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EFFECT OF PROCESSABILITY ON THE THERMAL STABILITY OF THE BLENDS BASED ON POLYURETHANE. Part II

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Abstract

Thermal stability of the blend of polyurethane with three other elastomers, having the reactive functional group, has been studied. Three different blending techniques have been employed to study the effect of processability on the thermal stability of the blend. IR spectral analysis revealed that interchain crosslinking takes place between the two elastomer phases. Thermal stability of the blend increased when preblending and preheating preblending techniques were applied, probably due to the formation of the interchain crosslink between the elastomer phases.

Keywords: caytur, interchain crosslinking, masterbatch, polyurethane, preblending, preblending–preheating , vulcanization

Introduction

Polymer blends have become an important area of research because of their wise use in the wide spectrum of industry. Blending has been the principal method for widening the range of properties of materials [1–4]. The mixing operation is an important step in the blend preparation and it is well known that certain properties strongly depend on it [5–10]. When two polymers containing the reactive functional groups are blended before addition of curatives, the blend is likely to have better performance properties derived from the interchain crosslinking reaction via the polar functional groups. Das *et al.* have already studied a series of blend systems where interchain crosslinking occur and showed how it affects the properties of the blends [11–20]. De and co-workers have reported that rubbers having appropriate functional groups when blended interact with each other and thus crosslink at high temperature in the absence of any curatives [21–29].

This paper relates to our investigation of thermal stability of the blends of polyurethane (AU) with other special elastomers, such as, ethylene acrylic elastomer (Vamac), polyacrylic elastomer (AR-31) and polychlorobutyl elastomers (CIIR), as determined by thermogravimetric analysis (TG) [30]. Polyurethane forms interchain crosslink bond with CSM [11], EPH [12] and CR [13] elastomers at high-temperature

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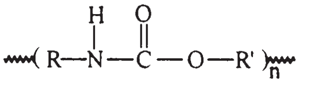
without any curatives. Degradation is normally regarded as a kinetic process. It is, however, accompanied by the chemical bond dissociation [31] and there is a definite correlation between the chemical structure of a polymer and its degradation temperature [32–33]. Considering this, blends of polyurethane were prepared to study the effect of interchain crosslink on the thermal stability of blends.

Experimental

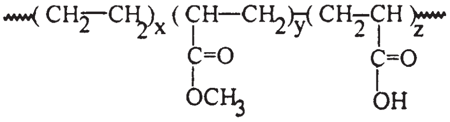
Materials used

Polyurethane: Vibrathane-5008 from Uniroyal Co. USA, Mooney viscosity ML 1+4 at 100°C is 45, specific gravity 1.15, chemical structure:



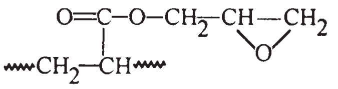
$$\sim(R-\overset{\overset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-O-R')_n\sim$$

Ethylene acrylic elastomer: Vamac B-124 from DuPont, USA. Mooney viscosity ML1+4 at 100°C is 34, specific gravity is 1.13, chemical structure:

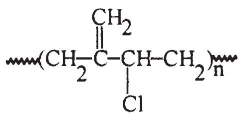


$$\sim(CH_2-CH_2)_x(\underset{\underset{\underset{OCH_3}{|}}{C=O}}{\underset{|}{CH}}-CH_2)_y(CH_2-\underset{\underset{\underset{OH}{|}}{C=O}}{\underset{|}{CH}})_z\sim$$

Polyacrylic elastomer: AR-31, from Nippon Zeon, Japan. Mooney viscosity ML1+4 at 100°C is 40, specific gravity is 1.10, chemical structure:



Chlorobutyl elastomer (CIIR): from Exxon Chemical Ltd. USA, Grade 1066, chemical structure:



$$\sim(CH_2-\overset{\overset{CH_2}{\|}}{C}-\underset{\underset{Cl}{|}}{CH}-CH_2)_n\sim$$

To study the effect of interchain crosslinking to the thermal stability of the blends, the (50:50) blends of (AU/Vamac), (AU/AR-31) and (AU/CIIR) were prepared in an internal mixer at room temperature (25°C) by three different blending technique, e.g. masterbatch technique, preblending technique and preheating preblending technique. The compounding formulations for the AU/Vamac, AU/AR-31 and AU/CIIR systems are:

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

Vamac (Phr): MDA-2, DPG-3.
AR-31 (Phr): TTFe-0.4, ZDC-0.9.
CIIR (Phr): MBTS-1.5, ZDC-1.5, ZnO-2, MgO-0.5, Stearic acid-1, S-2.

