

Polyblend Systems of Polyurethane (AU) and Ethylene Acrylic Elastomer (vamac) Using the Sulfur Cure Systems

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ABSTRACT: Blends of polyurethane (Vibrathane-5008, Uniroyal Co., USA) and ethylene acrylic elastomer (vamac B-124, du Pont, USA) prepared through three different blending techniques have been studied over the entire composition range. The processability and the aging properties of the polyurethane elastomer were improved as a result of blending with ethylene acrylic elastomer. IR spectral analysis of the (50:50) blend of the two elastomers, without any curatives, suggested that the interchain crosslinking reaction occurred between the two elastomers phases on heat treatment. The thermal stability of the blends also improved on heat treatment, before addition of curatives. Phase morphological study revealed that the extractability of the single phase by solvent was also restricted on preheating the preblends, probably due to the interchain crosslinking. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 2737–2745, 2001

Key words: polyurethane; vamac; masterbatch; preblending; phase morphology

INTRODUCTION

Mixing two or more polymers together to produce blends is a well-established strategy for achieving a specified portfolio of physical properties, without the need to synthesize specialized polymer systems.¹ It is an easy and inexpensive method of modifying various properties of a polymer such as processability, heat distortion, and impact strength.^{2,3} It offers an alternative way to develop new polymers with improved properties than the existing polymers to meet specific needs.^{4,5}

The aim of the present investigation is to study the blend of polyurethane (AU) and ethylene acrylic elastomer (vamac) with reference to the interchain crosslinking reaction on heat treatment and its effect on the properties of the blends. Recently Das et al. have studied several blend systems where interchain crosslinking takes

place and have shown how the blending technique dictated the blend properties.^{6–10}

Polyurethane has become an important class of organic compound because of its unique combination of unusual properties and its ability to be processed by almost all known manufacturing processes. The important outlets of polyurethane are in many branches of industry, and it is making an increasing contribution to our daily lives—for instance, as for abrasion resistant coating. Their unique property is combining high strength, high modulus with good resistance to attack by oil, petrol and many common non polar solvents.^{11,12} Wilcox has studied the blends of polyurethane elastomer with polybutadiene and nitrile rubber, and discussed the possible applications in tire tread.¹³

Ethylene acrylic elastomer (vamac), on the other hand, possesses heat- and oil-resistant properties and good low temperature properties, and the compounds are also highly resistant to deterioration by sunlight, water, and oxidation. Both forms of polymer—polyurethane and ethyl-

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Table I Compounding Formulations for the Masterbatch Technique^a

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

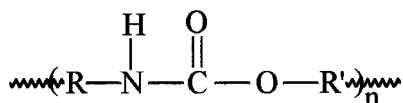
^a Curatives for AU (Phr): MBT-2, MBTS-4, ZDC-1, ZnO-1, Stearic acid-1.5, S-2, Caytur-0.5. Curatives for vamac (Phr): MDA-2, DPG-3.

ene acrylic elastomers—are polar in nature and expected to form interchain crosslink on heat treatment. Considering the above, blends were prepared to develop new polymeric material with enhanced performance properties that were explained through interchain crosslinking.

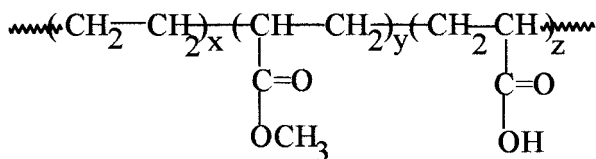
EXPERIMENTAL

Materials Used

Polyurethane: Vibrathane-5008 grade by Uniroyal Company, USA. Mooney viscosity, ML 1+4 at 100°C is 45, specific gravity is 1.15. Chemical structure:



Ethylene acrylic elastomer: vamac B-124 from du Pont, USA. Mooney viscosity, ML 1+4 at 100°C is 34, specific gravity is 1.13. Chemical structure:



Methods

Blends of polyurethane and vamac were prepared with different blend ratios in a two-roll open mixing mill at room temperature. Three different blending techniques have been employed: e.g., masterbatch technique, preblending technique, and preheating preblending technique.

