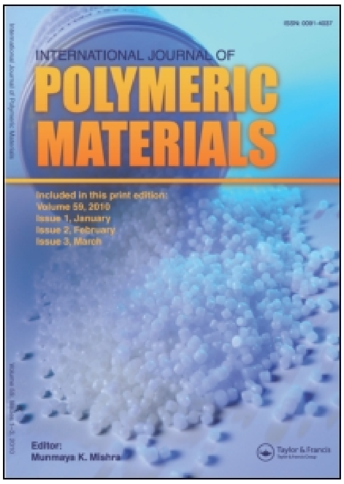

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Speciality Polymer Blends of Polyurethane and Chlorosulfonated Polyethylene (S-cure)

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Blends of polyurethane (vibrathane- 5008 Uniroyal Co., USA) and hypalon (CSM-350 Du Pont, USA) prepared by three different blending techniques, have been studied, over the entire composition range. The processability of the polyurethane rubber was improved as a result of blending with CSM. The IR spectral analysis suggested that on heat treatment, without curatives, interchain crosslinking reaction occured between the two elastomeric phases. Experimental data revealed that, preheating of the preblends, before addition of curatives, enhanced the thermal properties of the blends. The degradation process were delayed along with the retardation in weight loss. The extractability of the single phase by solvent was also restricted on preheating, due to interchain crosslinking reaction.

Keywords: Polyurethane; hypalon; blends; chlorosulfonated polyethylene

INTRODUCTION

Blending of two or more polymers is a novel technique in the field of polymer processing to produce a balanced combination of properties for the specific end use requirement. It offers an alternative way to develop new polymeric materials with enhanced performance properties rather than synthesizing new polymers. Blends of polymers may

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*Corresponding author.

also be used to reduce cost with only a slight loss and occasionally even a gain, in properties [1–3].

In the present work, efforts have been put forward to develop new polymeric material through the blending of polyurethane and CSM and to study the effect of the interchain crosslinking reaction on the blend properties. Polyurethane elastomers are of considerable commercial importance owing to their unique combination of unusual properties and the ability to be processed by almost all known manufacturing processes with wide range of properties, their valuable grades depending on stiffness and flexibility [4–7]. Versatility of polyurethane lies in five important applications in automobilies, furniture, construction, thermal insulation and footwear. On the otherhand, chlorosulfonated polyethylene (CSM) is best known for its exceptional environment and moisture resistant properties. Both the polymers are strongly polar in nature and expected to interact, thus may enhance the blend properties. Considering the above efforts have been made to develop improved blends.

EXPERIMENTAL

Blends had been prepared at room temperature in an internal mixer at a constant speed for a fixed period of time over the entire composition range by gradual replacement of polyurethane with CSM. The sulfur cure systems had been employed. The mix were sheeted in an open two-roll mixing mill. Blends were allowed to cure in a hot press at temperature 150°C upto optimum cure under constant pressure. The continuous cure characteristics were studied in a Monsanto Rheometer R-100 at 150°C. Physical properties of the blends like hardness (Å), modulus, tensile strength, elongation at break, *etc.*, were measured on cured sheets both before and after ageing. Ageing was performed in an air oven at 120°C for 40 hrs. The tensile properties were measured by a Universal Tensile Testing Machine. Swelling experiments [8, 9] had been carried out at ambient temperature for 48 hrs in DMSO and toluene solvent in order to study the phase adhesion between the two elastomers in the blend, following the Kraus equation:

$$\frac{V_{ro}}{V_{rf}} = 1 - M[\phi/(1 - \phi)]$$

where, V_{ro} = volume fraction of the elastomer in the swollen gel when any dispersed phase is absent; V_{rf} = volume fraction of the elastomer in the swollen gel when dispersed phase is present; ϕ = volume fraction of the dispersed phase in the vulcanizate; M = equation parameter.

Infrared Spectra of the thin films of pure (AU), pure CSM and the 50/50 blend of AU/CSM were taken using a Perkin Elmer Model 387. The phase morphology was studied for extracted samples with the help of SEM.

