# Carboxylated Nitrile Rubber as a Reactive Compatibilizer for Immiscible Blends of Poly(vinyl chloride) and Epoxidized Natural Rubber

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## SYNOPSIS

Blends of poly(vinyl chloride) (PVC) and epoxidized natural rubber (ENR) were prepared by melt-blending and studied using a Monsanto rheometer, infrared spectrophotometer, and dynamic mechanical analyzer. The PVC/ENR blends were found to be self-cross-linkable, but immiscible at 25/75, 50/50, and 75/25 blend ratios. However, addition of a third reactive polymer, such as carboxylated nitrile rubber (XNBR), can make the ternary blend miscible. The quantity of XNBR required to make the binary blend miscible depends on the blend ratio of the binary PVC/ENR blend and increases as the binary blend ratio changes through 25 : 75 to 50 : 50 to 75 : 25. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

Network formation is the predominant factor in elastomer vulcanization.[1] Formation of cross-links can be achieved through interchain reactions.[2,3] Recently, De and co-workers developed several self-cross-linkable blends from polymers having reactive functional groups.[4-9] Earlier it was reported that unstabilized poly(vinyl chloride) (PVC) and epoxidized natural rubber (ENR) form self-cross-linkable blends during high-temperature molding.[10] Such a blend was found to be immiscible even though the stabilized PVC/ENR blends are miscible both at the uncross-linked stage[11-13] and the cross-linked stage.[14] Again, carboxylated nitrile rubber (XNBR) has been reported to form self-cross-linkable and miscible blends with PVC.[15] It has also been reported that ENR and XNBR are able to cross-link between themselves during molding and form miscible self-vulcanizable rubber–rubber blends.[16] Accordingly, since the PVC/ENR system, in the absence of stabilizer, is immiscible, it was thought that the addition of XNBR to this system will have a profound effect on the miscibility of the resulting ternary blend.

Many of the ternary blends reported earlier deal with the study of the addition of a third component that is miscible with the components of an immiscible binary blend.[17-21] Studies on ternary blends with all the three miscible binaries have also been reported earlier.[22,23] Incorporation of ENR into an immiscible blend of polychloroprene and XNBR resulted in a ternary miscible blend system.[24] Similarly, incorporation of XNBR into an immiscible blend of chlorosulfonated polyethylene and ENR resulted in a miscible ternary blend.[25]

In this article, the results of studies on the miscibility of PVC/ENR binary blends and PVC/ENR/XNBR ternary blends are reported.

## EXPERIMENTAL

Table I gives the details of the materials used. Formulations and designations of the blends are given in Table II.

The blends were prepared in a Brabender plasticorder, Model PLE 330, fitted with a cam-type mixing head, at a rotor speed of 60 rpm and temperature of 180°C.

### Preparation of the PVC/ENR Blends

Prior to the blending, PVC was allowed to soften for about 2 min. Next, ENR was added and mixed for about 4 min.

**Table I  Details of the Materials Used**

| Materials | Description | Source |
|---|---|---|
| Poly(vinyl chloride) (PVC) | Suspension-polymerized PVC (NOCIL PVC Polymer S67-311), $K$-value 66–69. $\bar{M}_w = 3.5 \times 10^5$ | National Organic Chemical Industries Ltd., Bombay, India |
| Epoxidized natural rubber (ENR) | ENR-50, 50 mol % epoxidized natural rubber, specific gravity = 1.03. $\bar{M}_w = 4.7 \times 10^5$ | The Malaysian Rubber Producers' Research Association, England |
| Carboxylated nitrile rubber (XNBR) | Krynac-221, high level of carboxylated monomer (7 mol %) and medium-high bound acrylonitrile (28 mol %) rubber. $\bar{M}_w = 1.7 \times 10^5$ | Polysar Ltd., Sarnia, Canada |

## Preparation of the PVC/ENR/XNBR Blends

As discussed above, initially, PVC was allowed to soften for about 2 min and then ENR followed by XNBR were added and blended for about 4 min.

