

Effect of Blending Technique on the Properties of Polyurethane and Epichlorohydrin Blends (Sulfur Cure)

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ABSTRACT: Two elastomers having reactive functional groups may react with each other. Considering this, the blends of PU and EPH elastomers have been prepared where better performance properties can be tailored and optimized through the interchain crosslinking reaction. It is evident from the IR spectral analysis of the thin film of PU/EPH blend without curatives that an interchain crosslinking reaction occurs between the two elastomeric phases. Preheating of the preblends before addition of curatives enhances the properties of the blends. Thermal study revealed the delayed degradation with retardation in weight loss for the preheated, preblended samples. Preheating also restricted the extractability of the phases, by solvent, due to interchain crosslinking. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 1367–1376, 2000

Key words: polyurethane; epichlorohydrin; masterbatch; preblending; preheating; curing; morphology; vulcanisation; Caytur

INTRODUCTION

Homopolymers may not always satisfy all the end-use requirements for several practical applications. Suitable blending of two or more polymers can provide the required balance of properties, and such considerations form the basis of the study of polymer blends. From the standpoint of commercial applications and developments, polymer blending represents one of the fastest growing segments of polymer technology.^{1,2} In this article, efforts have been put forward to develop new polymer blends by blending polyurethane with epichlorohydrin rubbers.

The applications of polyurethane elastomers are in a wide variety of products. Millable polyurethane elastomer, in particular, is finding even more applications. Typical outlets are in many branches of industry including mechanical engineering, the petroleum industry, and increasingly

in everyday applications from foam insulation to shoe soles, car seats to abrasion-resistant coating, and exterior parts for automobiles.^{3–6}

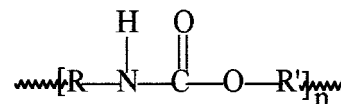
On the other hand, EPH polymers have a good balance of low-temperature flexibility, fuel, oil, and solvent resistance, high-temperature resistance, excellent ozone and weathering resistance, and very good dynamic properties. Both these polymers are strongly polar in nature, and expected to interact. Considering the above, blends were prepared to develop new kinds of materials to fit a wide range of engineering applications with enhanced performance properties.

EXPERIMENTAL

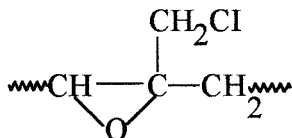
The elastomers used were polyurethane elastomer (AU): Vibrathane-5008 from the Uniroyal Company, USA.

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Epichlorohydrin elastomer (EPH): Gechron-3100 from M/S Nippon, Zeon, Japan.



Blends of polyurethane and epichlorohydrin were prepared by three different blending techniques. Mixing operations have been carried out in a two-roll open mixing mill for a fixed period of time at a constant friction ratio at ambient temperature. The polyurethane was blended with the epichlorohydrin elastomer to make blends over the entire composition range. The processability and the continuous cure characteristics of the blends have been studied in a Monsanto Rheometer (R-100) at a 150°C temperature. The state of cure [τ_{\max} (maximum torque) - τ_{\min} (minimum torque)] was calculated from the rheograph and plotted against percentage of epichlorohydrin elastomer. Blends were then allowed to cure in a hot press at a 150°C temperature up to their optimum cure time, as obtained from the rheograph, at a constant pressure (2800 psi). Physical properties of the blends like hardness, modulus, tensile strength, elongation at break, etc., were measured both before and after aging. Aging was performed in an air oven at 120°C temperature for 40 h. Tensile properties of the blends were measured in a Universal Tensile Testing machine. To study the phase adhesion between the two elastomers, the solvent swelling was performed in acetone and toluene at an ambient temperature, for 48 h, following the Kraus equation:

$$\frac{V_{ro}}{V_{rf}} = 1 - M \left[\frac{\Phi}{1 - \Phi} \right]$$

where V_{ro} is the volume fraction of the elastomer in the swollen gel when the dispersed phase is

Table I Compounding Formulations

Elastomers	I	II	III	IV	V
AU	80	60	50	40	20
EPH	20	40	50	60	80

Curatives for AU (100 phr): MBT-2; MBTS-4; ZDC-1; ZnO-1; stearic acid-1.5; Caytur-0.5; S-2.

Curatives for EPH (100 phr): ZnO-1; stearic acid-1; S = 1.5; MBT-1.5; TMTD-1.5.

