**DSC ANALYSIS OF THE THERMAL TREATMENT OF TERNARY MIXTURES OF
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DSC ANALYSIS OF THE THERMAL TREATMENT OF TERNARY MIXTURES OF EVA, PE AND AZODICARBONAMIDE

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Abstract

The different transitions and reactions involved in the thermal processing of ternary EVA-PE-ADC mixtures, with different concentrations of PE and azodicarbonamide (used as foaming agent), have been studied by means of differential scanning calorimetry (DSC).

The effect of the concentration of PE in the ternary samples is practically linear showing an increase in the fusion heat of the PE and the PE domains of the EVA. Contrarily, the mechanism of the thermal decomposition of the ADC that the ternary mixtures contain seems to be strongly dependent of its concentration in the sample showing clear deviations from linearity.

Keywords: EVA; PE; chemical blowing agent.

1. Introduction

As is very well known, the family of low-density microcellular compounds obtained by foaming and crosslinking of EVA copolymer has a large field of commercial application. Products such as the soles of sport shoes, bicycle helmets, toys, nautical buoys, gymnasium floors, hygienic stable floors, etc. 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 moulds, in the polymer selection/formulation and in the selection of the operating variables to obtain the product required [1-12].

In this work, the thermal behaviour of the ternary mixtures EVA-PE-foaming agent involved in the production of EVA foams has been systematically studied by differential scanning calorimetry. In the present study, azodicarbonamide has been used as foaming agent because it is very frequently used in the production of EVA-PE foams, due to the fact that its decomposition liberates a large volume of gas, which is trapped into the melt [13-15]. The decomposition of this chemical goes, according to Stevens and Emblem [16] and Lober [17], through the competitive and exothermic reaction pathways shown in Figure 1,

producing solids (urazol and hydrazodicarbonamide) and a gaseous mixture of nitrogen, carbon monoxide, cyanic acid and ammonia. This evolution of ammonia restricts the use of azodicarbonamides 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 favoured over others [14,16,18]. Typical parameters for the commercial azodicarbonamides provided by the suppliers are the particle size, the purity and the amount of gases (gas yield) evolved in an isothermal process at 210 °C for 15 minutes [19-21] collected in DOP (Di-Octyl Phthalate).

Taking into account that differential scanning calorimetry (DSC) is a powerful technique widely used to study the different transitions undergone by polymers such as melting, crystallisation, glass transitions or rearrangement in their structure [22-29], different DSC experiments with ternary samples, where the relative composition of PE and azodicarbonamide (ADC) were varied around typical values used in industrial applications, have been carried out. The thermal properties such as specific melting enthalpy and melting temperatures of non-foamed and foamed samples, the degradation temperatures for the ADC, and their dependence on the foaming agent concentration have been 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 paper allows for better knowledge of the processes involved and provides very useful information for the control and optimisation of the process, heat involved, cycles and formulations to be used.

2. Equipment and experimental procedure.

2.1. Materials

The polymers used were low-density polyethylene (LDPE) PE003 and EVA PA-539 ALCUDIA[®] copolymer, both supplied by REPSOL YPF[®]. Table 1 shows the properties of these two polymers according to the supplier.

The azodicarbonamide Unicell-D[®] supplied by LEDEX S.A.[®] was used in this study (Table 2). The decomposition of the ADC occurs after the melting of the PE and EVA respectively, i.e. in the molten polymer, producing the foaming process.

2.2. 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 3). The concentrations of the components were selected close to typical values used in industrial applications.

The mixtures were prepared, prior to experiments, in a Brabender[®] Plasticorder PL 2000 extruder at 398 K with a speed of 20 rpm, using a single screw. These conditions were chosen to achieve good homogenisation of the mixture, but avoiding the ADC degradation [30-32]. After the extrusion die, the mixture discharged was cut into pellets, immersed in a water bath and, after that, dried at room temperature.

In order to determine the density of the final foamed products, the mixtures prepared in the extruder were pressed in a heated plates press MECAMAQ[®] DE-200 at 448 K for 10 min, to carry out the foaming reaction.

2.3. Differential scanning calorimetry (DSC)

DSC tests were performed in a Perkin-Elmer[®] DSC 7 controlled by a PC AT compatible system. Samples of 8-9 mg were encapsulated in aluminium pans and treated at a heating rate of 10 K/min (according to Morisaki and Naito [21], the evolution of the decompositions 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 of 313-573 K was run. The sample was then cooled until 293 K and a second run was performed under the same heating rate, in order to analyse 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), in order to characterise the post-processing product.

