

Differential Scanning Calorimetry Analysis of the Thermal Treatment of Ternary Mixtures of Ethylene Vinyl Acetate, Polyethylene, and Azodicarbonamide

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Received 10 January 2008; accepted 31 May 2008

DOI 10.1002/app.28802

Published online 8 September 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The different transitions and reactions involved in the thermal processing of ternary ethylene vinyl acetate (EVA)–polyethylene (PE)–azodicarbonamide (ADC) mixtures with different concentrations of PE and ADC, which was used as a foaming agent, were studied by means of differential scanning calorimetry. The effect of the concentration of PE in the ternary samples was practically linear, which showed an increase in the fusion heat of the PE and the PE domains of the EVA.

On the contrary, the mechanism of the thermal decomposition of ADC that the ternary mixtures contained was strongly dependent on its concentration in the sample, which showed clear deviations from linearity. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 3217–3224, 2008

Key words: blends; blowing agents; density; differential scanning calorimetry (DSC); kinetics (polym.)

INTRODUCTION

As it is very well known, the family of low-density microcellular compounds obtained by the foaming and crosslinking of ethylene vinyl acetate (EVA) copolymer has a large field of commercial applications. Products such as the soles of sport shoes, bicycle helmets, toys, nautical buoys, gymnasium floors, and hygienic stable floors are typical examples of such a wide range of uses, where the density reduction can be turned directly into material/cost savings and more valuable products. On the other hand, the kinetic study and modeling of the reactions involved in the thermal processing of these crosslinking and foamed substances (transitions, melting, crosslinking, and foaming) are of paramount importance in the design of the molds, polymer selection/formulation, and selection of the operating variables to obtain the required product.^{1–12}

In this study, following an exhaustive investigation of the phenomena that happen in the industrial production of commercial EVA that we started in previous studies,^{9–12} the thermal behavior of EVA–polyethylene (PE)–foaming agent ternary mixtures

involved in the production of EVA foams was systematically studied by differential scanning calorimetry (DSC) to examine the possible effects of different compounds and mixtures on the foaming process. In this study, azodicarbonamide (ADC) was used as a foaming agent because it is very frequently used in the production of EVA–PE foams because its decomposition liberates a large volume of gas, which is trapped in the melt.^{13–15} The decomposition of this chemical goes, according to Stevens and Emblem¹⁶ and Lober,¹⁷ through the competitive and exothermic reaction pathways shown in Figure 1 to produce solids (urazol and hydrazodicarbonamide) and a gaseous mixture of nitrogen, carbon monoxide, cyanic acid, and ammonia. This evolution of ammonia restricts the use of ADCs in polymers or materials sensitive to degradation or corrosion produced by this gas. Depending on the process conditions and the state of the product, different paths may be favored over others.^{14,16,18} Typical parameters for commercial ADCs that are provided by the suppliers are the particle size, purity, and amount of gases (gas yield) evolved in an isothermal process at 210°C for 15 min^{19–21} collected in dioctyl phthalate.

Taking into account that DSC is a powerful technique widely used to study the different transitions undergone by polymers, such as melting, crystallization, glass transition, and rearrangement in their structures,^{22–29} we carried out different DSC experiments with the ternary samples, where the relative contents of PE and ADC were varied around typical values used in industrial applications. The thermal properties, including the specific melting enthalpy

Additional Supporting Information may be found in the online version of this article.

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Contract grant sponsor: Generalitat Valenciana; contract grant numbers: GRUPOS03/159, GV01-42, and GR01-36.