Masterbatch technique: In this technique, the individual elastomers were first mixed with the curatives and allowed to equilibrate for 24 h. The mixture was then blended at (50:50) ratio.

Preblending technique: In the preblending technique, the two elastomers were first blended at (50:50) ratio and allowed the blend to equilibrate for 24 h. The same amount of curatives as was in mater batch technique, was then incorporated in the blend.

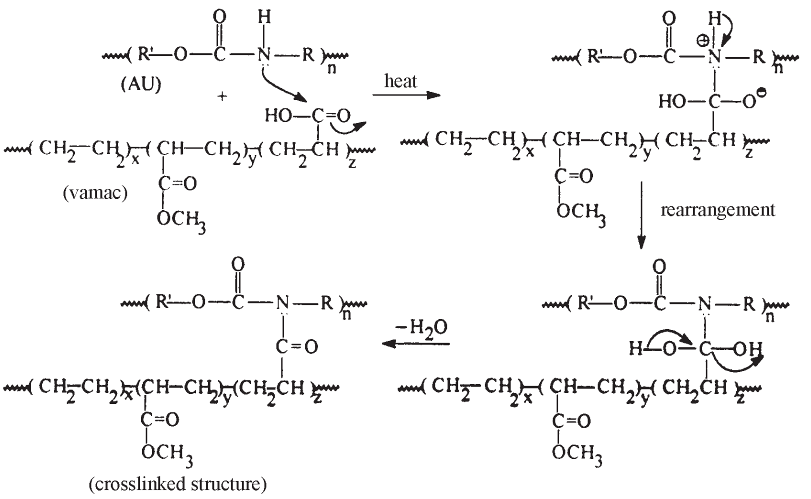
Preheating preblending technique: For the preheating preblending technique, the preblend was subjected to heat treatment at 150°C for 15 min and then the curatives were incorporated in the blend after cooling. The amount of curative was same as in the preblending technique.

The continuous cure characteristics and the processibility 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 (2800 psi) up to their optimum cure time. To study the interchain crosslinking reaction between the two elastomers, IR spectra of the pure elastomers and a (50/50) blend of the two were taken by using Perkin Elmer spectrophotomer, Model-387. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TG) of the blends has been studied through the Shimadzu Thermal Analyzer (DT-40) in air at a heating rate of 10°C min^{-1}, in the temperature range 25 to 600°C. To determine the glass transition temperature (T_g) of the blends, DSC was conducted in a Stanton Redcroft thermal analyzer, STA-625.

Results and discussion

IR spectral analysis of the (50:50) blends

The IR spectra of the thin films of pure elastomers and a (50:50) blend of the two (without any curatives), heated at 150°C are shown in Figs 1 and 2, respectively. Polyurethane showed characteristic peaks at 3140 cm^{-1} for the N–H stretching and 1690 cm^{-1} for the amide >C=O stretching. Vamac showed three characteristic 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) [34, 35]. In the (AU/Vamac) blend no peak was observed at 3140 and at 1690 cm^{-1} for N–H stretching and amide carbonyl (>C=O) 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 an imide type of linkage. A new peak at 1749 cm^{-1} in the blend for imide type of linkage also supported this. Thus the mechanism for the crosslinking reaction of polyurethane and Vamac may be written as follow.



Polyacrylic elastomer showed the peak for the ester carbonyl stretching and epoxy group at 1726 and at 1253 cm^{-1} respectively. In the blend no characteristic peaks were observed in the region of 3140, 1726 and 1253 cm^{-1}, for the –N–H stretching of