**Table II  Blend Composition in Parts by Weight**

| Blend Designation | PVC | ENR | XNBR |
|---|---|---|---|
| Binary blends (PVC/ENR) | | | |
| 25/75 | 25 | 75 | 0 |
| 50/50 | 50 | 50 | 0 |
| 75/25 | 75 | 25 | 0 |
| Ternary blends (PVC/ENR/ XNBR) | | | |
| 25/75/25 | 25 | 75 | 25 |
| 25/75/50 | 25 | 75 | 50 |
| 25/75/75 | 25 | 75 | 75 |
| 50/50/25 | 50 | 50 | 25 |
| 50/50/50 | 50 | 50 | 50 |
| 50/50/75 | 50 | 50 | 75 |
| 50/50/100 | 50 | 50 | 100 |
| 50/50/125 | 50 | 50 | 125 |
| 50/50/150 | 50 | 50 | 150 |
| 75/25/25 | 75 | 25 | 25 |
| 75/25/50 | 75 | 25 | 50 |
| 75/25/75 | 75 | 25 | 75 |
| 75/25/100 | 75 | 25 | 100 |
| 75/25/125 | 75 | 25 | 125 |
| 75/25/150 | 75 | 25 | 150 |
| 75/25/200 | 75 | 25 | 200 |
| 75/25/250 | 75 | 25 | 250 |

In the case of both the binary and ternary blends, the hot mix was quickly removed from the chamber after the mixing and sheeted out in the tight nip of a laboratory two-roll mill.

A Monsanto Rheometer R-100 was used to study the cure behavior of the blends at 170°C. Two additional compositions, 40/60 and 60/40 PVC/ENR, were also run in order to assess the trend in the rheometric behavior. The 50/50 and 75/25 PVC/ENR blends were molded for 60 min at 170°C. The 25/75 PVC/ENR blend was molded for 90 min at 170°C, since for up to 60 min the rise in rheometric torque for this blend was marginal. In the case of the 50/50 PVC/ENR blend, samples were also molded for 5 min in order to study the effect of molding time on miscibility between PVC and ENR. The ternary compositions were molded for 60 min at 170°C. The molding was done in a Labopress, Model 10T (Toyo Seiki Seisaku-Sho Ltd., Japan), at 10 MPa pressure. After the curing was over, the samples were cooled down to room temperature under pressure by cold water circulation through the platens.

Infrared (IR) spectra were obtained with a Perkin-Elmer 843 spectrophotometer. Thin films of 1 : 1 PVC/ENR and 1 : 1 : 1 PVC/ENR/XNBR blends were prepared by molding for 3 and 60 min at 170°C. The difference spectra of the blends were taken by subtracting the spectrum of the 3 min molded blend from that of the 60 min one. It is assumed that 3 min molding does not cause cross-linking between the polymers, whereas under the 60 min molding, substantial cross-linking occurs to cause changes in the difference IR spectra.

Rheovibron DDV-III-EP (Orientec Corp., Japan) was used to study the dynamic mechanical properties of the blends. The experiment was carried out at a double-strain amplitude of 0.1% (the double-strain amplitude is defined as the ratio of twice the displacement amplitude to the length of the test specimen; the displacement amplitude selected was 0.0025 cm) and a frequency of 3.5 Hz. Measurements were carried out over a temperature range of $-100$ to 200°C at a heating rate of 2°C per min.

## RESULTS AND DISCUSSION

### PVC/ENR Binary Blend

The Monsanto rheographs of 25/75, 40/60, 50/50, 60/40, and 75/25 PVC/ENR blends at 170°C are shown in Figure 1. The 25/75 PVC/ENR blend shows a marching modulus with no sign of reversion even up to 120 min. The rate of rise in torque increases with increasing PVC content. The composition dependence of the increase in torque in the rheographs indicates that the cross-linking reaction depends on the proportion of reactive functional groups in the polymer blend components.

The IR spectra of the 3 min molded 1 : 1 PVC/ENR blend subtracted from that of the same blend molded for 60 min is shown in Figure 2. The reduc-

tion in the peak, i.e., negative absorbance at 875 $cm^{-1}$, indicates that the epoxy group concentration was reduced when molded for 60 min and that the peak at 690 $cm^{-1}$ was reduced due to the decrease in C — Cl linkages.[26] Thus, the evolution of hydrogen chloride (HCl) from PVC causes an increase in the allylic chlorine groups in PVC and opens up the epoxy rings in ENR. The infrared spectrum of PVC alone when molded for 60 min showed changes in unsaturation (1660 $cm^{-1}$) and that of ENR alone showed slight furanization (1030 and 915 $cm^{-1}$), which may be due to the presence of residual acids from the epoxidation stage.