In the masterbatch technique, the polyurethane elastomer was first mixed with 24 phr carbon black. Then the black-filled polyurethane and

Table II Compounding Formulations for the Preblending and Preheated Preblended Technique

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

the vamac elastomers were mixed separately with the curatives systems. Blends were then prepared throughout the entire composition range by gradual replacement of polyurethane with vamac elastomer. The compounding formulation of the masterbatch technique is given in Table I.

In the preblending technique, the two polymers, polyurethane (24 phr carbon black loaded) and vamac were first mixed in the entire composition range and allowed to equilibrate for 24 h. The amount of the curatives was adjusted with the masterbatch technique depending on the percentage of elastomers present in the blend. Here to study the effect of blending technique on the blend properties, the (80:20), (50:50), and (20:80) AU/vamac blend systems have been considered. The compounding formulation is given in Table II.

In preheated preblended technique, the preblends of AU and vamac were heated at 150°C for 15 min and then the curatives were incorporated in the blends. Here to compare the blend proper-

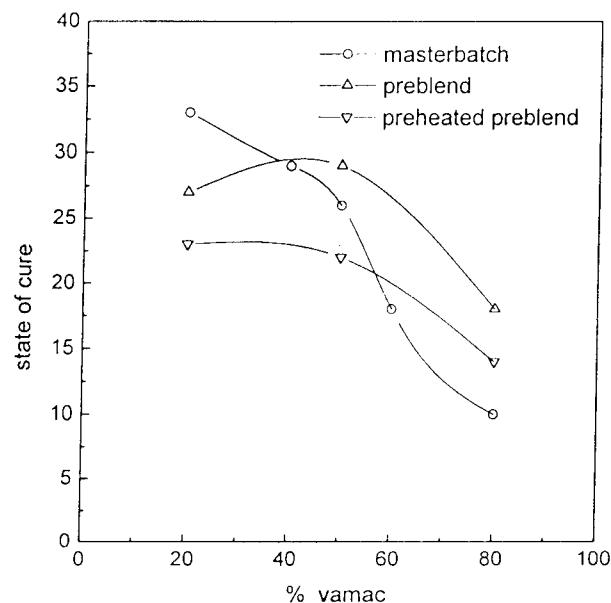
**Figure 1** State of cure vs percentage of vamac elastomer.

Table III Physical Properties of the Masterbatch Samples

Blends	Hardness (Å)	100% Modulus (N/m ² × 10 ⁻⁴)	Tensile Strength (N/m ² × 10 ⁻⁴)	Elongation at Break (%)
I	78	95.1	2177.6	520
II	70	74.5	1736.5	600
III	65	76.3	1336.3	610
IV	58	63.7	992.8	620
V	50	51.9	392.0	420

ties, the (80:20), (50:50), and (20:80) AU/vamac systems have been considered. The compounding formulation for the preheating preblending technique was same as with the preblended technique.

The processability and the continuous 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 under constant pressure (20 MPa) up to the optimum cure time. Physical properties of the blends like hardness, modulus, tensile strength, and elongation at break were measured on the cure sheets both before and after aging. Aging was performed at 120°C for 40 h in an air oven. A solvent swelling study^{14,15} was carried out to get an idea about the phase adhesion between the two elastomers phases, in acetone and toluene solvent for 48 h at room temperature following the Kraus equation:

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

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, Φ is the volume fraction of the dispersed phase in the vulcanizate, and M is the equation parameter.

To study the interchain crosslinking reaction between the two polymers, infrared spectra of the thin films of pure polymers and a (50:50) blend of the two (without any curatives) were taken using a Perkin Elmer Model 387. Phase morphology of the blends were studied with the solvent extracted samples with the help of scanning electron microscopy (SEM) (Cam Scan series auto sputter coater).

