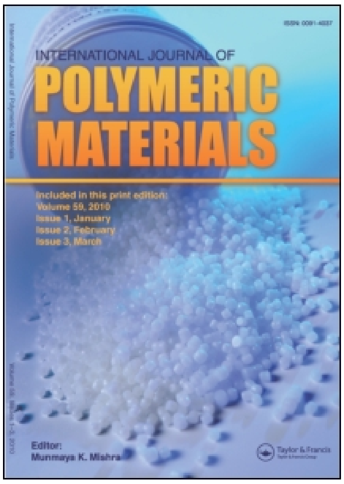

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Polyblends of Polyurethane and EVA Elastomers (Peroxide cure)

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Blends of polyurethane and EVA elastomers prepared by two different techniques, in different blend ratios, have been studied. Blend properties largely depended on the blend ratio and also blending techniques. Preheating technique offered better properties. IR spectral analysis revealed that on heating interchain crosslinking occured between PU and EVA. The degradation and weight loss were also retarded. Furthermore, preheating also restricted the extractibility of one phase by solvent extraction suggesting interchain crosslinking. Heat of vulcanization also confirmed the above view.

Keywords: Polyurethane; EVA elastomer; polyblends; structure; properties

1. INTRODUCTION

The modification of polymer properties through blending has been used increasingly in order to obtain comparatively low cost materials with improved properties. New materials with improved properties can be obtained by combining existing polymers to meet the specific applications [1, 2]. When two polymers containing polar functional groups are blended, the blend is likely to have better properties derived from interchain linking *via* functional groups [3]. Polyurethane (PU) have excellent abrasion resistance with good resistance to attack by oil, petrol and many common non-polar solvents have led to its use in wide spectrum of industries [4]. Ethylene vinyl acetate (EVA)

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elastomer on the other hand finds its application in cable sheathings, shoes *etc.*, because of its good heat and moisture resistant properties. The blends of EVA elastomers with other speciality elastomers have been studied by many authors [5, 6]. Recently Das *et al.* [7] have studied the XNBR/PU blends. The present paper reports the effect of blending technique on blend properties and the effect of interchain crosslinking reaction between PU and EVA on the blend properties.

2. EXPERIMENTAL

The PU-elastomer used was vibrathane 5004 variety by Uniroyal, USA and the EVA elastomer was Levaprene-450 by Bayer, Germany. Blends were prepared in an internal mixer at constant speed for fixed period of time by gradual replacement of PU with EVA over the entire composition range with dicumyl peroxide (Varox-40 KE) as a curative. The cured sheets were prepared by compression molding at 150°C to optimum cure time. The cure characteristics were studied on a Monsanto rheometer R-100 at 150°C. Physical properties were studied on cured sheets both before and after aging. Aging was performed in an air oven at 150°C for 48 hrs. The tensile properties were measured by Universal tensile testing machine.

Differential solvents swelling [8] in DMF and toluene were carried out followed by a Kraus plot [9] to study the phase adhesion. Infrared spectra of the thin film of pure PU, EVA and a (50:50) blend of PU/EVA (without curatives) were taken using a Perkin-Elmer model 837. The phase morphology was studied on extracted samples in toluene solvent with the help of an SEM (Camscun-Series 2 and E5200 Auto Sputter Coater). Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were conducted using a Shimadzu thermal analyser (DT-40) in air at the rate of 10°/min within the temperature range 25°C to 600°C. Differential scanning calorimetry (DSC) studies were carried out both at low and high temperature using a Stanton Redcroft thermal analyser STA-625 in a nitrogen atmosphere to determine the glass transition temperature (T_g) and heat of vulcanization. Two types of blending techniques were followed: (a) preblending techniques and (b) preheating of two elastomers (without curatives) followed by the addition of curatives.

3. RESULTS AND DISCUSSION

3.1. Preblending of PU and EVA

The elastomers PU and EVA were blended in their entire composition range and then the curative (DCP) was incorporated as per the compounding formulations shown in Table IA and the corresponding physical properties were given in Table IB respectively. The state of cure $(\tau_{\max} - \tau_{\min})$ of the blends gradually decreased with the addition of EVA dose. The modulus decreased with the addition of EVA in line with the state of cure. The tensile strength and elongation at break decreased with EVA dose. The hardness of the blends followed the same trend. The above results indicate that the extent of crosslinking decreases with addition of EVA. After aging in air, the hardness and modulus of the blend decreased, but the tensile strength and elongation at break increased in all the cases as shown in Table IC.