While considering the new peaks appearing in the longer-time molded blend, the peak at 3500 $cm^{-1}$ can be attributed to the hydroxyl groups formed; the peak at 1660 $cm^{-1}$, to the increased unsaturation in the PVC chain; and that at 1710 $cm^{-1}$, to the formation of keto, aldehyde, and carboxyl groups. The 1220 and 1130 $cm^{-1}$ bands are ascribed to the ether groups, and the 1030 and 915 $cm^{-1}$ bands, to that of furanized ENR.[26] Thus, the opening up of epoxy groups by HCl will result in chlorohydrin groups that can act as further reactive sites.[27] The following reactions can result in either cross-linking of ENR with PVC, or with ENR itself, or the furanization of ENR: It has been earlier reported that epoxy resins can cross-link with PVC.[28] Also, it has been
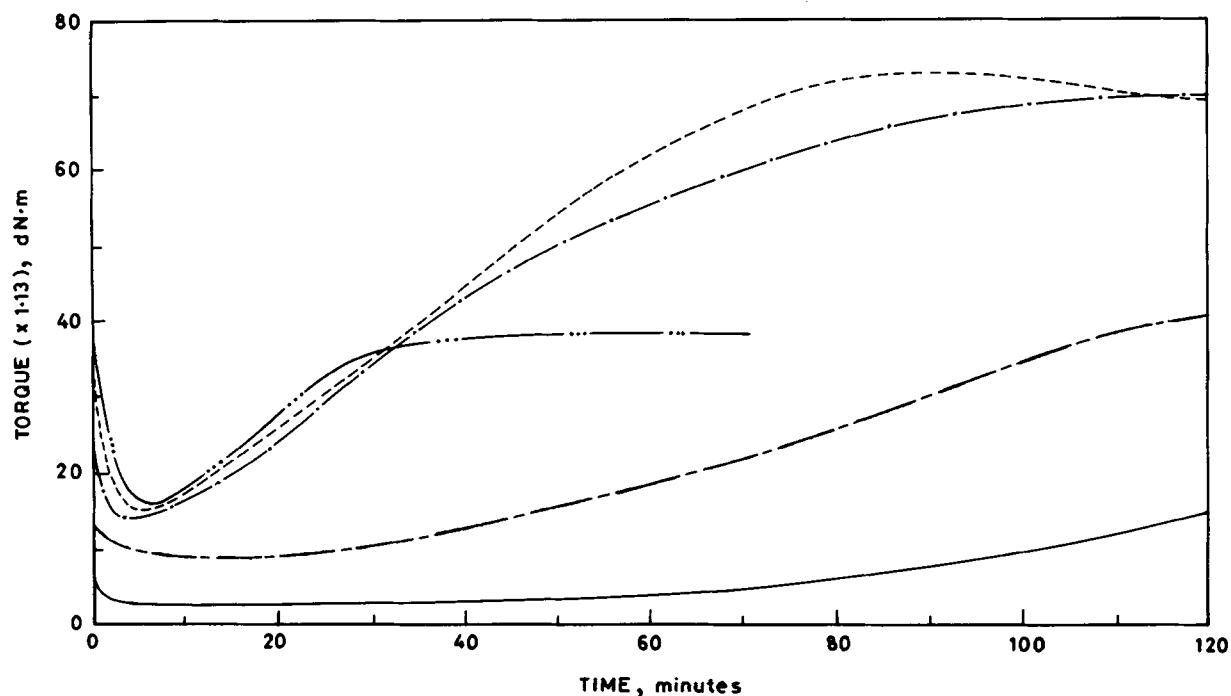


**Figure 1**   Monsanto rheographs of PVC/ENR blends at 170°C, PVC/ENR blends: (———)
25/75; (— — —) 40/60; (— · —) 50/50; (- - - - - -) 60/40; (— · · · —) 75/25.
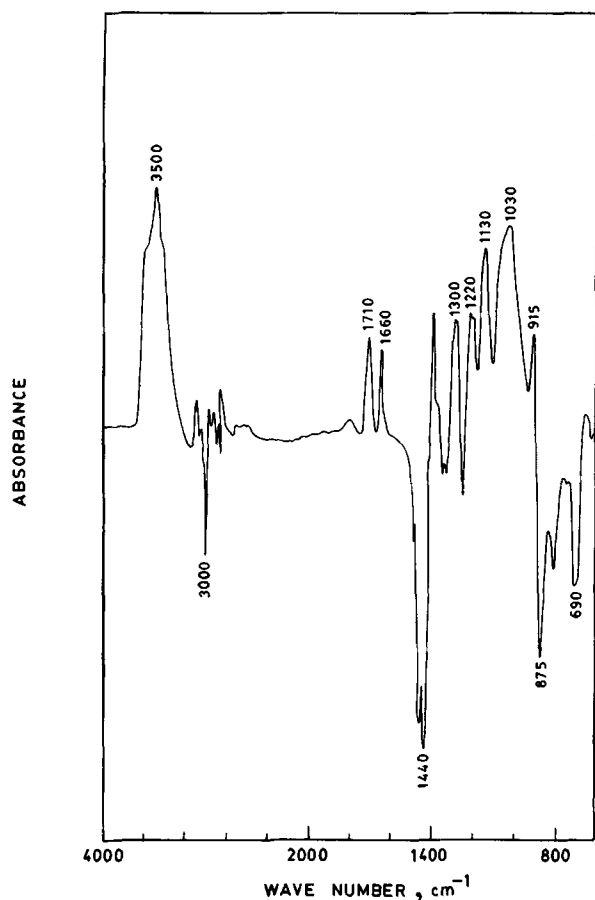
Figure 2    IR spectra of 3 min molded 1 : 1 PVC/ENR blend subtracted from that of 60 min.
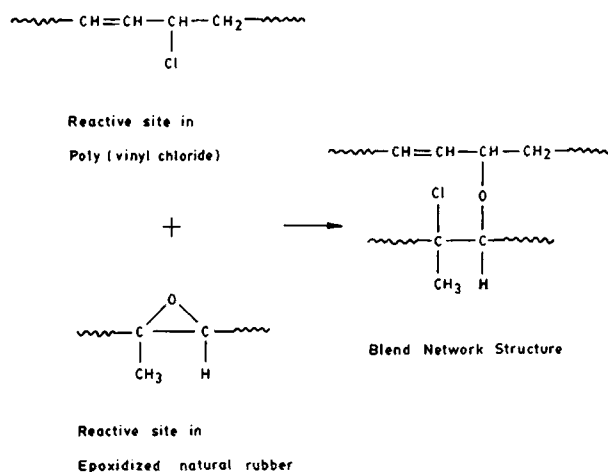