Differential Thermal Analysis (DTA) and Thermogravimetric Analysis (TGA) [10] were conducted using a Shimadzu Thermal Analyser (DT-40) in air at the heating rate of 10°C per minute within the temperature range 25°C to 600°C. Differential Scanning Calorimetry (DSC) studies had been conducted in a Stanton Redcroft Thermal Analyser STA-625 to determine the glass transition temperature (T_g) and the heat of vulcanization.

RESULTS AND DISCUSSION

Physical Properties of the AU-CSM Blend by Employing the Sulfur Curing System and the Effect of the Blending Technique on the Blend Properties

The blends of AU-CSM had been prepared throughout the entire composition range by three different blending techniques *e.g.*, masterbatch technique, preblending technique and preheating preblending technique. Physical properties of the blends like hardness, modulus, tensile strength and elongation at break were measured in all the cases. The compounding formulation for the masterbatch technique is given in Table Ia, whereas the same for the preblending and preheating preblending techniques are given in Table Ib. Curatives were adjusted based on the formulation given in Table Ia depending on the percentage of polymer used.

For the masterbatch technique, the individual elastomer was mixed with the curatives and then blended in different ratios. The state of cure ($\tau_{\max} - \tau_{\min}$) of the blend increased with increase in CSM content followed by a reversion both of which were maximum for (40:60) blend. Surprisingly, the hardness and the modulus showed a reverse trend where they decreased with the increase in CSM in the blend

TABLE Ia Compounding formulations: for masterbatch technique

Elastomer	*I*	*II*	*III*	*IV*	*V*
AU	80	60	50	40	20
CSM	20	40	50	60	80

Curatives for AU (100 gm):
MBT:2; MBTS:4; ZDC:1; ZnO:1; Stearic acid: 1.5; Caytur: 0.5; S:2.
Curatives for CSM (100 gm):
MBT:2; MBTS:2; ZDC:1; ZnO:2; Stearic acid: 1.5; S:2.

TABLE Ib Compounding formulations for preblending and preheating-preblending techniques

Elastomer	*I*	*II*	*III*
AU	80	50	20
CSM	20	50	80

attained minimum values at its 60% level and then increased at 80% level of CSM. Tensile strength also followed the similar trend (Tab. Ic). This may be due to the replacement of polyurethane, which is more thermoplastic in nature by CSM.

On ageing, the hardness decreased in the AU-rich blend and the CSM-rich blend showed the maximum hardness. The modulus and Tensile Strength of the ageing vulcanisates also decreased which was more prominent in the AU-rich blend. The percent change in properties on ageing are given in the following table (Tab. Id).

Preblending of AU and CSM Followed by Curatives Addition

In the preblending technique, the polymers were blended first in the entire composition range and allowed to rest for 24 hours to reach the equilibrium. Then the curatives were incorporated in the blends. The (80:20), (50:50) and (20:80) of AU-CSM blends were considered. The compounding formulations had been shown in Table Ib.

TABLE Ic Physical properties of the blends (masterbatch techniques)

Properties	*I*	*II*	*III*	*IV*	*V*
$\tau_{\max} - \tau_{\min}$ (dNM)	58	60	65	72	48
Hardness (Å)	53	51	47	45	48
200% Modulus kgf/cm^2	18.64	18.14	13.11	5.82	9.63
Tensile strength kgf/cm^2	86.0	77.0	62.06	17.47	48.2
Elongation at break (%)	400	500	500	850	450

TABLE Id Change in properties on ageing at 120°C for 40 hrs (masterbatch technique)

Properties	*I*	*II*	*III*	*IV*	*V*
Hardness (Å)	−18	−13	−7	−5	+7
200% Modulus	−85.11	−84.22	−78.87	−64.94	−55.55
Tensile strength (%)	−92.0	−87.0	−82.09	−82.48	−64.43
Elongation at break (%)	−37.5	−38	−30	−40.0	−28.88

The state of cure showed maximum value for (80:20) AU-CSM blend, decreased at the blend ratio of (50:50) and again increased for the (20:80) AU-CSM blend. However, the state of cure was higher for both AU rich and CSM rich blends as compared to that of masterbatch technique. Hardness and modulus showed the same trend. But the Tensile strength attained maximum value at (50:50) blend ratio as shown in table (Tab. Ie). Here again, tensile and modulus values were higher than that of masterbatch technique.