TABLE IA Compounding formulations

Sample	*A*	*B*	*C*	*D*	*E*
PU	80	60	50	40	20
EVA	20	40	50	60	80
DCP	2	2	2	2	2

TABLE IB Physical properties

	A	*B*	*C*	*D*	*E*
$\tau_{\max} - \tau_{\min}$ (dNm)	27	21	17	15	13
Hardness (Å)	45	42	39	38	35
Modulus 200% (kg/cm^2)	9.8	9.1	8.6	8.8	8.9
Tensile strength (kg/cm^2)	71.2	54.0	49.0	30.3	20.4
Elongation at break (%)	820	800	775	675	625

TABLE IC Percent change in properties after aging in air at 150°C for 48 hours

	A	*B*	*C*	*D*	*E*
Hardness (Å) (change in points)	−2	−5	−7	−5	−5
Modulus 200%	+8.4	−10.0	−11.6	−11.0	−11.1
Tensile strength	+24.0	+19.0	+14.7	+64.0	+175.4
Elongation at break	+6.2	+8.0	+12.9	+30.0	+40.0

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

In order to study the effect of interchain crosslinking on the blend properties, the preblend (blends of the two elastomers without curative) were heated and then the curatives were added. The compounding formulations were same as in Table IA and the corresponding physical properties were given in Table ID. The state of cure ($\tau_{\text{max}} - \tau_{\text{min}}$) of the preheating blend decreased as compared to preblend samples both for PU-rich blend and EVA-rich blend. But in case of (50:50) PU/EVA blend reverse effect was observed. The state of cure highly improved compared to the preblend sample of same ratio, resulting higher amount of effective crosslinking for this particular blend.

On heating the sample, the tensile strength, modulus and hardness decreased compared to the preblend sample in PU rich blends, while these properties were improved as the EVA dose increased. The tensile properties were improved remarkably in case of (50:50) PU/EVA blend. The elongation at break is decreased drastically in the case of (50:50) PU/EVA blend, while improving the modulus. On aging, all the physical properties of the preheated sample were found to decrease as shown in Table IE.

TABLE ID Physical properties

	A	*B*	*C*	*D*	*E*
$\tau_{\text{max}} - \tau_{\text{min}}$ (dNm)	14	18	38	16	11
Hardness (Å)	35	40	50	43	41
Modulus 200% (kg/cm^2)	3.4	6.0	12.2	5.8	4.3
Tensile strength (kg/cm^2)	37.8	52.0	63.0	50.2	46.2
Elongation at break (%)	850	700	625	780	900

TABLE IE Percent change in properties after aging in air at 150°C for 48 hours

	A	*B*	*C*	*D*	*E*
Hardness (Å) (change in points)	−1	−6	−10	−8	−9
Modulus 200%	−50.0	−42.1	−35.4	−49.0	−58.1
Tensile strength	−5.8	−15.0	−26.2	−47.2	−80.3
Elongation at break	−11.8	−17.1	−28.0	−26.2	−27.7

3.3. Differential Solvent Swelling

Differential solvent swelling with DMF and toluene were studied in order to assess the phase adhesion between the two elastomers and represented in Figures 1 and 2. In both the cases the swelling coefficient (left part of the Figs. 1 and 2) of the blend lie well below the average additive line for both preblend and preheated preblends. From the right hand portion of the Figures 1 and 2 the phase adhesion is confirmed for both PU rich blends and EVA rich blends as negative slopes have been obtained. This observations is valid for both the preblends and preheated preblends.

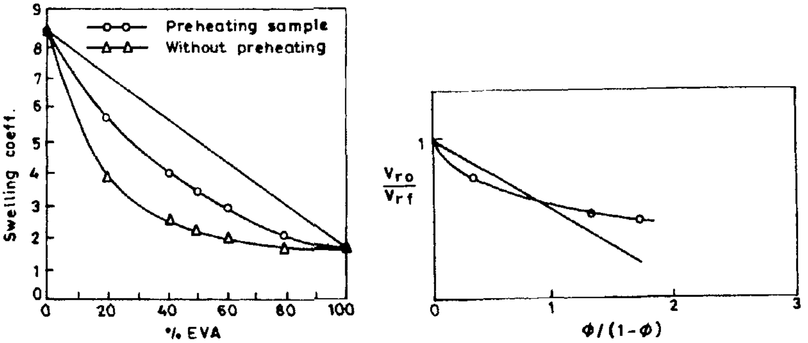


FIGURE 1 Plot of swelling coefficient against EVA and the Kraus plot of V_{ro}/V_{rf} against $\phi/(1-\phi)$ for PU/EVA blend in DMF solvent.

