanide,^{14–16} cyanide/carboxyl¹⁷ reactions, or even hydrolysis of cyanide groups. Figure 6 illustrates the effect of a thermal treatment (at 170°C for 60 min) on the intensity of C=N stretching of pure XNBR, pure HNBR, and the CSM/HNBR (50/50 w/w) blend. In the pure polymers, the thermal treatment does not produce any perceptible change in the intensity of the band at 2237 cm^{-1} . The (C=N) band in CSM/HNBR blend is, on the other hand, greatly affected by thermal treatment. Hence, it is logical to infer that CSM/XNBR does not contain any side products due to cyanide/cyanide or cyanide/carboxyl reactions. The decrease of the —CN concentration in the blends is therefore attributed to a partial hydrolysis of a cyanide groups¹⁸ by the split-out HCl gas from CSM during high-temperature heating [eqs. (2) and (3)] 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 PVC/NBR,¹⁹ as well as the PVC/HNBR²⁰ blends. A controlled HCl liberation from PVC favors the self-cross-linking by bringing about the hydrolysis of a cyanide groups to amides and acids. *In-situ* generated amides and carboxylic acids are capable of reacting with the allylic sites of degraded PVC.^{19,20}

An inspection of spectrum b (Fig. 5) reveals a new absorption band centered at 1553 cm^{-1} . This 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 —CONH groups.¹² Amide I band, which is ascribed to the C=O stretching mode of the amide group, generally occurs at the $1680\text{--}1630\text{ cm}^{-1}$ region.¹² In the present system, the amide I band cannot be detected because of the interference from the C=C stretching in the same region. It is also noteworthy that the amide present in the CSM/XNBR self-cross-linked blend is likely to be

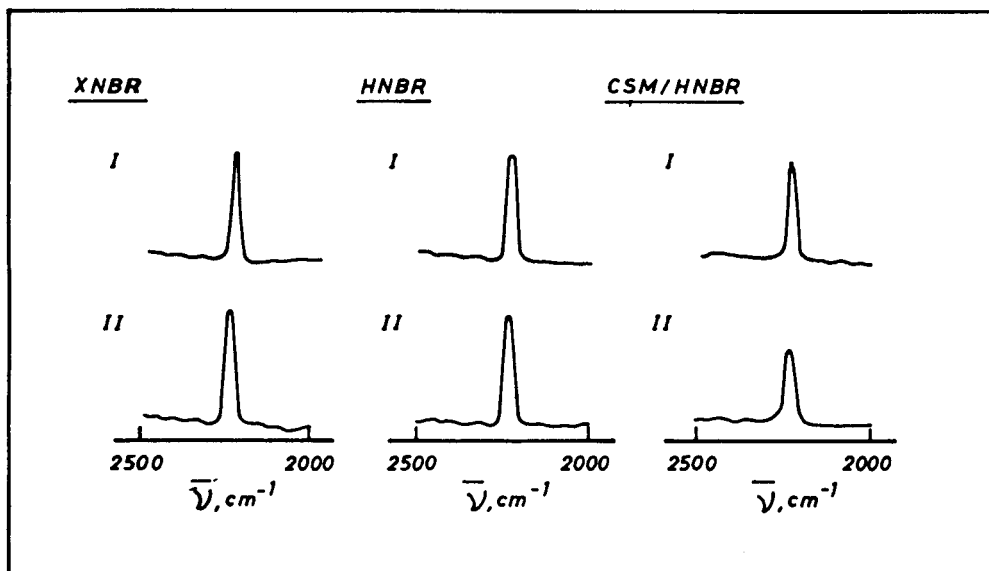
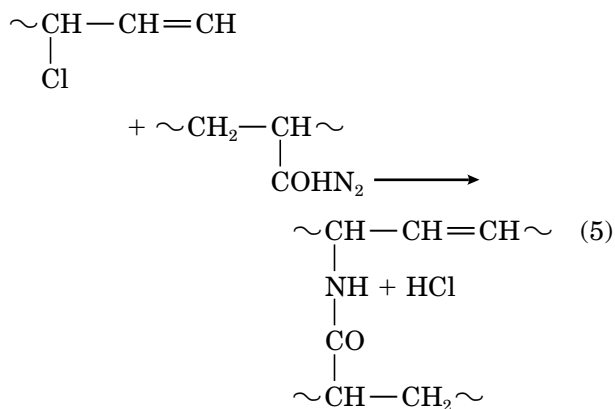
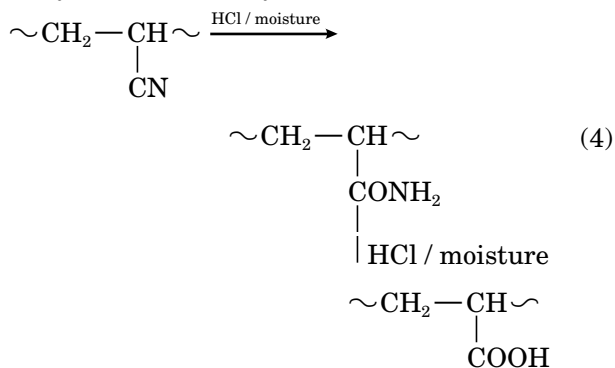


