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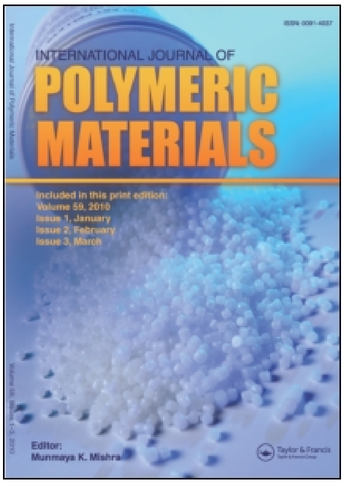

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Polyblend Systems of Polyurethane and HNBR Elastomers (Peroxide Cure)

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The blends of polyurethane elastomer (AU) with hydrogenated nitrile rubbers (HNBR) prepared by different blending techniques and different blend ratios have been studied. The processability and weather resistant properties of polyurethane elastomer was improved by blending with HNBR. Blend properties largely depend on the blend ratios and blending techniques. IR spectral analysis suggested interchain crosslinking by thermal activation between AU and HNBR. Preheating of the preblends before adding curatives improved the properties of the blends. The thermal stability of the blends were also improved. Preheating restricted the extractibility of the phases by solvent extraction as confirmed by the SEM analysis.

Keywords: Polyurethane; Nitrile rubbers; Elastomers; Blends

1. INTRODUCTION

There has been a significant advancement in the polymer blend technology because of technical and economic consideration which enables one to tailor and optimize the properties of the polymeric materials to the specific needs [1-4]. When two polymers each containing polar functional groups are blended, the blend is likely to have better properties derived from interchain crosslinking *via* functional groups. The combination of excellent mechanical strength and abrasion resistance makes the AU very attractive material for several applications [5]. Hydrogenated nitrile rubber (HNBR) is an

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easy processing high oil resistant speciality elastomer. HNBR is useful where an oil resistant polymers is required to have high modulus and tensile strength in a relatively easy processing materials. Wilcox [6] has studied the blends of AU elastomer with polybutadiene and nitrile rubber and discussed the possible applications. Recently Das *et al.*, have studied the blends of AU-XNBR elastomers [7] and EVA elastomers [8] and discussed the dependence of blend properties on the blending techniques. The present paper reports the effect of the blending techniques on the properties of blends and blend morphology and probable interchain linking.

2. EXPERIMENTAL

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The hydrogenated nitrile rubber (HNBR) used was Therban-1707 of Bayer Germany and the polyurethane elastomers (AU) was Vibrathane 5004 grade (ex. Uniroyal, USA). Blends were prepared in an open two-roll mixing mill at room temperature with uniform nip gap and speed by gradual replacement of AU with HNBR over the entire composition range using DCP (Varox 40 KE) as the curative. Blends were allowed to cure in a hot press at 150°C upto optimum cure under constant pressure. Measurement of cure characteristics were carried out at 150°C in a Monsanto Rheometer R-100.

Physical properties like hardness, modulus, tensile strength, elongation at break *etc.*, were measured on cured sheets both before and after aging. Aging was performed in an air oven at 120°C for 48 hrs. Solvent swelling [9] was studied in dimethyl formamide (DMF) and methyl ethyl ketone (MEK) at room temperature for 48 hrs to assess phase adhesion following the Kraus equation [10]. Infrared spectra were taken on virgin polymers and AU/HNBR blend (without any curative) using a Perkin Elmer Model 837. Phase morphology was studied on extracted samples in DMSO with the help of SEM (Camscan Series 2 and E 5200 Auto Sputter Coater). Differential Scanning Calorimetry (DSC) study was carried out using Stanton Redcroft Thermal Analyser STA- 625 to determine T_g values and high temperature DSC also performed to determine the thermal stability of the blend and heat of vulcanization. Two types of blending

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techniques were followed:

(i) preblending technique.
(ii) preheated preblending technique.

3. RESULTS AND DISCUSSION

3.1. Preblending Technique of AU and HNBR

The elastomers AU and HNBR were blended in their entire composition range and then the curatives were incorporated as per compounding formulations shown in Table IA.

The physical properties are given in Table IB. The state of cure ($Y_{\max} - Y_{\min}$) of the blends gradually decreased with the addition of HNBR as shown in Figure 1. The modulus decreased with the addition of HNBR in line with the state of cure. The hardness of the blends followed the same trend. AU rich blends showed high tensile strength compared to the HNBR rich blends. The elongation at break increased as HNBR is added to the blend. With the addition of HNBR the extent of crosslinking decreases, which resulted the above changes.

