Interchain Crosslinking Between NBR and Polyacrylic Rubber and Effect on (i) Processibility and Blend-Morphology

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SYNOPSIS

Flow behaviour of NBR and polyacrylic rubber blends have been studied throughout the entire composition ranges. The effect of preheating of the blends is also studied in order to understand the interchain crosslinking. Viscosity, extrudate swell, power law indices, have been studied as a function of shear rate and blend ratio. The shearing accompanied by blend ratio has a predominent effect on the rheological behaviour of the preheated blends due to microgel formation. From the rheological behaviour it appears that there is a phase inversion at around 50% of NBR, however, preheating does not change this trend. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The modification of polymer properties through blending has been used increasingly in order to obtain an inexpensive material with improved properties. When two polymers, each containing polar functional groups, are blended, the blend is likely to have better properties derived from interchain linking via functional groups.

Polyacrylonitrile butadiene rubber (NBR) has excellent performance at moderate temperatures and excellent oil resistance, but its high temperature application and ozone resistance are not satisfactory.[1] Blending of NBR with PVC and EPDM for better ozone and improved swell resistance have been examined by several authors.[2-5] Recently Tripathy et al.[6] have studied the blends of NBR and chlorosulphonated polyethylene to improve the ozone resistance and high temperature performance of NBR. It has been suggested that interchain cross-linking is responsible for improved ozone resistance.

In order to optimize the commercial operations, the rheology of polyblend systems must be known. Flow behaviour of polymeric fluids within a duct is at the heart of all extrusion processes. Thus viscosity of individual components plays a decisive role in the flow and forming of compounds. Several attempts have been made to predict the complicated rheological behaviour of polymer blends in view of its relevance to processing.[7-10] Uaki[11] has reviewed the rheology of multiphase flows. We have prepared the blends of NBR with polyacrylic rubber throughout the entire composition range and studied their rheological behaviour. We have reported a) the flow behaviour of preblends and preheated blends, b) the mechanism of interchain crosslinking, and c) the blend morphology.

EXPERIMENTAL

NBR (NBR-3309 from Synthetics and Chemicals Ltd., India) and polyacrylic rubber (Nipol AR-51, Nippon Zeon, Japan) were blended according to the formulations given in Table I. For the preparation of preblended stock the virgin polymers were well blended and for the preparation of preheated stocks, preblends were heated in a mould at 170°C for 40 min. Before studying the rheological behaviour both types of blends were kept for 24 h at ambient in order to attain an equilibrium. Blending was performed in an open mixing mill (keeping the nip gap

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Table I   Blend Formulations of Preblended Stock (Based on 100 phr Rubber)

Mix No.	A	B	C	D	E
NBR (3309)	80	60	50	40	20
AR-51 (Nipol)	20	40	50	60	80

Preheated blends are designated as superscripts W.

and friction ratio constant for all the blends) at ambient. Gottfart rheograph 2001 was used for rheological measurement of the curative free blends. The barrel temperature was fixed at 130°C and four shear rates (46.08, 115.2, 230.4, and 460.8 s^{-1}) were selected for the study of rheological parameters. The non-Newtonian index (n) and consistency index (k) were determined from shear stress and shear rates employing regression analysis. Extrudate samples were used to determine the swelling ratio (α) with the help of an optical microscope fitted with micrometer. Viscoelastic parameters such as stored elastic energy (W), shear modulus (G), relaxation time (t_R) were determined following the mathematical model as developed by Das et al.[12] namely,

