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OXIDATIVE DEGRADATION OF EVA COPOLYMERS IN THE PRESENCE OF CATALYSTS
Comparison among different zeolites and related materials

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A study of the catalytic degradation of EVA copolymers under air atmosphere has been carried out using thermogravimety (TG). Three commercial EVA copolymers and five zeolites and related materials catalysts have been selected. The degradation process in air atmosphere involves four main decomposition steps (as observed in TG), being more complex than the corresponding process in inert atmosphere. The presence of MCM-41, HY and H-β does not seem to noticeably affect to the overall degradation temperature, despite the temperature of maximum reaction rate for the second decomposition step being slightly displaced towards lower temperatures. Contrarily, the presence of HZSM-5 and HUSY zeolites seems to displace the main stage of the oxidative degradation process towards higher temperatures. Moreover, the relative importance of the second and third decomposition step is different depending on the amount and the nature of the zeolite mixed with the EVA sample. The results obtained show that the presence of the catalyst also enhances the formation of the carbonous residue.

Keywords: *degradation, EVA copolymers, MCM-41, oxidative, TG, zeolites*

Introduction

The pyrolysis of organic materials, such as plastic wastes, in the presence of air is an initial step in industrial incinerators. Therefore, the knowledge of such a process is very interesting to provide a better understanding of the behaviour of large scale polymer waste recycling incinerators.

The thermal oxidation of polymers has been studied by several authors [1–3], focusing the interest on the knowledge of the nature and mechanisms of the chemical reactions involved. Some of these studies have been centered in the analysis of the behaviour of ethylene-vinyl acetate copolymers (EVA) [2, 3]. On the other hand, the influence of the presence of zeolite catalysts in the oxidative degradation of EVA has been studied by Marcilla *et al*. [4, 5], showing that in the oxidative degradation of EVA with MCM-41 [4], four main reaction steps appear, 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. The shape of the curves obtained from thermogravimetric analysis (TG) [4], as well as the qualitative analysis by TG/FTIR of the evolution of the gas evolved in the oxidative pyrolysis process [5], suggested that in the first degradation stage, the loss of acetoxy groups of the VA units occurs, with the major formation of acetic acid, CO and CO_2, and also other carbonylic compounds. The second and third decomposition steps correspond to the degradation of the polymeric chain resulting from the previous step and which involves different oxidation reactions. Finally, the fourth reaction step corresponds to the slower oxidation of the carbonous residues formed in the previous stages. The results obtained also indicated that the presence of solid acid catalysts enhances the cracking processes which occur simultaneously to the oxidation and, consequently, reduce the CO and CO_2 content in the gas evolved.

The ability of TG as a tool to study the decomposition of several materials [6, 7] as well as to compare the behaviour of different catalysts in degradation processes has been already demonstrated in the bibliography [4, 8, 9]. The objective of this work is to use this analytical technique for the study of the effect of the concentration of five zeolites and related materials in the degradation of EVA copolymers under air atmosphere. With this purpose, three commercial EVA copolymers with different vinyl acetate (VA) content and melt flow index (MFI) have been selected. The five materials have been chosen among materials with catalytic activity for the pyrolysis of polymers, and trying to screen some range of chemical and structural properties. With this purpose, HY, HZSM-5, H-β and HUSY zeolites and mesoporous MCM-41 have been selected. Previous studies carried out using these materials as catalysts for the pyrolysis of

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EVA [10, 11] showed a clear relationship between the solid characteristics and the corresponding catalytic activity, covering a wide range. In this work, the objective was to study the effect of these catalysts on the oxidative degradation of EVA and compare that effect with that observed in the degradation processes carried out under N_2 and air atmospheres. When these materials were studied as catalysts for the pyrolysis of EVA copolymers [10, 11], the following decreasing order of the catalytic activity was observed: MCM-41>H-β>HY>HUSY>HZSM-5. This order was explained considering that the catalytic activity increases as the specific surface, the accessibility of the active sites located in the inner of pores and the acidity of the material increase, and according to the following considerations [10, 11] (Table 1 for the characteristics of the catalysts):

- MCM-41 has the higher activity due to its greater pore size, which provides a considerable specific surface and minimizes the influence of the eventual steric hindrances.
- The lower activity of HZSM-5 is in agreement with the lower pore size and specific area.
- HY and H-β have intermediate activities, according to its intermediate values of specific area and SiO_2/Al_2O_3 ratios, but H-β showing higher external surface area [10].
- The unexpected low activity of HUSY, despite its high acidity (i.e., its low SiO_2/Al_2O_3 ratio) and relatively high specific surface, is related to the existence of some early deactivation processes occurring during the first step of EVA pyrolysis, with the result that the catalyst reaches the second decomposition step (i.e., the main decomposition step) with a fraction of the initial active sites deactivated.