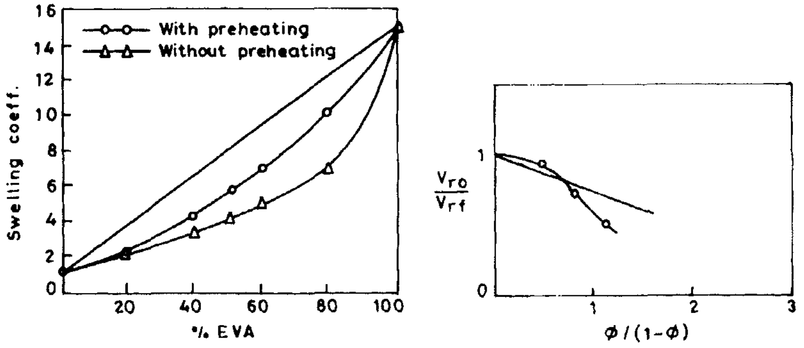


FIGURE 2 Plot of swelling coefficient against EVA and the Kraus plot of V_{ro}/V_{rf} against $\phi/(1-\phi)$ for PU/EVA blend in toluene solvent.

3.4. IR Spectral Analysis

The IR spectra of the thin film of pure PU, pure EVA and a (50:50) blend of PU/EVA (without curative) heated at 150°C for 30 minutes are shown in Figure 3. There is peak at 1716 cm^{-1} for the presence of 2° amide $> C{=}O$ and a broad peak at 3510 cm^{-1} for the 'N—H' stretching in pure PU [10]. In the pure EVA there were peaks at 1720 cm^{-1} for ester $> C{=}O$ and 1241 cm^{-1} for 'C—O' stretchings [11]. There is drastic shift of the amide peak 1740 cm^{-1} in blend indicates the presence of 2° amide $> C{=}O$ in different environment of blend than in pure PU. PU itself has a broad peak at 3510 cm^{-1} which is absent in the blend thus supporting the crosslinking through 'N—H' in PU with EVA. This is also supported by the presence of one additional peak at 1525 cm^{-1} in the blend which may be due to the formation of crosslinked 'C—N' bond between the two elastomers. The absence of EVA peak at 1728 cm^{-1} in the blend suggest the elimination of acetate group. A probable mechanism for the interchain crosslinking reaction may be cited as below in Scheme 1.

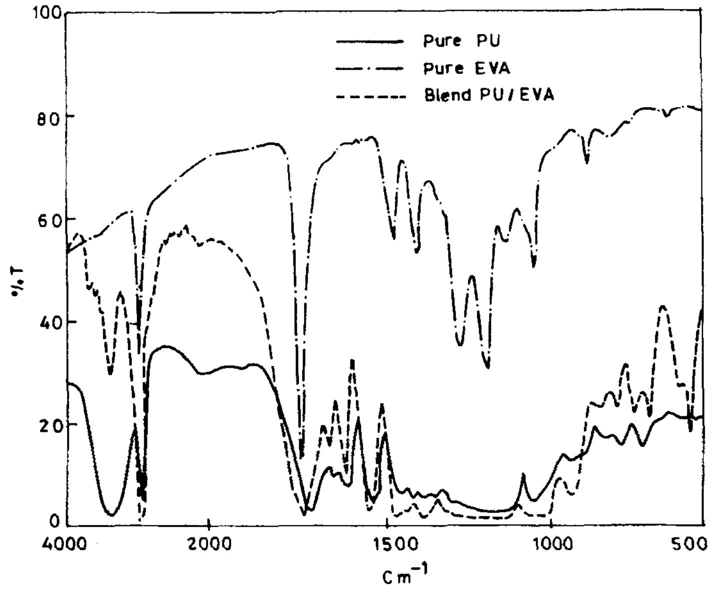
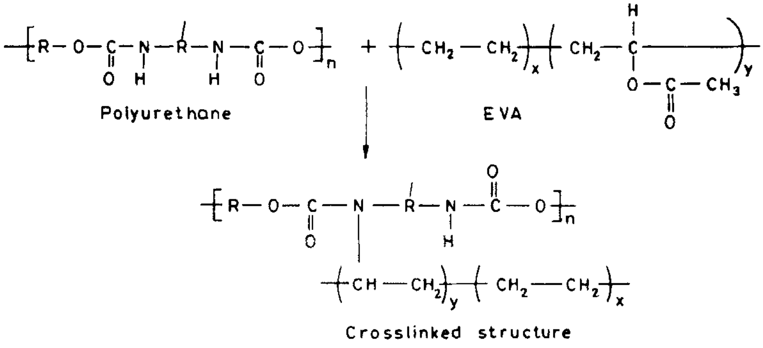