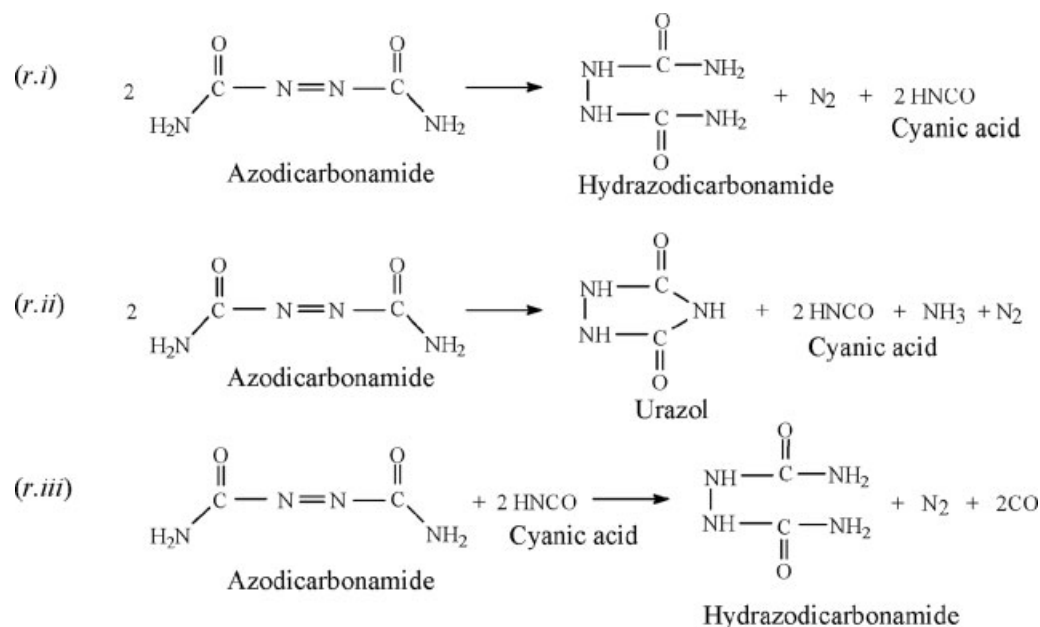


Figure 1 Reactions of the decomposition of ADC (from refs. 16 and 17).

and melting temperatures of nonfoamed and foamed samples, the degradation temperatures for ADC, and the dependence on the foaming agent concentration, were studied. The density evolution of the foamed samples was also determined to quantify the efficiency of the foaming process.

The DSC analysis presented in this article will provide better knowledge of the processes involved and very useful information for the control and optimization of the process conditions, including the heat involved, temperatures, cycles, and formulations to be used.

EXPERIMENTAL

Materials

The polymers used were low-density polyethylene (LDPE) PE003 and EVA PA-539 Alcudia copolymer (vinyl acetate content = 18 wt %), both supplied by Repsol YPF[®] (Madrid, Spain). Table I shows the

TABLE I
Technical Data for LDPE PE003 and EVA PA-539
(Alcudia, Repsol YPF)

Property	PE	EVA
Melt flow index (g/10 min)	2	2
Vicat temperature (°C)	92	64
Crystallinity (%)	44	18
Density at 23°C (g/cm ³)	0.920	0.937
Melting temperature (°C)	113	90
Thermogravimetric analysis peak temperatures (°C) in a nitrogen environment (45 STP mL/min) ¹¹	474	366 and 474

properties of these two polymers according to the supplier.

The ADC Unicell-D, supplied by Ledex S. A.[®] (Barcelona, Spain), was used in this study (Table II) because of its industrial use, which corresponds to an activated ADC (normally with a metal oxide, e.g., ZnO or MgO). In this sense, the decomposition of the ADC occurred before 200°C (to reduce the heat requirements) but after the melting of PE and EVA, respectively, that is, in the molten polymer to produce the foaming process.

Sample preparation

Ternary mixtures of EVA with three different concentrations of PE (5, 10, and 15 phr) and ADC (1, 2, and 4 phr) were studied (Table III). The concentrations of the components were selected to be close to typical values used in industrial applications.

Pellets of the different formulations studied were prepared by melting, before the experiments and after the manual mixing of the different compounds, in a Brabender[®] Plasticorder PL 2000 extruder (Duisburg, Germany) at 398 K at a speed of 20 rpm with a

TABLE II
Technical Properties of the Activated ADC: Unicell-D
(Ledex S. A.)