Table 1 Characteristics of the catalysts studied

Molecular sieve	Pore size[1]/ Å	SiO_2/Al_2O_3[2]	Specific area[3]/ $m^2\ g^{-1}$
H-ZSM-5	5.1×5.5 5.3×5.6	30	420
HUSY	7.4	6	790
HY	7.4	12	750
H-β	5.6 7.7×6.6	25	625
MCM-41	27	43	1357

[1]Nominal values for HZSM-5, HUSY, HY and H-β, measured by the BJH method from the N_2 adsorption isotherm at 77 K for MCM-41. [2]Determined by XRF. [3]Measured by BET method from N_2 adsorption isotherm at 77 K

Experimental

Table 1 shows the structural characteristics of the five catalysts selected and Table 2 shows the main characteristics (as provided by the supplier) of the three commercial EVA studied and the notation used in this work. HY, HUSY and H-β zeolites and mesoporous MCM-41 were synthesized as described elsewhere [10] and HZSM-5 zeolite was supplied by Grace GmbH and Co. KG. The acidity of these materials is related to the respective SiO_2/Al_2O_3 ratios (Table 1), and is in the following decreasing order: HUSY>HY>H-β>HZSM-5>MCM-41 [10]. For each EVA+catalyst system, the influence of the catalyst content has been studied, and three mixtures with different catalyst percentage have been analyzed. The catalyst content was varied in order to study the eventual influence of the zeolite presence as well as the effect of the concentration, as will be seen in the next section.

Mixtures of powdered copolymer and catalyst of around 5 mg were pyrolysed in an air atmosphere (21% O_2 and 79% (*v*/*v*) air, 99.995% minimum purity) using a TG Netzsch TG209 and at a heating rate of 10 K min^{-1}. The samples were placed in open Al_2O_3 pans and a flow rate of carrier gas of around 0.5 cm^3 STP s^{-1} was used. To ensure the measurement of the actual sample temperature, a calibration was performed using the Curie-point transition of standard metals. Table 3 presents the experiments carried out, and the polymer, catalyst, concentration and peak temperatures observed.

Results and discussion

Study of EVA0 containing systems

Figures 1a–5a, respectively, show the TG curves obtained at 10 K min^{-1} for EVA0 and three different mixtures of EVA0 with each one of the catalysts studied in this work, whereas Figs 1b–5b show the corresponding derivative curves (DTG curves), and Table 3 reports the corresponding peak temperatures. As

Table 2 Characteristics of the three commercial EVA copolymers studied

Commercial name of polymer	VA/%	MFI* (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

*MFI=melt flow index (g/10 min)

Table 3 Temperatures of maximum decomposition rate for each decomposition step in the oxidative degradation of several EVA+ catalyst mixtures