$$\gamma_m = \sqrt{(1/2c)\,(\alpha^4 + 2\alpha^{-2} - 3)}.$$

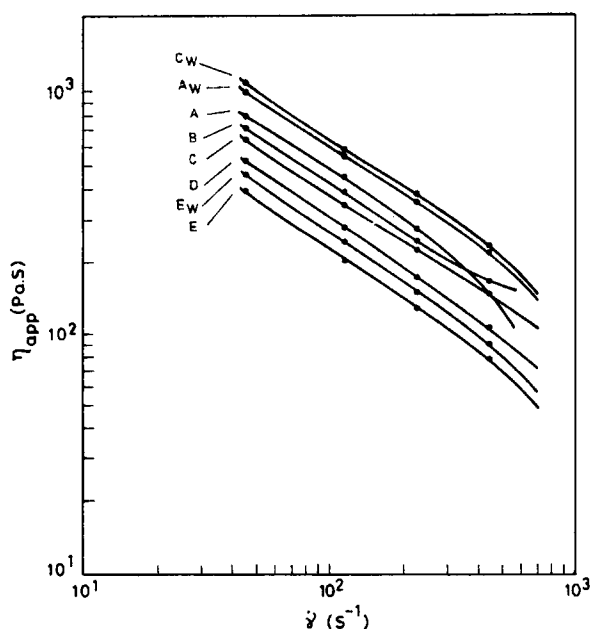where $c = (3n + 1)/4(5n + 1)$ and γ_m is recoverable deformation,

Figure 1   Variation of apparent viscosity $(\eta_{app.})$ with shear rate.

$$W = c\gamma_m \tau.$$

$$G = 2W/(\alpha^4 + 2\alpha^{-2} - 3),$$

$$t_R = [1/(\tau^{(1-n)/n})] \cdot [(n \cdot K^{1/n})/$$

$$G(1 - n) \cdot \{\exp[(1 - n)/n] - 1\}.$$

Cure characteristics were measured using a Monsanto R-100 Rheometer. Phase morphology was studied for extracted samples in acetone with the help of SEM (Camscan Series 2 and E 5200 Autosputter Coater). DSC studies were carried out using Stanton Redcraft Thermal Analyser STA-652, version C 4.20 in a nitrogen atmosphere to determine the heat of cross-linking reaction. FTIR spectra were obtained with transparent films of the blended polymers.

RESULTS AND DISCUSSION

Flow Behaviour of Preblends and Preheated Blends

Effect of Shear Rate and Blend Ratio on the Melt Viscosity

Variation of apparent viscosity with shear rates for various blends are shown in Figure 1. The viscosity decreases with shear rates for all the blends. This decrease may be attributed to the disentanglement of chains at higher shear regions or to the breaking of microgels. Variation of melt viscosity with the blend ratio for both the preblends and preheated blends are shown in Figure 2. There are two distinct stages in viscosity change with the addition of NBR in the blend. First, there is a rapid rise of viscosity with initial addition of NBR, then beyond ~ 50%
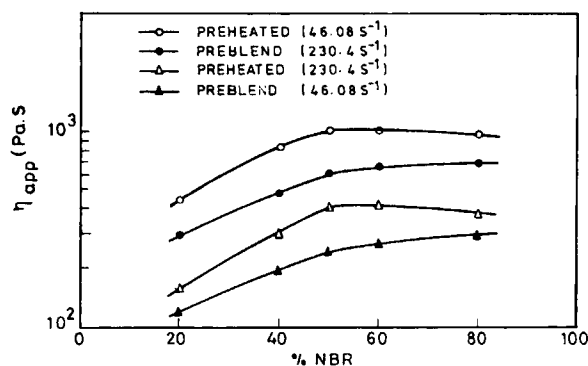

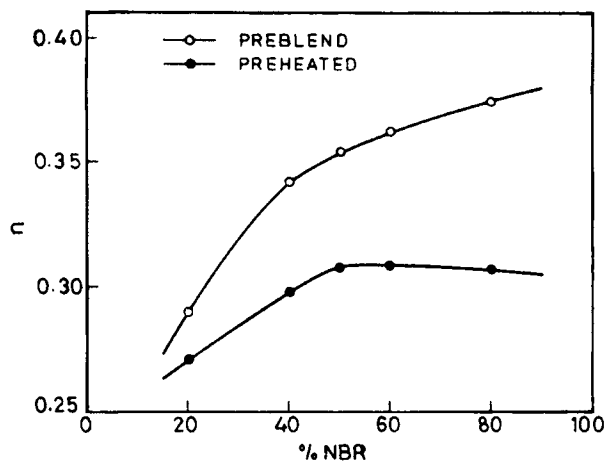**Figure 2**   Variation of apparent viscosity $(\eta_{app.})$ with percent NBR.

Figure 3   Variation of non-Newtonian index (n) with percent NBR.