Property	Value
ADC (wt %)	91.1
Decomposition temperature (K)	460
Ashes (%)	5.85
Gas yield (cm ³ /g; isothermal at 210°C for 15 min)	160
Particle size (µm)	7
Density (g/cm ³)	1.65

TABLE III
EVA-PE-ADC Ternary Mixtures: Compositions, Codes, and Densities

Composition (phr)			Codes	Density (g/cm ³)	
EVA	PE	ADC			
100			EVA	0.938	
	100		PE	0.923	
100	5	2	I	EP(5)A(2)	0.323
100	10	2	II	EP(10)A(2)	0.341
100	15	2	III	EP(15)A(2)	0.368
100	10	1	IV	EP(10)A(1)	0.429
100	10	4	V	EP(10)A(4)	0.215

Samples were pressed at 175°C for 10 min.

single screw (extruder type = 19/25D, 3z; screw 4/1; die type = Roundcap 15/1). These conditions were chosen to achieve a good homogenization of the mixture and to avoid ADC degradation.^{30–32} After the extrusion die, the discharged mixture was cut into pellets, immersed in a water bath, and then dried at room temperature.

To determine the densities of the final foamed products, the mixtures prepared in the extruder were pressed in a heated plate press (Mecamaq[®] DE-200) (Madrid, Spain) at 448 K for 10 min to carry out the foaming reaction.

DSC

DSC tests were performed in a PerkinElmer[®] DSC 7 instrument controlled by a Personal Computer Advanced Technology compatible system. Samples of 8–9 mg were encapsulated in aluminum pans and treated at a heating rate of 10 K/min (according to

Morisaki and Naito,²¹ the evolution of the decomposition heat of ADC may be only slightly influenced by the heating rate when the rate exceeds 3°C/min).

The atmosphere used was nitrogen with a flow rate of 45 STP mL/min. Two consecutive runs were performed on each sample. Initially, an experiment within the temperature range 313–573 K was run (to avoid the decomposition of the polymeric compounds; Table I). The sample was then cooled to 293 K (at 10 K/min), and a second run was performed at the same heating rate to analyze the effect of the foaming agent not only before and during the foaming process (first run) but also on the final foamed polymer (second run) to characterize the postprocessing product.

All of the experiments were repeated to determine their reproducibility and showed very good results with a maximum deviation between the repeated runs of about 2%.

Density measurement

The density of the different mixtures was measured after processing with a Afora[®] glass pycnometer (Valencia, Spain) at 298 K. The variation coefficient for the measured densities was estimated to be 0.005 g/cm³.

RESULTS AND DISCUSSION

Thermal properties and analysis (DSC experiments)

Figure 2 shows the DSC curve of the ADC used in this study from 300 to 550 K. This curve showed two overlapped and exothermic peaks (p1 and p2) and one endothermic peak (p3), which indicated

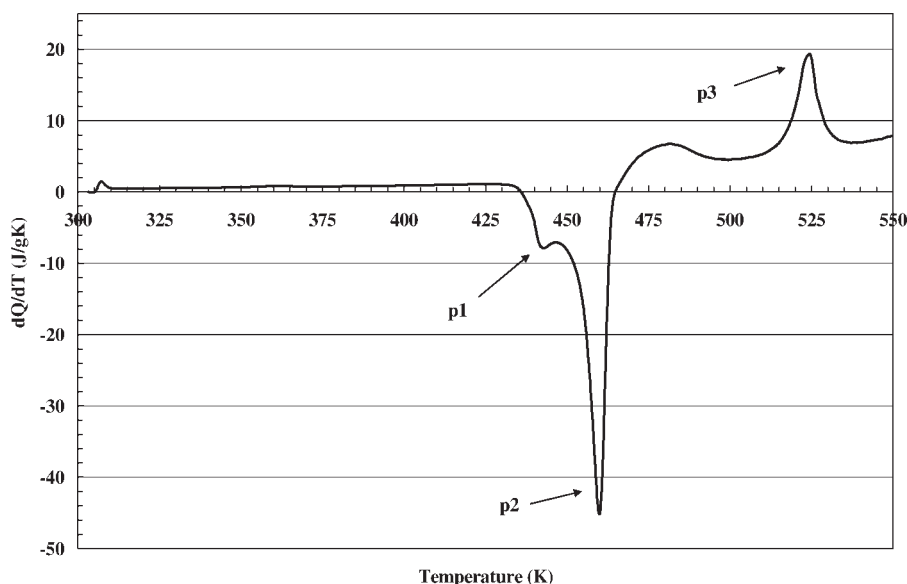


Figure 2 DSC curve of the activated ADC Unicell-D (Ledex S. A.).

