

Interchain Crosslinkable Polymer Blends of Polyurethane and Polyacrylic Elastomer (Sulfur Cure)

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ABSTRACT: Blends of polyurethane and polyacrylic elastomers prepared by three different blending techniques have been studied in different blend ratios. The processability of the polyurethane elastomer was improved as a result of blending with the polyacrylic elastomer. The blending technique has a significant role in determining the physical properties of the blends. Improvement of physical properties was observed in the blends containing the interchain crosslink bonds. IR spectral analysis suggested the formation of interchain crosslink between the two elastomers phases on heat treatment, before the addition of any cura-

tives. Thermal stability of the blends was also improved when preblending and preheating techniques were applied. The extraction of the single phase by solvent was also restricted to a significant extent for the preheated sample probably due to the interchain crosslinking. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 845–853, 2004

Key words: polyurethanes; elastomers; crosslinking; thermogravimetric analysis (TGA); phase behavior; infrared spectroscopy

INTRODUCTION

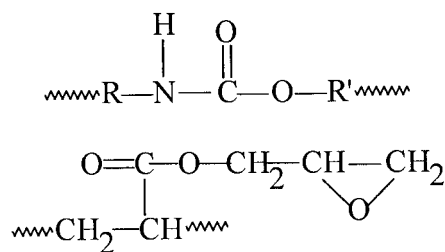
A considerable amount of research has been made over the last several years with a view to obtaining new polymeric materials with enhanced specific properties for specific applications or a better combining of different properties. After the synthesis of polymers from new monomers had been largely explored, efforts were focused on multiphase polymeric systems.^{1–5} Much attention is currently being devoted to the route for combining outstanding properties of different existing polymers, that is, the formation of polymer blends.^{6–11} It is an easy and inexpensive method of modifying various properties of a polymer such as processability, heat distortion, etc.^{12–15}

Recently, several blend systems where interchain crosslinking occur^{16–20} has been studied. Polyurethane elastomers are widely utilized as engineering materials in many industries, and are well known for their excellent wear and tear properties and good oil resistance. Polyurethane finds its applications in solid tires and rollers, automotive industry, sealing applications, conveyor belts, aircraft industry, and from shoe soles to household requirements.^{21–23} Polyacrylic elastomer, on the other hand, is a special-purpose rubber featuring resistant to heat, oil, and ozone. The important outlets of polyacrylic rubber are in roll, shaft seal,

oil pan gasket, crankshaft seal, oil return hose, torque converter hose, air control hose, tube, diaphragm, boots, etc. Both the polymers have a polar functional group and are expected to undergo interchain crosslinking reaction on heat treatment. Considering this, blends of polyurethane with polyacrylic rubber were prepared by interchain crosslinking reaction to develop new polymers with enhanced properties that were explained through the interchain crosslinking reaction.

EXPERIMENTAL

Materials used



Blend of polyurethane (AU) and polyacrylic elastomers (AR-31) were prepared in an open two-roll mixing mill throughout the entire composition range at room temperature and at a constant shear rate. The polyurethane phase was gradually replaced by the polyacrylic elastomer. The sulfur cure systems have been employed. Blends were prepared by three different blending techniques, for example, masterbatch

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TABLE I
Compounding Formulations for the
Masterbatch Technique

Elastomers (wt/wt)	I	II	III	IV	V	VI
AU	80	70	60	50	30	20
AR-31	20	30	40	50	70	80

Curatives for AU (Phr): MBT-2, MBTS-4, ZDC-1, ZnO-1, Stearic acid-1.5, S-2, Caytur-0.5.

Curatives for AR-31 (Phr): TTFc - 0.4, ZDC- 0.9.

technique, preblending technique, and preheating preblending technique. The processability and the cure characteristics of the blends were studied in a Monsanto Rheometer (R-100) at 150°C. Blends were then allowed to cure in a hot press at 150°C up to the optimum cure under 20 MPa pressure. Physical properties of the blends like hardness, modulus, tensile strength, and percent elongation at break were measured on the cure sheets both before and after aging. Aging was performed in an air oven at 120°C for 40 h. Tensile properties of the blends were measured in a universal tensile testing machine. Solvent swelling study^{24,25} was performed in tetrahydrofuran and toluene at ambient temperature for 48 h, and covulcanization was studied following the Kraus equation:²⁴

$$\frac{V_{ro}}{V_{rf}} = (1 - M) \frac{\Phi}{(1 - \Phi)}$$

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

Infrared spectra of the thin films of virgin polymers and a 50 : 50 blend of AU/AR-31, without curatives, were taken using a Perkin-Elmer Model-837 to establish the interchain crosslinking reaction between the two elastomers. High-temperature Differential Scanning Calorimetry (DSC) and Thermogravimetric analysis (TGA) of the blends were studied²⁶ through the