EVA sample	Catalyst	Catalyst content/mass%	Temperature/K			
			1st step	2nd step	3rd step	4th step
EVA0	no catalyst	–	619.4	699.0	730.2	803.5
	MCM-41	5.8	622.5	694.3	725.9	810.2
	MCM-41	12.6	622.6	686.2	722.2	802.1
	MCM-41	19.2	622.5	686.3	721.8	802.1
	HY	5.8	614.4	691.7	714.8	804.5
	HY	16.6	618.5	684.2	726.6	800.8
	HY	22.4	614.7	695.9*	695.9*	800.9
	H-β	5.3	600.0	678.8	714.5	783.1
	H-β	10.1	607.7	679.0*	679.0*	791.3
	H-β	19.8	611.6	682.8	720.4	791.3
	HZSM-5	2.9	615.6	674.4	726.1	805.7
	HZSM-5	12.5	617.5	676.6	720.2	811.8
	HZSM-5	14.7	620.5	695.0	710.7	809.7
	HUSY	2.3	619.3	678.4	725.8	809.5
	HUSY	6.7	623.2	694.4	721.9	809.5
	HUSY	14.6	619.4	686.2	733.5	866.3
EVA1	no catalyst	–	617.4	720.7*	720.7*	808.7
	MCM-41	5.7	626.5	718.3*	718.3*	810.2
	MCM-41	15.3	618.6	714.2*	714.2*	802.2
	MCM-41	34.4	622.1	681.9*	681.9*	805.7
	HY	4.9	618.7	711.6	727.1	806.8
	HY	6.5	624.3	713.6	728.8	804.9
	HY	14.4	617.4	706.2	729.5	807.6
	H-β	10.4	614.7	714.1	735.8	810.2
	H-β	12.4	614.8	718.2	730.2	806.3
	H-β	26.9	614.8	722.1*	722.1*	806.4
	HZSM-5	7.3	627.0	729.9*	729.9*	829.8
	HZSM-5	23.5	617.3	715.9	731.6	815.6
	HZSM-5	37.7	621.2	711.9	735.7	811.6
	HUSY	4.3	623.1	718.2	726.1	813.7
	HUSY	9.2	619.3	714.3	729.9	809.7
	HUSY	22.3	619.2	718.1	730.0	809.6
EVA2	no catalyst	–	622.8	718.9*	718.9*	802.3
	MCM-41	2.5	622.7	718.4	726.3	818.3
	MCM-41	13.0	621.7	705.2*	705.2*	813.4
	MCM-41	18.2	622.7	710.2*	710.2*	818.4
	HY	2.5	619.7	722.6*	722.6*	822.1
	HY	9.5	614.6	703.5*	703.5*	812.5
	HY	22.7	620.4	709.4	724.8	802.8
	H-β	2.1	630.6	722.6	730.4	814.4
	H-β	8.5	622.8	714.4	726.3	818.4
	H-β	21.6	629.6	717.4*	717.4*	813.3
	HZSM-5	11.6	627.1	718.4	726.2	809.8
	HZSM-5	19.0	627.2	714.1	725.9	817.8
	HZSM-5	33.3	627.1	710.3*	710.3*	821.9
	HUSY	13.7	625.2	735.7*	735.7*	823.6
	HUSY	24.3	623.2	741.5*	741.5*	837.9
	HUSY	31.4	623.1	722.1*	722.1*	809.5

*results of the overlapping between 2nd and 3rd peaks of the DTG curve

can be seen, all the cases show the existence of the already known four main reaction steps [4, 5]. As has been reported previously [4, 5], the analogy with the mass loss and the behaviour observed in an EVA pyrolysis process (i.e., under inert atmosphere) as well as measurements by TG/FTIR of the gas evolved in the oxidative degradation process, allow us to relate the first decomposition step mainly to the acetate groups loss. According to Figs 1b–5b, this step is almost not affected by the presence of the zeolite, and the temperature of maximum reaction rate for this stage, obtained from the temperature of the first peak of the DTG curves, is around 600–623 K. No attempt to analyze the differences among the temperatures for the first degradation step has been carried out because of the width of the corresponding DTG peaks difficulting the measurement of the peak temperatures; despite this, it seems that this step occurs at lower temperatures in the presence of H-β (Table 3).

The second and third decomposition steps occur at very close temperatures and in many cases produce overlapped peaks in the DTG curves, which cannot always be clearly distinguished. Figures 1b to 3b show that, in the thermal process and in the presence of MCM-41 and HY and H-β zeolites, the third decomposition step appears in the DTG curves as a shoulder at around 715–730 K, and its location seems to be independent of the presence of the zeolite. Contrarily, in the presence of HZSM-5 and HUSY zeolites, the main peak of the DTG curves corresponds to the third decomposition step, and also appears at around 711–734 K, whereas in these cases the shoulder is related to the second stage of the process. According to the previous results [4, 5], the second and third decomposition steps could be associated to the decomposition of the polymeric chain formed once the VA groups have been eliminated in the first decomposition step, and occur yielding CO_2 though reactions with a different degree of oxidation, being the complete oxidation processes more predominant in the third step than in the second one.