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) of the blends¹⁶

were studied through the Shimadzu Thermal Analyzer (DT-40) in air, at a heating rate of 10°C/min in the temperature range 25–600°C. To determine the glass transition temperature (T_g) and the heat of vulcanization of the blends, differential scanning calorimetry (DSC) was conducted in a Stanton Redcroft Thermal Analyzer, STA-625.

RESULTS AND DISCUSSION

Physical Properties of the AU/vamac Blends Both Before and After Aging

Masterbatch Samples

The state of cure ($\tau_{max} - \tau_{min}$) decreased with the increase in vamac content in the blend, showing a minimum value at (20:80) AU/vamac blend ratio (Fig.1). Hardness of the blends decreased with increase in vamac content in the blend. Modulus (100%) and tensile strength of the blends also showed a good agreement with the hardness. Elongation at break of the blend increased slightly with the addition of vamac in the blend up to (40:60) AU/vamac ratio and then it again decreased at (20:80) AU/vamac blend (Table III).

On aging in air at 120°C for 40 h, all the physical properties of the blend changed. Hardness of

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

Blends	Hardness (Change in Points)	100% Modulus	Tensile Strength	Elongation at Break
I	-10	-45.0	-48.0	-38.4
II	-7	-33.4	-40.0	-41.6
III	-3	-16.5	-31.0	-37.7
IV	+4	+11.2	-25.1	-31.1
V	+8	+20.2	+3.3	-40.5

Table V Physical Properties of the Preblended Samples

Blends	Hardness (Å)	100% Modulus (N/m ² × 10 ⁻⁴)	Tensile Strength (N/m ² × 10 ⁻⁴)	Elongation at Break (%)
I	64	76.0	1800.2	570
II	70	86.2	1006.0	500
III	60	70.5	670.3	520

the blend containing higher amounts of polyurethane decreased more whereas the blends containing higher amounts of vamac showed an increase in hardness on aging. Modulus and tensile strength also followed the same trend with the hardness. Elongation at break of all the blends decreased on aging (Table IV).

Preblended Samples

Rheometric study of the blends showed that the state of cure ($\tau_{\max} - \tau_{\min}$) increased slightly with the addition of vamac elastomer in the blend up to a (50:50) blend ratio and then decreased again at the (20:80) AU/vamac ratio. The state of cure of the (50:50) AU/vamac preblended sample was higher than that obtained through the masterbatch technique of same elastomer ratio (Fig.1).

The hardness of the preblends showed the reverse trend than that obtained from the masterbatch technique. Here the hardness of the blends increased with the increase in vamac content in the blend up to a (50:50) blend ratio and then again decreased at the (20:80) AU/vamac ratio. Hardness of the (80:20) AU/vamac preblended sample was lower than the (80:20) AU/vamac masterbatch sample but the (50:50) and (20:80) AU/vamac preblended sample showed higher hardness than the masterbatch sample of same elastomer ratio. The modulus (100%) also followed the same trend with the state of cure and the hardness. The tensile strength of the preblends decreased with the increase in vamac content in the blend (Table V).

The aging properties are given in Table VI. The decrease in hardness was more in the (80:20) AU/vamac blend ratio. Modulus and tensile strength decreased more in the AU-rich blend (80:20 AU/vamac), whereas the blend containing the higher amount of vamac (20:80 AU/vamac) showed an increase in properties on aging.

Effect of Heat Treatment on the Properties of the Blends

The state of cure of the preheated preblends ($\tau_{\max} - \tau_{\min}$) was found to decrease with the increase in

vamac content in the blend and was lower than those obtained from the preblending technique (Fig.1). Hardness of the preheated preblended samples decreased with increase in vamac content in the blend. Modulus (100%), tensile strength, and elongation at break also followed the same trend with the hardness. All these properties are given in Table VII.