After aging in air the elongation at break of the blend decreased, but the hardness, modulus and tensile strength are increased in all the cases as shown in Table IC.

TABLE IA Compounding formulations of AU/HNBR (g/g) blend

	1	2	3	4	5
AU	80	60	50	40	20
HNBR	20	40	50	60	80
DCP	2	2	2	2	2

TABLE IB Physical properties

	1	2	3	4	5
$Y_{\max} - Y_{\min}$ (dNm)	21	17	14	11	8
Hardness (Å)	44	42	41	39	40
Modulus 200% (kg/cm^2)	9.0	8.6	4.9	3.8	4.6
Tensile strength (kg/cm^2)	110.0	78.0	58.0	48.2	43.1
Elongation at break (%)	1050	1120	1140	1300	1400

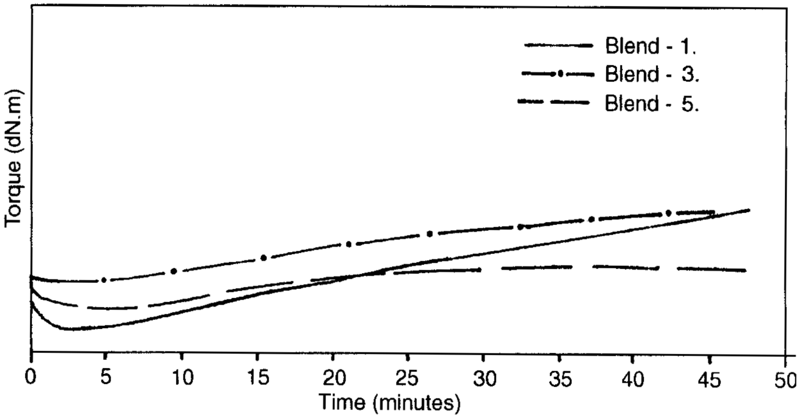

FIGURE 1 Variation of Rheomatric torque with cure time. (1) (80 : 20) AU/HNBR preblended sample, (3) (50 : 50) AU/HNBR preblended sample, (5) (20 : 80) AU/HNBR preblended sample.

TABLE IC Percent change in properties after aging in air at 120°C for 48 hrs

	1	2	3	4	5
Hardness change (in points)	+6	+6	+4	+3	+1
Modulus 200% (kg/cm^2)	+5.5	+7.6	+18.36	+12.4	+6.5
Tensile strength (kg/cm^2)	+4.5	+20.4	+55.0	+30.3	+16.0
Elongation at break (%)	−4.8	−6.5	−10.52	−13.2	−17.1

3.2. Effect of Heat Treatment on the Properties of the Blends

In order to study the effect of preheating of the blend properties, AU and HNBR were blended in their entire composition range then heated at 150°C for 15 min. The curatives were then incorporated into the preheated blends. The compounding formulations were same as shown in Table IA and the corresponding physical properties were given in Table ID.

On preheating the preblends, the state of cure ($Y_{\max} - Y_{\min}$) decreases while the elongation at break increases in all the cases. The tensile strength, hardness and modulus decreased compared to the preblend sample in AU rich and also HNBR rich blends. On preheating there might be a certain extent of interchain crosslinking between the AU and HNBR phases. Hence after the addition of

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TABLE ID Physical properties

	1	2	3	4	5
$Y_{max} - Y_{min}$ (dNm)	18	16	10	9	5
Hardness (Å)	39	38	33	30	29
Modulus 200% (kg/cm^2)	7.6	6.9	4.3	4.0	3.2
Tensile strength (kg/cm^2)	74.2	64.0	45.6	41.0	24.0
Elongation at break (%)	1800	1950	2100	2200	2400

TABLE IE Percent change in properties after aging in air at 120°C for 48 hrs

	1	2	3	4	5
Hardness change (in points)	+7	+5	+5	+4	+4
Modulus 200% (kg/cm^2)	+6.3	+12.0	+14.6	+9.0	+3.1
Tensile strength (kg/cm^2)	+9.0	+24.0	+32.2	+30.0	+25.0
Elongation at break (%)	+11.1	+13.0	+14.28	+16.0	+16.7

curatives the state of cure does not increase so much since some of the curing sites are consumed during the heating and thus physical properties are being modified accordingly. On aging hardness, modulus and tensile strength and elongation at break of the preheated samples were found to increase as shown in Table IE.