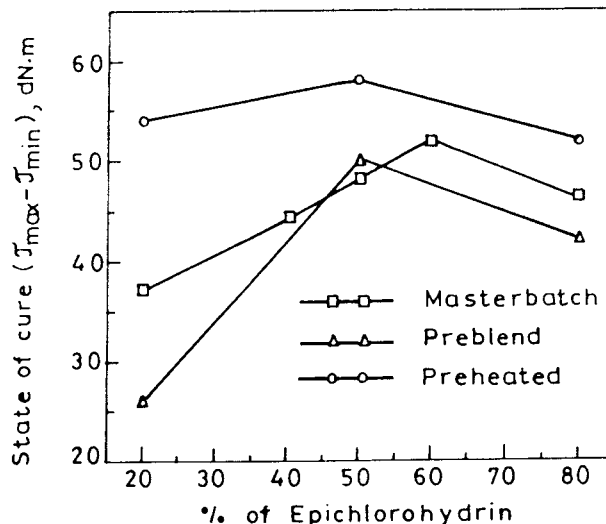


Figure 1 Plot of state of cure against percentage of the epichlorohydrin elastomer.

absent. V_{rf} is the volume fraction of the elastomer when the dispersed phase is present. Φ is the volume fraction of the dispersed phase in the unswollen vulcanisate, and M is the equation parameter.^{7,8}

IR spectral analysis was carried out with the thin film of pure polyurethane, pure epichlorohydrin, and a 50/50 blend of AU/EPH using a Perkin-Elmer model 837. Phase morphology of the blends were studied with the solvent extracted samples by SEM.

Thermal studies of the blends viz., differential thermal analysis and thermogravimetric analysis, were carried out in air, by using a Shimadzu Thermal Analyser (DT 40), within a temperature range 25 to 60°C at a heating rate of 10°C/min. To determine the glass transition temperature (T_g) and heat of vulcanization reaction, Differential Scanning Calorimetry studies (DSC) were conducted using a Stanton Redcroft Thermal Analyser, STA 625.

RESULTS AND DISCUSSION

Blends of AU/EPH Using a Sulfur Curing System and Its Effect on the Blending Technique

Masterbatch Techniques

In the masterbatch techniques, the individual elastomers (AU and EPH) were mixed with the curatives system. Then the mixed compounds were blended in different ratios. Sulfur curing

Table II Physical Properties of Masterbatch Samples

Blend Ratio (AU/EPH)	Hardness (°A)	100% Modulus (N/m ² × 10 ⁻⁴)	200% Modulus (N/m ² × 10 ⁻⁴)	Tensile Strength (N/m ² × 10 ⁻⁴)	Elongation at Break (%)
80 : 20	63	137.2	215.6	617.4	430
60 : 40	55	78.4	137.2	284.2	320
50 : 50	51	78.4	127.4	333.2	400
40 : 60	58	117.6	166.6	499.8	470
20 : 80	58	98.0	196.0	294.0	380

systems have been employed. The compounding formulation is given in Table I.

The state of cure ($\tau_{\max} - \tau_{\min}$) increased for all the blends (Fig. 1) with the increase in EPH content up to the (40/60) AU/EPH blend. The hardness of the blends became a maximum for the AU-rich blend (80/20), and was found to decrease gradually with the replacement of polyurethane by epichlorohydrin up to a 50/50 blend ratio, and beyond this, hardness again increased. The modulus also followed the same trend with the hardness, and beyond the 50/50 AU/EPH blend ratio, all the physical properties were improved. Percent elongation of the blends decreased up to the 60/40 (AU/EPH) level, and beyond this ratio percent elongation of the blends was found to increase, which became maximum at the (40/60) AU/EPH blend. The physical properties are given in Table II.

Aging in air at 120°C for 40 h decreased the hardness of all the blends. The decrease in hardness was more in the AU-rich blends. The modulus and tensile strength of the aged samples also decreased more in the AU-rich blend than the EPH-rich blends. Elongation of the blend containing a higher percentage of polyurethane (AU) increased upon aging, and was maximum in the (80/20) AU/EPH blend. The percent elongation of the EPH-rich blends was found to decrease. The

change in properties on aging are given in Table III.

Blends of AU/EPH by the Preblending Technique

The polymers (AU and EPH) were first blended throughout the entire composition range and allowed to reach equilibrium for 24 h. Then the sulfur curing systems were incorporated into the blends. To study the properties of the blends and the effect of blending technique on blend properties, the (80/20), (50/50), and 20/80 (AU/EPH) have been considered. The compounding formulation of the preblending technique is given in Table IV. The amount of curatives were taken according to the percentage of elastomers (both) used, as was in the masterbatch technique.