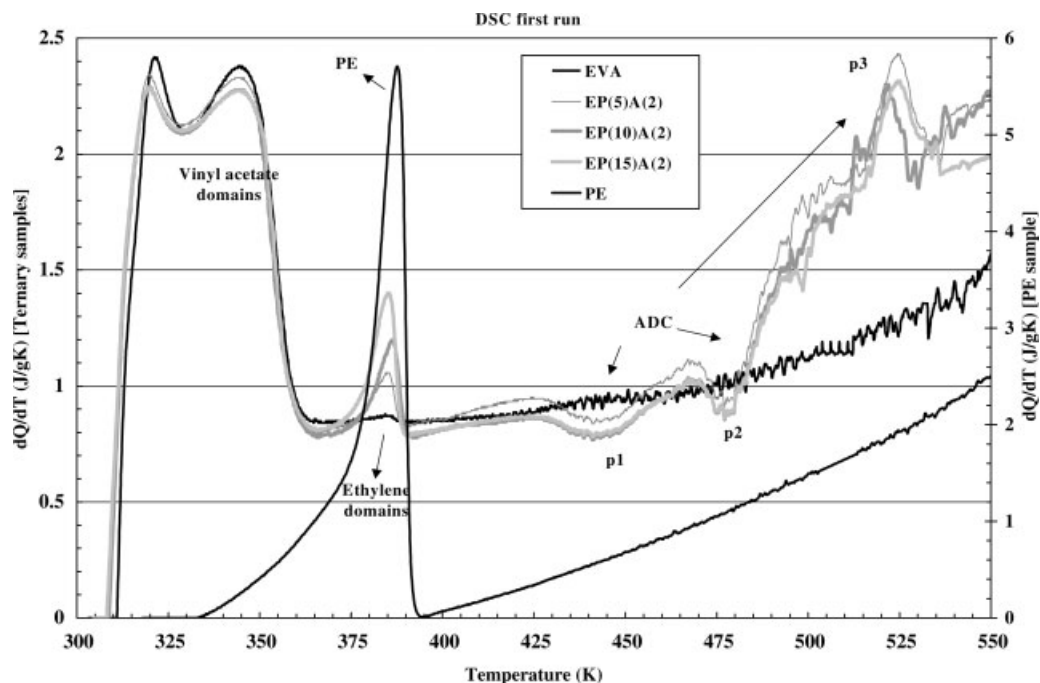


Figure 3 DSC results (first runs) for the pure polymers and ternary EVA-PE-ADC mixtures with various PE contents (5, 10, and 15 phr).

that the complete thermal decomposition of the ADC took place in different steps according to the accepted scheme of the three competitive reactions shown in Figure 1.³³

Figures 3–6 show the DSC curves for the ternary EVA-PE-ADC mixtures studied with various PE

and ADC contents, respectively, and include the curves corresponding to the pure polymers. Table IV shows the melting temperatures (or reaction temperature in the case of the foaming agent) and heats (i.e., area under the corresponding peak) determined by DSC for all of the samples studied, including the

