Studies on Thermal Degradation Behaviour of EVA/LDPE Blend

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ABSTRACT: Degradation of ethylene vinyl acetate copolymer (EVA; 28% VA content), low density polyethylene (LDPE) and their blends has been studied through thermogravimetric analysis (TGA/DTG). Pure EVA and its blends show a two stage decomposition, where the first stage is ascribed to the acetic acid elimination, i.e., the weight loss is proportional to the amount of acetate group present in the system. The second stage of decomposition is due to main chain scission when blends exhibit better thermal stability compared to pure polymers. The activation energy (E_a) of second stage decomposition is calculated according to Freeman and Carroll's method. The maximum E_a is observed for pure EVA. The experimental E_a values of the blends are much greater than the theoretically calculated values based on the law of additivity. Among different blends maximum thermal stability is observed for the 50:50 EVA/LDPE system. Infrared spectrophotometry has been used to investigate about the possible reason behind the higher thermal stability of the blends compared to pure components. The effect of crosslinking and two different atmospheres, namely nitrogen and air, on thermal degradation have also been studied.

KEY WORDS: blend, TGA, activation energy, IR spectroscopy, crosslinking, atmosphere.

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0095–2443/94/02 0168-15 $06.00/0

INTRODUCTION

ETHYLENE VINYL ACETATE copolymer (EVA) undergoes thermal decomposition through elimination of acetic acid. Extensive work has been reported on the thermal degradation of EVA [1–6]. McNeill et al. [1] found that deacetylation starts at bout 290°C for EVA containing 12–33% VA. Razuvaev et al. [2] reported a considerable deacetylation rate at 260°C under isothermal conditions for EVA containing 33% vinyl acetate. The process of deacetylation may be catalyzed by some acidic materials like HCl and to some extent by evolved acetic acid, but inhibitors of radical reactions cannot influence the deacetylation rate. A literature review revealed that the degradation of EVA took place through a crosslinking mechanism [3]. Detailed reports can be found concerning decomposition products and the possibility of molecular enlargements during degradation of EVA [4–6]. No acetate containing fragments are produced during main chain scission of EVA. The lowest temperature at which deacetylation could be traced in EVA is 150°C. For isothermal decomposition at 333°C the process of deacetylation is complete within 30 minutes. The deacetylation rate increases with an increase in temperature and VA content.

The degradation of LDPE takes place according to a random chain scission mechanism [5,7–10]. Holmstrom and Sorvik [9] reported that molecular enlargement reactions also take place simultaneously during PE degradation.

Thermal degradation behaviour of EVA/LDPE blends in a N_2 atmosphere has been reported in the present study. The effects of curing and different atmospheres on thermal decomposition have also been studied. These two polymers have a high degree of misciblity when blended in a molten condition. The detailed mechanical, dynamic mechanical, electrical and morphology of blends of these two polymers have already been reported [11]. These blend systems may find application as cable insulants. Hence, this study has some practical significance.

EXPERIMENTAL

Materials Used

The materials used for the experiments and their specifications are given in Table 1.

Preparation of the Blends

Formulations of the blends are given in Table 2. The blends are designated as P_0, P_{30}, P_{50}, P_{70} and P_{100}, where the subscripts denote the

weight percent of LDPE in the blend. Blending was carried out in a Brabender Plasticorder PLE-330 using a cam type rotor. Temperature of mixing was set at 130°C with rotor speed of 60 r.p.m. The details of blending have been described elsewhere [12].

IR Spectrophotometric Studies

Pure EVA and a 50:50 EVA/LDPE blend were exposed to a temperature of 370°C for 15 minutes in a nitrogen atmosphere. Subsequently, the samples were taken from the oven and subjected to infrared spectrophotometry in a Perkin-Elmer-843 IR machine. The scan was taken in the range 1600–1900 cm^{-1}. EVA and the 50:50 EVA/LDPE blend processed at 170°C were also subjected to IR analysis. The spectral resolution was kept at 2.40 cm^{-1} and the scan was taken at room temperature.

Thermogravimetric Analysis

Thermogravimetric analysis (TGA/DTG) of different blends and pure components were carried out using a DuPont 951 Thermogravimetric Analyser in nitrogen atmosphere and in air at a heating rate of 20°C min^{-1}. About 10 mg of sample were used for each experiment.