The state of cure (Fig. 1) gradually increased with increase in epichlorohydrin content and became maximum at the (50/50) AU/EPH level, which was higher than the blend obtained by the masterbatch technique. Physical properties of the blends obtained by this technique have been measured. Hardness of the preblended vulcanisates were almost of the same values as obtained from the vulcanisate made via the masterbatch techniques. The modulus of the (50/50) AU/EPH preblended sample slightly increased compared to that of the masterbatch technique, while the mod-

Table III Percent Change in Properties on Aging at 120°C for 40 h of the Masterbatch Samples

Blend Ratio (AU/EPH)	Hardness (Change in Points)	100% Modulus	200% Modulus	Tensile Strength	Elongation at Break (%)
80 : 20	-13	-79.0	-60.22	-55.0	+4.65
60 : 40	-10	-48.7	-51.42	-33.3	+18.75
50 : 50	-6	-62.1	-30.76	-23.52	-12.5
40 : 60	-11	-50.0	-21.42	-50.98	-25.53
20 : 80	-12	-53.9	-40.0	-53.2	-15.78

Table IV Compounding Formulations for the Preblending Technique

Elastomers	I	II	III
AU	80	50	20
EPH	20	50	80

ulus of the (80/20) AU/EPH preblended sample decreased to an extent. However, the tensile strength of the preblended sample was found to be lower than the masterbatch technique having the same compounding formulation. Elongation at break of the (50/50) AU/EPH vulcanisate remain almost unaffected, but the elongation at break of the (80/20) AU/EPH blend decreased to a remarkable extent compared to the masterbatch technique. Physical properties of the preblended samples are given in Table V.

Upon aging in air at 120°C temperature for 40 h, all these physical properties of the preblended samples decreased. The change in hardness was more in the AU-rich blend, i.e., the (80/20) AU/EPH preblended sample. The percent change in modulus (both 100 and 200%) and tensile strength of the aged samples was also in line with the hardness. This may be due to the presence of higher amounts of polyurethane, which is thermally less stable. However, elongation at break of the aged samples was found to decrease with increase in EPH content in the blend, the extent of which was highest in the (50/50) AU/EPH blend ratio. In the case of the blends prepared by the masterbatch technique, the retention in physical properties, on aging, was better than the blends prepared by the preblending technique. The change in properties on aging are given in Table VI.

Effect of Heat Treatment on the Properties of the Blends

To study the effect of preheating on the properties of the blends, the preblends of polyurethane and

epichlorohydrin elastomers without any curatives were heated at a 150°C temperature for 20 min. The same sulfur curative systems (as in the masterbatch and preblended techniques) were then incorporated to these preheated preblended samples. Here, to compare the properties of the preheated blends with the blends obtained by the masterbatch and preblending techniques, the (80/20), (50/50), and (20/80) AU/EPH blends have been considered. The compounding formulations were similar to that of the Preblending technique, and given in Table IV.

The state of cure ($\tau_{\max} - \tau_{\min}$) gradually increased with the addition of epichlorohydrin in the blend (Fig. 1). Again, the state of cure of the preheated preblended samples was higher than that of the masterbatch and preblended samples having the same compounding formulations with the same blending ratios. This may be due to the higher extent of crosslinking in the preheated sample. The cure rate of the blends of the same ratio, obtained by the masterbatch technique were lower than that of preheated preblended samples. However, the cure rate of (80/20) and (50/50) AU/EPH preheated, preblended samples were much lower than the cure rate of the preblended samples having the same compounding formulations with the same elastomer ratio. This may be due to the effect of preheating the preblends at 150°C, resulting in a crosslinking reaction to an extent during heat treatment and thereby lowering the cure rate.

The hardness of the preheated blends decreased with a decrease in polyurethane content in the blends. This may be due to the replacement of polyurethane, which was more thermoplastic in nature, by EPH. The hardness of the blends remain almost the same as the blends obtained from the masterbatch and preblended technique having the same elastomer ratio. Modulus (both 100 and 200%) and tensile strength of the preheated samples increased with increase in epichlorohydrin content in the blend, whereas the modulus and the tensile strength of the blends

Table V Physical Properties of the Preblended Samples

Blend Ratio (AU/EPH)	Hardness (°A)	100% Modulus (N/m ² × 10 ⁻⁴)	200% Modulus (N/m ² × 10 ⁻⁴)	Tensile Strength (N/m ² × 10 ⁻⁴)	Elongation at Break (%)
80 : 20	62	88.2	147.0	215.6	280
50 : 50	52	88.2	137.2	205.8	420
20 : 80	56	107.8	186.2	205.8	390