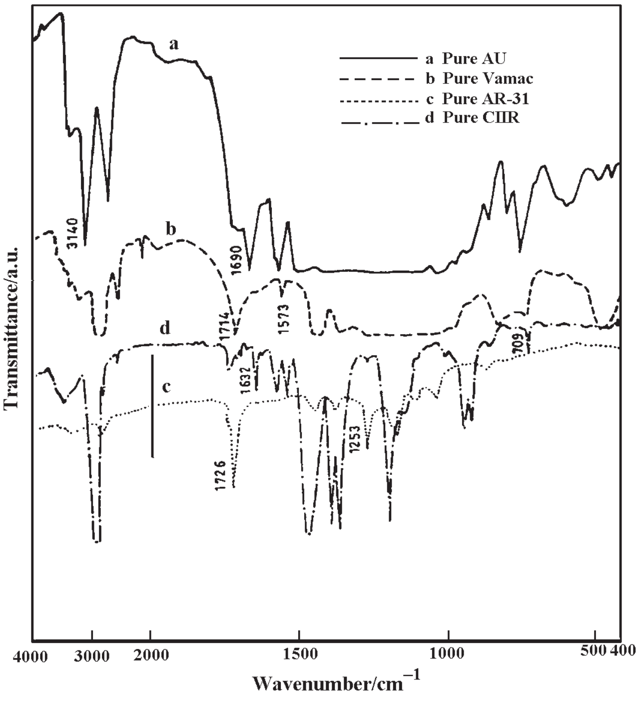
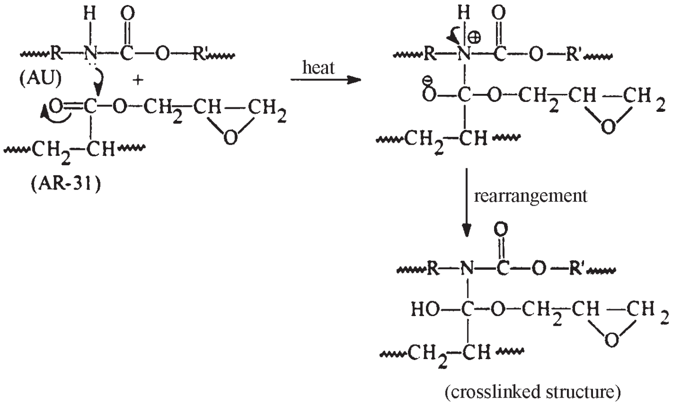
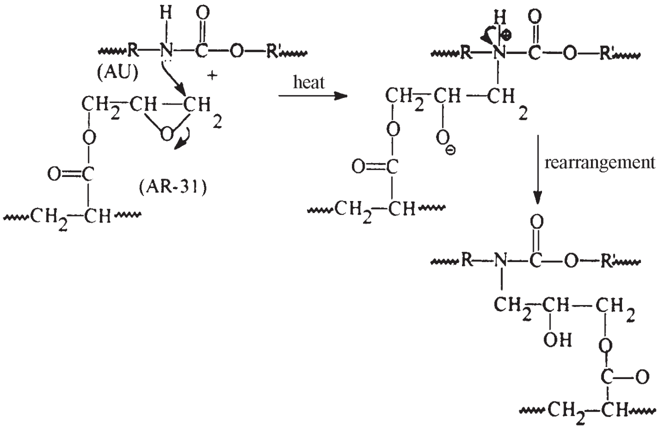


Fig. 1 IR Spectral analysis of the thin films of pure elastomers

pure AU and ester carbonyl (>C=O) and epoxy type of linkage in pure AR-31. The absence of the peaks at 1726 and at 1253 cm^{-1} in the blend suggested the involvement of ester ($-CO_2R$) 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 hydroxyl (–OH) group, supported this. The shifting of the amide carbonyl (>C=O) peak of pure AU from 1690 to 1749 cm^{-1} also provided a supporting evidence for the crosslinking reaction. Thus a plausible mechanic pathway for the interchain crosslinking reaction may be suggested as