3.3. Differential Solvent Swelling Study

Differential solvent swelling with DMF and MEK were studied in order to study the phase adhesion between the two elastomers and represented in the Figures 2 and 3. It was observed that in MEK the

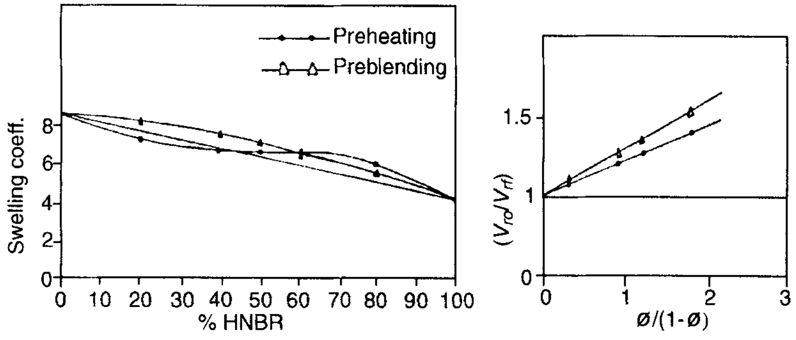

FIGURE 2 Plot of swelling coefficient against HNBR and the Kraus plot of V_{ro}/V_{rf} against $\phi/1-\phi$ for AU/HNBR blend in DMF solvent.

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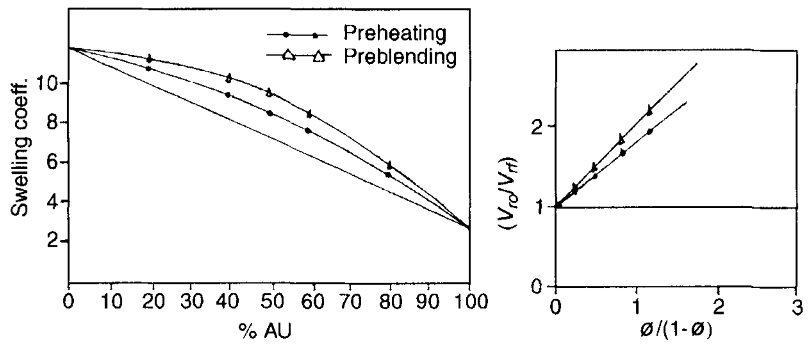

FIGURE 3 Plot of swelling coefficient against AU and the Kraus plot of V_{ro}/V_{rf} against $\phi/1-\phi$ for AU/HNBR blend in MEK solvent.

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percent volume swell decreases with increase of AU. The swelling coefficient of the blend lie well above the average additive line. It is observed from Figure 2 swelling in DMF, that the swelling coefficient of the preblended sample lie above the additive average line whereas in the case of the preheated preblended sample there is a transition at around (60:40) AU/HNBR. However the corresponding Kraus plot showed the positive slope for both the types of techniques used, again suggesting the lack of covulcanisation.

3.4. IR Spectral Analysis

The IR spectra of the thin films of pure AU, pure HNBR and AU/HNBR (50:50) blend (without any curative) heated at 150°C for 30 minutes are shown in Figure 4. AU shows a broad peak at $1716\,\mathrm{cm}^{-1}$ for the presence of 2° amide $>\mathrm{C{=}O}$ stretching and at $3510\,\mathrm{cm}^{-1}$ for 'N—H' stretching [11]. In HNBR there was a sharp peak at $2230\,\mathrm{cm}^{-1}$ for $-\mathrm{CN}$ group [12]. The blend showed shift of the peak to $2290\,\mathrm{cm}^{-1}$ for $-\mathrm{CN}$ group and $1740\,\mathrm{cm}^{-1}$ for $>\mathrm{C{=}O}$ stretching clearly indicate that they are present under different environment. The peak at $3510\,\mathrm{cm}^{-1}$ for 'N—H' stretching of AU was absent in the blend suggesting the crosslinking occurs through 'N' in AU. The appearance of one additional new peak at $1520\,\mathrm{cm}^{-1}$ in the blend may be due to the formation of crosslinked 'C—N' bond between the two elastomers. A plausible mechanism for the interchain crosslinking reaction may be cited below in the Scheme I.