Ageing properties (Tab. If) suggested the lower percentage drop in the case of AU rich blend. However, beyond (50:50) level the ageing characteristics were more or less same.

Effect of Heat Treatment on the Properties of the Blends

The objective of heat treatment was to study the effect of interchain crosslinking reaction on the properties of the blends. To perform this, preblends (blends of AU-CSM without curatives) were heated at 150°C for 15 minutes and then the curatives were incorporated. The

TABLE Ie Physical properties of the blends of preblending technique

Blends	$\tau_{max} - \tau_{min}$	*Hardness (Å)*	200% *modulus, kgf/cm²*	*Tensile strength kgf/cm²*	*Elongation at break,* (%)
I	66	60	21.05	82.89	500
II	52	48	12.76	127.8	650
III	60	50	15.6	118.2	600

TABLE If Percent change in properties on ageing at 120°C for 40 hrs

Blends	*Hardness in points*	200% *modulus*	*Tensile strength*	*Elongation at break,* (%)
I	−5	−60.42	−81.57	−20.00
II	−13	−79.93	−93.97	−44.61
III	−2	−58.00	−68.00	−27.00

(80:20), (50:50) and (20:80) AU-CSM blends were considered for comparison. The compounding formulation and the physical properties were given in Table Ib.

Torque rheometry showed that the state of cure (Tab. Ig) decreased with the increase in CSM content at its 50% level but further increased at its 80% level. Modulus and hardness followed the same trend. However, the tensile strength showed the maximum value for the CSM rich blend. In this case the technical properties were much less than that of the preblended technique. However, the tensile values had an edge over the masterbatch technique for the CSM rich blend. The percent change in properties on ageing, as shown in Table Ih, suggested the much lower degradation as compared to both the preblend and masterbatch technique. The lower values of the technical properties in the case of preheated preblended sample may be due to the loss of functional groups, because of their mutual interaction which were usually responsible for the crosslinking of the individual elastomer. This loss of functional groups were not probably compensated by the properties which had been developed by their mutual interaction of the individual polar functional group.

IR Spectral Analysis

IR spectra of the thin film of AU, CSM (hypalon) and a (50:50) blend of AU-CSM without any curatives, heated at 150°C had been studied

TABLE Ig Physical properties of the blends prepared by preheating preblending technique

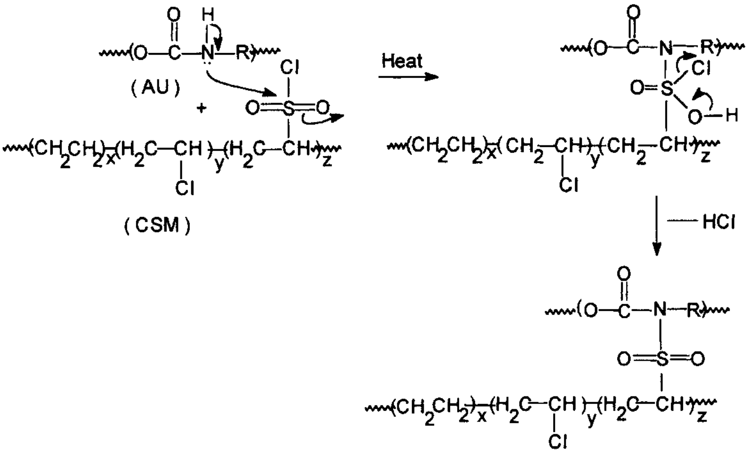
Blends	$\tau_{max} - \tau_{min}$ *(dNM)*	*Hardness (Å)*	200% *modulus, kgf/cm^2*	*Tensile strength, kgf/cm^2*	*Elongation at break,* (%)
I	14	42	7.89	23.68	480
II	12	38	5.67	53.90	750
III	16	45	9.20	56.80	780