All the experiments were replicated in order to determine their reproducibility, showing very good results with a maximum deviation between the repeated runs of about 2%.

2.4. Density measurement.

The density of the different mixtures was measured after processing using a glass picnometer at 298 K. The variation coefficient for the measured densities was estimated to be 0.005 g/cm³.

3. Results and discussion.

3.1. Thermal properties and analysis (DSC experiments)

Figure 2 shows the DSC curve of the azodicarbonamide used in this work from 300 to 550 K. This curve shows two overlapped and exothermic peaks (p1 and p2) and one endothermic peak (p3), which indicates that the complete thermal decomposition of the ADC takes place in different steps according to the accepted scheme of the three competitive reactions shown in Figure 1 [33].

Figures 3-4 and 5-6 show the DSC curves for the ternary mixtures of EVA-PE-ADC studied varying the PE and ADC content, respectively, and including the curves corresponding to the pure polymers. Table 4 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 the samples studied including pure components, non-foamed 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, corresponding to the transitions of the vinylacetate (VA) domains [9], and a third endothermic peak at 386 K (much smaller) corresponding to the melting of the ethylene domains of the EVA copolymer (totally coincident with the melting process of the pure PE [9] (Table 4).

Analysing the first run for the EVA-PE-ADC ternary mixtures studied (Figures 3-4 and Table 4), the peaks corresponding to the thermal transitions of the polymeric matrix are similar (number of peaks, reaction temperatures and heat) to those corresponding to the pure polymers used and binary mixtures EVA-ADC [9,12], since the ADC is still unaltered at this temperature, but taking into account the expected increase of the area corresponding to the endothermic peak at 386 K, due to the presence of additional PE in the ternary sample.

After melting of the polymer (Figures 3-4), different peaks appear in the first run of the DSC curves, which correspond with the exothermic (primary) and endothermic (secondary) decompositions of the ADC. Most samples show three decomposition peaks (p1-p3) as does the pure ADC (Figure 2). But contrary to the pure ADC, at low concentrations of ADC, the first exothermic peak (p1) is much more evident than the second (p2) that increases with the ADC content (the EVA matrix seems to alter the mechanism of the ADC primary exothermic thermal decomposition). Even more, the sample with the lower content of ADC, EP(10)A(1), shows only two peaks for the ADC decomposition: one exothermic peak at 460K corresponding to the primary decomposition of the ADC (peaks p1 and p2, in Figure 2, are in this case totally overlapped in a wide peak) and another one, endothermic, at 534K (p3).

In Figure 3, it can be observed that the variation of the PE content of the ternary sample does not affect the ADC decomposition temperatures (i.e. temperatures of maximum heat flow rate), and also that the effect of the PE over the base line is 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.

From this Figure 7 (and Figure 4) it can be observed that in the case of the sample with lower ADC content, all the processes (p1-p3) appear 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 when increasing the ADC content, furthermore the peak temperatures of the p1 and p3 processes pass 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 two different effects:

1. The effect of the polymeric matrix in the heat transfer inside the sample that contributes to the delay of the peaks in the samples with PE as compared with pure ADC.
2. According to the azodicarbonamide degradation reactions shown in Figure 1, the heterogeneous reaction (iii) could introduce an auto-accelerating effect [13,14,18,34] when the concentration of ADC in the sample increases, due to 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 accelerate the global decomposition of the ADC, and produce the observed shift to lower temperatures.

With respect to the heat evolved, when the composition of the PE changes (Figure 3), the heat corresponding to the EVA and ADC processes remain almost constant and only the PE melting heat increases lineally with the PE content (Table 4). In the case of the ternary samples varying the ADC content (Figure 4), the heat corresponding to the melting of the polymers remains almost constant regardless of the ADC content. Regarding the extension of the reactions of the ADC decomposition and assuming that, according to the trend observed, the heat evolved in the overlapped peak in the experiment with 1 phr de ADC corresponds mainly to the first process, the heat (J/g_{sample}) of the first exothermic process (p1) presents a continuous decrease with respect to the ADC concentration (Table 4). On the other hand, the heat corresponding to the second exothermic process (p2) increases strongly with the amount of ADC in the sample. Thus, the decomposition of the ADC in the sample with 4 phr of ADC

(Figure 4) presents a behaviour similar (regarding the relative intensity of the peaks p1, p2 and p3) to the one observed before for the pure ADC (Figure 2). The reaction heat corresponding to the third event (p3) increases with the ADC content, but with a lower rate than that corresponding to the linear trend.