Table VI Percentage Change in Properties on Aging at 120°C for 40 h of the Preblended Samples

Blend Ratio (AU/EPH)	Hardness (Change in Points)	100% Modulus	200% Modulus	Tensile Strength	Elongation at Break (%)
80 : 20	-16	-80.22	-76.2	-75.68	+10.71
50 : 50	-4	-63.8	-69.28	-72.38	-28.57
20 : 80	-9	-55.3	-58.7	-61.0	-18.6

obtained through the masterbatch and preblended technique decreased with increase in epichlorohydrin content. Elongation at break was almost the same as the blends obtained by the masterbatch and preblending techniques. All these physical properties are given in Table VII.

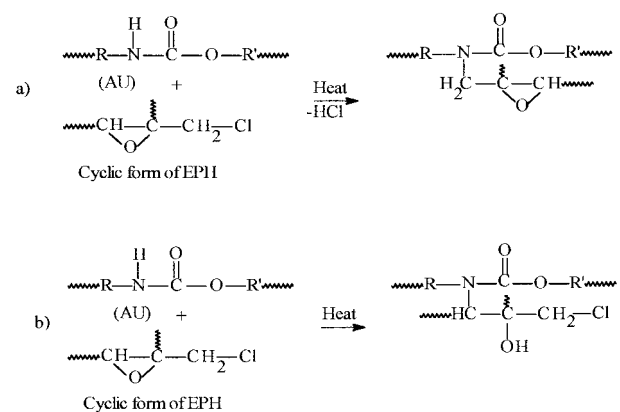
Upon aging in air at 120°C for 40 h all the physical properties were found to decrease (Table VIII). Here, also, the change in hardness (in points) and modulus (both 100 and 200%) was more in the AU-rich blend (80/20, AU/EPH). Tensile strengths also followed the same trend with hardness and modulus. Elongation at break was more in the AU-rich blend and decreased with increase in EPH content in the blend, the extent of which was more in the 50 : 50 (AU/EPH) blend ratio.

IR Spectral Analysis

To study the interchain crosslinking reaction between polyurethane and epichlorohydrin elastomer, IR spectra of the thin films of pure polyurethane, pure epichlorohydrin, and a (50/50) blend of polyurethane and epichlorohydrin without any curatives, heated at 150°C, were studied (Figure 2). It was observed from the spectral analysis that polyurethane showed characteristic peaks at 3140 cm^{-1} and 1690 cm^{-1} for N—H and amide $>\text{C}=\text{O}$ stretching. Epichlorohydrin showed several peaks at 745 cm^{-1} , 1252 cm^{-1} , 2915 cm^{-1} , and 1644 cm^{-1} for C—Cl, epoxide

group, ethoxy linkage ($-\text{O}-$), and pendant $-\text{C}=\text{C}-$, respectively.

In epichlorohydrin, the reactive site may be the C-atom containing the epoxy linkage, or bonded with the $-\text{Cl}$ atom where the $-\text{N}$ atom of polyurethane can attack and thereby form a $-\text{C}-\text{N}$ linkage. Thus, the plausible reactions may be as follow:



Thus, the reactive sites of AU and EPH are expected to be the $-\text{N}-$ and $-\text{C}-$ atoms, respectively, as shown above. Absence of the N—H peak at 3140 cm^{-1} also suggested the above view. Now the reaction may proceed through path (a) or (b), as stated above.

In the IR spectra of the blend, the peak at 745 cm^{-1} remain unchanged, as it was in EPH, which

Table VII Physical Properties of the Preheated Preblended Samples

Blend Ratio (AU/EPH)	Hardness ($^{\circ}\text{A}$)	100% Modulus ($\text{N/m}^2 \times 10^{-4}$)	200% Modulus ($\text{N/m}^2 \times 10^{-4}$)	Tensile Strength ($\text{N/m}^2 \times 10^{-4}$)	Elongation at Break (%)
80 : 20	62	107.8	161.7	343.0	330
50 : 50	52	98.0	166.6	431.2	410
20 : 80	54	117.6	196.0	480.2	400

Table VIII Percent Change in Properties on Aging at 120°C for 40 h of the Preheated Preblended Samples

Blend Ratio (AU/EPH)	Hardness (Change in Points)	100% Modulus	200% Modulus	Tensile Strength	Elongation at Break (%)
80 : 20	-12	-84.1	-78.78	-84.9	+6.06
50 : 50	-6	-31.5	-19.41	-54.54	-26.82
20 : 80	-10	-35.7	-25.2	-57.4	-21.54

suggested the nonparticipation of $-C-Cl$ group in the crosslinking reaction. Hence, the reaction did not follow the path (a). Again, absence of the peak at 1252 cm^{-1} for epoxide linkage in the blend, and the presence of a new peak at 3340 cm^{-1} , which may be due to the $-OH$ group in polymeric association, supported the reaction to occur through path (b) and not through path (a), as stated earlier.