The percent change in properties on aging are given in Table VIII. Hardness and elongation at break decreased more in the (50:50) blend ratio. Modulus and tensile strength decreased more in the (80:20) AU/vamac blend on aging.

IR Spectral Analysis

In order to study the interchain crosslinking reaction between polyurethane and vamac elastomers, IR spectra of the thin films of pure polyurethane, pure vamac, and a (50:50) blend of the two (without any curatives), heated at 150°C were taken (Fig. 2). Polyurethane showed characteristic peaks nearly at 3140 cm⁻¹ for the N—H stretching and 1690 cm⁻¹ for the amide >C=O stretching. vamac showed three characteristics peaks for the —COOH group. The acid carbonyl (>C=O) group appeared at 1714 cm⁻¹ and the acid —OH group appeared at 1573 cm⁻¹ (strong peak) and at 2685 cm⁻¹ (weak peak).^{17,18}

In the blend of the two (50:50 AU/vamac, without curatives), no peaks was observed at 3140 and at 1690 cm⁻¹, which were the characteristic peak for N—H stretching and amide carbonyl (>C=O)

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

Blends	Hardness (Change in Points)	100% Modulus	Tensile Strength	Elongation at Break
I	-6	-34.2	-33.3	-32.1
II	-4	-13.0	-21.0	-34.0
III	+2	+18.0	+5.2	-30.0

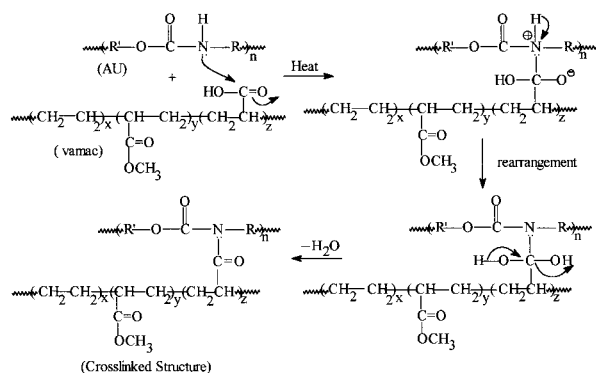
Table VII Physical Properties of the Preheated Preblended Samples

Blends	Hardness (Å)	100% Modulus (N/m ² × 10 ⁻⁴)	Tensile Strength (N/m ² × 10 ⁻⁴)	Elongation at Break (%)
I	68	93.1	1303.4	580
II	65	81.6	884.6	500
III	60	60.7	741.9	450

stretching of polyurethane. Again the peak for —OH group of vamac in the region of 1573 and 2685 cm⁻¹ were absent in the blend. These spectral changes indicated that the interchain crosslinking reaction occurred through the —N atom of polyurethane and —COOH group of vamac, and thereby forming a

substituted amide type of linkage. A new peak at 1749 cm⁻¹ in the blend for amide type of linkage also supported this. The shifting of the amide carbonyl (>C=O) peak to the higher region is due to the attachment of electron withdrawing group (—O—CO—) with the —N atom.¹⁸

Thus based on the aforesaid spectral analysis, the plausible mechanism for the crosslinking reaction of polyurethane and vamac may be written as follows:



Solvent Swelling Study of the Blends

In order to study the phase adhesion between the two elastomers phases, the solvent swelling was carried out in toluene and tetrahydrofuran solvents where vamac and polyurethane were soluble respectively. In toluene, the swelling coefficient values for all the three types of blend lie well above the additive average line (Fig. 3). The masterbatch samples showed higher swelling coefficient values than the preblended and preheated preblended samples. The Kraus plot of the blends (Fig. 3 RHS) in toluene exhibited a positive slope

for all the blends, suggesting the lack of phase adhesion in the vamac-rich blends.