TABLE Ih Change in properties on ageing at 120°C for 40 hrs

Blends	*Hardness in points*	200% *modulus*	*Tensile strength*	*Elongation at break,* (%)
I	−2	−44.10	−51.09	−12.50
II	−3	−49.73	−84.10	−38.66
III	+2	−38.00	−48.00	−10.20

(Fig. 1). Polyurethane (AU) showed a broad peak at 3140 cm^{-1} for N—H stretching and at 1690 cm^{-1} for amide carbonyl (>= O) stretching. Hypalon showed two characteristic peaks at 721 cm^{-1} and 1180 cm^{-1} for the presence of C—Cl and SO_2Cl group respectively. The IR spectra of the blend of (50:50) AU-CSM revealed the formation of a new S—N bond as indicated by the shifting of amide >= O peak from 1690 cm^{-1} to higher region (1728 cm^{-1}), probably due to the more electronegative atom sulfur bonded to —N— in place of —H atom, and thereby forming S—N bond. Absence of the peaks at 3140 cm^{-1} and 1180 cm^{-1} for N—H and SO_2Cl, in the blend also supported this. The peak for C—Cl in the blend appeared at 721 cm^{-1} as was in the IR spectra of CSM (Hypalon) indicating that it was not taking part in the reaction.

Based on the aforesaid spectral analysis, a plausible mechanism for the reaction of AU-CSM can be suggested as follow.



Crosslinked structure.

Solvent Swelling Study

The Differential Solvent Swelling Study were carried out to study the covulcanisation between the two elastomers in the blend. The two solvents were used where each individual polymer was soluble. The left portion of the figure (Fig. 2), in DMSO showed that both for

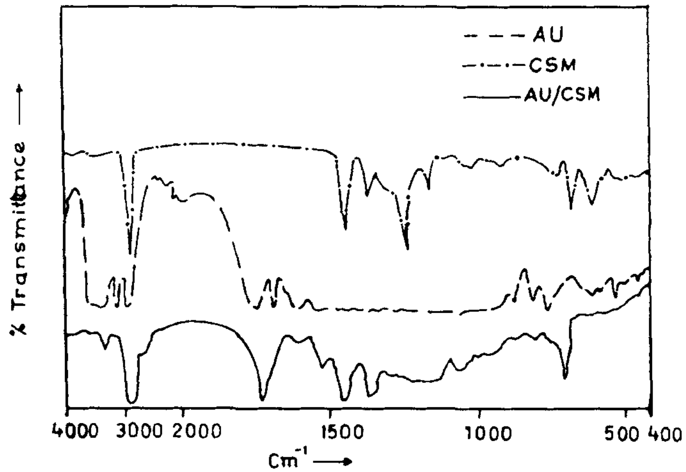


FIGURE 1 IR Spectral analysis of pure AU, pure CSM and a blend (50:50) AU:CSM without curatives.

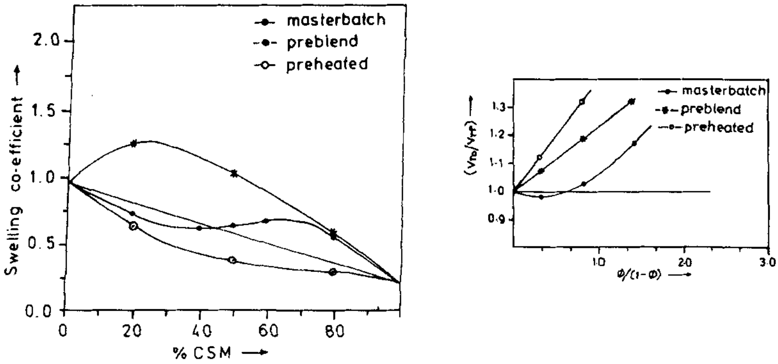


FIGURE 2 Plot of swelling coefficient against CSM and V_{ro}/V_{rf} against $\phi/1-\phi$ for AU-CSM system in DMSO.

masterbatch and preheated preblended compounds, the swelling coefficient lie nearer to the additive average line. Whereas for preblended compound the swelling coefficient of the compound lie well above the additive average line specially at the low CSM dose. The right side of the figure (Fig. 2) suggested phase adhesion in the case of masterbatch compound particularly in the region of low CSM content blend.