Solvent Swelling Study

The volume coefficient of swelling for the blends in acetone were found to be lying nearer to the additive average line. The corresponding Kraus plot on the right-hand portion of Figure 3 showed

the positive slope for all the three different types of blending, suggesting the lack of phase adhesion between the two elastomers, particularly for AU-rich blends. However, preheating preblending had an edge over the other two.

The solvent swelling in toluene is shown in Fig. 4. It was found that the volume coefficient of swelling for the blends lay well below the additive average line, and the corresponding Kraus plot showing the negative slope for all the three types of blending suggesting the existence of phase adhesion, particularly for the EPH-rich blends. From the slope it can be inferred that preheating enhances the phase adhesion between the two elastomers.

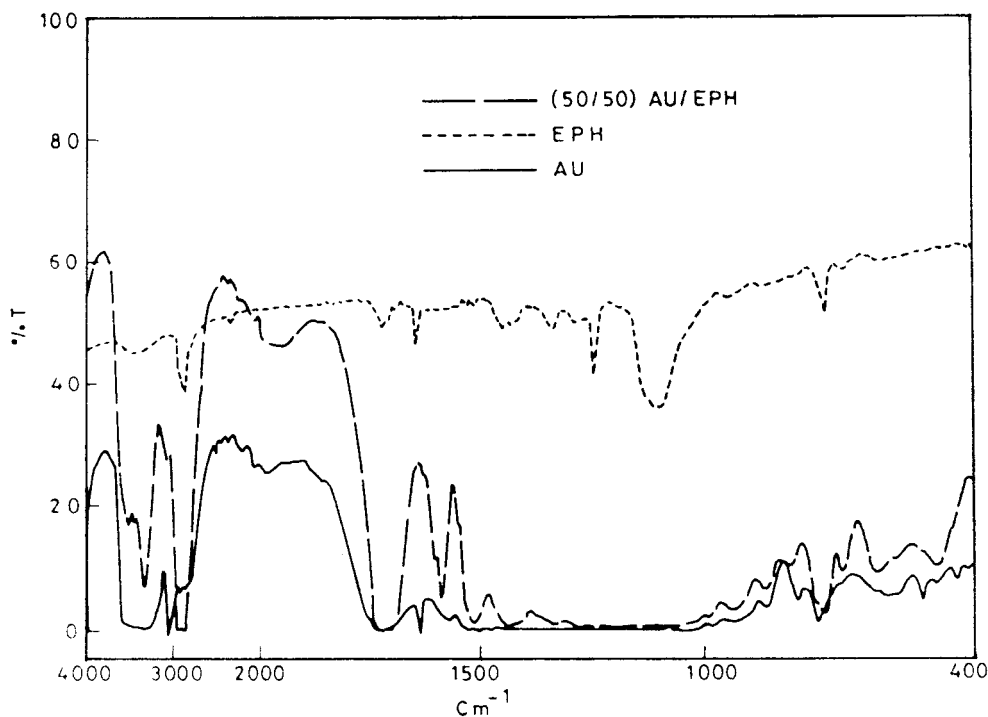


Figure 2 IR spectral analysis of pure AU, pure EPH, and the (50 : 50) AU : EPH blend without curatives.