RESULTS AND DISCUSSIONS

Thermal Decomposition in Nitrogen

Thermal decomposition characteristics of different uncured blends and pure polymers in nitrogen atmosphere are presented in TGA and DTG plots (Figures 1 and 2). Pure EVA and its blends exhibit two stage decomposition whereas a single stage decomposition is observed for pure LDPE. The first stage decomposition in EVA containing compositions is due to deacetylation of the pendant acetate groups of EVA. The

Table 1. Materials used in the investigation.

	Trade Name	Characteristics	Producer
EVA copolymer	Pilene 2806	28% VA content MFI = 6g/10 min. d = 0.95g/c.c.	PIL, India
LDPE	Indothene 20CA002	MFI = 0.2g/10 min. d = 0.92g/c.c.	IPCL, India
Dicumyl Peroxide	DCP	98% pure	Akzo chemi, Holland

Table 2. Formulation of the blends.

	P_0	P_{30}	P_{50}	P_{70}	P_{100}	P_0 (c)	P_{30} (c)	P_{50} (c)	P_{70} (c)	P_{100} (c)
LDPE (gm)	0	18	30	42	60	0	18	30	42	60
EVA (gm)	60	42	30	18	0	60	42	30	18	0
DCP (gm)	—	—	—	—	—	1	1	1	1	1

second stage decomposition is due to thermal scission of the backbone methylenic chain. Three characteristic temperatures can be identified from TGA and DTG plots: T_i–temperature at which decomposition initiates; T_{max}–temperature corresponding to the maximum rate of decomposition (weight loss/time), i.e., the peak temperature in DTG plot; and T_{50}–where 50% of the initial weight has been lost.

These characteristic temperatures for first and second stage decomposition have been presented in Table 3. It has been found that the initial decomposition temperature, T_i, of first stage (where $\approx 2\%$ decomposition occurs) increases with LDPE concentration in the blend up to 50

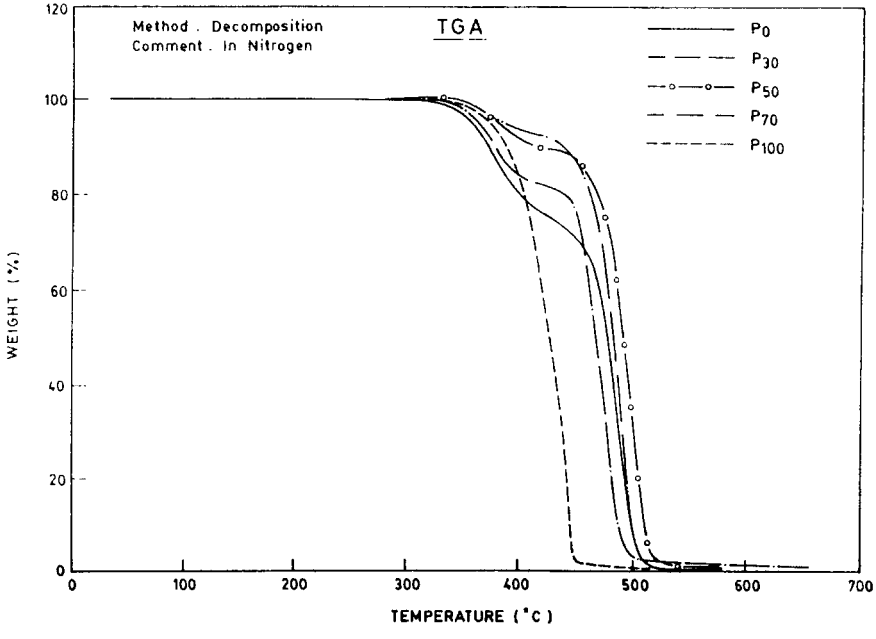


FIGURE 1. TGA curves of uncured compositions in nitrogen.