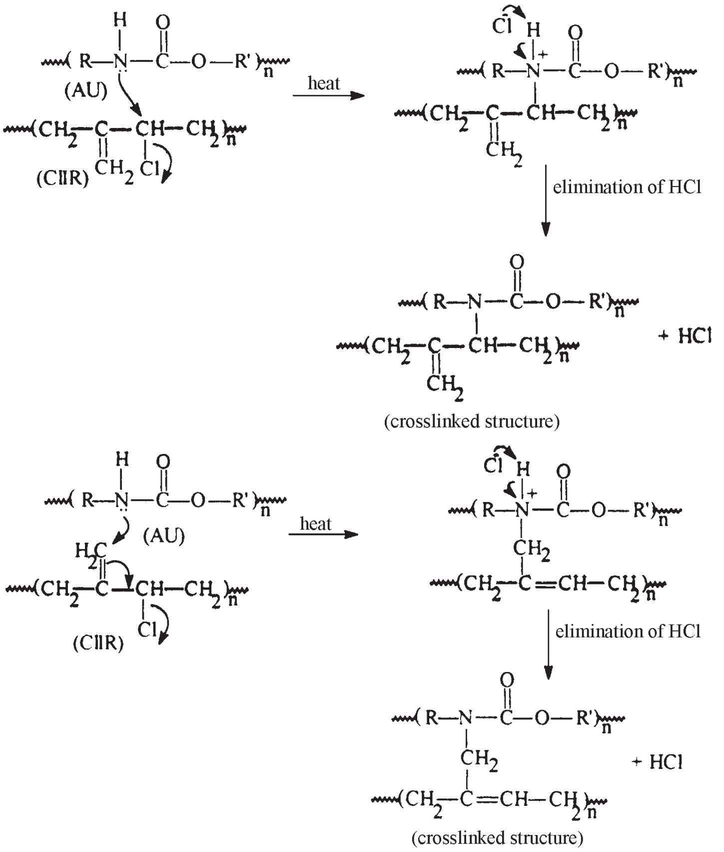


An alternative mechanic pathway for the crosslinking reaction that involves the epoxy group of AR-31 and thereby forming the –OH group can also be taken into consideration as below.



Polychlorobutyl elastomer exhibited characteristic peaks for the >C=C< and C–Cl group at 1632 and 709 cm^{-1}, respectively. In the blend no peak was observed at

3140 and 709 $\mathrm{cm^{-1}}$, which were the characteristic peaks of the N–H group of pure polyurethane and C–Cl of pure polychlorobutyl elastomers, confirming the crosslinking reaction via N–H group of polyurethane and C–Cl of the polychlorobutyl elastomer. Thus the mechanic pathway for the crosslinking reaction may be proposed as,



Thermal analysis of the AU/Vamac blends

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 –36.2 and at –17.6°C. The T_g values of the preblended sample, having the same elastomer ratio, appeared at –36 and at –13.2°C. For the preheated preblended sample, the T_g value appeared relatively at higher temperature, –30.3 and –9.6°C. The T_g value may be shifted to the higher temperature due to the crosslinking of the two elastomers phases by the addition of curatives. In 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 cross-linking reaction and thereby shifted the T_g values to the higher temperature.

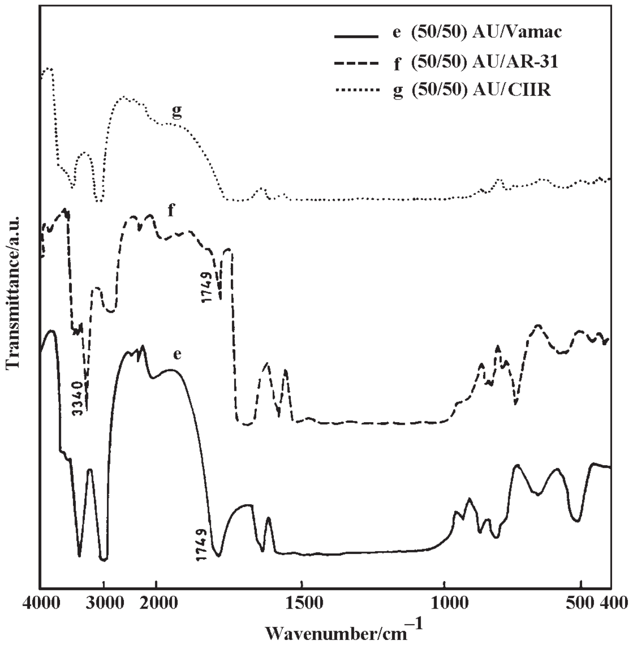


Fig. 2 IR Spectral analysis of the thin films of (50:50) blends of polyurethane and other elastomers without curatives