As can be seen in Figs 1–3, mixtures of EVA0 with MCM-41, HY and H-β show similar behaviour, and the presence of the catalyst does not seem to significantly affect the temperature of the process, with the only exception of the second degradation step, which is slightly displaced to lower temperatures in the presence of the catalyst. This displacement increases as the catalyst percentage increases, and can be related to the existence of catalytic cracking reactions, occurring with low O_2 consumption. The temperature of maximum decomposition rate for each decomposition step in these systems is shown in Table 3. As can be seen, the corresponding ranges are:

- First step: at around 600–623 K.
- Second step: 699 K for the pure EVA0 and in the range 679–694 K, for the different mixtures of EVA0 and the zeolite.
- Third step: at around 715–727 K.
- Fourth step: at around 783–866 K.

As commented previously, the DTG peak corresponding to the third decomposition step appears as a shoulder, overlapped with the second step DTG peak, indicating that the main mass loss related to the degradation process occurs through the second reaction step.

Mixtures of EVA0 with HZSM-5 or HUSY zeolites showed different behaviour to the above-mentioned for mixtures with the other selected catalysts. As can be seen in Figs 4 and 5, the TG characteristics (i.e., the peak temperatures and the shape of the curves) observed for the first and fourth decompo-

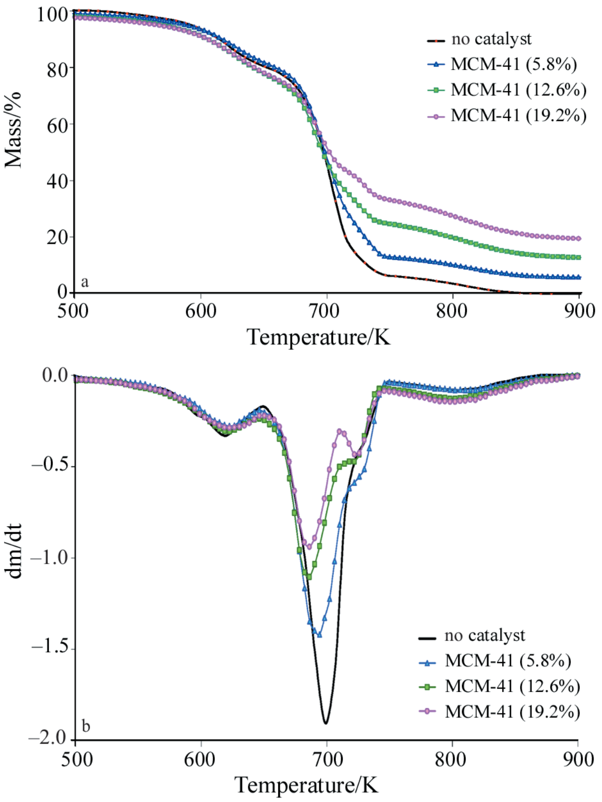

Fig. 1 a – TG and b – DTG curves obtained for different EVA0+MCM-41 mixtures at 10 K min^{-1}

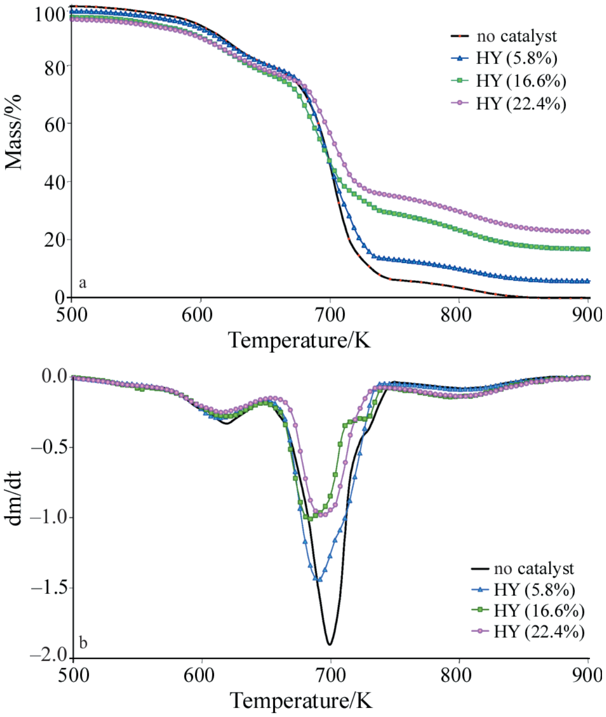

Fig. 2 a – TG and b – DTG curves obtained for different EVA0+HY mixtures at 10 K min^{-1}