TABLE II
Physical Properties of the Masterbatch Samples

Blends	Hardness (Shore A)	200% Modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
I	58 ± 0.2	1.5 ± 0.1	5.2 ± 0.1	520 ± 14
II	52 ± 0.1	1.4 ± 0.1	4.8 ± 0.2	550 ± 16
III	44 ± 0.1	1.1 ± 0.2	3.7 ± 0.1	600 ± 12
IV	38 ± 0.3	0.9 ± 0.1	2.8 ± 0.1	610 ± 10
V	35 ± 0.2	0.8 ± 0.1	2.6 ± 0.2	630 ± 14
VI	32 ± 0.1	0.7 ± 0.1	2.4 ± 0.2	640 ± 16

TABLE III
Percent Change in Properties on Aging
of the Masterbatch Samples

Blends	Hardness (loss in points)	200% Modulus (% loss)	Tensile strength (% loss)	Elongation at break (% loss)
I	13	62.4	75.1	23.0
II	10	57.8	68.4	21.8
III	8	49.1	62.7	25.0
IV	6	41.6	57.2	27.8
V	5	38.5	52.4	28.6
VI	3	36.0	49.8	30.4

Shimadzu thermal analyzer in air, at a heating rate of 10°C/min. Low-temperature DSC study was conducted using a Stanton Redcroft Thermal analyzer, STA 625 to determine the glass transition temperature (T_g) values of the blends. Phase morphology of the blend was studied with solvent extracted samples with the help of a SEM (Camscan series 2 and E 5200 auto sputter coater).

RESULTS AND DISCUSSION

Physical properties of the AU/AR-31 blends prepared by the masterbatch technique

The individual elastomers were first mixed with the curatives and allowed to equilibrate for 24 h. Then the mixed compounds were blended in the ratios given in Table I.

The state of cure of the blends were increased with the increase in AR-31 content in the blend up to a 70 : 30 AU/AR ratio and then again decreased at its 80% level. The hardness of the blends decreased with the increase in AR-31 content in the blend. This decreasing tendency in hardness may be due to the replacement of polyurethane elastomer, which is more thermoplastic in nature, by AR-31. Modulus (200%) and tensile strength of the blends also followed the same trend with the hardness. However, elongation at break was increased slightly with the increase in AR-31 content in the blend (Table II).

On aging in air, all the physical properties were decreased. The hardness, modulus, and the tensile strength decreased more in AU rich blends, whereas elongation at break decreased more in the AR-31 rich

TABLE IV
Compounding Formulations for the Preblending
and Preheating Preblending Technique

Elastomers (wt/wt)	I	II	III
AU	80	50	20
AR-31	20	50	80

TABLE V
Physical Properties of the Preblended Samples

Blends	Hardness (Shore A)	200% Modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
I	52 ± 0.2	1.8 ± 0.1	6.3 ± 0.2	500 ± 12
II	42 ± 0.2	1.4 ± 0.2	3.9 ± 0.1	550 ± 10
III	35 ± 0.1	1.0 ± 0.2	3.3 ± 0.2	580 ± 10

blend (Table III). This decrease in properties is due to the instability of polyurethane elastomer at the aging temperature (120°C). Nonreversible destructive changes occur in the chemical structure of the polyurethane²¹ elastomers at above 80°C that reduces the mechanical properties.

Physical properties of the AU/AR-31 blends prepared by the preblending technique

In this technique, the two polymers were first blended in different ratios and then the curatives were incorporated. Three different blend ratios have been considered as indicated in Table IV. The amount of curatives was adjusted with the masterbatch technique, depending on the percentage of elastomers used in the blends.

The state of cure of the blends were decreased with the increase in AR-31 content in the blend and were higher than that obtained through the masterbatch technique having the same blend ratio. The hardness of the preblends was found to decrease with the increase in AR-31 content in the blend. The 80 : 20 AU/AR-31 preblended sample showed the lower hardness value than the masterbatch sample of same elastomer ratio, whereas the 50 : 50 and 20 : 80 AU/AR-31 ratio showed a reverse trend. Modulus (200%) and the tensile strength values were decreasing with the increase in AR-31 content in the blend, and were higher than that obtained by the masterbatch technique having the same elastomer ratio. Elongation at break was increased with the increase in AR-31 content in the blend, and was lower than the Masterbatch samples of the same elastomer ratio (Table V).