The swelling coefficient values in tetrahydrofuran (Fig. 4, left-hand side) followed a sigmoidal pattern for the masterbatch samples. For the polyurethane-rich blends, the swelling coefficient values lie below the additive average line whereas after 40% vamac, the swelling coefficient values are lying above the additive average line. However, for the preblended and preheated preblended samples, the swelling coefficient values lie below the additive average line. The Kraus plot (Fig. 4, right-hand side) of the blends in tetrahydrofuran exhibited a negative slope for the preblended and preheated preblended samples in the AU-rich blends (60% AU), suggesting the presence of phase adhesion, the extent of which was more in the preheated preblended samples.

Thermal Analysis

The low temperature DSC of the (50:50) AU/vamac blends prepared through the three different blending techniques have been carried out to study the effect of blending technique on the compatibility of the blends. In all the three cases two T_g were observed. The masterbatch sample showed the T_g values at -36 and at -18°C . The T_g values of the preblended sample, having the same elastomer ratio, appeared at -36 and at -13°C . For the preheated preblended sample, the T_g values appeared

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

Blends	Hardness (Change in Points)	100% Modulus	Tensile Strength	Elongation at Break
I	-3	-38.0	-35.0	-20.7
II	-5	-18.0	-25.1	-23.0
III	+2	+5.1	-11.4	-21.1

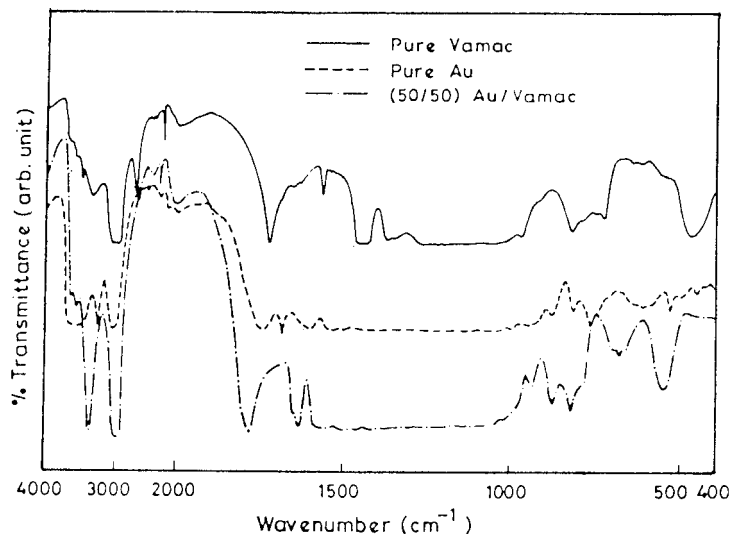


Figure 2 IR spectral analysis of pure AU, pure vamac, and (50:50) AU/vamac blend of the two without curatives.

relatively at the higher temperature, -30 and -10°C . The T_g value may be shifted to the higher temperature due to the crosslinking of the two elastomers phases due to the addition of curatives. In the case of the preblended sample, some sort of extra crosslinking was there in the blend before addition of curatives via the functional groups. The effect of the heat treatment to the preblend, before addition of curatives, again enhanced the crosslinking reaction and thereby shifted the T_g values to the higher temperature.

High temperature TGA/DTG of the (50:50) AU/vamac blends prepared through the three different blending techniques have been studied to find the thermal stability of the blends. In each case, the degradation occurred in three steps. For the (50:50) AU/vamac blend prepared by the masterbatch technique, the degradation started at 239 and continued up to 354°C , where the second degradation started. The third degradation occurred at 450°C and 50% of the sample degraded at 445°C (Fig. 5).