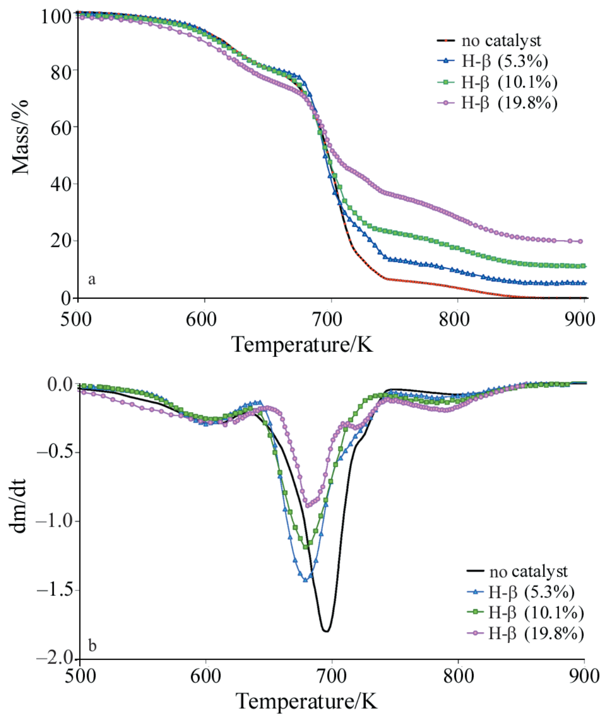

Fig. 3 a – TG and b – DTG curves obtained for different EVA0+H-β mixtures at 10 K min^{-1}

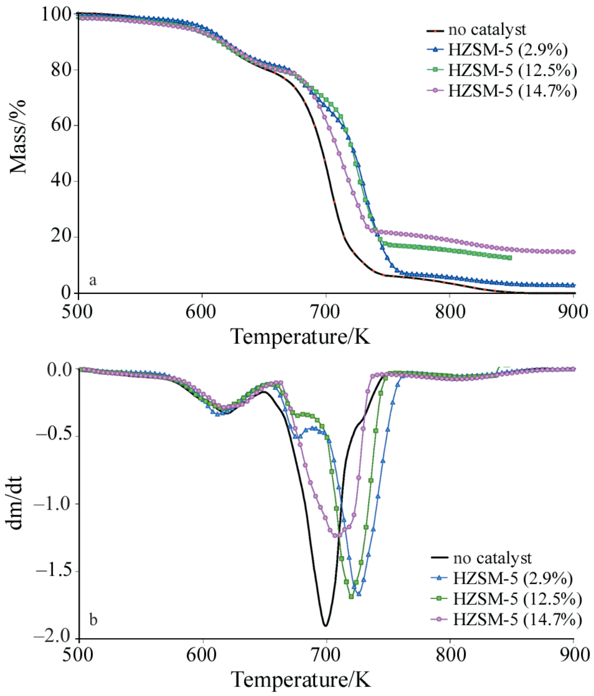

Fig. 4 a – TG and b – DTG curves obtained for different EVA0+HZSM-5 mixtures at 10 K min^{-1}

sition steps are close to those described for the previous systems. However, the second and third decomposition steps show noticeable differences. In fact, in the presence of HZSM-5 and HUSY zeolites, the main mass loss associated to the oxidative degradation process occurs through the third decomposition step. Despite the fact that the overlapping between the DTG peaks corresponding to the second and third decomposition steps makes a detailed analysis of the curves difficult, some considerations may be taken into account. In both cases, the temperature of maximum reaction rate for the second degradation step is at around 674–695 K, in the same range as the values observed for the previous systems, and no clear correlation with the catalyst content has been observed in the presence of HUSY zeolite, despite the fact that the peak temperature seems to increase as the catalyst content increases. It must be noted that the peak corresponding to the second step in the presence of HZSM-5 and HUSY – as occurred with that corresponding to the third step in the presence of MCM-41, HY or H-β – are a shoulder on the main peak, and thus, they are very influenced by the location or the displacements of the main peak.