Figure 4   Variation of extrudate swell (α) with percent NBR.

of NBR, viscosity increases slowly except for the preheated blends where viscosity decreases marginally at the higher level of NBR.

Effect of Blend Ratio on Power Law Indices

The non-Newtonian index n is plotted against the blend ratio in Figure 3. We see that for both the preblends and the preheated blends, the n value increases with NBR content up to about 50% of NBR. Beyond this, whereas preblend shows a continued increase in n value at a slower rate, the preheated blends seem to show a saturation in n value. The low values of n may be attributed to the interchain cross-linking at higher levels of NBR in the blends.

Effect of Shear Rate and Blend Ratio on Swelling Ratio

Representative plots of the extrudate swelling ratios with NBR content are shown in Figure 4 as a function of shear rate for both types of blends. At a high shear rate, the die swell increases as NBR content increases, attains a maximum at 50% NBR, and then decreases on further increase in NBR. However, at low shear rates, the swelling ratio tends to decrease marginally with the increase in NBR content in the blend. We see that preheating of blends decreases the swelling in all shear rates. Here again there is an inflexion point at 50 : 50 level for the preblends (without heating) at low shear rate.

Effect of Shear Rate and Blend Ratio on Rheological Parameters

The rheological parameters with blend compositions are shown in Figures 5–7. The relaxation time in-

creases with the increase in NBR content up to a 50% level for both the preblends and preheated blends. Comparing the preblends and preheated blends, we see that the relaxation time decreases from 40 to 50% of NBR and then increases gradually up to 100% of NBR for the preblends at all the shear rates studied; but there is a clear inflexion point around 50 : 50 ratio for the preheated blends. Preheating of the blends increases the relaxation time.

Shear modulus is also changed with the blending type (Fig. 6). Preheated blends provide higher modulus than the preblends. It is obvious that shear modulus either decreases or remains the same at the
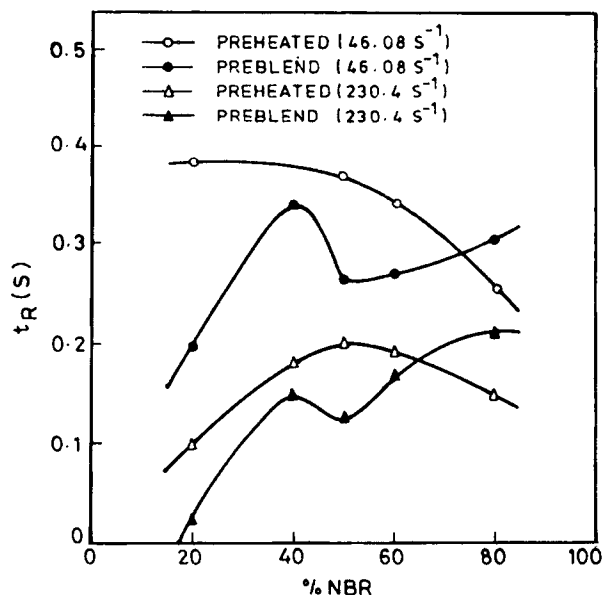
Figure 5   Variation of relaxation time (t_R) with percent NBR.

Figure 6   Variation of shear modulus (G) with percent NBR.

initial level of NBR for preblends, but beyond 45% of NBR there is a further rise in the G value irrespective of shear rates; whereas at the lower shear rate preheated blends show the continuous rise in the shear modulus for the entire composition range.

Stored elastic energy (Fig. 7) also increases with shear rate both for preblends and preheated blends. Here again, we see that the W values increase
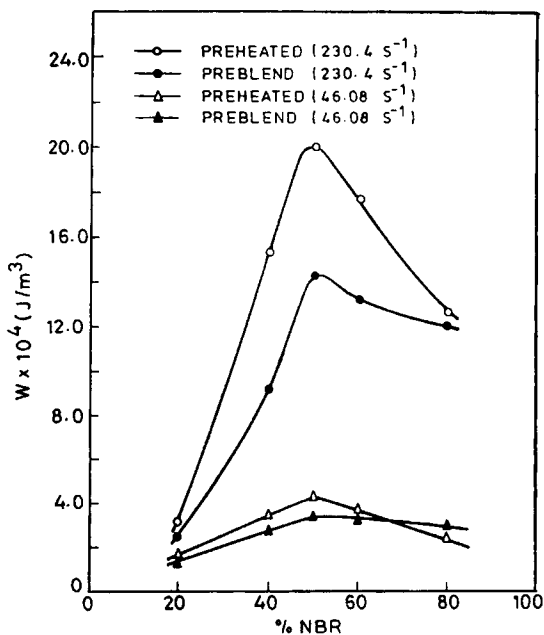
Figure 7   Variation of stored elastic energy (W) with percent NBR.