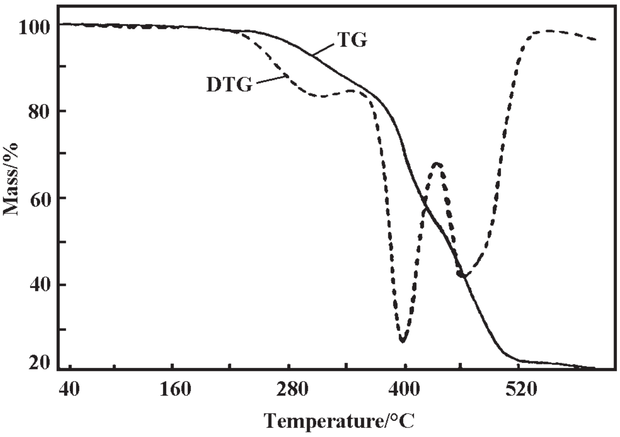


Fig. 3 DTG/TG plot of the (50:50) AU/Vamac masterbatch sample

Table 1 Degradation temperatures of the (50:50) AU/Vamac blends

Blends	T_1/	T_2/	T_3/	T_{50}/
	°C			
Masterbatch	239	354	450	445
Preblend	245	354	454	435
Preheated preblend	243	353	455	437

High temperature TG/DTG of the (50:50) AU/Vamac 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. A typical TG plot for the (50:50) AU/Vamac masterbatch sample is shown in Fig. 3. The degradation temperatures of the three types of blends were calculated from the TG plots. The temperatures for the initial degradation (T_1), second degradation (T_2), third degradation (T_3) and 50% degradation (T_{50}) of blend were calculated and given in Table 1. From the results it was found that the initial degradation temperature increased when the blend was prepared by the preblending and preheating preblending technique, have the same elastomer ratio.

Table 2 Onset temperature, exothermic heat of reaction of the blends

Blends	Blend ratio	Onset temperature/°C	Exothermic heat of vulcanization/J g^{-1}
	80:20	186	49
AU/Vamac	50:50	95	20
	20:80	72	14
	80:20	140	26
AU/AR-31	50:50	118	40
	20:80	92	31
	80:20	117	220
AU/CIIR	50:50	98	94
	20:80	126	150

Heat of vulcanisation of the AU/Vamac blends, without curatives, have been studied (Table 2). 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 elastomer phases, the extent of which depends on the blend ratio.

Thermal analysis of the AU/AR-31 blends

The (50:50) 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 preblending and preheating preblending technique were adapted. The (50:50) AU/AR-31 blend prepared by the preblending technique showed the T_g at –9.0°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 the addition of curatives as discussed in IR section.

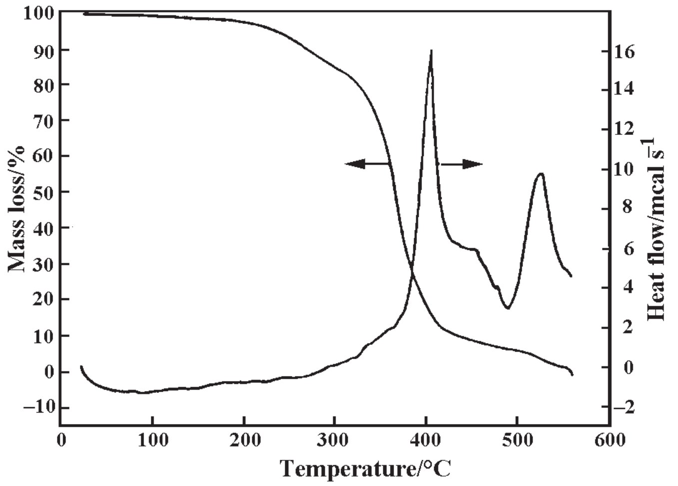


Fig. 4 DSC/TG plot of the (50:50) AU/AR-31 masterbatch sample

High temperature DSC/TG study showed that the degradation occurred mainly in two steps for all the three types of blends. However, a third step is also occurred after almost 80% degradation, which is technically less important. A typical DSC/TG plot of the AU/AR-31 masterbatch sample is shown in Fig. 4. The degradation temperatures were calculated and given in Table 3. From the thermal analysis it was found that masterbatch sample degraded at lower temperature. Delayed degradation occurred in case of the preblended and preheated preblended samples. However, 90% degradation (T_{90}) of the AU/AR-31 masterbatch sample occurred at higher temperature than that of preblended and preheated preblended samples.

Table 3 Degradation temperatures of the (50:50) AU/AR-31 blends

Blends	T_1/	T_2/	T_{50}/	T_{90}/
	°C			
Masterbatch	237	353	378	510
Preblend	241	362	380	443
Preheated preblend	248	355	389	476

The DSC study revealed that the heat evolved for the oxidative degradation was maximum in case of the preblended sample (1997.5 J g^{-1}) and minimum for the preheated preblended sample (1465.8 J g^{-1}). The masterbatch sample evolved 1646.4 J g^{-1} of heat during its degradation. Thus the ease of degradation was the highest for the preblended sample and lowest for the preheated preblended sample. However, the blend prepared by the masterbatch technique, was thermally less stable than preheated preblended sample but higher stability towards thermal degradation than the preblended sample.