Aging properties are given in Table VI. Here also

TABLE VI
Percent Change in Properties on Aging of the Preblending Technique

Blends	Hardness (loss in points)	200% Modulus (% loss)	Tensile strength (% loss)	Elongation at break (% loss)
I	8	52.3	66.4	24.0
II	5	46.5	58.6	30.0
III	3	34.6	47.8	27.5

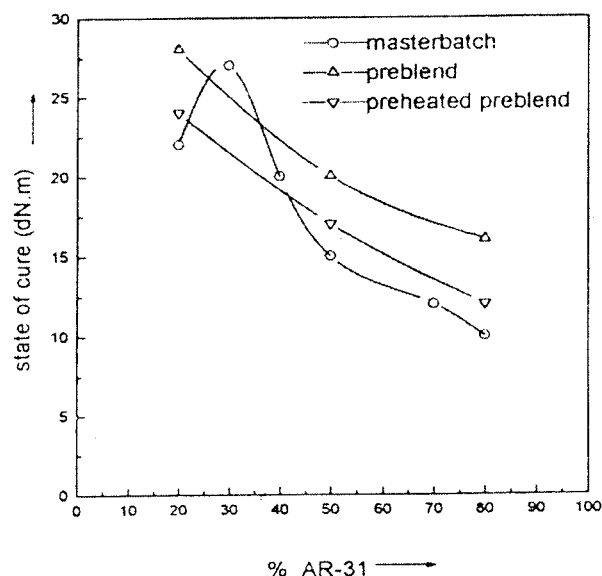


Figure 1 State of cure vs percentage of AR-31 elastomer.

the decrease in properties like hardness and modulus were more in the AU-rich blend. This reduction in properties on aging was because of lower stability of polyurethane elastomer at this temperature. Elongation at break was found to decrease more in case of the 50 : 50 AU/AR-31 blend.

Physical properties of the preheated preblended samples

To study the effect of heat treatment on the properties of the AU/AR-31 blends, the preblends of the two were heated at 150°C for 15 min before the addition of the curatives. Here to study the effect of heat treatment, three different blending ratios have been considered. The compounding formulation corresponds to Table IV.

The state of cure (Fig. 1) of the blend was found to decrease with the increase in AR-31 content in the blend, and was lower than that of the preblended samples of the same elastomer ratio. The hardness of the blends was higher than that obtained through the preblended technique having the same blending ratio. The AU-rich blend showed the higher hardness value and decreased with the increase in AR-31 content in

TABLE VII
Physical Properties of the Preheated Preblended Samples

Blends	Hardness (Shore A)	200% Modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
I	55 ± 0.1	1.6 ± 0.1	5.4 ± 0.2	460 ± 14
II	44 ± 0.2	1.0 ± 0.1	3.2 ± 0.1	530 ± 10
III	38 ± 0.2	0.8 ± 0.2	2.8 ± 0.1	560 ± 12

TABLE VIII
Percent Change in Properties on Aging of the Preheated
Preblended Samples

Blends	Hardness (loss in points)	200% Modulus (% loss)	Tensile strength (% loss)	Elongation at break (% loss)
I	10	54.6	67.1	26.0
II	5	38.7	54.9	25.4
III	2	32.1	44.2	26.5

the blend. We consider that the increased hardness of preheated preblended sample is due to interchain crosslinking between the two elastomers as a result of heat treatment before addition of curatives, as shown in IR spectral analysis. Modulus (200%) and tensile strength were higher than that of the masterbatch samples but lower than the preblended samples of same elastomer ratio. This may be due to some degradation of polyurethane phase upon preheating the preblend at 150°C for 15 min. Elongation at break was increased with the addition of an AR-31 elastomer in the blend and was lower than the masterbatch and preblended samples having the same elastomer ratio (Table VII).