FIGURE 3 IR spectra of pure PU, pure EVA and a blend of (50:50) PU/EVA without curatives.



SCHEME 1

3.5. Thermal Analysis

The DTA/TGA plot of the (50:50) PU/EVA blend with and without preheating of the preblend are shown in Figure 4. It was observed that for the blend without preheating, early degradation occurs starting at 420°C, and at 530°C the whole sample is degraded, whereas for the blend with preheating, the degradation is delayed and starts at 475°C and finally at 550°C the whole sample is degraded. It may be assumed that the degradation process is being delayed due to the interchain crosslink, in the case of preheated sample, as shown earlier. The heat of vulcanization have been studied for PU/EVA blends. The PU and EVA have been blended without any curatives. Three different cases are considered to study the effect of blend ratio on the onset temperature of the crosslinking reaction and the heat of vulcanization. The onset temperature and the heat of crosslinking reaction were given in Table IF. All the blends showed the exothermic peaks. The heat of reaction is maximum for the 80:20 PU/EVA blend ratio which is lowered of (50:50) ratios and again shoots up to 20:80 PU/EVA ratio. Similarly the onset temperature of interchain crosslinking is higher for (50:50) PU/EVA blend which dropped at both extreme ends of the blend ratio *i.e.*, (80:20) PU/EVA and (20:80) PU/EVA blend ratios. It reveals that some reaction occured between the two elastomeric phases in absence of curatives at high temperature, the extent of which depends on the blend ratio.

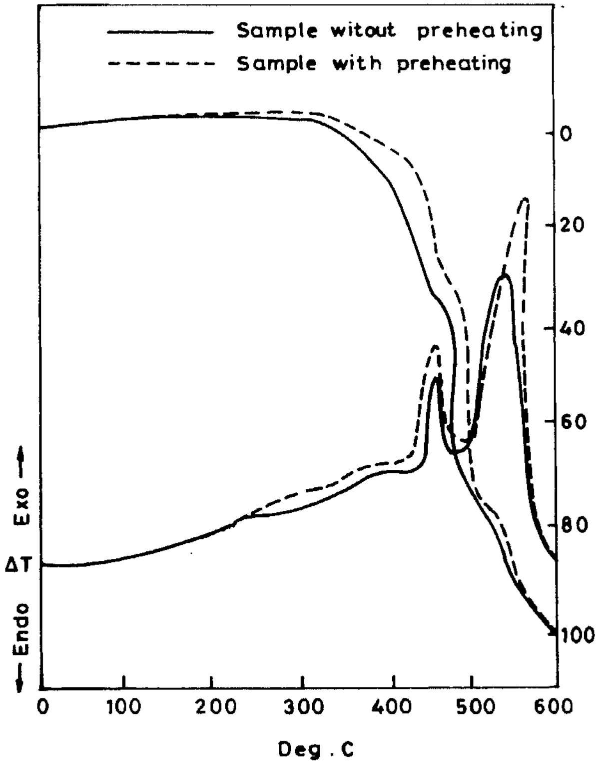


FIGURE 4 DTA/TGA plots of the (50:50) PU/EVA blend with and without heating of the blend.