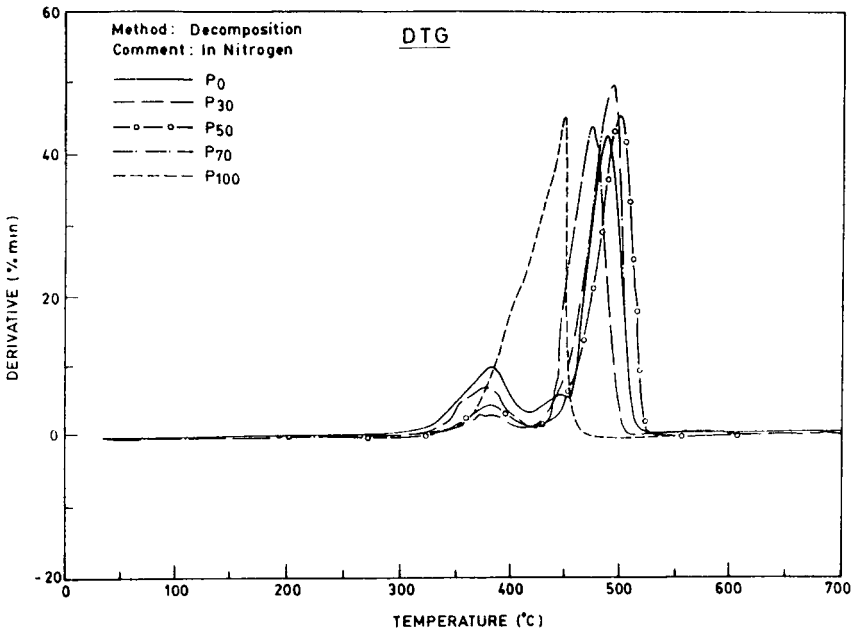


FIGURE 2. DTG curves of uncured compositions in nitrogen.

wt.% and beyond that remains constant. There is only marginal variation of T_{max} with composition during deacetylation process. As expected, the weight loss is directly proportional to vinyl acetate content of the blend composition.

The onset temperature for second stage decomposition, i.e., the breakdown of main backbone chain, is found to increase with EVA concentration in the blend up to 50 wt.%. However, some drop in onset temperature is observed for the blend containing 70 wt.% EVA. T_{max} for this

Table 3. Thermal decomposition of uncured samples in nitrogen atmosphere.

	1st Stage		2nd Stage		
	T_i (C)	T_{max} (C)	T_i (C)	T_{max} (C)	T_{50} (C)
P_0	346	380	456	489	476
P_{30}	350	376	436	474	466
P_{50}	366	380	455	502	493
P_{70}	366	376	438	493	483
P_{100}	—	—	360	446	426

stage is found to increase with EVA concentration and attains maximum value at 50 wt.% EVA. T_{50}–the temperature corresponding to 50% wt. loss exhibits a similar trend as that of T_{max} for second stage of decomposition.

Activation Energy and Order of the Second Stage Decomposition

Activation energy requirement for the degradation of the main chain backbone can be determined from TGA curves by Freeman and Carroll's method [13].

The Freeman and Carroll method uses the expression:

$$\Delta \log \frac{dw}{dt} = n\Delta \log Wr - \left(\frac{E}{2.3R}\right) \cdot \Delta\left(\frac{1}{T}\right) \tag{1}$$

where

dw/dt = rate of decomposition
n = order of reaction
R = universal gas constant
E = activation energy of the process
T = absolute temperature
Wr = proportional to the amount of reactant remaining

Dividing Equation (1) by $\Delta \log Wr$

$$\left(\Delta \log \frac{dw}{dt}\right) \Big/ \Delta \log Wr = n - \left(\frac{E}{2.3}\right) \Delta\left(\frac{1}{T}\right) \Big/ \Delta \log Wr \tag{2}$$

Thus, a plot of the left hand side of Equation (2) versus $[\Delta(1/T)]/(\Delta \log Wr)$ gives the values of n and E.

The order of the reactions are found to be unity and the activation energies for the degradation of different compositions have been evaluated from the slope of the curves. The order and activation energy of different compositions are shown in the Table 4. It is seen that the activation energy (E_a) of pure EVA (P_0) is maximum whereas it is minimum for pure polyethylene (P_{100}). The activation energy of different blends lies in between the activation energies of pure components. Among the blends, P_{50} exhibits a higher activation energy than either P_{30} or P_{70}. This shows that the thermal stability is highest in P_{50} where EVA and LDPE are in equal proportion by weight. This may be explained as follows.

Table 4. Order of reaction and the activation energy of different blend compositions of second stage decomposition in nitrogen atmosphere.

Composition	Order of Reaction	Energy of Activation (KJ/mole)
P_0	1.00	302
P_{30}	1.00	274
P_{50}	1.00	298
P_{70}	1.00	275
P_{100}	1.00	165

Thermogravimetric analysis can be employed for establishing polymer-polymer compatibility in blends through the measurement of activation energy [14, 15]. Activation energy of thermal degradation of a multicomponent polymer blend (E_B) is given by the relation

$$E_B = W_1E_1 + W_2E_2 + \ldots \pm \Delta E$$

Where W_1, W_2 . . . are weight fractions of individual components in the blend system.