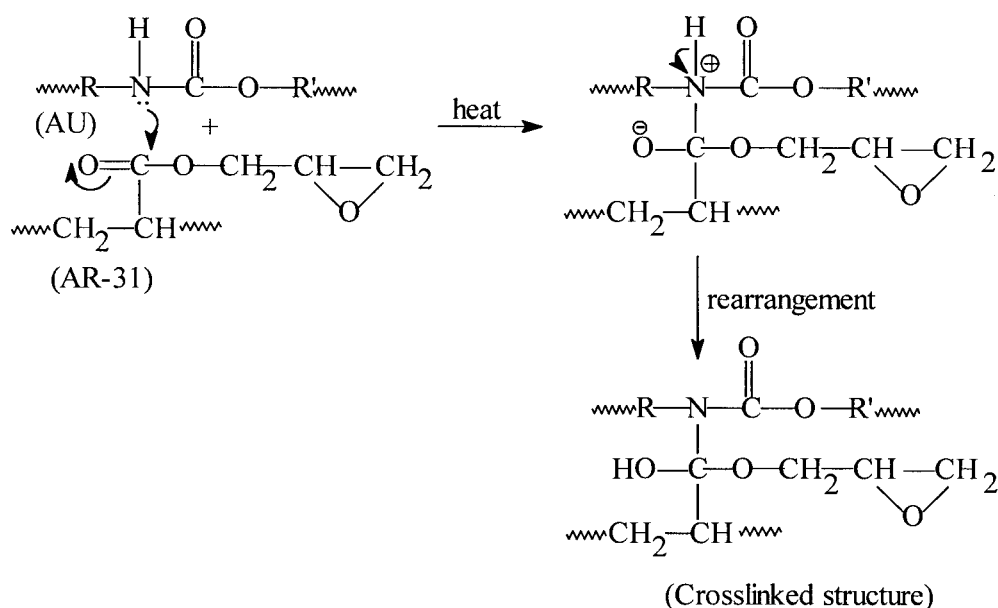
On aging, all the physical properties were decreased. The decrease in properties was more in the case of the AU-rich blend than that of the AR-31-rich blend (Table VIII). Above 80°C there is a gradual permanent decrease in properties for the oxidative cleavage of the polyether and polyester linkages in the polyurethane main-chain backbone.²¹ Hence, aging at 120°C for 40 h may cause oxidative degradation of the

polyurethane phase. Thus, the properties of the polyurethane-rich blend decreased more on aging.

IR spectral analysis

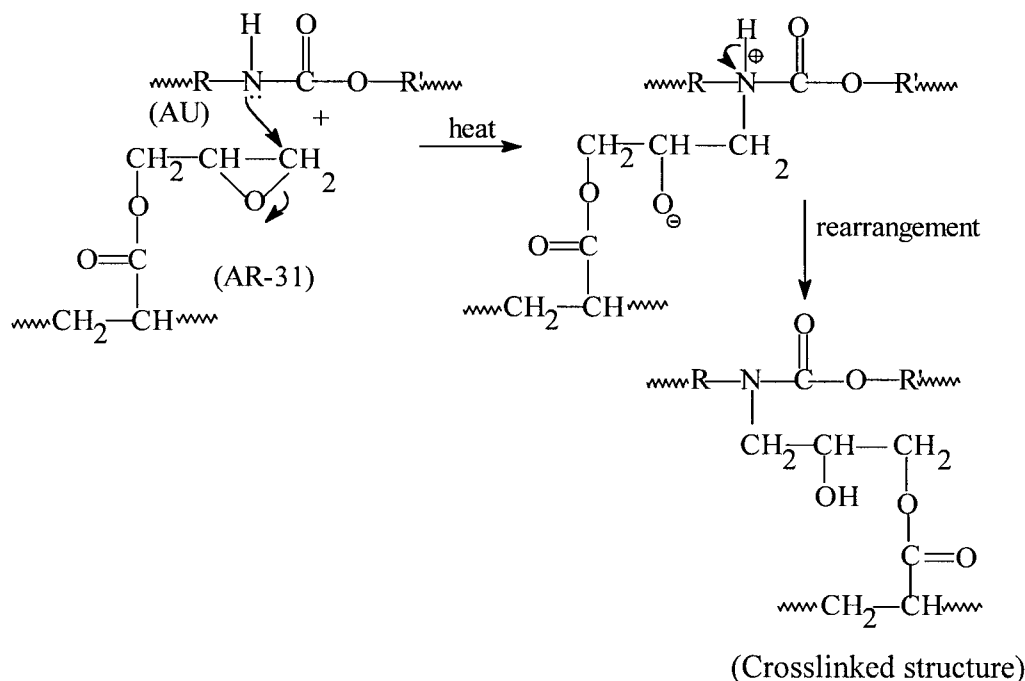
To study the interchain crosslinking reaction between the two elastomeric phases of polyurethane (AU) and polyacrylic elastomers (AR-31), IR spectra of the thin films of pure AU, pure AR-31, and a 50 : 50 blend of the two without any curatives (Fig. 2) were recorded. Polyurethane showed characteristic peaks at 3140 cm^{-1} and at 1690 cm^{-1} for the N—H stretching and amide carbonyl ($\text{C}=\text{O}$) stretching vibrations. Polyacrylic rubber showed characteristic peaks for the ester carbonyl group at 1726 cm^{-1} and epoxy linkage at 1253 cm^{-1} .^{27,28}