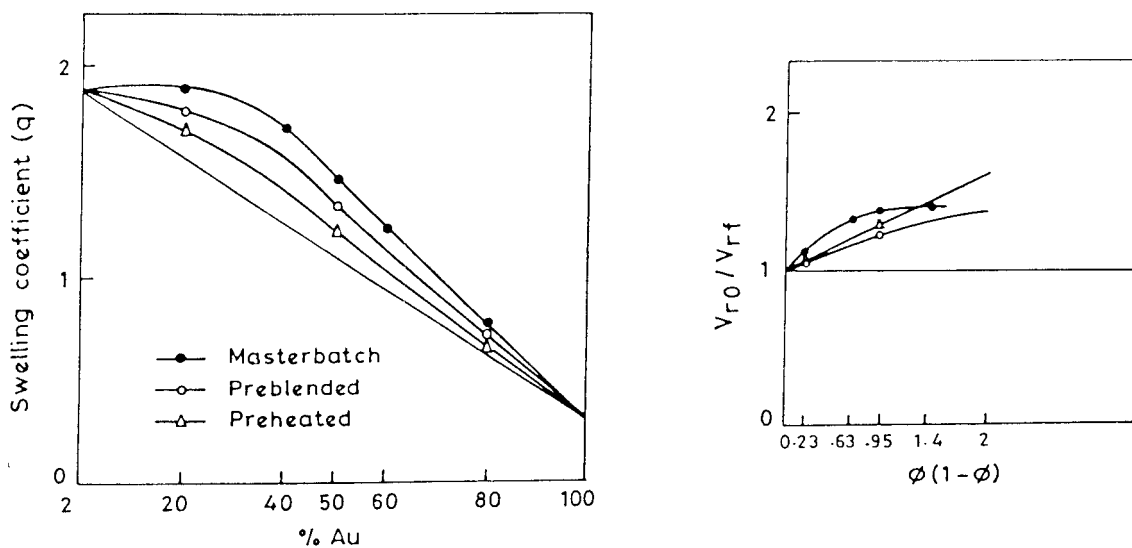


Figure 3 Plot of swelling coefficient against AU and (V_{r0}/V_{rf}) against $\Phi/(1-\Psi)$ for the AU/vamac system in toluene.

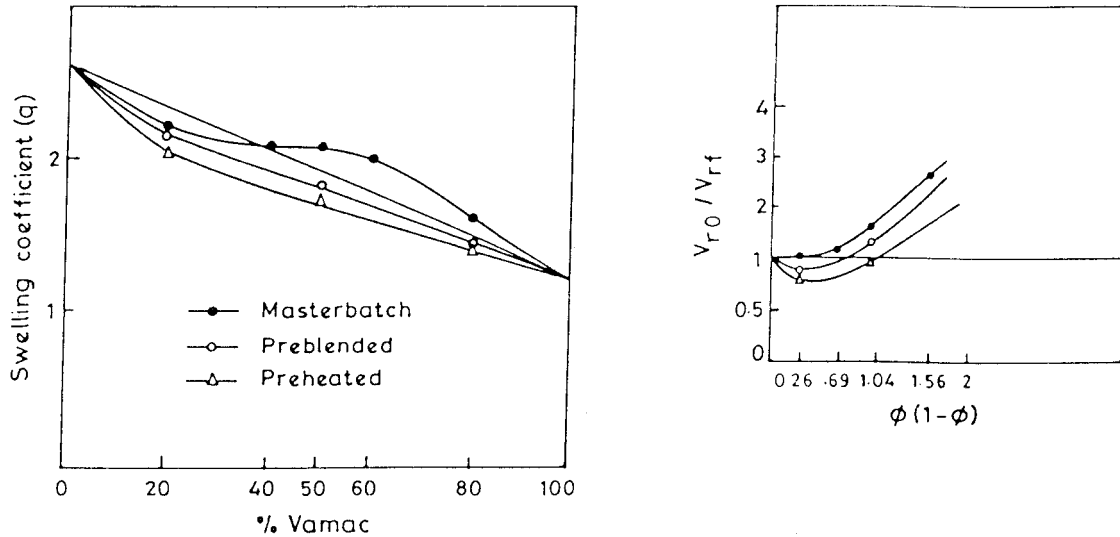


Figure 4 Plot of swelling coefficient against vamac and (V_{r0}/V_{rf}) against $\Phi/(1 - \Phi)$ for the AU/vamac system in tetrahydrofuran.