Figure 3    Possible mechanism of cross-linking between PVC and ENR.

ENR blends form an immiscible system at all blend ratios studied.

Dynamic mechanical analysis of the 50/50 PVC/ENR blend, molded for 5 min at 170°C, was carried out and the results are also shown in Figure 4. The dynamic mechanical analysis plots for this blend
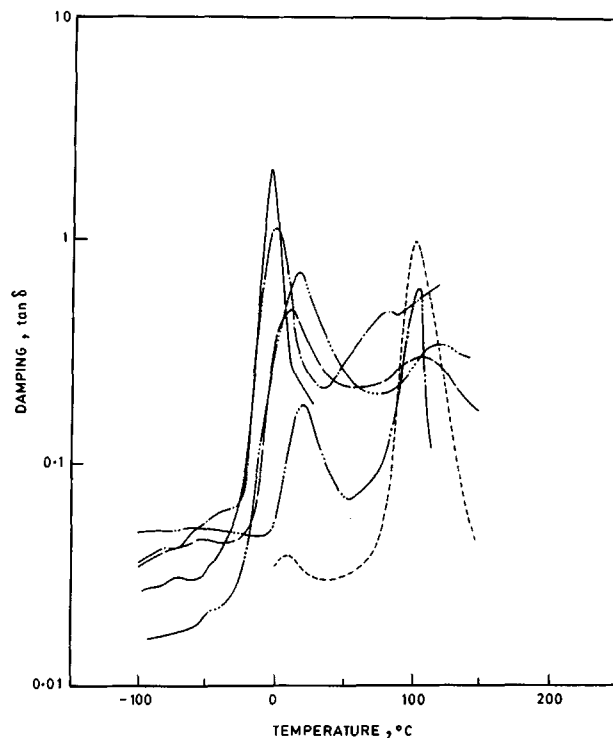
shown that the allylic moieties of 4-chloro-2-hexene and 2-chloro-3-hexene (as prototypes for the reactive segments of the PVC chains) can react with cyclohexene oxide (as a prototype for the epoxy resin) to form an ether,[29] thereby confirming that epoxy resin and PVC can react together to form ether cross-links. A probable mechanism of cross-linking between PVC and ENR is shown in Figure 3. The blend network, however, consists of furanized ENR and cross-linked ENR, along with the cross-linked PVC/ENR.

An idea about the miscibility of the components in the blend was obtained by the dynamic mechanical analyses. The loss tangent, tan $\delta$, vs. temperature plots for the 25/75, 50/50, and 75/25 PVC/ENR blends are shown in Figure 4. All compositions show two transition peaks corresponding to the two phases of the components present. The glass transition temperatures ($T_g$) as obtained from the temperature corresponding to the tan $\delta_{maximum}$ for the blends and the individual components are summarized in Table III. Thus, it is evident that PVC/



Figure 4    Temperature dependence of tan $\delta$ of PVC/ENR system: (——) ENR; (-----) PVC; PVC/ENR blends: (— · —) 25/75; (— —) 50/50; (— · · —) 75/25. (— · · · —) indicates 50/50 PVC/ENR blend molded for 5 min.