In the IR spectra of the 50 : 50 blend of AU/AR-31, no characteristic peaks were observed in the region of 3140 cm^{-1} , 1726 cm^{-1} and 1253 cm^{-1} , for the —N—H stretching of pure AU and ester carbonyl ($\text{C}=\text{O}$) and epoxy linkage in pure AR-31. The absence of the peaks at 1726 cm^{-1} and at 1253 cm^{-1} in the blend suggested the involvement of ester ($-\text{CO}_2\text{R}$) group as well as the epoxy group of AR-31 in the crosslinking reaction where the N-atom of AU may attack on heat treatment. The appearance of a new peak at 3340 cm^{-1} in the blend, which may be due to the presence of the hydroxyl ($-\text{OH}$) group, supported this. The shifting of amide carbonyl ($\text{C}=\text{O}$) peak of pure AU from 1690 cm^{-1} to 1749 cm^{-1} also provided supporting evidence for the crosslinking reaction. Thus, a plausible mechanistic pathway for the interchain crosslinking reaction may be suggested as:



An alternative mechanistic pathway for the crosslinking reaction that involves the epoxy group of

AR-31 and thereby forming the —OH group can also be taken into consideration as below.



Solvent swelling study

To study the phase adhesion and the covulcanization of the blends, solvent swelling was carried out in tetrahydrofuran (THF) and toluene solvents where polyurethane and polyacrylic rubbers are soluble, respectively. The variation of the swelling coefficient values of the masterbatch and preheated preblended samples in THF followed a sigmoidal pattern with the insoluble fraction of the blends. The swelling coeffi-

cient values lie below the additive average line up to 50% of the insoluble fraction. For the preblended samples the swelling coefficient values lie well below the additive average line (Fig. 3). The Kraus plot (Fig. 3, right-hand side) of all the three types of blends in THF exhibited a negative slope, indicating the presence of phase adhesion in the AU-rich blend.

The swelling coefficient values of the masterbatch and preheated preblended samples in toluene also exhibited a sigmoidal pattern with the insoluble fraction of the blends. The swelling coefficient values of the masterbatch and preheated preblends lie above the additive average line up to 70 and 60% of the insoluble fraction. However, the swelling coefficient of the preblended samples lie below the additive average line through out the composition range (Fig. 4). The Kraus plot (Fig. 4, right-hand side) of the blends exhibited a positive slope for all the three types of blends, indicating the lack of phase adhesion in the AR-31-rich blend.

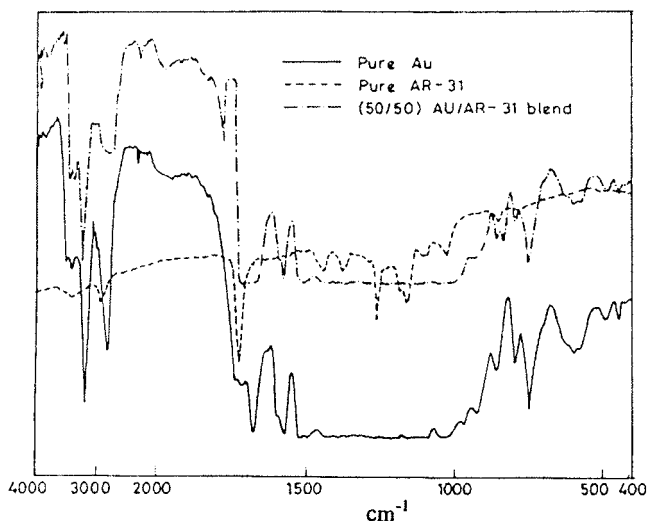


Figure 2 IR spectral analysis of Pure AU, Pure AR-31, and (50 : 50) AU/AR-31 blend without curatives.