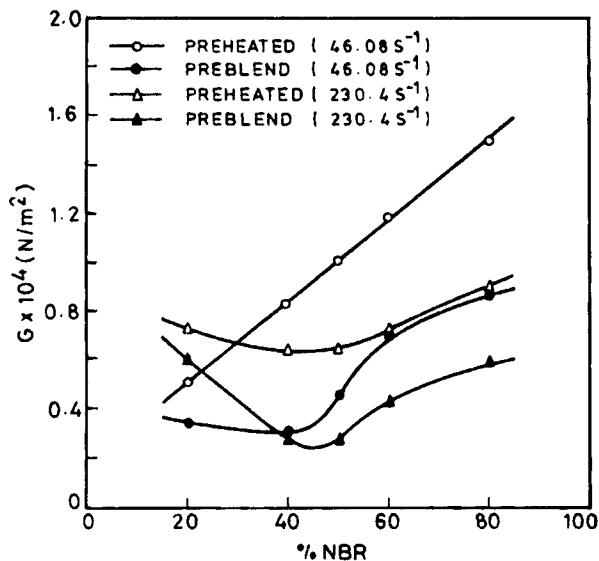sharply with NBR, attain a maximum at 50 : 50 level, and beyond 50% NBR the stored elastic energy decreases.

From the above rheological parameters it appears that there is a phase inversion at around a 50 : 50 blend ratio of NBR and polyacrylic rubber. However, preheating does not seem to change the position of this inversion point. These rheological parameters change appreciably with the blend ratio for the preheated blends particularly at high shear rate region. This may be due to shear induced structural changes in the blend. It may be assumed that preheating induces microgels in the blend, depending on the blend ratio, that are prone toward shear rate at its higher level. This type of shear sensivity may be absent in the preblends.

Mechanism of Interchain Cross-linking

In order to study the interchain cross-linking the continuous cure characteristics of the blends (Table I) in absence of curatives were studied (shown in Fig. 8). Rheometric torque (state of cure) gradually increases with time for all the blends, although to a different extent depending on the blend ratio. This variation in rheometric torque with the blend ratio probably suggests the cross-linking between the two polymers that has already been described in the earlier section. The above view of interchain cross-linking has been confirmed by FTIR spectral analysis of the individual polymers and the blends that have been preheated in the mould (at 170°C, 40 min).

