Thermal Stability of Ethylene–Vinyl Acetate and Ethylene–Propylene–Diene (EVA–EPDM) Blends

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ABSTRACT: The thermal behavior of ethylene-vinyl acetate (EVA) and ethylene propylene-diene (EPDM) blends have been studied by thermogravimetry in nitrogen. The activation energy, preexponential factor, and lifetime have been calculated using software-based on the Flynn and Wall isoconversional procedure. The maximum thermal stability in nitrogen atmosphere was observed for the EV80–EP20 blend. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1829–1835, 1998

Key words: ethylene-vinyl acetate (EVA); ethylene-propylene-diene (EPDM); thermal stability, thermogravimetry

INTRODUCTION

There is an increase in the use of polymeric materials for high-temperature applications. The modification of ethylene-vinyl acetate (EVA) copolymer with ethylene-propylene-diene (EPDM) elastomer improves environmental stress cracking. The beading in automobiles and linings in solar ponds are major areas for the application of EVA-EPDM blends. Associated with these hightemperature applications, there is a need for test procedures to assess and predict performance under service conditions. While assessing the thermal stability and lifetime, it should also be considered that physical properties, such as the mechanical strength, are directly related to its weight loss. Thermogravimetric analysis (TGA) experiments are capable of providing information on the kinetics of the thermal decomposition of

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polymers and insight into the complex degradation mechanism. $^{1\!-\!5}$

In this work, we have studied the thermal stability of EVA-EPDM blends by performing a detailed TG kinetic study for a series of different compositions. To assess the importance of the pyrolytic process, the weight-loss curves were measured in a nitrogen atmosphere. Fundamental kinetic information is, therefore, needed regarding the thermal behavior of EVA-EPDM blends before its widespread acceptance in demanding high-temperature applications.

EXPERIMENTAL

EVA (PIL, 2806; vinyl acetate = 28%; MFI = 6 g/10 min) and EPDM elastomer (JSR, 21; ethylene, 64%; ethylene norbornene, 6.7%; Mooney viscosity, 20 mL₁₊₈^{127°C} were mixed in appropriate ratios using an internal mixer (Torque Rheometer, Haake Rheocord-90). Dicumyl peroxide (DCPO) is recrystallized with methanol, then used for the dynamic curing purpose. Blends with 0, 20, 40,

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Figure 1 Thermogravimetric analysis of EVA–EPDM blends: (1) EV100; (2) EV80–EP20; (3) EV60–EP40; (4) EV40–EP60; (5) EV20–EP80; (6) EP100 in nitrogen atmosphere.

60, 80, and 100% by weight of EPDM (designated EV100–EP0, EV80–EP20, EV60–EP40, EV40–EP60, and EV100–EP0, respectively) were mixed at 150°C with a rotor speed of 50 rpm for 10 min, and the rotor is stopped for a while to attain a melt temperature of 160°C; then, in all cases, 1% by weight DCPO is added, mixing continued for 8 min more. The degradative kinetics of these dynamically cured blends were studied by nonisothermal thermogravimetry (DuPont TGA 951) with heating rates 5, 10, and 15°C/min under a nitrogen atmosphere, and the temperature range was from room temperature to 600°C. The sample weight was set in all the cases of 6–7 mg.

RESULTS AND DISCUSSION

Typical results for TG on various composition of dynamically cured EVA–EPDM blends in nitrogen atmosphere at a heating rate of 10°C/min are shown in the Figure 1. The plots in the nitrogen atmosphere show degradation in the range of 323–570°C. It is observed from the thermograms that the onset temperature decreases with increase in EVA%, which is a consequence of acetic acid evolved from EVA.⁶

The kinetic values obtained in three different heating rates are based on the methods Flynn and Wall⁷ and Doyal.⁸ Figures 2-5 represent isoconversion (Ozawa) plots [log(heat rate) ver-1000/T] for EV0-EP100, EV60-EP40, sus EV80-EP20, and EV100-EP0, respectively, in a nitrogen atmosphere. Almost all these figures show two sets of parallel lines, that is, up to 5% and higher conversions. This is a consequence of moisture and low molecular fraction evolution up to 5% conversion, and major degradation occurs after that. One important aspect is that, as EVA% increases, the distance between two sets of isoconversion lines, that is, up to 5 or 10% and higher conversion is the consequence of increase in acetic acid evolution in a nitrogen atmosphere.