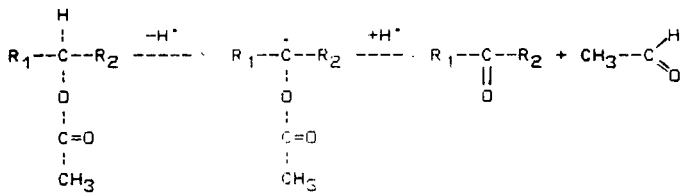
E_1, E_2 . . . are the activation energies of thermal degradation of each component.

ΔE is the difference between the actual activation energy and that of weighted average value, in other words it is a measure of deviation from weighted average values in a blend. This energy difference is ascribed to the formation of some new polymer-polymer bonds due to interactions among the components. Table 4 shows that the experimental values of E_a of the blends are always higher than the weighted average values. This indicates the existence of some interaction between LDPE and EVA in their blends. This difference between theoretical and experimental values is maximum for 50:50 EVA/LDPE blend which shows that at this blend composition the interaction is greatest between the constituents.

IR Analysis of Aged and Unaged EVA/LDPE Blend

Figure 3 represents the IR spectra of 1900–1600 cm^{-1} region of pure EVA and 50:50 blend of EVA and LDPE processed at 170°C. The spectra of pure EVA shows two distinct carbonyl peaks at 1746 cm^{-1} and 1729 cm^{-1}. The 1746 cm^{-1} peak is assigned to the >C=O stretching vibration of the vinyl acetate group [16]. The second peak at 1729 cm^{-1} is assigned to the keto carbonyl stretching vibration [5,16]. The forma-

tion of ketone from pure EVA during processing can be schematically represented by the following reaction scheme:



The above mechanism has been proposed by Sultan and Sörvik [5] based on similar observations.

It is interesting to note that the 50:50 EVA/LDPE blend processed under the same conditions shows a single well-resolved >C=O stretch-

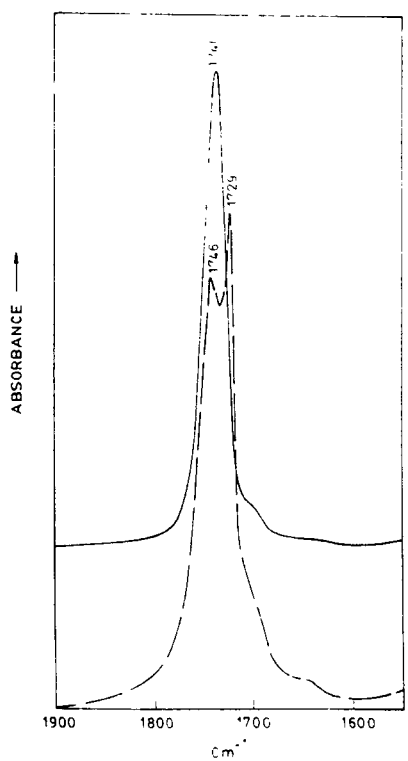
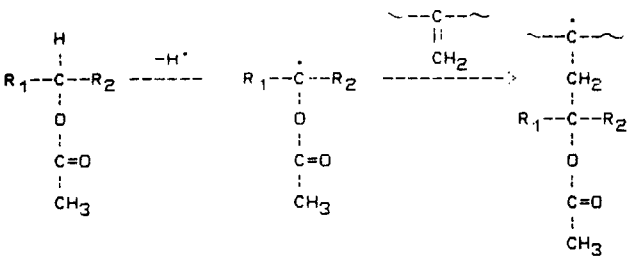


FIGURE 3. IR spectra of EVA (- -) and 50:50 EVA/LDPE blend (–) processed at 170°C.

ing band at 1740 cm^{-1} which signifies that there is no trace of the keto-carbonyl group. The absence of the keto group in the blend may be ascribed to the reaction of the macroradical (formed during processing through abstraction of α-H atoms of EVA) with the vinylidene group of LDPE [5].