TABLE IF Heat of vulcanization of PU/EVA blend

Sl. No.	*Blend ratio PU/EVA*	*Onset temp. of curing, °C*	*Heat of vulcanization exothermic (m Cal/mg)*
1	80:20	101	7.47
2	50:50	125	0.80
3	20:80	120	2.20

The low temperature DSC plot of (50:50) PU/EVA blend with and without preheating is shown in Figure 5. It was observed from the Figure 5 that there is one prominent T_g for the sample and the position of T_g varies slightly depending upon the condition of the blending. In the case the blend without preheating, T_g is observed at around −18°C, while the preheated preblend sample at around 13°C.

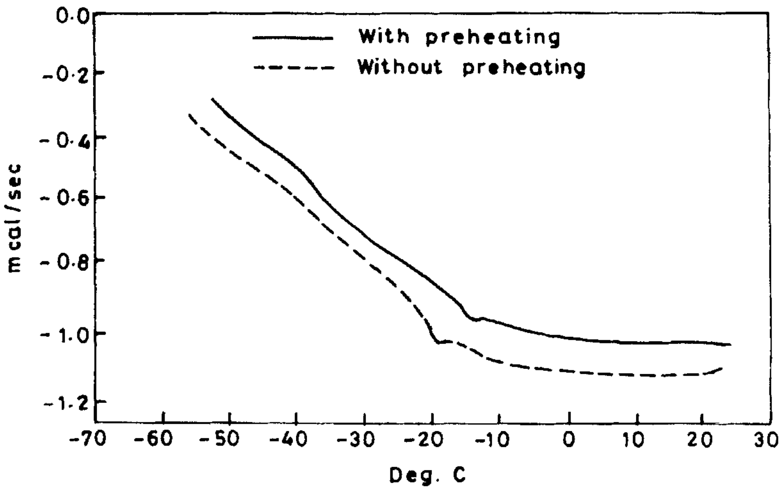


FIGURE 5 Plot of T_g curves of (50:50) PU/EVA blend with and without heating of the blend.

Preheating of the blend shifts the position of T_g to the higher temperature side, although to a very small extent, clearly indicated the interchain crosslinking between the two elastomers.

3.6. SEM Study

The samples were extracted by toluene to remove the EVA phase and then SEM study was conducted. The blend morphologies were shown in Figures 6 and 7 for the (50:50) PU/EVA preblend and preheated preblend samples respectively. The Figure 6 suggested the presence of EVA phase as larger domain which could be extracted out easily. The extraction of EVA phase is being restricted after (Fig. 7) the preheating of the blends system, probably due to the formation of interchain linking through the mechanism as discussed earlier.

4. CONCLUSION

The processability of PU was improved by blending it with EVA. The incorporation of EVA improved the solvent resistance. The interchain

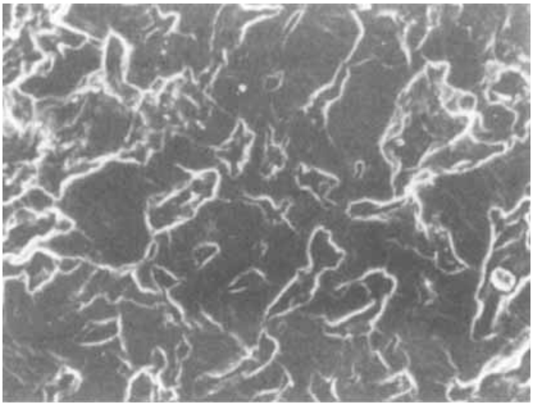


FIGURE 6 SEM photograph of solvent (toluene) extracted (50:50) PU/EVA blend without heating sample.

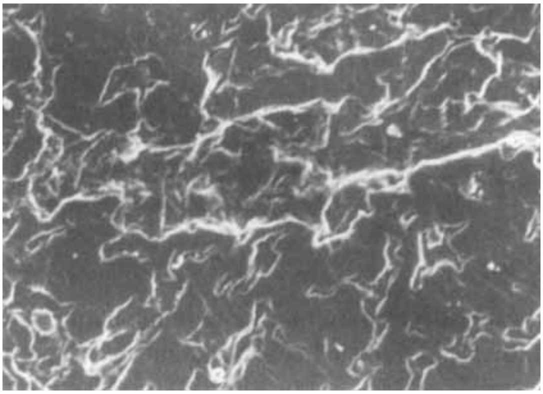


FIGURE 7 SEM photograph of solvent (toluene) extracted (50:50) PU/EVA blend with preheating sample.

crosslinking improved the properties of the blend. The preheating of the preblends delays degradation under high temperature conditions.

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