**Table III    $T_g$s of the Binary Blends**

| Blend Composition PVC/ENR | $T_g$ (°C) from tan $\delta$ vs. Temperature Plots |
|---|---|
| 0/100 | −5 |
| 25/75[a] | −1, around 90°C |
| 50/50[b] | 9, 105 |
| 75/25[b] | 19, 103 |
| 100/0 | 101 |

[a] Molded at 170°C for 90 min.
[b] Molded at 170°C for 60 min.

also show two separate transitions, indicating that the blend is not miscible even in the nearly uncross-linked state.

The findings on the miscibility of the PVC/ENR blend in the present case are different from those reported earlier in the cases of both solution-cast and melt-mixed blends, which were reported to be miscible.[11-13] The difference between the present observations and the earlier studies lies in the presence of the PVC stabilizer. Although earlier workers have dealt with the PVC/ENR blends containing a PVC stabilizer, the present studies deal with the blends without a PVC stabilizer. It may be argued that the decrease in intermolecular interactions due to both the reduction in C—Cl groups in PVC and the opening up of epoxy groups in ENR, the cross-linking of ENR alone, and the furanization of ENR

all contribute to the phase separation in such blends. Thus, the immiscibility can be attributed to the physicochemical changes occurring in the blend during blending and curing. In the blends of amine cross-linked epoxy resin–poly(ethylene oxide), the phase separation observed during cross-linking was ascribed to the physical and chemical changes of the epoxy resin during cross-linking.[30] It is interesting to note that even in the 5 min molded PVC/ENR blend immiscibility was observed, and this suggests that in the absence of a PVC stabilizer the change occurring during plasticorder-blending and 5 min molding is sufficient to cause the phase separation.

## PVC/ENR/XNBR Ternary Blends

Representative rheographs of the ternary blends are shown in Figure 5. Some of the compositions, especially with low PVC content, show a marching modulus without reversion even up to 120 min. The difference between the maximum and minimum torque values differ with blend ratio, indicating the extent of the dependence of the chemical cross-linking reaction on blend composition.

The IR spectra of the PVC/ENR/XNBR 50/50/50 blend molded for 3 min subtracted from that of the 60 min molded blend is shown in Figure 6. The reduction in peak absorptions at 860 and 690 cm$^{-1}$ is due to reduction in concentration of epoxy groups and —C—Cl groups, respectively.[26] The increase in the hydroxyl stretching vibration at 3530
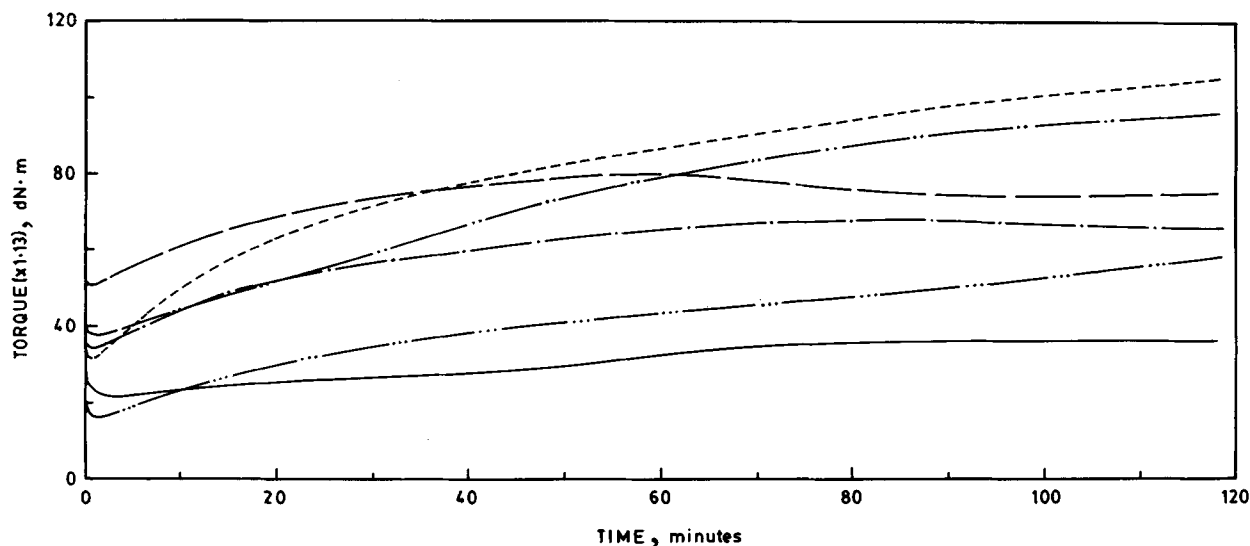