It is observed from Figure 9 that polyacrylic rubber contains ester ($-CO_2R$) and $C-Cl$ bonds. The corresponding peaks are 1726 cm^{-1}(s) and 1233 cm^{-1}(s) for $>C-O$ and $-C=O$ bonds in ester[13] and 704 cm^{-1}(s) for $C-Cl$ bond.[14] In addition to this there are other peaks such as 2933 cm^{-1}(s) for $C-H$ stretching, 858 cm^{-1}, 776 cm^{-1}(s) for $C-H$ deformation.
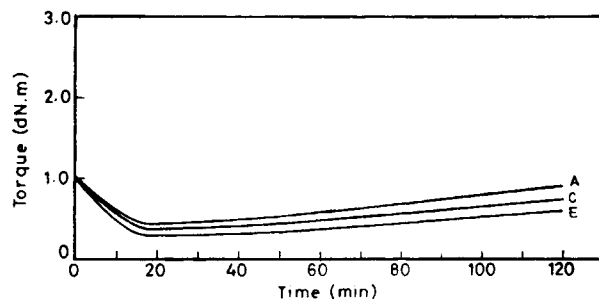
Figure 8   Rheometric torque versus cure time.
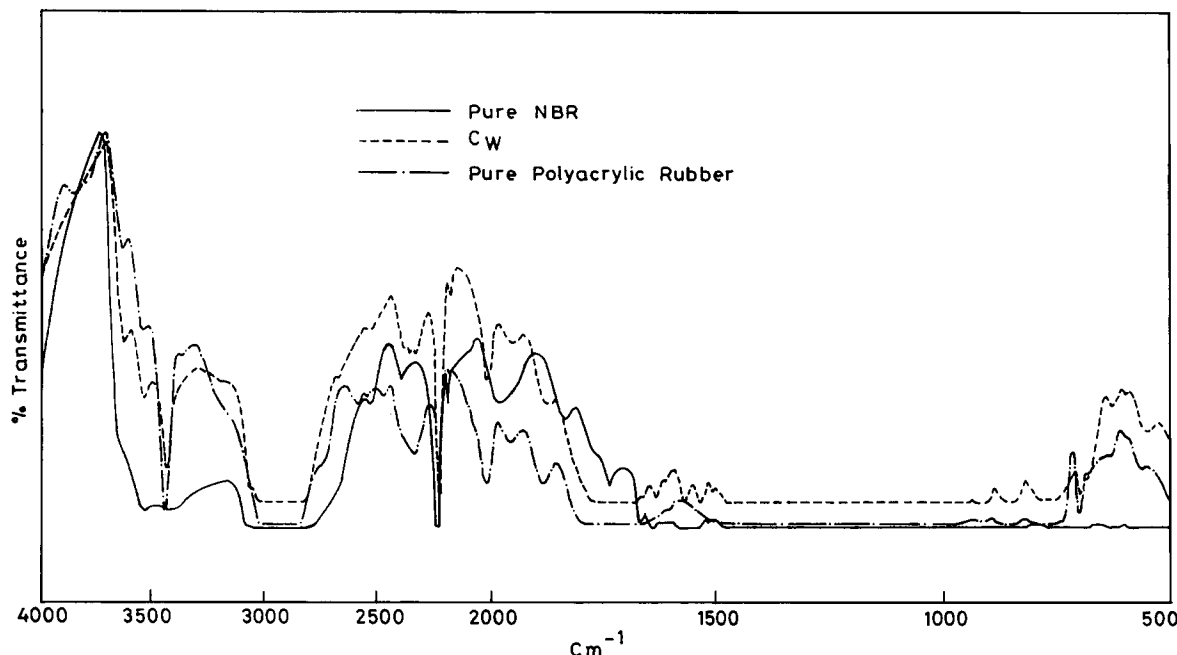
Figure 9 FTIR spectra of C_w, pure NBR, and pure polyacrylic rubber.

NBR has the nitrile (— C≡N) group and C=C bond in the main chain. The corresponding peaks are 2238 cm^{-1}(s) and 1628 cm^{-1}(s), respectively.[15]

The absence of 1726 cm^{-1}(s) and 1233 cm^{-1}(s) frequencies for ester group suggests the involvement of —CO_2R in the interchain cross-linking reaction when the blends are heated. Similarly, the presence of 3442 cm^{-1}(s) for N—H (secondary) and 1729 cm^{-1}(s) for >C=O in amide suggests that —CO_2R may be converted into amide with —C≡N of NBR. But the presence of 2236 cm^{-1}(s) suggests that —C≡N are a remaining excess or nonreacting. Amide formation and percentage transmittance shows that —C≡N is undergoes the reaction. The presence of 1639 cm^{-1}(s) of C=C that is obtained in the blend hints that C=C of NBR is converted or rearranged after interchain cross-linking to have a most stable compound.[16] Besides these above peaks there are other secondary peaks such as 1576

cm^{-1}(s) and 1540 cm^{-1}(s) for N—H bending, and 859 cm^{-1} and 772 cm^{-1} for C—H deformation. The presence of 702 cm^{-1} indicates that the C—Cl bond remains intact. Considering the above fact the following may be the probable mechanism of the interchain cross-linking reaction. The presence of a polar group in the polymers' ionic mechanism has been taken into account.