For the EVA0+HZSM-5 mixtures (Fig. 4), the DTG peak temperature corresponding to the third decomposition step seems to decrease as the HZSM-5 content increases, and appears in the range 711–726 K. The EVA0+HUSY mixtures (Fig. 5) show that the temperature of maximum reaction rate for the third step is around 722–734 K, and no clear relation between temperature and catalyst content has been observed. Table 3 shows the DTG peak temperatures corresponding to each peak in the different systems studied.

In accordance with the previous comments, and from Figs 1–5, the general conclusion is that, despite the fact that the presence of MCM-41 or HY and H-β zeolites slightly advances some processes involved in the oxidative degradation of EVA0 (i.e., those involved in the second decomposition step), these materials do not noticeably modify the overall temperature of the processes, which are very similar to the oxidative degradation in the absence of catalyst. However, the presence of HZSM-5 or HUSY causes a different behaviour, modifying the relative importance of the chemical processes involved in each degradation step, and increasing the differences with respect to the thermal process, which occurs at an overall temperature lower than in the presence of these zeolites, thus revealing noticeable differences in the mechanisms of reaction with respect to the former group of catalysts. The differences between the behaviour of the group of MCM-41, HY and H-β and the group of HZSM-5 and HUSY were also observed previously from TG and TG/FTIR data corresponding to EVA pyrolysis experiments [10, 11], and were related to the lower catalytic effect of HZSM-5 and HUSY zeolites on the cracking reactions occurring without oxygen consumption.

The possible formation of cross-linked structures in the thermal pyrolysis of EVA [12] or in the

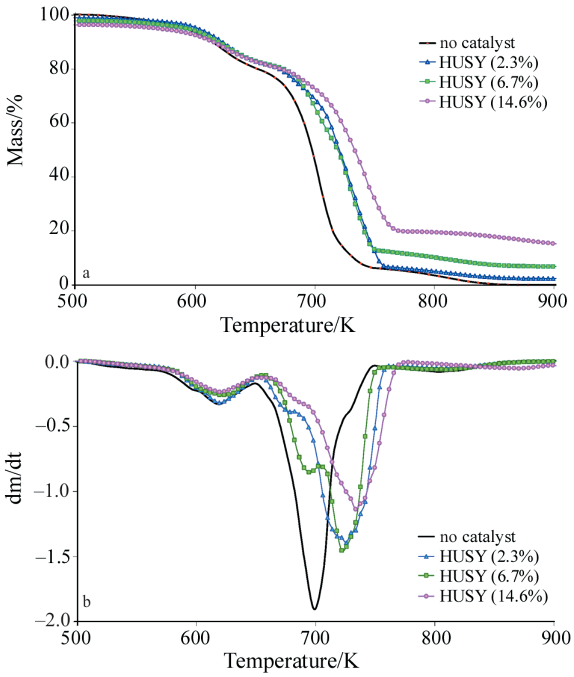

Fig. 5 a – TG and b – DTG curves obtained for different EVA0+HUSY mixtures at 10 K min^{-1}

catalytic pyrolysis of EVA [13] has been reported in the literature, and in the case of the oxidative degradation of EVA, could be enhanced by the known formation of hydroperoxides in the first stages of the oxidative degradation process [1, 2]. On the other hand, as has been above-commented in the Introduction section, the decrease of the catalytic activity of HUSY zeolite in the pyrolysis of polymers, related to the fast deactivation processes reported previously [14], as well as the low catalytic activity of the HZSM-5 zeolite in the pyrolysis of EVA, related to its low pore size, low specific area and relatively high SiO_2/Al_2O_3 ratio (Table 1) [11], may support the differences observed in the case of HZSM-5 and HUSY. In this way, for these materials, the active sites could have enough catalytic activity to initiate the chain reactions involved in the degradation processes, but not to permit the fast degradation of the polymeric chains. In these cases, the croslinking processes could play a role as a termination stage of the chain reaction mechanisms.