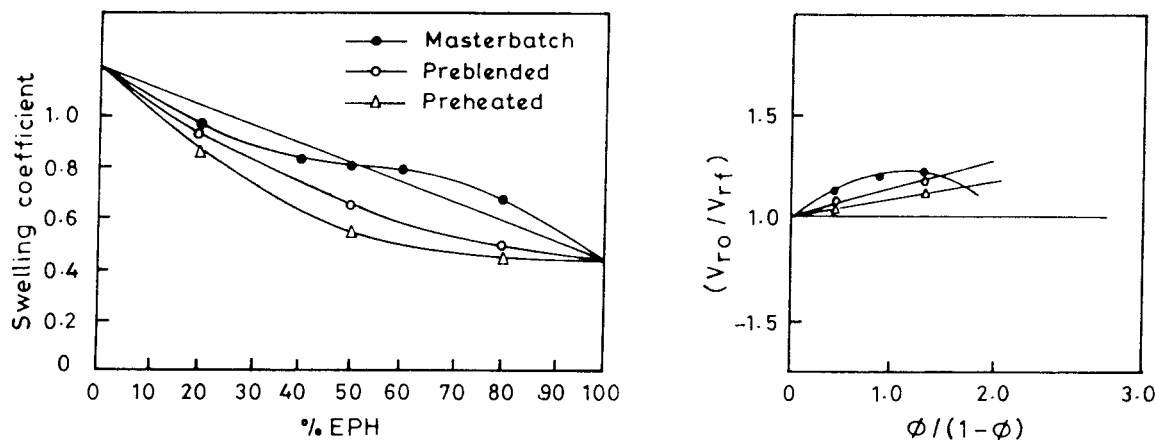


Figure 3 Plot of the swelling coefficient against EPH and (V_{ro}/V_{rf}) against $\phi/(1-\phi)$ for the AU/EPH system in acetone.

Thermal Analysis

To study the compatibility of the blend with reference to the effect of preheating the preblend, the low temperature DSC of the (50/50) polyurethane and epichlorohydrin has been studied. In the present study, two different cases have been considered, for example, blends obtained by the masterbatch techniques and by preheating followed by curatives addition, having the same compounding formulations with the same elastomer ratio.

In both the cases only one prominent T_g was observed, the position of which varied slightly, depending on the blending techniques. The (50/50) AU/EPH blend (masterbatch technique) showed the single T_g at -11°C , indicating a better compatibility of the blend. In case of the blend of (50/50) AU/EPH

preheating followed by curative addition, the T_g shifted slightly to the higher temperature of -6°C . The T_g value may have been shifted to the positive side due to crosslinking by the addition of curatives. But in the case of the preheated preblended technique, a higher shifting of the T_g is observed. This is probably because of the interchain crosslinking reaction occurring between the two elastomers phases during the heat treatment. That again, enhances the phase adhesion, affecting the segmental motion, as observed from the solvent swelling study.

High-temperature DSC/TGA analysis were carried out to study the degradation pattern of the (AU/EPH) blends with reference to the effect of heating the preblends. Blends prepared by three different blending techniques with the same compounding formulations and elastomer ratio

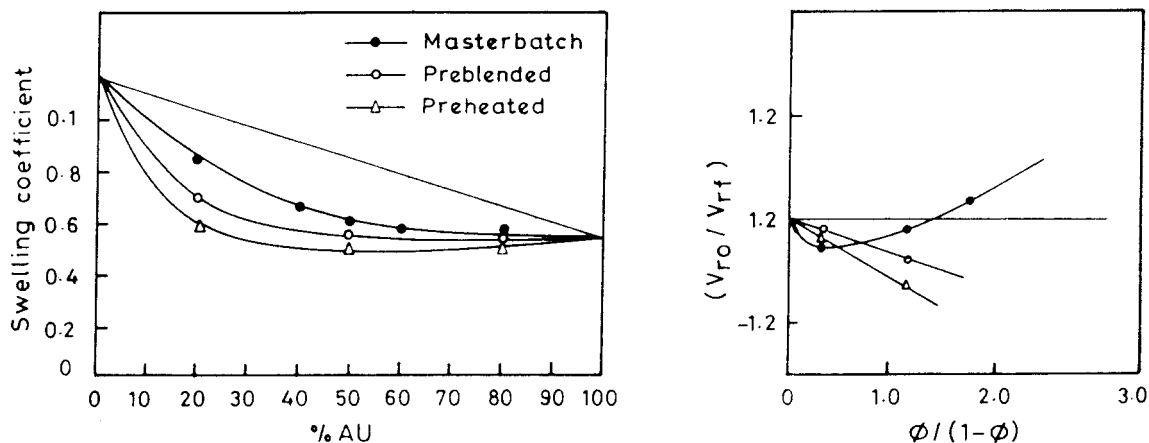
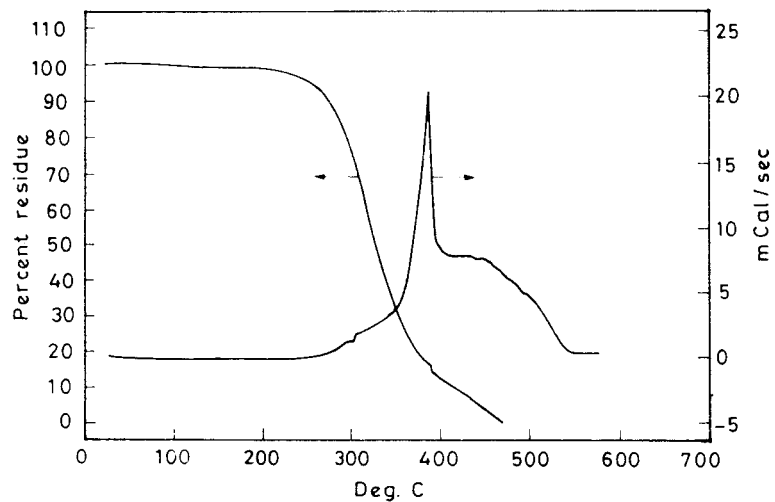
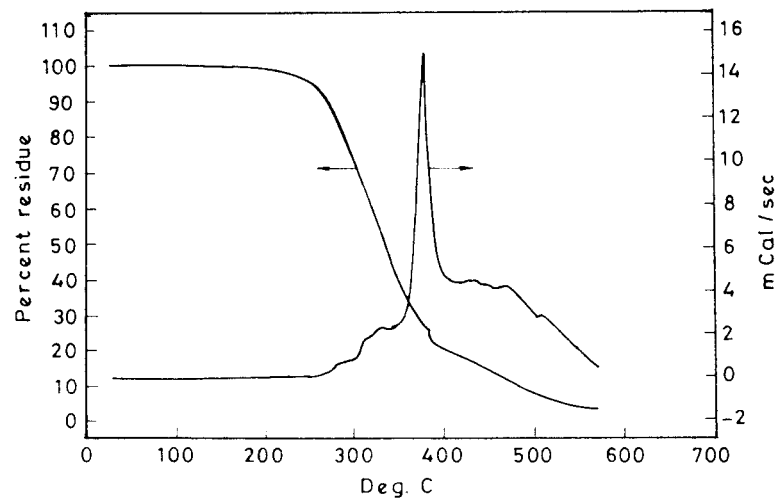