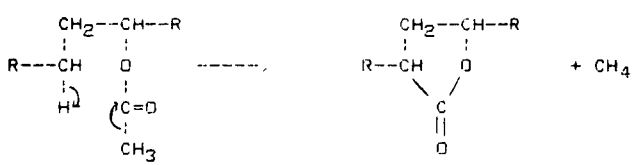
The reaction may be represented schematically:



The macroradical thus formed may terminate in either of the following ways: (a) addition of a H· radical, (b) reaction with an EVA macroradical or (c) liberation of a H· radical from an adjacent methylene group. Case (b) may be ruled out due to steric factors. The possibility of liberation of a H· radical as mentioned in (c) may also be eliminated which leaves the possibility of (a)–the bond energy of C–H is $\approx$100 Kcal/mole compared to $\approx$60 Kcal/mole for >C=C< [17]. It may be concluded from IR analysis that under the action of heat and mechanical shearing at the process condition, EVA-g-LDPE is formed.

Thus, in EVA-g-LDPE, another bulky alkyl group is attached to the α-carbon replacing the α-hydrogen atom of EVA. This bulky alkyl group obviously exerts an electron donating effect to the >C=O group of ester resulting in enriched electron density and decreased frequency of absorption of >C=O group from 1746 to 1740 cm^{-1} [18].

Figure 4 depicts the IR spectra in the 1900–1600 cm^{-1} region for EVA and EVA/LDPE blend treated at 370°C for 15 minutes in a nitrogen atmosphere. It is clearly visible from the spectra that for EVA/LDPE blend an additional peak at 1786 cm^{-1} has appeared while in case of pure EVA the region only shows a shoulder. This absorption band corresponds to γ-lactone [16]. The mechanism of formation of γ-lactone during the aging of EVA has been suggested by Sörvik et al. [5] which may be represented as follows:



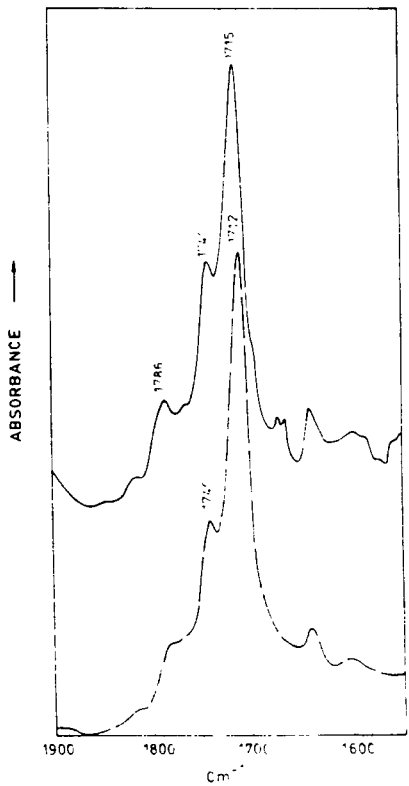


FIGURE 4. IR spectra of EVA (- -) and 50:50 EVA/LDPE blend (—) treated at 370°C in nitrogen atmosphere for 15 minutes.

The distinguishing feature of lactone formation is that it does not involve the abstraction of α-hydrogen atoms. Due to the grafting reaction in the blend leading to formation of EVA-g-LDPE, the concentration of α-hydrogen atoms per unit vinyl acetate moiety is considerably less compared to pure EVA. As a result reactions through the abstraction of α-hydrogen atoms, e.g., the ketone formation, is also less. Moreover, during processing at 170°C there is no evidence of lactone formation in either case, which means that lactone formation is a higher temperature phenomenon compared to ketone formation. Thus at lower temperatures the degradation taking place apart from deacetylation is via ketone formation [4]. But the probability of ketone formation is low in EVA-g-LDPE due to less availability of α-hydrogen atoms per unit vinyl