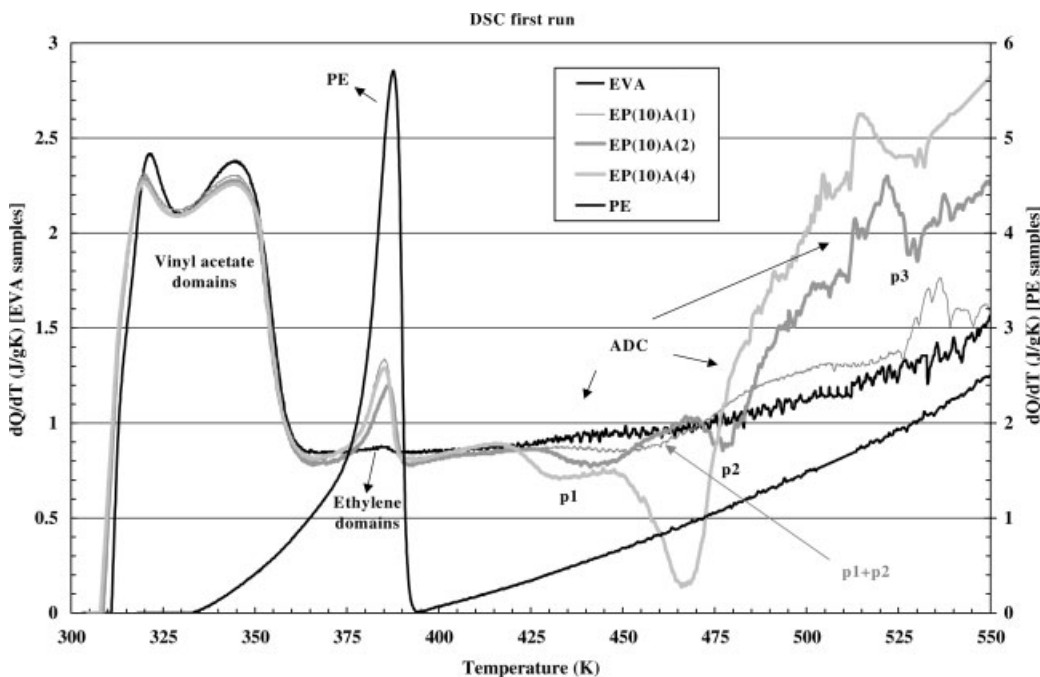


Figure 4 DSC results (first runs) for the pure polymers and ternary EVA-PE-ADC mixtures with various ADC contents (1, 2, and 4 phr).

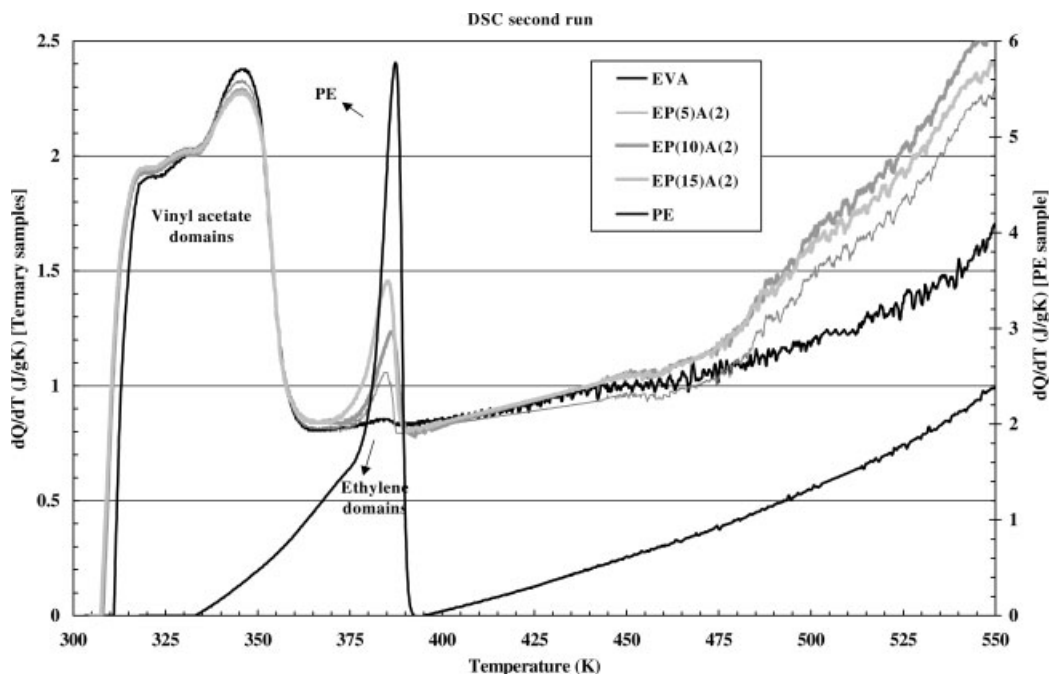


Figure 5 DSC results (second runs) for the pure polymers and ternary EVA-PE-ADC mixtures with various PE contents (5, 10, and 15 phr).

pure components, nonfoamed samples (first DSC run), and foamed samples (second DSC run).

DSC first runs

DSC curves for a typical EVA copolymer show two endothermic and overlapped peaks at 321 and 344 K, which correspond to the transitions of the vinyl acetate

domains,⁹ and a third endothermic peak at 386 K (much smaller), which corresponds to the melting of the ethylene domains of the EVA copolymer (totally coincident with the melting process of the pure PE⁹; Table IV).