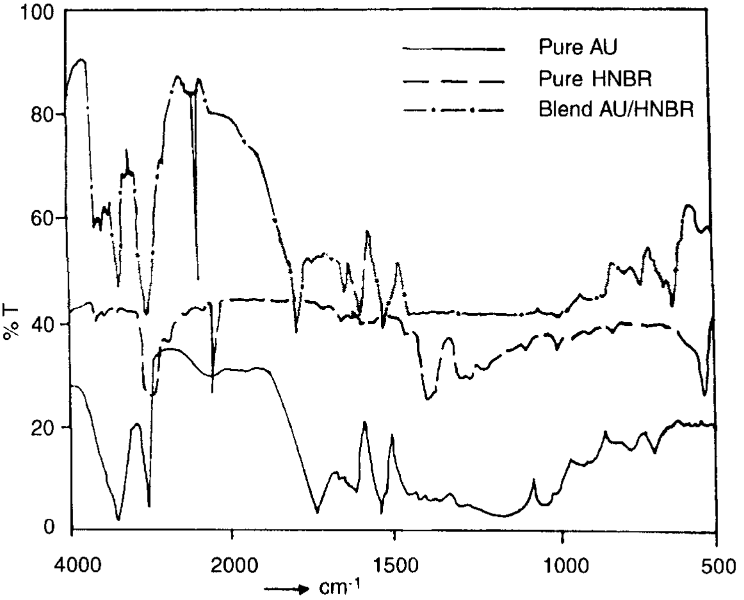
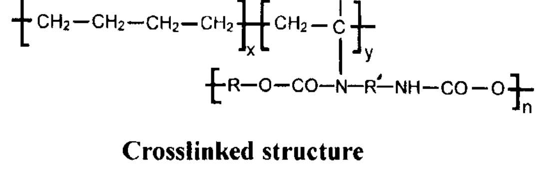


FIGURE 4 IR spectra of pure AU, pure HNBR and a blend of (50:50) AU/HNBR without curatives.



SCHEME I

3.5. Thermal Analysis

The high temperature DSC plot of the AU/HNBR (50:50) blend with and without preheating is shown in the Figure 5. It was observed

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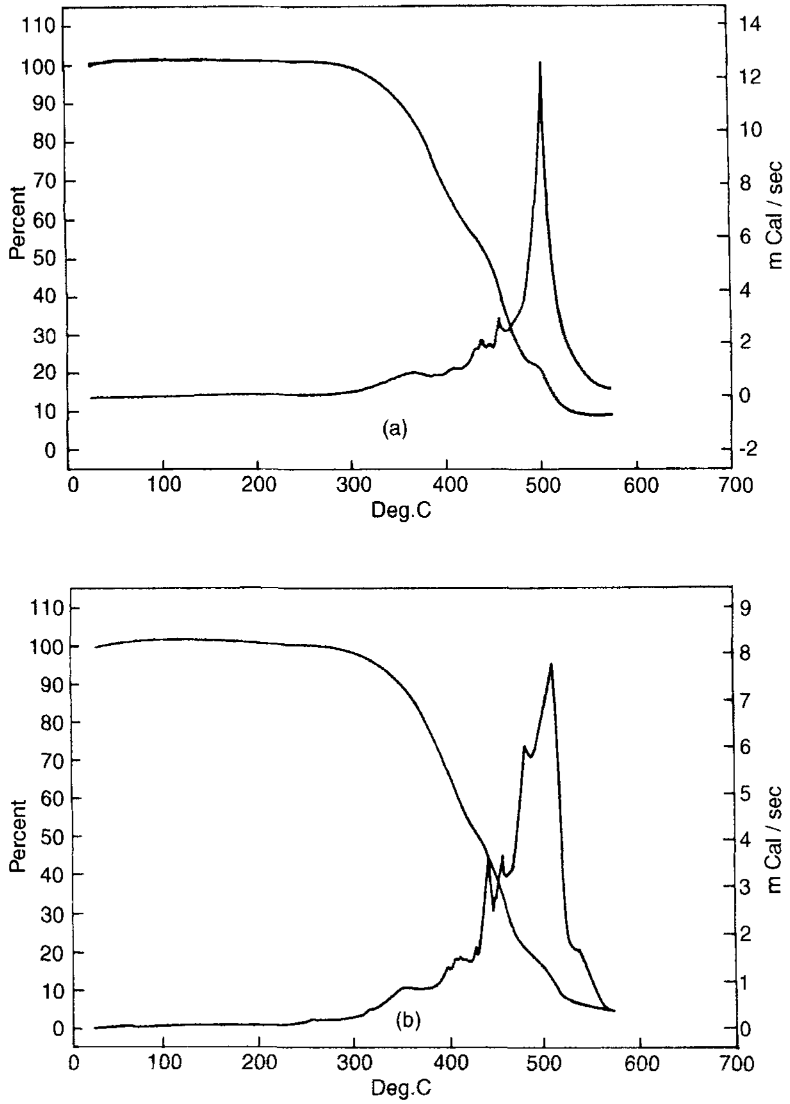