**Figure 5**    Monsanto rheographs for some representative ternary blends at 170°C; PVC/ENR/XNBR blends: (— · · · —) 25/75/25; (-------) 25/75/75; (— · · —) 50/50/25; (— · —) 50/50/150; (— —) 75/25/25; (———) 75/25/250.
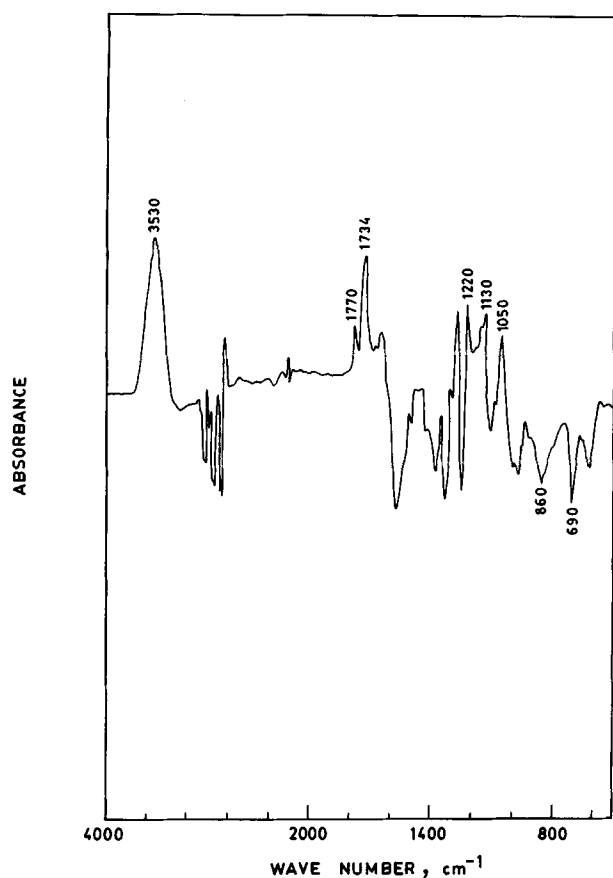
**Figure 6**  IR spectra of 3 min molded 1 : 1 : 1 PVC/ENR/XNBR blend subtracted from that of 60 min.

$cm^{-1}$ is due to the formation of hydroxyl groups in ENR by the opening up of epoxy groups by HCl and due to the hydroxyl groups formed during the ENR-XNBR cross-linking reaction. The peaks at 1220 and 1130 $cm^{-1}$ are due to ether formation, whereas those at 1770 and 1734 $cm^{-1}$ are due to ester formation.[26] The 1050 $cm^{-1}$ can be assigned to that of furan groups.[26] Thus, the blend network structure consists of different types of cross-links: PVC–ENR (ether cross-links), PVC–XNBR (ester cross-links), and ENR–XNBR (ester cross-links). Also, it contains furanized ENR and ENR–ENR cross-links (ether type). The probable cross-linking reaction is shown in Figure 7.

The miscibility of the ternary blends of different compositions was examined by dynamic mechanical analyses.