When the blend with the same elastomer ratio was prepared by the preblending technique, the degradation occurred at a relatively higher temperature, 246°C. The second degradation started at 354°C and continued up to 454°C, where the third degradation occurred. Fifty percent of the sample degraded at 436°C (Fig. 6). In the case of the blend prepared through the preheating preblending technique, with the same elastomer ratio, the initial degradation started at 244°C. The second degradation started at 353 and continued up to 456°C, where the third degradation occurred. Fifty percent of the sample degraded at 437°C (Fig. 7).

Heat of vulcanization of the AU/vamac blends, without curatives, have been studied. Three different cases have been considered. Table IX represents the onset temperature and the heat of interchain crosslinking reaction with the blending ratio. The heat of reaction varied with the blend ratio, associated with the exothermic peak in each case. The onset temperature and the exothermic heat of reaction were maximum for the (80:20) AU/vamac blend ratio. The exothermic heat of reaction revealed that some reaction occurred between the two elastomers phases, the extent of which depends on the blend ratio.

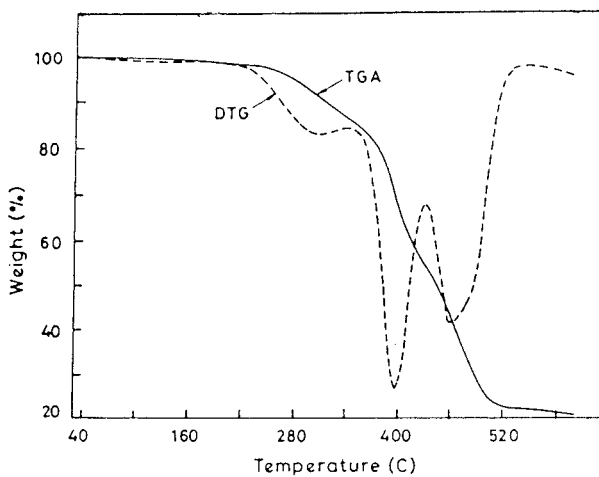


Figure 5 High temperature DTG/TGA plot of the 50:50 AU/vamac masterbatch sample.

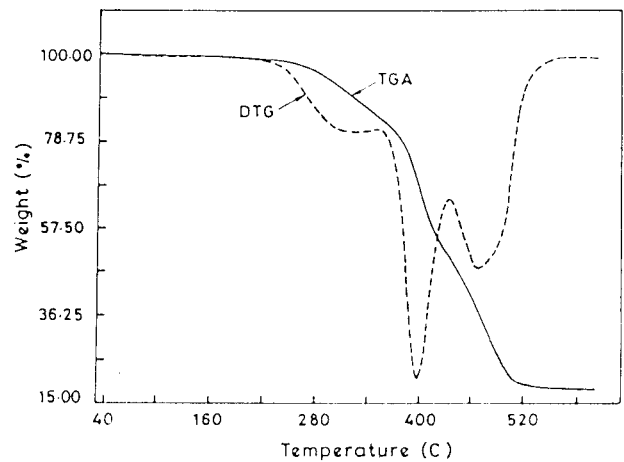


Figure 6 High temperature DTG/TGA plot of the (50:50) AU/vamac preblended sample.

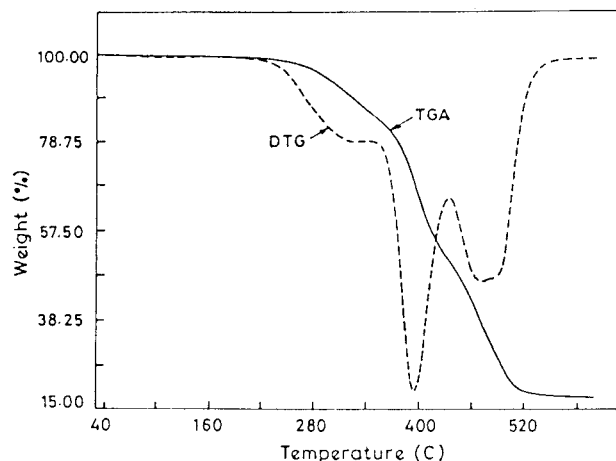


Figure 7 High temperature DTG/TGA plot of the (50:50) AU/vamac preheated preblended sample.