In the analysis of the first run for the EVA-PE-ADC ternary mixtures (Figs. 3 and 4 and Table IV), the peaks corresponding to the thermal transitions of the polymeric matrix were similar (number of

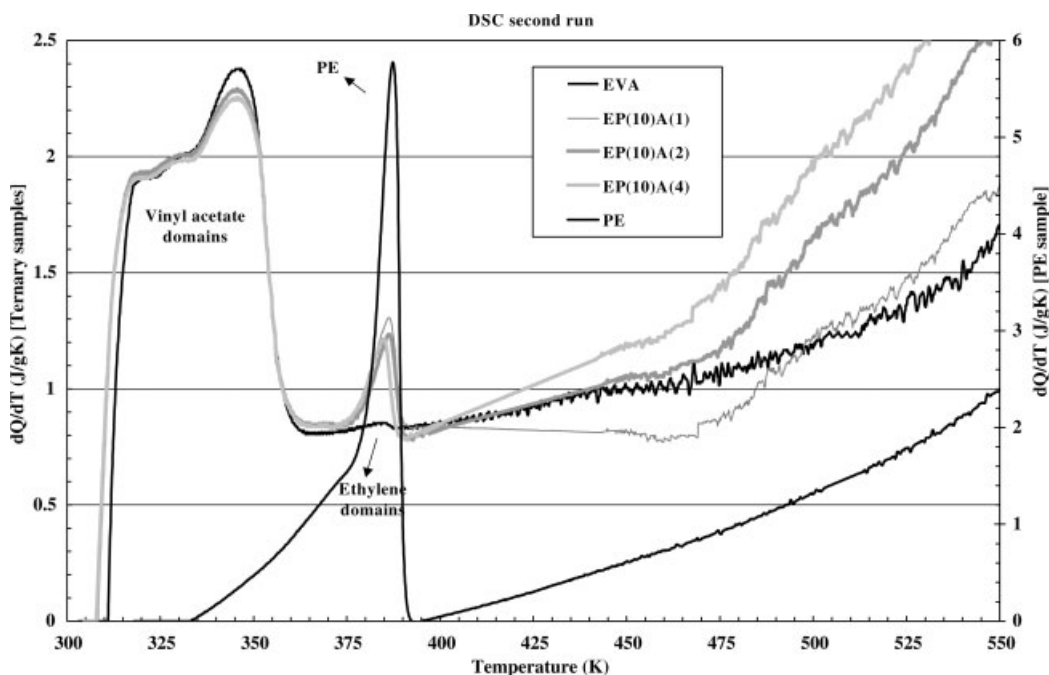


Figure 6 DSC results (second runs) for the pure polymers and ternary EVA-PE-ADC mixtures with various ADC contents (1, 2, and 4 phr).

TABLE IV
DSC Results (First and Second runs) for Pure EVA and PE and the Ternary EVA-PE-ADC Mixtures^a

DSC peaks	Sample code						
	EVA	PE	I	II	III	IV	V
EVA domains							
$\Delta H_{\text{melt EVA}}$ (J/g)	57 (53)		59 (52)	59 (52)	57 (52)	57 (52)	57 (52)
$T_{\text{trans EVA}}$ (K)	322 (322)		318 (321)	321 (322)	319 (321)	319 (322)	319 (322)
$T_{\text{melt EVA}}$ (K)	345 (345)		346 (346)	347 (347)	346 (346)	347 (347)	347 (347)
PE domains							
$\Delta H_{\text{melt PE}}$ (J/g)	0.8 (0.8)	81.3 (79.7)	4.2 (4.0)	8.7 (8.5)	11.9 (11.5)	8.6 (8.5)	8.6 (8.4)
$T_{\text{melt PE}}$ (K)	386 (386)	388 (388)	386 (386)	388 (388)	386 (386)	387 (387)	386 (386)
ADC exothermic decompositions							
ΔH_{p1} (J/g)			-21.7 ^b	-21.2 ^b	-21.3 ^b	-8.4 ^b	-41.3 ^b
$T_{\text{peak p1}}$ (K)			447	447	448	466*	438
$T_{\text{peak p2}}$ (K)			480	479	479		469
ADC endothermic decomposition							
ΔH_{p3} (J/g)			6.4	7.9	7.0	4.3	6.3
$T_{\text{peak p3}}$ (K)			526	525	525	537	519

^a The values in parentheses correspond to the DSC second runs.