## Incorporation of XNBR into 25/75 PVC/ENR Blend

This section deals with the 25/75/25, 25/75/50, and 25/75/75 PVC/ENR/XNBR ternary blends. The temperature dependence of loss tangent of the blends is given in Figure 8. The ternary blends show a single transition in tan $\delta$ vs. temperature and loss modulus vs. temperature plots at all compositions studied. The $T_g$ values from damping peak maxima are given in Table IV. Therefore, the ternary blends from PVC, ENR, and XNBR are miscible at 25/75/25, 25/75/50, and 25/75/75 PVC/ENR/XNBR blend compositions.
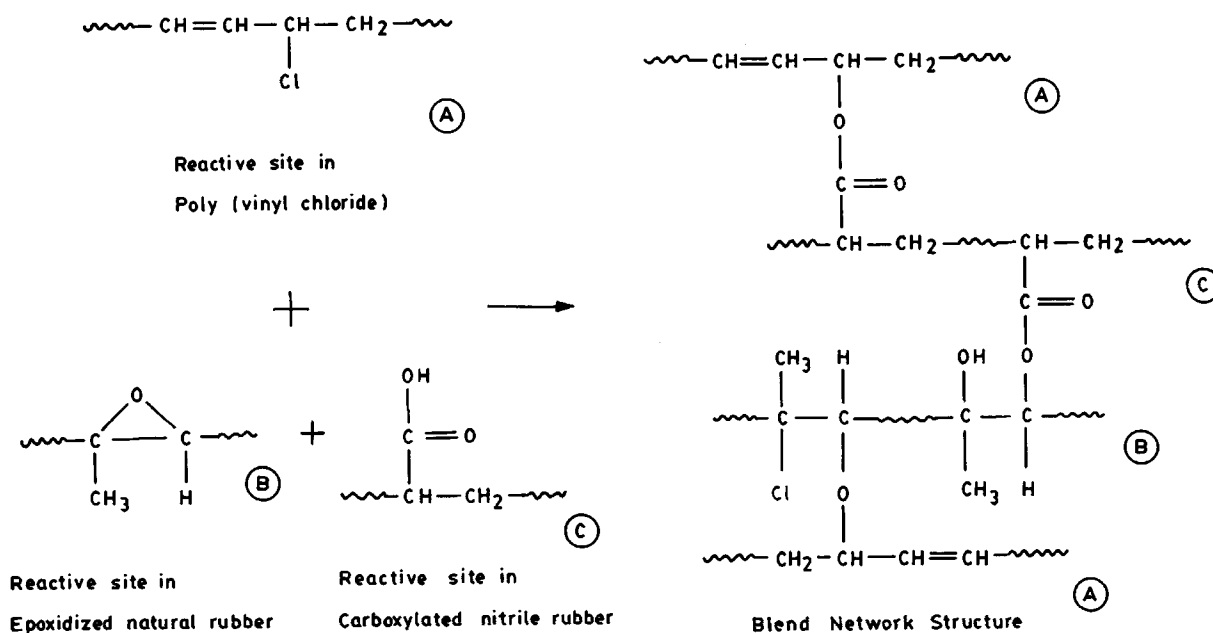


**Figure 7**  Possible mechanism of cross-linking between PVC, ENR, and XNBR.
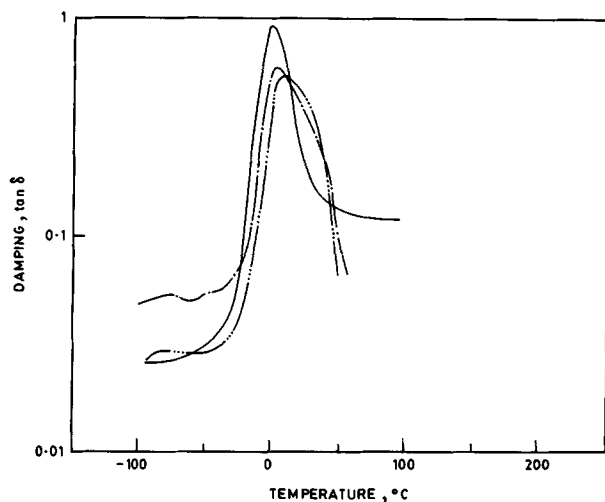
**Figure 8**   Tan $\delta$ vs. temperature plots for PVC/ENR/
XNBR blends: (——) 25/75/25; (— · —) 25/75/50;
(— · · · —) 25/75/75.

## Incorporation of XNBR into 50/50 PVC/ENR Blend

Results of dynamic mechanical analyses of the 50/
50/25, 50/50/50, 50/50/75, 50/50/100, 50/50/
125, and 50/50/150 PVC/ENR/XNBR blends are

shown in Figure 9. Close examination of these plots
reveals that the immiscible binary blend becomes
progressively miscible by the addition of the third
reactive polymer component; XNBR. As XNBR
content increases, the two damping peaks merge and,
accordingly, the 50/50/75 PVC/ENR/XNBR
blend possesses high damping capability over a broad
temperature range. Further increase in XNBR con-
tent reduces the broadness of the transition region.

## Incorporation of XNBR in 75/25 PVC/ENR Blend

Figure 10 shows the results of dynamic mechanical
analyses for the 75/25/25, 75/25/50, 75/25/75, 75/
25/100, 75/25/125, 75/25/150, 75/25/200, and
75/25/250 PVC/ENR/XNBR blends. Low XNBR
content does not alter the immiscibility of the 75/
25 PVC/ENR blend. But as the XNBR content is
increased to 200 parts per hundred parts of the PVC/
ENR blend, the resulting ternary blend shows a
broad damping transition. It can be seen from the
damping plots that several PVC/ENR/XNBR
compositions possess high damping capability over
a broad temperature range. The blend becomes mis-
cible at 250 parts of XNBR and shows a single
damping peak at 3°C.