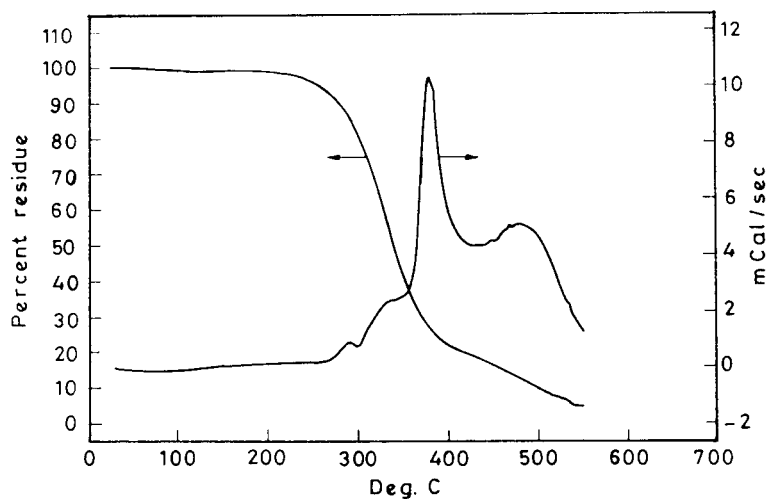
Figure 4 Plot of swelling coefficient against AU and (V_{ro}/V_{rf}) against $\phi/(1-\phi)$ for the AU/EPH system in toluene.



(a)



(b)



(c)

Figure 5 (a) High-Temperature DSC/TGA plot of the (50 : 50) AU : EPH masterbatch sample. (b) High-temperature DSC/TGA plot of the (50 : 50) AU : EPH preblended sample. (c) High-temperature DSC/TGA plot of the (50 : 50) AU : EPH preheated preblended sample.

Table IX Onset Temperature, Heat of Interchain Crosslinking Reaction with the Blending Ratio

Sl. No	Blend Ratio (AU : EPH)	Onset Temperature (°C)	Exothermic Heat of Vulcanization (mcal/mg)
1	80 : 20	92	3.59
2	50 : 50	100	9.09
3	20 : 80	98	5.80

have been considered to correlate the effect of the blending technique on the thermal stability. In the present study, the (50/50) (AU/EPH) blends were taken for consideration. In each case, single-step degradation occurred, associated with the exothermic peak in the DSC/TGA curves as shown in Figure 5. In the case of the (50/50) AU/EPH blend obtained from the masterbatch techniques, the degradation started at a 260°C temperature and continued up to a 375°C temperature at a faster rate [Fig. 5(a)]. For the preblended sample of (50/50) AU/EPH without any heat treatment, the degradation occurred at a 266°C temperature and continued up to 380°C at a faster rate [Fig. 5(b)]. But in the case of the blend obtained by heating the preblend followed by the curatives addition, the degradation started at a relatively higher temperature, 275°C, and continued up to 395°C at a faster rate [Fig. 5(c)].