Reaction:

∼CH_2—CH=CH—CH_2—CH_2—CH∼
                                    |
                                    C≡N

[NBR]

+   ⟶

R—O
   |
O=C
   |
∼CH_2—CH—CH_2—CH∼
                    |
                    O—CH_2—CH_2Cl

[PAR]

∼CH_2—CH=CH—CH_2—CH_2—C∼ + H⁺ ⟶
                                    ‖
                                    C=N
                                    |
                              R—O—C—O⁻
                                    |
              ∼CH_2—CH—CH_2—CH∼
                         |
                         O—CH_2—CH_2Cl

Table II Heat of Cross-linking Reaction

Blend Ratio (NBR : PAR)	80 : 20 (A)	50 : 50 (C)	20 : 80 (E)
Heat of reaction (exo.) (mcal/mg)	0.19	0.49	0.39
Onset temperature (°C)	134	100	115

$$\sim CH_2-CH=CH-CH_2-\overset{\overset{\displaystyle H}{|}}{CH}-\overset{\overset{\displaystyle |}{C}}{\underset{\underset{\displaystyle C=N}{\|}}{}}\sim \; + \; ROH \longrightarrow$$

$$\underset{\underset{\underset{\underset{\underset{O-CH_2-CH_2Cl}{|}}{\sim CH_2-CH-CH_2-CH\sim}}{|}}{C=O}}{C=N}$$

$$\sim CH_2-CH=CH-\underset{\underset{\displaystyle H}{|}}{CH}-CH=\underset{\underset{\underset{\underset{\underset{O-CH_2-CH_2Cl}{|}}{\sim CH_2-CH-CH_2-CH\sim}}{|}}{C=O}}{\underset{\underset{\displaystyle C=N}{|}}{H-C}}\sim \longrightarrow$$

$$\sim CH_2-CH=CH-CH=CH=\underset{\underset{\underset{\underset{\underset{O-CH_2-CH_2Cl}{|}}{\sim CH_2-CH-CH_2-CH\sim}}{|}}{C=O}}{\underset{\underset{\displaystyle CH-N-H}{\|}}{C}}\sim$$

From the reaction, it seems that the interchain cross-linking occurs via amide formation out of the —C≡N in NBR and the —CO₂R of polyacrylic rubber. The C—Cl bond also remains unaffected by this reaction. This is confirmed by FTIR spectra showing the presence of amide, C—Cl bond, C=C, and the absence of —CO₂R.

Heat of Interchain Cross-linking Reaction

Heat of reaction and onset temperatures of the interchain crosslinking are reported in Table II. In each of the three blends, exothermic peaks are observed within this temperature range depending on blend ratios. The heat of interchain cross-linking rises from the 80 : 20 (NBR:PAR) level to the 50 : 50 (NBR:PAR) level then decreases again at the 20 : 80 level of the blend ratio. The onset temperature of curing traces the reverse trend where the early reaction is encountered in the case of the 50 : 50 blend maintaining the higher onset temperatures at both ends. This study clearly reveals that there is a reaction between the two types of polymer chains (confirmed by FTIR) and the extent of reaction depends on the blend ratio.

Blend Morphology

The SEM of the acetone extracted (polyacrylic rubber is soluble) samples of 80 : 20 (NBR:PAR) both

Figure 10 SEM fractogram of the extracted blend "A" (500×).

with and without heating are shown in Figures 10 and 11. The simple blending with no heating (preblends) (Fig. 10) removes the PAR phase to a considerable extent that are in larger domain size. However, preheating of blends restricts the extraction of PAR that has comparatively lower domain size (Fig. 11). This is accompanied by more or less smooth surface texture as compared to the blends of without heating.

CONCLUSION

NBR reduces the elastic response and enhances the processibility of polyacrylic rubber. Heat treatment of the preblend may be preferred because of enhanced phase adhesion due to interchain cross-linking. This interchain cross-linking, which leads to microgel formation, has a predominant effect on the processability, especially at higher shear rate regions. Preheating of the blends results in the higher viscosity, relaxation time, shear modulus, and lessens the die-swell than the blends without heating. Preheating, however, restricts the extraction of the PAR phase in ketonic solvent. The interchain cross-linking occurs throughout the entire composition ranges, although this cross-linking is predominant at a 50 : 50 ratio of the blends. We also see that

Figure 11 SEM fractogram of the extracted blend "Aw" (500×).

there is a phase inversion at around the 50 : 50 level of the blend irrespective of blending type.

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