^b Corresponding to the p1 + p2 ADC peaks.

peaks, reaction temperatures, and heat) to those corresponding to the pure polymers used and EVA-ADC binary mixtures^{9,12} because the ADC was still unaltered at this temperature; they also included the expected increase in the area corresponding to the endothermic peak at 386 K due to the presence of additional PE in the ternary sample.

After the melting of the polymer (Figs. 3 and 4), different peaks appeared in the first run of the DSC curves, which corresponded to the exothermic (primary) and endothermic (secondary) decompositions of the ADC. Most samples showed three decomposi-

tion peaks (p1–p3), as did the pure ADC (Fig. 2). However, contrary to the pure ADC, at low concentrations of ADC, the first exothermic peak (p1) was much more evident than the second (p2), which increased with ADC content. Even more, the sample with the lower content of ADC [EP(10)A(1); see Table II for explanations of each sample code] showed only two peaks for the ADC decomposition: one exothermic peak at 460 K, which corresponded to the primary decomposition of the ADC [peaks p1 and p2 (Fig. 2) were, in this case, totally overlapped in a wide peak], and another endothermic one at 534 K (p3).

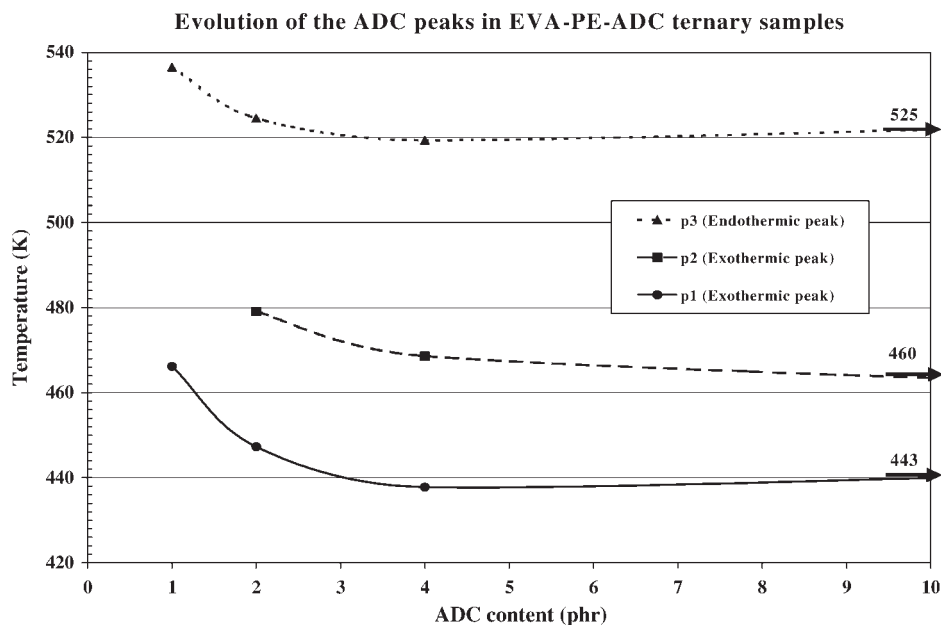


Figure 7 Evolution of the peak temperatures for the ADC thermal decomposition in the EVA-PE-ADC ternary samples.

As shown in Figure 3, the variation of the PE content of the ternary sample did not affect the ADC decomposition temperatures (i.e., temperatures of maximum heat flow rate), and also, the effect of the PE over the baseline was lower than the effect of the foaming reaction. Figure 7 shows the variations of the peak temperature of the three ADC decomposition processes as a function of the concentration of ADC. The temperature for the pure ADC is also shown and corresponds to the asymptotic value for the infinite ADC content.

As shown in Figure 7 (and Fig. 4), in the case of the sample with lower ADC content, all of the processes (p1–p3) appeared at higher temperatures than the same peaks in the DSC of the pure ADC. On the other hand, these temperatures of the maximum rate decrease with increasing ADC content; furthermore, the peak temperatures of the p1 and p3 processes passed through a minimum with respect to the ADC concentration.