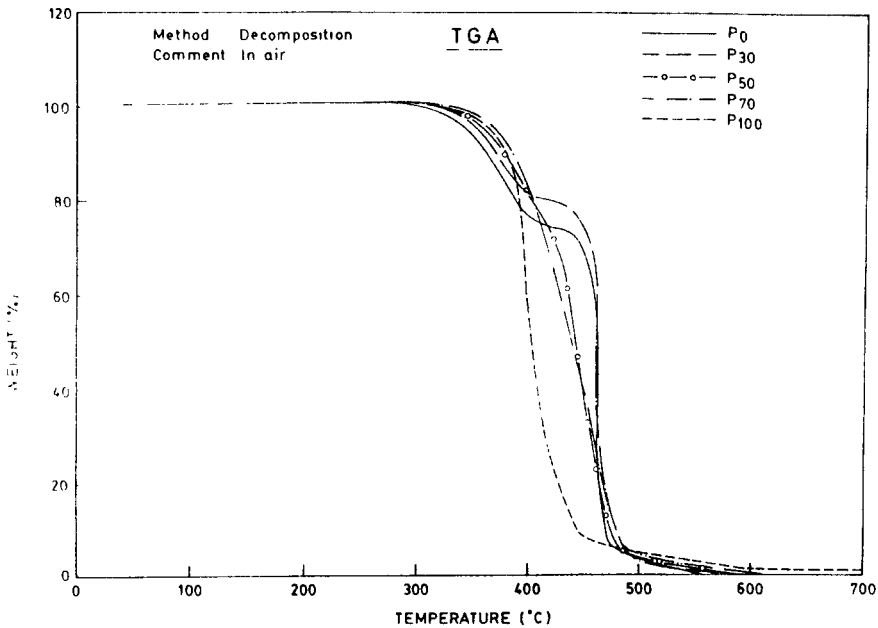


FIGURE 5. TGA curves of uncured compositions in air.

acetate moiety. This may be the reason for higher thermal stability of the EVA/LDPE blend compared to pure EVA.

Thermal Decomposition in Air

Thermal decomposition characteristics of different uncured blends and pure polymers are presented in Figure 5. Different characteristic temperatures for first and second stage decomposition have been presented in Table 5. The extent of degradation during the deacetylation

Table 5. Thermal decomposition of uncured samples in air.

	1st Stage		2nd Stage		
	T_i (C)	T_{max} (C)	T_i (C)	T_{max} (C)	T_{50} (C)
P_0	316	380	440	460	462
P_{30}	333	361	436	463	460
P_{50}	336	380	400	440	440
P_{70}	350	—	350	470	440
P_{100}	—	—	340	392	400

process for blends is somewhat higher for decomposition carried out in air compared to that in nitrogen. Onset of both the decomposition stages starts at considerably lower temperature in air than that in nitrogen; the difference in T_i between the two atmospheres for any composition at the first stage is about 20°C but for second stage this difference is found to be as high as 50°C (for P_{50} blend). The effect of atmosphere on T_{50} and T_{max} for the second stage decomposition is found to be at a maximum for the 50:50 blend. There is an appreciable reduction in T_{50} and T_{max} values when decomposition is carried out in air instead of nitrogen for all compositions.

Thermal Decomposition of Crosslinked Blends in Nitrogen and Air

TGA curves of different cured compositions in nitrogen and air are shown in Figures 6 and 7 respectively. Different characteristic temperatures for thermal decomposition of cured compositions in two different atmospheres are shown in Tables 6 and 7 respectively. T_i for first stage decomposition in nitrogen is not affected by crosslinking (Table 6). But

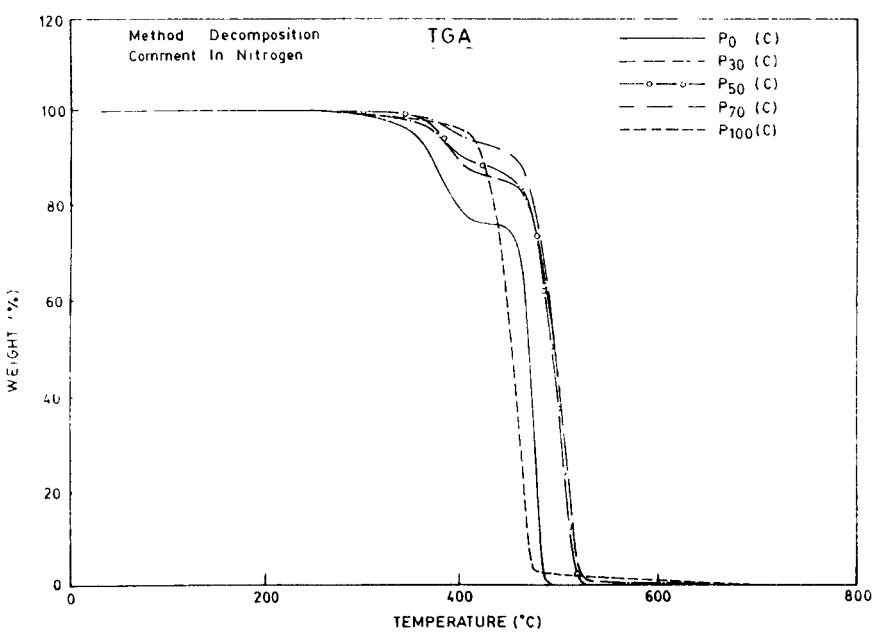


FIGURE 6. TGA curves of cured compositions in nitrogen atmosphere.