The left portion of figure (Fig. 3) in toluene, showed that the swelling coefficient of the blends lie more or less nearer to the additive average line for both the CSM and AU rich blends. However, the right portion of the figure (Fig. 3) suggested the probable phase adhesion although to a smaller extent in the region of high AU containing blend. However, the Kraus plot in both the cases suggested the lack of phase adhesion for the preblended and preheated-preblended compounds.

Thermal Analysis

The low temperature DSC of the (50:50) AU:CSM blend had been carried out to study the compatibility of the blends with reference to the effect of preheating. Two different cases of the AU:CSM blends had been considered having the same compounding formulations and blend ratio in order to study the effect on the compatibility of the blends of preheating followed by the curatives addition and the blends without preheating.

Low temperature DSC plot of (50:50) AU:CSM preheated sample showed only one prominent T_g at –9.15°C for the sample indicating the better compatibility of AU and CSM in the blend. In case of the blends (50:50) and (20:80) AU:CSM, without any heat treatment, prepared by the masterbatch techniques, the DSC plots showed two T_g values in the vicinity of –17.04°C and –11.30°C and –18.45°C and –10.41°C respectively. This study indicated that the compatibility of

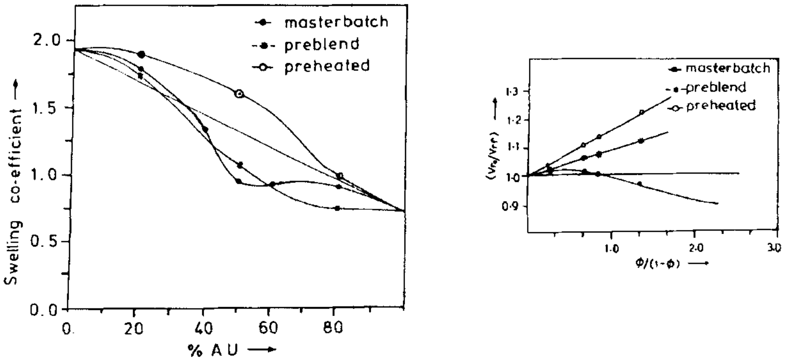


FIGURE 3 Plot of swelling coefficient against AU and V_{ro}/V_{rf} against $\phi/1-\phi$ for AU-CSM system in toluene.

the blends can be enhanced by preheating the blends followed by the curatives addition.

The high temperature DSC of (50:50) AU:CSM blends, prepared by three different blending techniques, had been studied to find the degradation pattern of the blends. The high temperature DSC plots are given in figure (Fig. 4). From the DSC plots it was evident that the degradation occured in two steps in each blends having the same blending ratio. For (50:50) AU:CSM blend prepared by the masterbatch technique, the first degradation started at a temperature of 183.67°C and about 50% of the sample degraded in this step with a faster rate while the second degradation occured at 418°C (Fig. 4a)

In case of (50:50) AU:CSM preblended sample, the first degradation started at 214.3°C with a comparatively slower rate which lead to the second degradation to occur at 421.33°C (Fig. 4b). In case of the preheated sample followed by the curative addition, the initial degradation started at 216.05°C with much slower rate as compared to both the above processes and lead to second degradation at 428.67°C (Fig. 4c).

