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Qualitative study of the evolution of the composition of the gas evolved in the thermal and HY-catalytic oxidative degradation of EVA copolymers

A. Marcilla, A. Gómez-Siurana*, S. Menargues

Dpto. Ingeniería Química, Universidad de Alicante, Apdo. 99, 03080 Alicante, Spain

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Abstract

In this work, a study of the evolution with the temperature of the qualitative composition of the gas evolved in the degradation of ethylene-vinyl acetate (EVA) copolymers under air atmosphere has been carried out using on-line analysis by thermogravimetry (TGA) combined with FTIR spectrometry (TGA/FTIR). Three commercial EVA copolymers were selected, and the results obtained in the experiments performed in the presence and in the absence of HY zeolite are compared. The air atmosphere causes significant differences among the thermal and catalytic pyrolysis. The oxidative pyrolysis involves four main decomposition steps, and each of them also involves different types of reactions. In the first stage, the loss of acetoxi groups of the VA units occurs, with formation of acetic acid, but also CO, CO_2 and carbonylic compounds are produced, increasing the formation of these compounds as the VA content of the copolymer decreases. The second and third decomposition steps, which are better distinguished as the VA content of the copolymer increases, correspond to the degradation of the polymeric chain which results from the previous step, and involves cracking reactions, without O_2 consumption, as well as oxidation reactions. Finally, the fourth reaction step corresponds to the slower oxidation of the carbonous residues formed in the previous stages. The presence of the HY zeolite contributes to a decrease of the CO and CO_2 formation, or in other words, to an increase of the reactions without oxygen consumption.

Keywords: EVA copolymers; Oxidative degradation; TGA; FTIR; HY zeolite

1. Introduction

The importance and interest of the study of the possible recycling of ethylene-vinyl acetate (EVA) copolymers wastes by catalytic pyrolysis or by oxidative thermal degradation, in order to obtain useful energetic products or valuable chemicals has been shown previously [1–3]. The study of the oxidative pyrolysis has added interest since it is always present in the earlier stages of the combustion processes, which are important waste disposal alternatives to be considered on many occasions. Moreover, the ability of the combination of thermogravimetric analysis (TGA) and FTIR spectrometry (TGA/FTIR) as a technique for showing the evolution with the time or the temperature of the composition of the gas evolved in pyrolysis processes has also been demonstrated in bibliographies [4–6], and interesting conclusions related to the nature of the chemical reactions involved in the degradation processes can be obtained from the analysis of the changes in the IR absorption bands corresponding to the functional groups or the chemical bonds present in the volatile products evolved from the TGA furnace.

The mechanisms involved in the thermal oxidation of polymers have been studied by several authors [1,7,8]. According to Allen et al. [8], the thermal oxidation of EVA copolymers proceeds by an initial loss of acetic acid, followed by oxidation and breakdown of the main chain. FTIR spectroscopic analysis of the oxidized EVA shows the evidence for deacetylation followed by the concurrent formation of hydroxil/hydroperoxide species, ketone groups, α–β

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* Corresponding author. Tel.: +34 965903400x2953; fax: +34 965903826.
E-mail address: Amparo.gomez@ua.es (A. Gómez-Siurana).

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unsaturated carbonyl groups, conjugated dienes, lactones and various substituted vinyl groups. The hydroperoxide evolution follows typical auto-oxidation kinetics forming ketonic species. Moreover, García and Font [1] showed that the pyrolysis and combustion processes of an EVA refuse can be perfectly simulated by two series reactions, the second reaction beginning when the first one has almost finished.

Prior results [9] showed that in the oxidative degradation of EVA with MCM-41, four main reaction steps appear, with and without catalyst, and the presence of the catalyst does not seem to significantly affect the peak temperature of the processes, with the only exception of the second one, which is slightly displaced to lower temperatures in the presence of the catalyst. By analogy with the weight loss and the behaviour observed in the EVA pyrolysis process (i.e., in the presence of inert atmosphere), the first decomposition step was related to the acetate groups' loss [3]. The second and third decomposition steps occurred at very close temperatures and produce overlapped peaks in the derivative of the TGA curves (DTG curves), which cannot always be distinguished, and that were associated to the decomposition of the polymeric chain formed once the acetate groups have been eliminated in the first decomposition step, through reactions with and without oxygen consumption. Finally, the last decomposition step was related to a slow oxidation of non-volatile residues formed in the previous steps.