Thermal analysis

The low-temperature DSC of the 50 : 50 AU/AR-31 blends was carried out to study the compatibility of the blends with reference to the effect of preheating the preblend. Three different cases of AU/AR-31 blend have been considered, keeping the blend ratio constant to study the effect of the blending technique on the compatibility of the blend. The 50 : 50

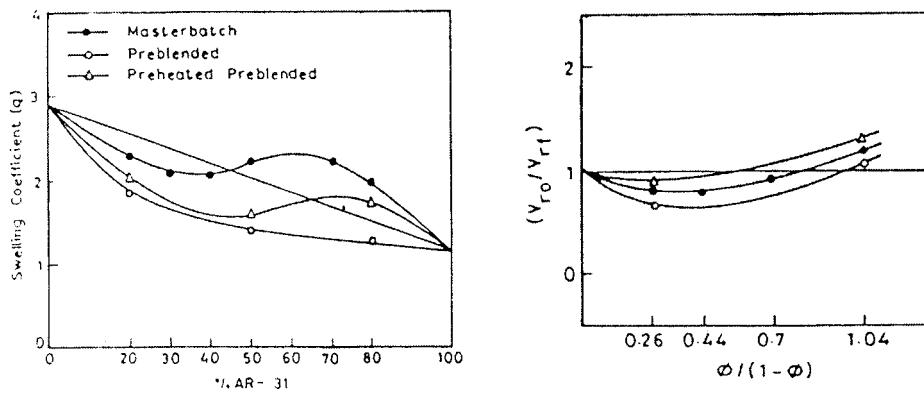


Figure 3 Plot of swelling coefficient against AU and (V_{r0}/V_{rf}) against $\Phi/(1-\Phi)$ for the AU/AR-31 system in THF.

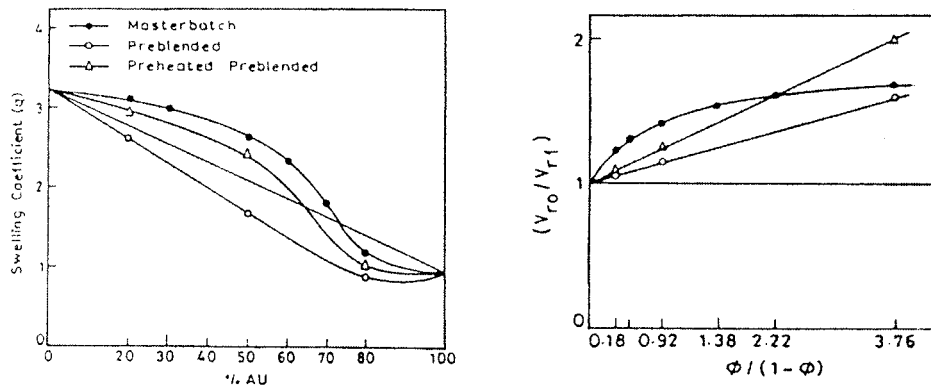


Figure 4 Plot of swelling coefficient against AR-31 and (V_{r0}/V_{rf}) against $\Phi/(1-\Phi)$ for the AU/AR-31 system in toluene.

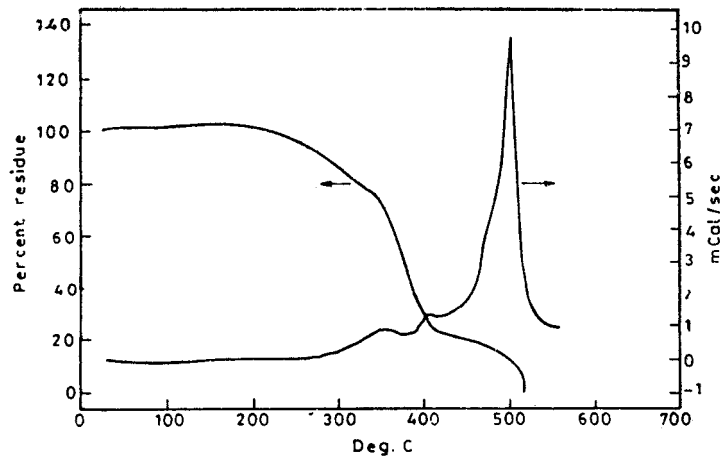


Figure 5 High-temperature DTG/TGA plots of (50 : 50) AU/AR-31 masterbatch sample.