On the other hand, there exists a progressive increase of the final base line slope (at high temperatures) when the concentration of the ADC in the sample is increased (Figure 4). This phenomenon can be explained in terms of the heat transfer within the sample: when the ADC content increases, a higher amount of the gases entrapped is obtained, yielding a progressively more foamed sample, which can decrease the observed thermal conductivity and increase the observed base line slope.

DSC of second consecutive runs

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

It can also be observed that, for all the second run experiments, no more significant peaks appear indicating that the ADC was consumed completely during the first run.

On the other hand, the base lines after the polymer peaks for both runs of each sample are very similar. Therefore, the base line slope should depend mainly on the gas that continues encapsulated in the sample and the inert components of the ADC, certifying the closed-cell structure of this kind of foam.

3.2. Physical properties of the foamed samples

In order to confirm the effect of the foaming reaction with a different concentration of ADC, samples were processed in a heated plate press, and the densities of the final foamed product were determined. These results are shown in Table 3. Obviously, the extension of the foaming process increases with the concentration of ADC, as the values of densities indicate. The decreasing of the density with the ADC concentration in the sample is pronounced for the samples studied, showing the important effect of the low melt viscosity of the EVA in the foaming process.

4. Conclusions.

Investigation of the thermal properties of the non-foamed ternary samples showed that the melting point, heat of fusion and crystallinity of the pure polymer are not significantly modified by the presence of the PE and azodicarbonamide, before and after the foaming process. However, the peaks corresponding to the ADC decomposition and also the thermal conductivity of the foamed sample at high temperatures present a strong variation with the ADC content. Regarding the thermal decomposition of the samples, only the foamed samples present a soft evolution in the temperatures of the EVA decompositions when increasing the PE content. As expected, the samples present an important decrease of the density when increasing the ADC content in the initial mixture.

Appendix. Supplementary figures and data, following similar kinetic analysis and modelling as presented in previous papers [9-11], could be found for possible on-line extra information.

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Notation

<i>DSC</i>	Differential scanning calorimetry.
<i>EVA</i>	Polyethylene vinyl acetate copolymer.
<i>PE</i>	Polyethylene or polyethylene domains in EVA.
<i>phr</i>	Parts per hundred of resin.
<i>VA</i>	Vinyl acetate domains in the EVA copolymer.

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FIGURE CAPTIONS

Figure 1. Reactions of decomposition of the azodicarbonamide (from [16,17]).

Figure 2. DSC curve of the azodicarbonamide Unicell-D® (LEDEX S.A.®).

Figure 3. DSC results (1st runs) for the pure polymers and ternary mixtures EVA-PE-ADC varying the PE content (5, 10, and 15 phr).

Figure 4. DSC results (1st runs) for the pure polymers and ternary mixtures EVA-PE-ADC varying the ADC content (1, 2, and 4 phr).

Figure 5. DSC results (2nd runs) for the pure polymers and ternary mixtures EVA-PE-ADC varying the PE content (5, 10, and 15 phr).

Figure 6. DSC results (2nd runs) for the pure polymers and ternary mixtures EVA-PE-ADC varying the ADC content (1, 2, and 4 phr).

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

TABLE TITLES

Table 1. Technical data for LDPE PE003 and EVA PA-539 (ALCUDIA®, Repsol YPF).

Table 2. Technical properties azodicarbonamide Unicell-D® (LEDEX S.A.).

Table 3. Composition, code and density of the EVA-PE-ADC ternary (pressed samples at 175 °C during 10 min).

Table 4 DSC results (1st and 2nd runs) of pure EVA, PE and ternary EVA-PE-ADC mixtures.

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Table 1. 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
Cristallinity (%)	44	18
Density at 23°C (g/cm ³)	0.920	0.937
Melting temperature (°C)	113	90

Table 2. Technical properties azodicarbonamide Unicell-D[®] (LEDEX S.A. [®]).

Properties	Value
wt % ADC	91.1
Decomposition Temperature (°C)	187
% Ashes	5.85
Gas Yield (cm ³ /g) (isothermal at 210°C during 15 min.)	160
Density (g/cm ³)	1.65

Table 3. Composition, code and density of the EVA-PE-ADC ternary (pressed samples at 175 °C during 10 min).

Compositions (phr)					Density (g/cm ³)
EVA	PE	ADC	Code:		
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

Table 4. DSC results (1st and 2nd runs) of pure EVA, PE and ternary EVA-PE-ADC mixtures.

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

 ΔH (J/g) and T (K).

*corresponding to p1+p2 ADC peaks.

♦The values in brackets correspond to the DSC second runs.