In the present work, the thermal and catalytic degradation of EVA copolymers under air atmosphere has been studied using TGA/FTIR analysis, in order to confirm the different types of reactions involved. In this way, three commercial EVA copolymers with different vinyl acetate (VA) content and melt flow index (MFI), and a HY zeolite have been selected. HY zeolite has been selected because is a catalyst widely studied for the pyrolysis of polymers, and especially for the pyrolysis of EVA [10,11]. In previous works, we have studied the thermal [6] and HY-catalytic pyrolysis [10,11] of EVA copolymers. In the present work, we focus on the thermal and catalytic oxidative pyrolysis of such copolymers in order to study the influence of the oxidative atmosphere and the presence of the catalyst in the pyrolysis process.

2. Experimental

Table 1 shows the main characteristics (as provided by the supplier) of the three commercial EVA studied and the notation used in this work. HY zeolite was prepared by conventional hydrothermal synthesis as described elsewhere [12] and has a pore size of 7.4 Å, a specific area of 750 m^2/g and a molar ratio SiO_2/Al_2O_3 of 12.

Mixtures of powdered copolymer and catalyst of around 5 mg, with around 10% (w/w) of HY zeolite, were pyrolysed in an air atmosphere (21%, v/v, O_2 and 79%, v/v, air; 99.995% minimum purity) using a TGA Netzsch TG209 and at heating rate of 35 K/min. To ensure the measurement of the actual sample temperature, a calibration of the temperature was performed using the Curie-point transition of standard metals. With this equipment, the accuracy of the measurements of the sample temperature was less than 0.5 K, with a resolution of 0.1 K. The nominal resolution of the mass measurement was 0.1 μg. On the other hand, all the experiments were replicated at least twice to ensure its reproducibility.

The output of the inert gas from the TGA was connected to a Bruker Tensor 27 FTIR spectrometer through a heated line, as described in bibliography [13]. The low volumes in the thermobalance microfurnace, transfer line and gas measurement cell permit low carrier gas flowrates to be used and allow the detection of the gases evolved in the pyrolysis process. In all the experiments, the transfer line and the gas measurement cell were maintained at 473 K, in order to avoid the condensation of the less volatile compounds.

3. Results and discussions

3.1. Analysis of the GS and DTG curves

The selection of the analysis conditions (i.e., the heating rate) is a matter of great importance in order to interpret the results provided by the different analytical techniques. According to Berbenni et al. [14], high heating rates are required to obtain adequate concentration in the FTIR spectrometer coupled with the thermobalance to be correctly detected. Nevertheless, in such conditions, the processes observed by the weight loss analysis are likely to be overlapped. Thus, a type of compromise solution must be adopted in order to enable the objective of the study to be reached. In this case, we focus on the analysis of the FTIR data and, consequently, we have selected a high heating rate (i.e., 35 K/min). In a previous work [9] and focusing on the analysis of the weight loss data, we selected 10 K/min that allowed better representation of the processes in the TGA. In this work, we corroborate and clarify previous results obtained.

Fig. 1 shows the TGA and Gram–Schmidt (GS) curves obtained for the oxidative degradation of the three EVA studied, both in the presence and in the absence of HY zeolite.

Table 1
Characteristics of the three commercial EVA copolymers studied

Commercial name of polymer	VA%	MFI[a] (ASTM D1238)	Hardness (Shore A)	Nomenclature
EVA BASF LUPOLEN U-3510-K	13	4	84	EVA0
EVA EXXON ESCORENE UL-15028-CC	27.5	145	69	EVA1
EVA ESCORENE UL-00728	27.5	7	78	EVA2

[a] MFI: melt flow index (g/10 min).