From the thermal analysis it was clear that the blends prepared by the masterbatch techniques degraded earlier whereas for the preblended sample and preheated preblended sample, the delayed degradation

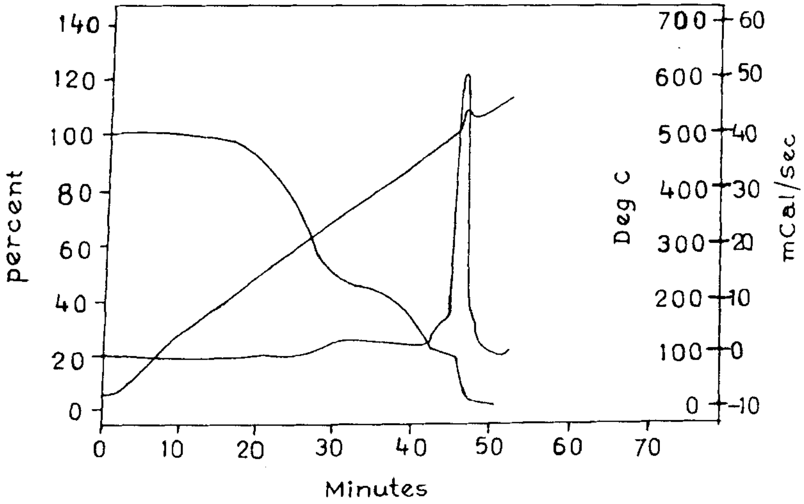


FIGURE 4a DTA/TGA plots of the 50:50 AU:CSM masterbatch sample.

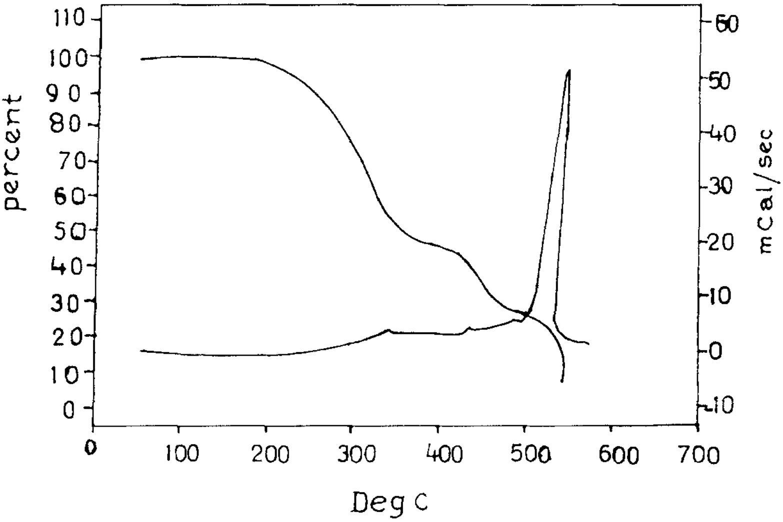


FIGURE 4b DTA/TGA plots of the 50:50 AU:CSM preblended sample.

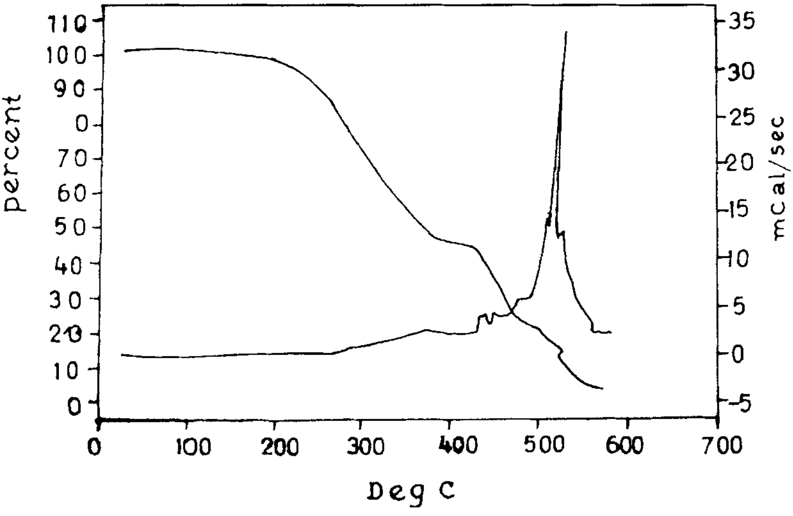


FIGURE 4c DTA/TGA plots of the 50:50 AU:CSM preheated preblended sample.

occured, the extent of which was more in case of the preheated preblended sample. Thus preheating retarded the degradation process.