Figure 6 Effect of heat treatment on the intensity of C=N stretching in IR (I) before heat treatment and (II) after heat treatment.

a secondary amide because the amide II band of the primary amide (in the condensed phase) occurs at $1650\text{--}1620\text{ cm}^{-1}$, while the corresponding absorption due to a secondary amide¹² (solid) takes place at $1570\text{--}1515\text{ cm}^{-1}$. This indicates a chemical reaction between *in-situ* generated primary amides and allyl chlorides.



The hydrolysis of cyanide group, therefore, increases the concentration of reactive species in XNBR and thereby facilitates the self-cross-linking process and contributes to extra cross-linking.

In-situ amide formation and its reaction with allyl chloride from CSM, therefore, accounts for the gel formation, even in the CSM/NBR and CSM/HNBR blend systems.

Cis-trans isomerization of double bonds is a typical phenomenon generally prevalent in the presence of sulfur compounds, particularly SO_2 .²¹⁻²³ It has been observed that some of the residual *cis*-1,4-isoprene units in ENR get converted to the corresponding *trans*-isomer during self-cross-linking of CSM/ENR blend.²⁴ Similar behavior is also expected in the CSM/XNBR blend. *Cis-trans* isomerization of polybutadiene is, in fact, more favorable than that of polyisoprene.^{21,23} The butadiene moiety in the XNBR exists mostly in *trans*-1,4-form (66%, *trans*-1,4; 22%, *cis*-1,4~; and 12%, 1,2-butadiene units). The intense peak at 968 cm^{-1} due to *trans*-isomer^{9,12,13} is strongly attenuated upon self-cross-linking of the blend. This is, therefore, consistent with the *cis-trans* isomerization of *trans*-butadiene units of XNBR in the blend. In the uncross-linked blend, the =C-H out-of-plane deformational mode of *cis*-1,4-CH=CH unit at 748 cm^{-1} and CH_2 rocking at $740\text{--}720\text{ cm}^{-1}$ overlap and give a composite band at 746 cm^{-1} ; whereas in the cross-linked blend, these two vibrational modes interact and give a single band at 725 cm^{-1} . Hence, the corre-

sponding increase of the *cis*-content owing to *cis-trans* isomerization cannot be detected.

CONCLUSIONS

- 1) CSM/XNBR (50/50 w/w) is a thermally induced self-cross-linking blend as exhibited by an appreciable amount of gel formation.
- 2) CSM/XNBR (50/50 w/w) shows a single glass transition in DMA, indicating the homogeneity of the blend.
- 3) Infrared studies show that cross-linking takes place in two ways: one through allyl chloride and carboxylic group [eqs. (2) and (3)]; the other through allyl chloride and amide produced due to hydrolysis of $-C=N$ group [eqs. (4) and (5)]. *Cis-trans* isomerization is also exhibited during cross-linking of the blend.

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