Phase Morphology Study

Phase morphology of the blends of polyurethane and vamac has been studied using a scanning electron microscope. The (50:50) AU/vamac blends prepared through three different blending techniques have been considered. The blends were first extracted with tetrahydrofuran solvent to remove the polyurethane phase and then the SEM photographs were taken after suitable gold sputtering. From the SEM photograph of the masterbatch sample, it was clear that the extraction of the polyurethane phase was easier. It was indicated by the larger voids in the SEM photograph (Fig. 8). 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). Again, the extraction of the polyurethane phase was limited to a negligible extent when the preblend was given heat treatment before addition of curatives

Table IX Blend Ratio, Onset Temperature and Exothermic Heat of Vulcanization of the (AU/vamac) Blends Without Curatives

S1. No.	Blend Ratio (AU/vamac)	Onset Temperature (°C)	Exothermic Heat of Vulcanization (J/gm)
1	80 : 20	186	49
2	50 : 50	95	20
3	20 : 80	72	15

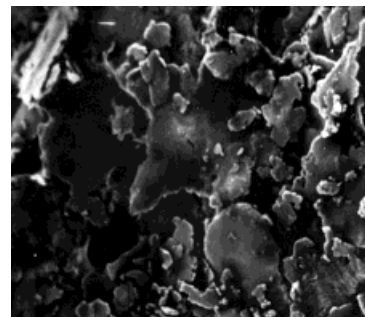


Figure 8 SEM photograph (800 \times) of the THF-extracted sample of the (50:50) AU/vamac blend prepared by the masterbatch technique.

(Fig.10). These differences in the extractability of the single phase by solvent clearly suggested the 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 the vamac elastomer. The properties of the blends were dictated by the blending technique. IR spectral analysis of the thin film of (50:50) AU/vamac blend without any curatives revealed that interchain crosslinking occurred between the two elastomers phases on heat treatment. Thermal stability of the blends was increased for the preblended and preheated preblended samples. Blend prepared by the masterbatch technique degraded at a lower temperature compared to the blends made via the preblending and preheated preblended technique. The extraction of the single phase by solvent was

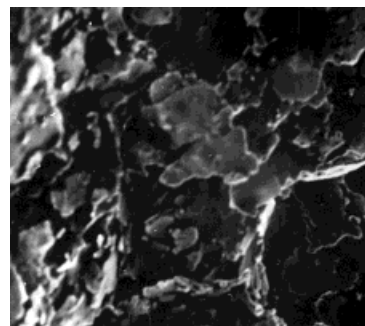


Figure 9 SEM photograph (800 \times) of the THF-extracted sample of the (50:50) AU/vamac blend prepared by the preblending technique.

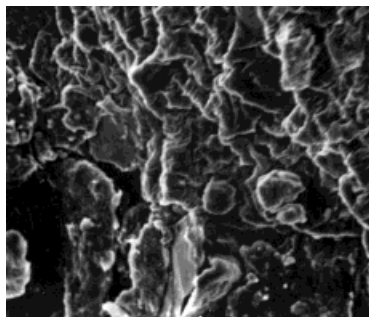


Figure 10 SEM photograph (800 \times) of the THF-extracted sample of the (50:50) AU/ vamac blend prepared by the preheated preblended technique.

also restricted for the preblended and preheated preblended samples, probably due to the inter-chain crosslinking, the extent of which was more in the preheated preblended sample.

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