Table I shows that the activation energy increases with increase in the percentage of conver-



Figure 2 Isoconversion plot of the EV0-EP100 blend in a nitrogen atmosphere.

sion except for two cases, EV0–EP100 and EV100–EP0. This is attributed to the less chance of crosslinking for the EV100–EP0 blend. In the case of the EV0–EP100 blend, steric crowding between two crosslinked EPDM chains results in a weakening of interchain C—C bonds. The per-

oxide molecule, despite being in the vicinity, cannot penetrate deep into the bulk of the dispersed phase (EPDM) as its viscosity is very high and, hence, there is less chance of crosslinking. However, the ease of crosslinking is very high in EPDM due to the very large number of tertiary



Figure 3 Isoconversion plot of the EV60-EP40 blend in a nitrogen atmosphere.



Figure 4 Isoconversion plot of the EV80-EP20 blend in a nitrogen atmosphere.

hydrogen atoms per chain. The exceptionally high activation energy for degradation in the case of EV80–EP20 blend ($E_a = 194.1$ kJ/mol for 5% conversion) might be due to low viscosity, and higher penetration by the peroxide molecule between EPDM chains takes place, resulting in a

higher degree of crosslinking for this particular blend. This is also evidenced by lifetime estimates, as explained later.

Table II summarizes ideas about the starting stage for degradation of all blends. The EV0-EP100 blend shows the least rate constant



Figure 5 Isoconversion plot of the EV100-EP0 blend in a nitrogen atmosphere.

Conversion Percentage	Energy of Activation E_a (kJ/mol)						
	EV100– EP0	EV80– EP20	EV60– EP40	EV40– EV60	EV20– EP80	EV0– EP100	
1.0	104.6	188.5	159.2	161.7	111.7	103.6	
2.5	166.6	192.8	159.3	162.5	111.9	82.5	
5.0	107.6	194.1	159.5	158.2	95.9	82.7	
10.0	111.2	202.9	159.7	123.0	132.1	84.3	
20.0	116.0	345.9	210.0	228.3	151.6	85.8	
30.0	150.8	370.5	226.7	251.3	159.2	87.2	
40.0	138.2	365.3	229.5	256.4	167.6	89.8	
60.0	127.3	337.3	238.5	266.2	181.1	92.9	
80.0	126.6	331.2	266.1	276.2	193.6	92.7	
99.0	126.6	277.5	251.2	271.0	228.4	94.6	

Table IActivation Energy at Different Conversion Levels for Various Dynamically Cured EVA(EV)-EPDM (EP) Blends in Nitrogen Atmosphere

amongst the all blends. This factor is attributed to EVA evolving acetic acid in the initial stage of degradation, and the rate constant is almost same in all the cases, except for EV0–EP100. Hence, this series of rate constants for 5% conversion in nitrogen atmosphere describing the starting degradation is almost same and higher than the EV0–EP100, as the latter does not contain EVA and a heterogeneously crosslinked phase.

LIFETIME PREDICTION

Using the kinetic data derived in this study and a software package, life estimates for all the blends in nitrogen atmosphere were generated. The maximum temperatures at which the lifetime is a century for 5% conversion are shown in Table II. The EV80–EP20 blend is stable up to a century at 170°C and is the most stable among the blends heated in a nitrogen atmosphere (Fig. 6). This blend is followed by the EV60–EP40 blend in a nitrogen atmosphere (Fig. 7). Again, this is evidenced by the lifetime estimate plot, and this shows a century lifetime temperature maximum of 143°C, heating in nitrogen.

CONCLUSIONS

Thermogravimetry is capable of providing some very useful information on thermal stability of these blends provided that care is taken in the

 Table II
 Summerized Degradative Kinetic Results at 5% Conversion Level for Various Dynamically

 Cured EVA (EV)-EPDM (EP) Blends in Nitrogen Atmosphere

Various Dynamically Cured Blends	Onset Degradative Temp (°C)	Rate Constant for 5% Conversion at Onset Degradative Temp (1/min)	Half-Life for 5% Conversion at Onset Degradative Temp (min)	E_a at 5% Conversion (kJ/mol)	Max Temp at Which Cured Lifetime is a Century for 5% Conversion (°C)
EV100-EP0	323.5	$2.32 imes 10^{-3}$	298.7	107.6	85
EV80-EP20	331.4	$1.556 imes10^{-3}$	445.0	194.1	170
EV60-EP40	334.4	$1.924 imes10^{-3}$	307.3	159.5	143
EV40-EP60	323.4	$1.88 imes10^{-3}$	583.3	158.2	135
EV20–EP80	334.4	$2.58 imes10^{-3}$	268.0	95.9	75
EV0-EP100	332.4	$5.366 imes10^{-4}$	129.2	82.7	55



Figure 6 Lifetime of the EV80-EP20 blend with respect to temperature.



Figure 7 Lifetime of the EV60–EP40 blend with respect to temperature.

interpretation. The TGA kinetics data for the EV80-EP20 blend heated in nitrogen indicate that the material has excellent thermal stability.

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