AU/AR-31 blend prepared through the masterbatch technique showed two T_g values in the vicinity of -24.3 and -12.4°C . However, only one T_g was observed for the blends when the preblending and preheating preblending techniques were adapted. The 50 : 50 AU/AR-31 blend prepared by the preblending technique showed the T_g at -9.05°C and the 50 : 50 AU/AR-31 preheated preblended sample

showed the T_g at -9.3°C . Thus, the compatibility of the blend can be enhanced through the preblending and preheating preblending techniques. The shifting of the T_g values to the higher temperature region for the preblend and preheated preblend may be due to the interchain crosslinking between the two elastomer phases before addition of curatives as discussed in IR section.

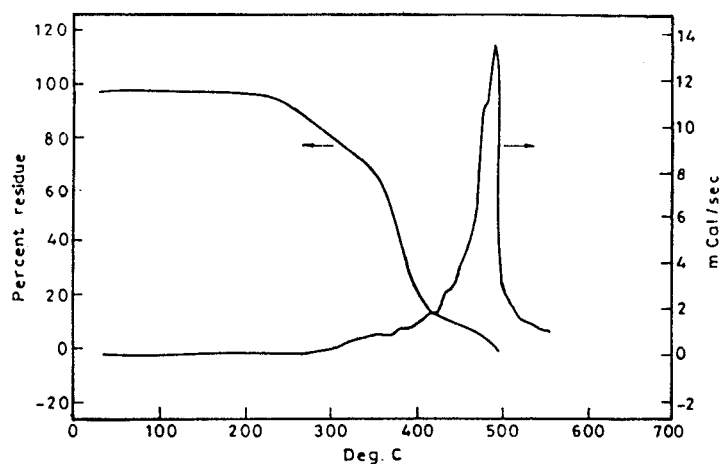


Figure 6 High-temperature DTG/TGA plots of (50 : 50) AU/AR-31 preblended sample.

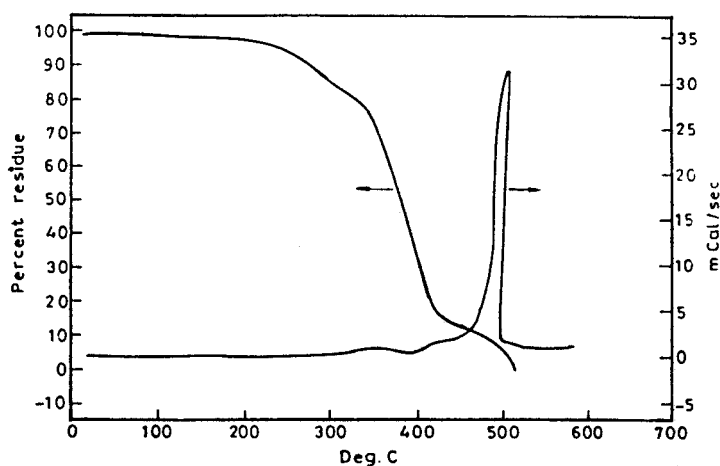


Figure 7 High-temperature DTG/TGA plots of (50 : 50) AU/AR-31 preheated preblended sample.

The degradation pattern of the blends has been studied with special reference to the effect of preheating the preblends. The degradation occurred mainly in two steps for all the three types of blends. However, a third step also occurred after almost 80% degradation, which is technically less important. The DSC/TGA plot of the 50 : 50 AU/AR-31 masterbatch sample showed the initial degradation at 237.9°C and continued up to 353°C at a slower rate. By this time almost 24% of the sample was lost. The second degradation, which started at 353°C, continued up to 400°C at a faster rate. In this step almost 77% of the sample was degraded and the degradation was completed at 515°C (Fig. 5). For the preblended sample the first degradation started at 241.3°C and continued up to 362°C at a slower rate where the second degradation started. In this step almost 34% of the sample was degraded. The second degradation continued up to 406°C at a relatively faster rate. By this time almost 86% of the sample was lost and the degradation was completed at 500°C (Fig. 6). In case of the blend pre-

pared by preheating the preblend, the degradation was started at a higher temperature, 248 °C and continued up to 355 °C where the second degradation was started. Almost 22% of the sample was degraded in this step. In the second step almost 85% of the sample was lost at a faster rate, which continued up to 420.6°C, and the degradation was almost completed at 517.2°C (Fig. 7).