FIGURE 5 High temperature DSC plots: (a) (50 : 50) AU/HNBR preblended sample, (b) (50 : 50) AU/HNBR preheated preblended sample.

that the degradation occurs in two steps. In the case of the blend without preheating early degradation occurs starting at 306°C and at 520°C the whole sample is degraded, whereas for the blend with preheating the degradation is delayed and starts at 315°C and at

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550°C the whole sample is degraded. In all cases the degradation is characterized by exothermic peaks. Heat of oxidation as measured from the DSC plot, have been found to be 746 mcal/mg and 799 mcal/mg for preheated and preblended samples respectively suggesting only the preblended samples to be more prone towards oxidative degradation. Thus preheating make the blend stable towards thermal degradation.

The heat of vulcanization has been studied for the AU/HNBR blends. Onset temperature and heat of interchain crosslinking reaction were shown in Table IF. Three different cases are considered to study the effect of blend ratio on the onset temperature and heat of reaction. In all the cases exothermic peaks are observed. As the HNBR content in the blend is increased the interchain crosslinking reaction starts at a lower temperature region and the heat of reaction is also higher suggesting probable reaction between the two elastomers in absence of curatives at high temperature, the extent of which depends on the blend ratio.

If two polymers are not compatible, T_g shows the presence of two separate peaks corresponding to the T_g values of individual polymers [13]. For highly compatible blend T_g shows only a single peak lying between the $T_g s$ of the component polymers, whereas in partially compatible system a broadening of T_g is observed [14]. Low temperature DSC suggested the variation of T_g values depending on both the blend ratios and the blending techniques. Two T_g values (around −35°C and −21°C) are observed for (80:20) of AU/HNBR preblended sample. (50:50) blend ratio showed also the two $T_g s$ around −35°C and −23°C suggesting the blend to be incompatible. Whereas in the case of (50:50) AU/HNBR preheated sample both values of $T_g s$ were shifted to higher side *i.e.*, around −27°C and −8°C. This shifting of the respective $T_g s$ to the higher temperature side may be due to introduction of certain amount of crosslinking between the phases.

TABLE IF Heat of vulcanization in AU/HNBR blends

Sl. No.	*Blend ratio AU:HNBR*	*Onset temperature of curing*	*Heat of vulcanisation (exothermic), mcal/mg*
a	80:20	100	1.0
b	50:50	60	6.5
c	20:80	48	8.7

3.6. SEM Study

The blends were extracted with a solvent DMSO in which one phase (AU) is soluble so as to remove one phase. Then the phase morphologies were studied by SEM and shown in the Figures 6 and 7 for the (50:50) AU/HNBR preblend and preheated preblend samples respectively. When this extracted samples were examined by SEM, the extracted portion appeared as holes in the photographs, the size of which depended on the size of the extracted phase. As observed in Figure 6 the extraction of AU phase was evident, but restricted to limited extent when the blend was given heat treatment (Fig. 7). This clearly suggests crosslinking between the two elastomeric phases.

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FIGURE 6 SEM photograph of solvent (DMSO) extracted (50:50) AU/HNBR blend without heating sample. (800 ×).

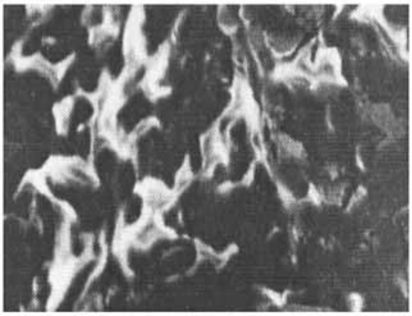

FIGURE 7 SEM photograph of solvent (DMSO) extracted (50:50) AU/HNBR blend with preheating sample. (800 ×).

4. CONCLUSION

The incorporation of HNBR improves the aging properties and heat resistance properties of the blends at the initial stages. The blend properties largely depend on the blend ratio and the blending techniques. The state of cure of preheated preblended sample was not improved due to loss of functional groups. IR spectrum confirmed certain amount of interchain crosslinking. Thermal stability was increased in the preheated sample due to interchain crosslinking. SEM also corroborated the above mentioned phenomena.

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