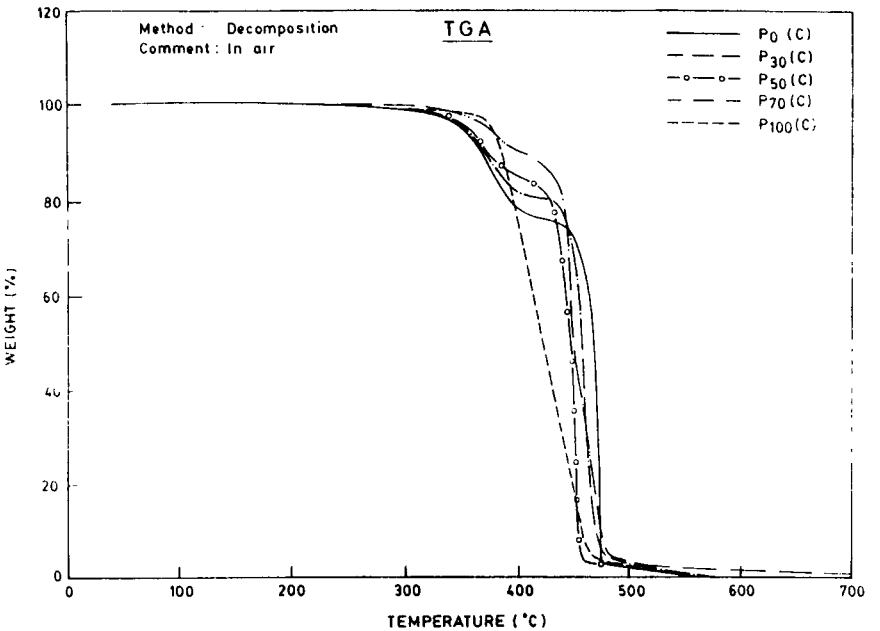


FIGURE 7. TGA curves of cured compositions in air.

the initiation of decomposition is retarded for cured systems compared to uncured ones in the second stage degradation. However, crosslinking has a somewhat adverse effect on both the initiation temperatures of pure EVA. T_{max} and T_{50} for both of the stages are higher for cured systems (except in pure EVA) compared to uncured ones. The extent of first stage decomposition is reduced on curing only for EVA rich blends. On average, the cured blends show greater thermal stability than the pure components as observed for decomposition of uncured compositions in nitrogen.

Table 6. Thermal decomposition of cured samples in nitrogen.

	1st Stage		2nd Stage		
	T_i (C)	T_{max} (C)	T_i (C)	T_{max} (C)	T_{50} (C)
P_0	323	381	446	469	470
P_{30}	365	392	460	508	496
P_{50}	357	389	461	507	496
P_{70}	377	388	450	506	496
P_{100}	—	—	365	461	454

Table 7. Thermal decomposition of cured samples in air.

	1st Stage		2nd Stage		
	T_i (C)	T_{max} (C)	T_i (C)	T_{max} (C)	T_{50} (C)
P_0	325	373	446	468	468
P_{30}	325	370	433	453	456
P_{50}	325	366	420	446	448
P_{70}	350	370	420	443	450
P_{100}	—	—	360	400	420

In air, T_i for the first stage is not affected much between cured and uncured compositions (Table 7). However, there is a slight delay in the onset of second stage decomposition for cured systems compared to uncured ones. This difference is more pronounced in LDPE rich blends. Thus, curing has a marginal effect on both T_{max} and T_{50}. The extent of decomposition in the first stage is slightly retarded on curing in air.

CONCLUSION

Uncured blends in nitrogen show greater thermal stability than the pure components. Activation energy of the blends shows a positive deviation from the theoretically calculated values based on additivity which is indicative of a strong interaction between EVA and LDPE in their blends. IR analysis supports this as well. For cured compositions, greater thermal stability is observed for the blends than for the pure components. The process of degradation is facilitated in air compared to that in an inert nitrogen atmosphere. Crosslinking increases the thermal stability of the blends to second stage decomposition in a nitrogen atmosphere.

ACKNOWLEDGEMENTS

The authors are grateful to the Department of Science and Technology, India, and Polyolefins Industries Ltd., India, for financial assistance.

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