The heat of vulcanisation and onset temperature of the AU/AR-31 blends without any curatives were studied (Table 2). The onset temperature and heat of vulcanization were maximum for the (80:20) and (50:50) AU/AR-31 blend ratio, respectively. This study revealed that crosslinking reaction occurred between the two elastomer phases the extent of which depends on blending ratio.

Thermal analysis of the AU/CIIR blends

In all the cases, the degradation mainly occurred in two steps, associated with the exothermic peak in the DSC curve. Although a third step was also found in the TG plot for each blend, after 80% degradation, which is technically less important. A typical DSC/TG plot of the (50:50) AU/CIIR masterbatch sample is shown in Fig. 5. The degradation temperatures of the three types of blends are shown in Table 4. The results showed that the masterbatch sample degraded at a lower temperature. The degradation temperatures were delayed for the blends prepared by the preblending and preheating preblending technique.

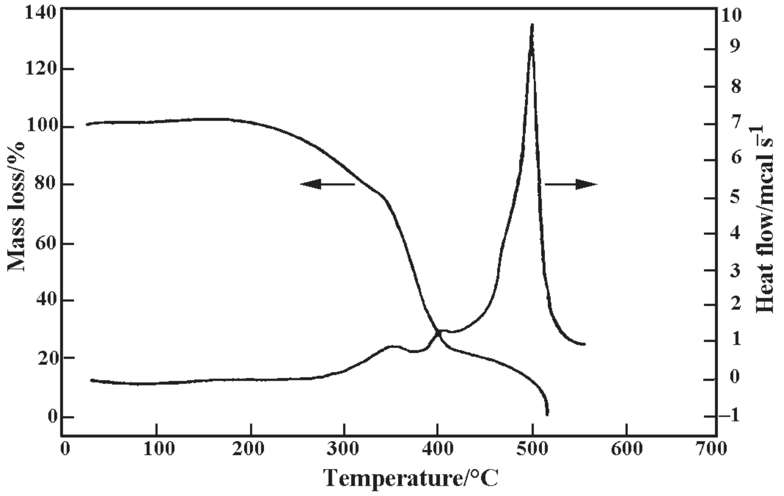


Fig. 5 DSC/TG plot of the (50:50) AU/CIIR masterbatch sample

From the DSC plot it was observed that the heat evolved for the oxidative degradation of the blends was maximum in case of the masterbatch sample (1395.6 J g^{-1}) and minimum for the preblended sample (1056.7 J g^{-1}). The preheated sample evolved 1326.4 J g^{-1} of heat during its degradation. The exothermic heat of degradation revealed that the ease of degradation was the highest for the masterbatch sample and the lowest for the preblended sample. However, the blend prepared by the preheated preblended technique, was thermally less stable than the preblended sample but higher stability towards thermal degradation than the masterbatch sample.

Table 4 Degradation temperatures of the (50:50) AU/CIIR blends

Blends	T_1/	T_2/	T_{50}/	T_{90}/
	°C			
Masterbatch	229	326	352	426
Preblend	233	330	363	474
Preheated preblend	241	336	356	465

The heat of vulcanization and onset temperature of the AU/CIIR blends without any curatives are shown in Table 2. Three different blend ratios have been considered. The onset temperature and heat of vulcanisation were maximum for the (20:80) and (80:20) AU/CIIR blend ratio, respectively. This study revealed that crosslinking reaction occurred between the two elastomer phases, the extent of which depends on blending ratio.

Conclusions

The degradation temperature of the blends largely depends on the blending technique. Blend prepared through the different blending technique, with same elastomer ratio, differs towards the thermal stability. Blend prepared by the masterbatch technique degrades at a lower temperature compared to those of the preblended and preheated preblended one, with the same elastomer ratio. This may be due to the formation of the interchain crosslink bonds in the blend of the two elastomers having reactive functional groups as a results of blending before addition of curatives. The extent of cross-linking is again increased when the preblended sample is subjected to heat treatment before the curative addition. This interchain crosslinking enhances the thermal stability and the degradation temperature of the preblended and preheated preblended samples.

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