From the above thermal study it is observed that the masterbatch sample degraded at a lower temperature,

TABLE IX
Blend Ratio, Onset Temperature, and Exothermic Heat of Vulcanization

Sl. No.	Blend ratio (AU/AR-31)	Onset temperature (°C)	Exothermic heat of vulcanization (J/g)
1	80:20	140	30
2	50:50	119	41
3	20:80	93	32

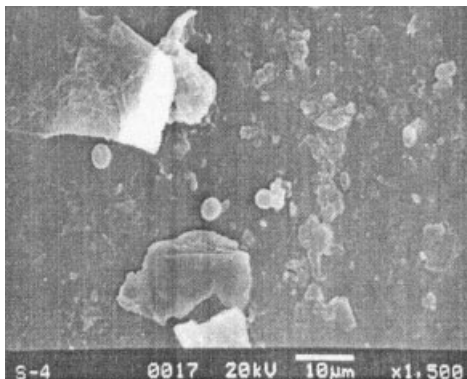


Figure 8 SEM photograph (1500 \times) of the THF extracted sample of (50 : 50) AU/AR-31 blend prepared by the masterbatch technique.

whereas the degradation processes were delayed when the blend was prepared by the preblending and preheating preblending technique. This increase in thermal stability in preblend and preheated preblend samples is related to the interchain crosslink bonds presented in these blends (as discussed in IR spectral analysis section). Thus, the thermal stability of the blend depends on the blending technique.

The heat of vulcanization and onset temperature of the AU/AR-31 blends without any curatives have been studied (Table IX). The onset temperature and heat of vulcanization were highest for the 80 : 20 and 50 : 50 AU/AR-31 blend ratio, respectively. This study revealed that crosslinking reaction occurred between the two elastomers phases, the extent of which depend on blending ratio.

Study of phase morphology by SEM

Phase morphology of the blends of polyurethane and polyacrylic elastomer, has been studied using a scanning electron microscope. The 50 : 50 AU/AR-31

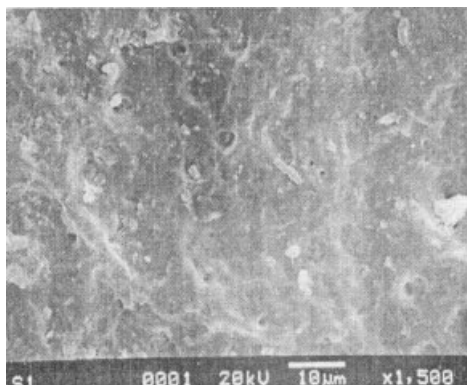


Figure 9 SEM photograph (1500 \times) of the THF extracted sample of (50 : 50) AU/AR-31 blend prepared by the preblended technique.

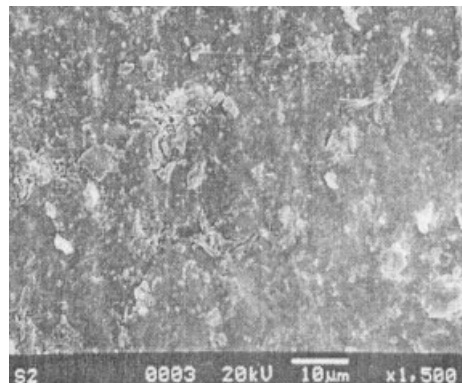


Figure 10 SEM photograph (1500 \times) of the THF extracted sample of (50 : 50) AU/AR-31 blend prepared by the preheated preblended technique.

blends prepared through three different blending techniques have been considered. The blends were first extracted with tetrahydrofuran where the polyurethane phase was removed out and then the SEM photographs were taken after suitable gold sputtering. The SEM photograph of the masterbatch sample showed the larger voids (Fig. 8), indicating the easy extraction of the polyurethane phase by solvent. When the blend was prepared through the preblending technique, the extraction of the polyurethane phase became restricted. The reduction in the domain size in the SEM photograph indicated this (Fig. 9). The extraction of the polyurethane phase was limited to a negligible extent when the preblend was given heat treatment before addition of curatives (Fig. 10). These differences in the extractability of the single phase by solvent clearly suggested that interchain crosslinking reaction occurred between the two phases at the domain boundary on heat treatment.

CONCLUSION

The processability of the polyurethane elastomer was improved by blending with polyacrylic elastomer. Masterbatch samples showed poorer physical properties than the preblended and preheated preblended samples, probably due to the cure rate mismatch. Delayed degradation occurred when the preblend was given heat treatment, probably due to interchain crosslink between the elastomeric phases, as discussed in the IR spectral analysis.

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