Heat of vulcanisation of the AU:CSM blends had been studied. The following table (Tab. Ii) represents the onset temperature and the heat of interchain crosslinking reaction of the blends. Three different cases had been considered without curatives having different AU:CSM ratio. The heat of reaction varied with the blend ratio, associated with the exothermic peak in each case. The heat of reaction was maximum for the 80:20 blend ratio, decreased with CSM addition and again increased at its 80% level while the onset temperature of reaction had maximum value at 50:50 level. The exothermic peaks revealed that some reaction occured between the two elastomeric phases the extent of which depends on the blend ratio.

SEM Study

In order to study the phase morphology of the blends, the blends were extracted with a specific solvent where only one phase of the blends were removed and then the blends were SEM photographed after suitable gold sputtering. The blends, prepared by three different blending techniques *viz*. Masterbatch, preblending and preheating-preblending, having the same blending ratio (50:50, AU:CSM) were toluene extracted (where CSM phase dissolved out) and the SEM photographs were taken. The SEM photographs of the masterbatch samples (Fig. 5) showed larger domains indicating easy extraction of the single phase by solvent. When the blend was prepared by the preblending technique the extraction of the CSM phase is slightly restricted as observed from the SEM photograph (Fig. 6). In case of the heating of the preblended samples the extraction of the CSM phase by solvent (toluene) become much more restricted as evident from the more uniform in SEM

TABLE Ii Heat of vulcanisation

Sl. No.	*Blend ratio (AU/CSM)*	*Onset temp. (°C)*	*Heat of vulcanization (mcal/mg)(exothermic)*
1	80:20	99.65	23.06
2	50:50	107.11	16.60
3	20:80	105.20	20.40

FIGURE 5 SEM photograph of toluene extracted sample of 50:50 AU:CSM blend, prepared by masterbatch technique (×800).

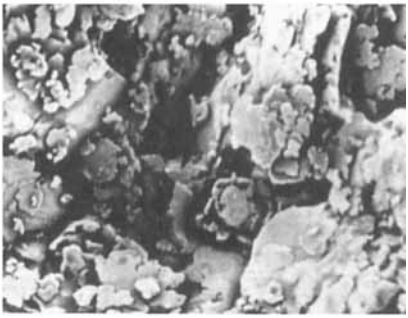


FIGURE 6 SEM photograph of toluene extracted sample of 50:50 AU:CSM blend, prepared by preblending technique (×800).

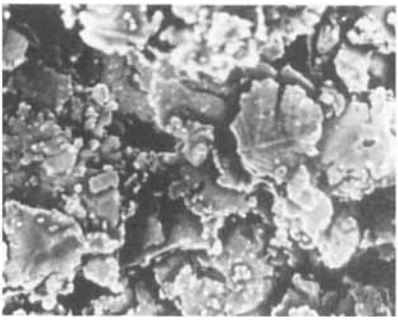


FIGURE 7 SEM photograph of toluene extracted sample of 50:50 AU:CSM blend, prepared by preheating-preblending technique (×800).

photograph (Fig. 7) which clearly indicated the formation of interchain crosslinks between the two blend partners on heating.

CONCLUSION

The processability of polyurethane was improved by blending with chlorosulfonated polyethylene. Blends properties largely depends on the blending techniques and on blending ratio. The thermal stability of the preblended compounds were greater than that of the masterbatch compounds. Heat treatment of the preblend improved thermal stability of the blends. On heating the preblends the extraction of the single phase became restricted indicating the interchain crosslinking reaction occured between the two elastomeric phases.

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