**Table IV    $T_g$s of the Ternary Blends[a]**

| Blend Composition PVC/ENR/XNBR | $T_g$ (°C) from tan $\delta$ vs. Temperature Plots |
|---|---|
| 100/0/0 | 101 |
| 0/100/0 | −5 |
| 0/0/100 | −8 |
| 25/75/25 | −1 |
| 25/75/50 | 3 |
| 25/75/75 | 9 |
| 50/50/25 | 16, 85 |
| 50/50/50 | 13, 73 |
| 50/50/75 | Broad |
| 50/50/100 | 5 |
| 50/50/125 | 3 |
| 50/50/150 | 3 |
| 75/25/25 | 11, 99 |
| 75/25/50 | 6, 87 |
| 75/25/75 | −1, 87 |
| 75/25/100 | −9, 75 |
| 75/25/125 | −7 and broad |
| 75/25/150 | −8 and broad |
| 75/25/200 | Broad |
| 75/25/250 | 3 |

[a] Molded for 60 min at 170°C.



**Figure 9**   Temperature dependence of tan $\delta$ of PVC/
ENR/XNBR blends: (——) 50/50/25; (— · —) 50/50/
50; (— · · · —) 50/50/75; (— —) 50/50/100; (— · · —)
50/50/125; (------) 50/50/150.

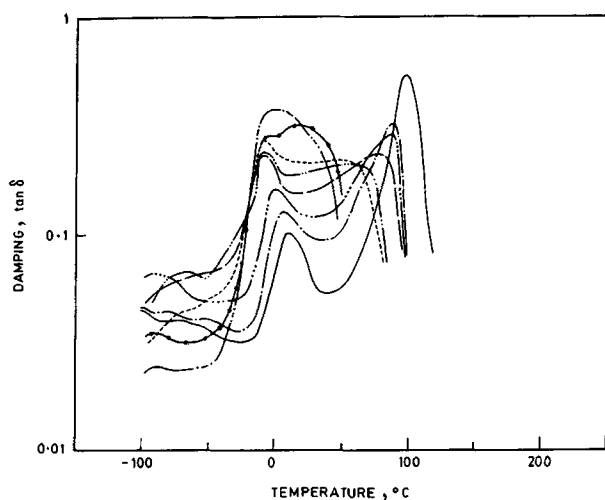**Figure 10** Tan $\delta$ vs. temperature plots for PVC/ENR/
XNBR blends: (———) 75/25/25; (— · —) 75/25/50;
(— · · · —) 75/25/75; (— —) 75/25/100; (— · · —)
75/25/125; (------) 75/25/150; (—▲—) 75/25/200;
(— · – · —) 75/25/250.

The level of XNBR required for compatibilization
depends on the PVC/ENR blend ratio. Also, the
quantity of XNBR required increases as the PVC/
ENR blend ratio changes from 25 : 75 to 50 : 50 to
75 : 25. The reasons for these observations can be
attributed to the structural changes occurring in the
blend during blending and molding. At high PVC
contents, the HCl liberated from PVC favors struc-
tural changes in ENR as discussed earlier. As seen
in the case of PVC/ENR binary blends, PVC-ENR
cross-links cause immiscibility in blends in the ab-
sence of a stabilizer. Therefore, even though PVC/
XNBR and ENR/XNBR blends are miscible, PVC/
ENR networks make the ternary system immiscible.
The increase in XNBR content means relative low-
ering of the PVC content, which decreases the
chances of the structural changes in ENR and the
relative cross-link density of PVC/ENR binary
blends. Therefore, with increase in XNBR content,
the blend changes initially to a partially miscible
system and then to a completely miscible system.
The broadness in the loss tangent plots is a conse-
quence of the superposition of the different relax-
ations of the various blend networks.

It was observed that some of the blend compo-
sitions register high mechanical damping over a
broad temperature range, a behavior not observable
with individual rubber systems. Such ternary blend
compositions may be interesting in respect to vi-
bration damping applications over a wide spectrum
of service conditions.

## CONCLUSIONS

A Brabender plasticorder-mixed blend of PVC/
ENR is self-cross-linkable in the absence of any
cross-linking agent. The extent of cross-linking
varies with composition and the blends possess very
good processing latitude. The blend is immiscible at
PVC/ENR blend ratios of 25/75, 50/50, and 75/
25. XNBR acts as a reactive compatibilizer for the
PVC/ENR system. The self-cross-linkable ternary
blends of PVC/ENR/XNBR can be made miscible
and the quantity of XNBR required to make the
ternary system miscible increases as the PVC con-
tent in the binary PVC/ENR blend increases. The
immiscibility has been ascribed to the furanization
of ENR taking place during the cross-linking reac-
tion in the absence of a PVC stabilizer. Presence of
XNBR prevents this furanization reaction, presum-
ably through formation of self-cross-linkable binary
PVC/XNBR and ENR/XNBR blends.

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