From the thermal analysis it is evident that the degradation temperature depends on the blending techniques. Early degradation occurred in the blends obtained by the masterbatch techniques, whereas in the case of the preblended and preheated preblended samples, the degradation processes were delayed, the extent of which was more in the case of the preheated, preblended sample.

The heat of the vulcanization was studied for the AU/EPH blends without any curative addition. Three different cases have been considered, having different elastomer ratios. Table (Table IX) represents the onset temperature, the heat of the interchain crosslinking reaction with the blending ratio. In all cases exothermic peaks were observed. The heat of the vulcanization is highest in the case of the 50/50 (AU/EPH) blend, suggesting that interchain crosslinking reaction occurred between the elastomers without any curative, the extent of which depended on the blending ratio.

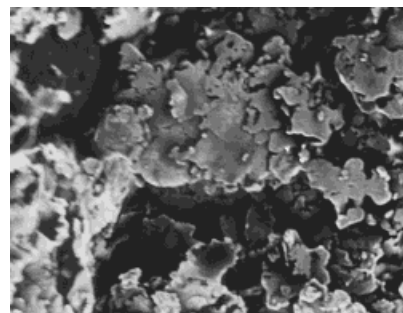


Figure 6 SEM photograph (800×) of the toluene extracted sample of the (50 : 50) AU : EPH blend, prepared by the masterbatch technique.

Phase Morphology of the Blends

Phase morphological study was carried out on the blends prepared by three different blending techniques having the same elastomer ratio and the same compounding formulations by extracting one phase in a specific solvent, toluene, for 48 h, and then the extracted samples were SEM photographed after suitable gold sputtering.

In the case of the masterbatch techniques, the easy extraction of the single phase by the solvent was possible, as indicated by the larger voids in the SEM photograph (Fig. 6). Easy extraction of the single phase by the solvent became restricted in the preblended sample, as observed from the SEM photograph (Fig. 7). The restriction in the single phase extraction became maximum in the preheated preblended sample as observed from the smaller voids in the SEM photograph (Fig. 8), which indicated the interchain crosslinking reaction occurred between the two elastomer phases as a result of the heat treatment. Again, it is clear from the SEM photograph that the extent of phase distribution was higher in the case of pre-

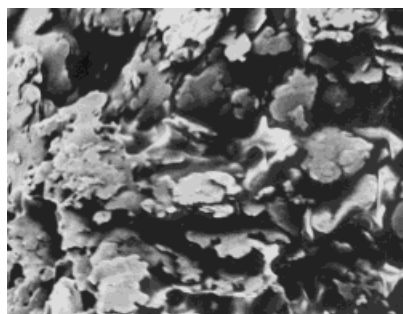


Figure 7 SEM photograph (800×) of the toluene extracted sample of the (50 : 50) AU : EPH blend, prepared by the preblending technique.

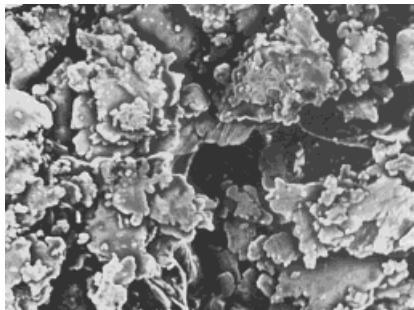


Figure 8 SEM photograph (800 \times) of the toluene extracted sample of the (50 : 50) AU : EPH blend, prepared by the preheating preblending technique.

heated preblended sample, and the phase distribution was found to be minimum in the case of the masterbatch sample. These observations again provide supporting evidence in favor of a phase adhesion between the two elastomers, which occurred also by virtue of an interchain crosslinking reaction upon heat treatment.

CONCLUSIONS

The incorporation of epichlorohydrin elastomer improved the processability of the polyurethane elastomer. A blending technique had a significant

role on the properties of the blend. Preheating improved the thermal stability of the blend. The extraction of the single phase by the solvent was also restricted in the preblended and preheated preblended samples, which indicated the interchain crosslinking reaction occurred between the two elastomeric phases upon heat treatment.

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