The shift of the peaks associated with the ADC thermal decomposition in the mixtures studied compared with the pure ADC might be explained as a result of different effects:

1. There existed an initial effect of the polymeric matrix in the heat transfer inside the sample that contributed to the delay of the peaks in the ternary mixtures as compared with pure ADC.
2. Additionally, the EVA matrix seemed to alter the mechanism of the ADC primary exothermic thermal decomposition (different relative intensities of peaks p1 and p2) that apparently went through different paths than those of the pure components.
3. According to the ADC degradation reactions shown in Figure 1, the heterogeneous reaction iii introduced an autoaccelerating effect^{13,14,18,34} when the concentration of ADC in the sample increased because of a higher probability of reaction (higher contact time) between the non-reacted ADC and the HNCO gas generated from reactions i and ii in Figure 1. This reaction may have accelerated the global decomposition of the ADC and produced the observed shift to lower temperatures.

With respect to the heat evolved, when the composition of the PE changed (Fig. 3), the heat corresponding to the EVA and ADC processes remained almost constant, and only the PE melting heat increased linearly with the PE content (Table IV). In the case of the ternary samples with various ADC contents (Fig. 4), the heat corresponding to the melting of the polymers remained almost constant regardless of the ADC content. Regarding the extension of the reactions of the ADC decomposition and

with the assumption that, according to the trend observed, the heat evolved in the overlapped peak in the experiment with 1 phr of ADC corresponded mainly to the first process, the heat (J/g of sample) of the first exothermic process (p1) represented a continuous decrease with respect to the ADC concentration (Table IV). On the other hand, the heat corresponding to the second exothermic process (p2) increased strongly with the amount of ADC in the sample. Thus, the decomposition of ADC in the sample with 4 phr of ADC (Fig. 4) represented a behavior similar (regarding the relative intensity of peaks p1, p2, and p3) to the one observed before for pure ADC (Fig. 2). The reaction heat corresponding to the third event (p3) increased with ADC content but with a lower rate than that corresponding to the linear trend.

On the other hand, there existed a progressive increase of the final baseline slope (at high temperatures), mainly when the concentration of ADC in the sample increased (Fig. 4). This phenomenon can be explained in terms of the heat transfer within the sample: when the ADC content increased, a higher amount of the gases entrapped was obtained, which yielded a progressively more foamed sample, which could have decreased the observed thermal conductivity and increased the observed baseline slope.

DSC of second consecutive runs

If the second consecutive heating run of the mixtures is considered (Figs. 5 and 6), the first peak for EVA contribution appeared at the same temperature but underwent a notable decrease in its height and total area, in the same way that happened in the case of pure EVA.⁹ The second and third peaks coincided (temperature and area) with those of the first run. Therefore, the melting processes and crystallinity for the EVA copolymer did not apparently undergo any modification as a consequence of the foaming process in the DSC capsule.

We also observed that, for all of the second run experiments, no more significant peaks appeared, which indicated that the ADC was consumed completely during the first run.

On the other hand, the baselines after the polymer peaks for both runs of each sample were very similar. Therefore, the baseline slope depended mainly on the gas, which continued to be encapsulated in the sample, and the inert components of the ADC, which certified the closed-cell structure of this kind of foam.

Densities of the foamed samples

To confirm the effect of the foaming reaction with different concentrations of ADC, the samples were

processed in a heated plate press, and the densities of the final foamed products were determined. These results are shown in Table III. Obviously, the extension of the foaming process increased with the concentration of ADC, as the densities values indicate. The decrease in the density with ADC concentration in the sample was pronounced for the samples studied, which showed the important effect of the low melt viscosity of EVA in the foaming process.

CONCLUSIONS

The investigation of the thermal properties of the nonfoamed ternary samples showed that the melting point, heat of fusion, and crystallinity of the pure polymer were not significantly modified by the presence of PE and ADC before or after the foaming process. However, the peaks corresponding to the ADC decomposition and also the thermal conductivity of the foamed sample at high temperatures presented a strong variation with ADC content. With regard to the thermal decomposition of the samples, only the foamed samples presented a soft evolution in the temperatures of the EVA decompositions when the PE content was increased. As expected, the samples shown an important decrease in the density when the ADC content was increased in the initial mixture.

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