According to Figs 1–5, the last decomposition step is very slow (i.e., the mass loss occurs through a wide range of temperature – or time) and gives rise to very wide peaks in the DTG curves. Therefore, the assignment of the temperature of maximum decomposition rate in this case is more uncertain than in the previous ones. However, it does not seem to be affected by the presence of the catalyst and always occurs around 783–866 K. This step must be related to a slow oxidation of non volatile residues formed in previous steps.

Comparison among different EVA containing systems

TG and DTG curves corresponding to the oxidative degradation of EVA1 and EVA2 show a general behaviour similar to the above-commented for EVA0. However, there are some interesting differences, which can be attributed to the specific characteristics of the EVA considered or to the nature of the interaction between the two species, the EVA and the zeolite. These differences are described in the following paragraphs. As an example, Figs 6 and 7 show, respectively, the TG and DTG curves corresponding to different mixtures of EVA1 and EVA2 with the five catalysts selected in this work. In order to reduce the number of figures shown in this paper, only a mixture for each EVA+catalyst system has been selected and considered as representative of the other mixtures studied, with different catalyst percentage. When the results obtained suggested a possible influence of the catalyst content on the behaviour of the system, it is mentioned. Table 3 shows the corresponding DTG peak temperatures.

An overview of Figs 6 and 7 shows that in both cases, i.e., for EVA1 and EVA2 systems, it is difficult to observe the existence of the two degradation steps involved in the main mass loss stage (i.e., those previously described as second+third decomposition steps) from the TG and DTG curves corresponding to the thermal process. Nevertheless, it can be observed in some EVA+catalyst systems, thus showing that these processes, which clearly appeared differentiated in the systems including EVA0, are also involved in the oxidative degradation of EVA1 and EVA2. These two copolymers have higher VA content than EVA0 (Table 2), and it can be concluded that this is responsible for the above-mentioned differences and for the increase of the overlapping among the reaction steps. Therefore, the results obtained in this work suggest that the increase of the PE content in the EVA copolymers contributes to an increase in the differentiation between the processes involved in the main degradation step in the oxidative pyrolysis of EVA. In good agreement with these comments, Figs 6 and 7 show that in both cases, despite the fact that some global displacement of the main DTG peaks towards lower temperatures in the presence of MCM-41, HY and H-β is observed, the effect of the presence of HZSM-5 and HUSY on the main peak of the DTG curves is lower for EVA1 and EVA2 than for EVA0.

As Table 3 reflects, the temperatures of maximum decomposition rate obtained from the DTG peaks of Figs 6 and 7 are the following, and with the only exception of the second decomposition step, there are no significant differences between EVA0, EVA1 and EVA2 containing systems:

- First step: at around 614–630 K.

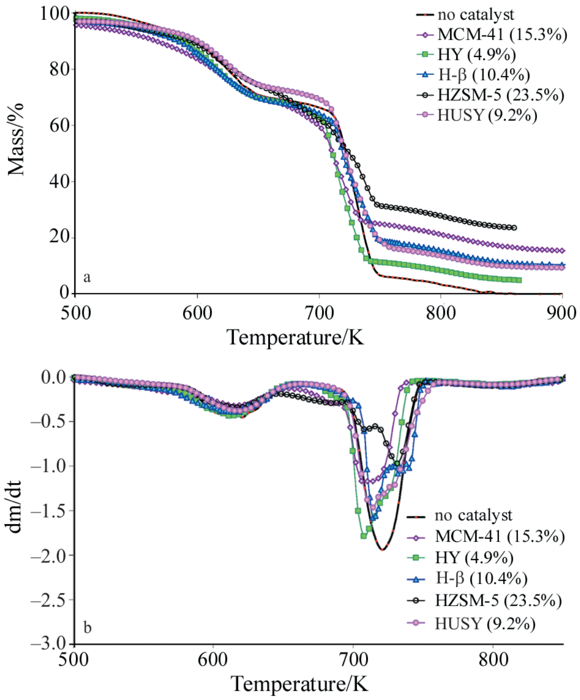

Fig. 6 a – TG and b – DTG curves obtained for different EVA1+catalyst mixtures at 10 K min^{-1}

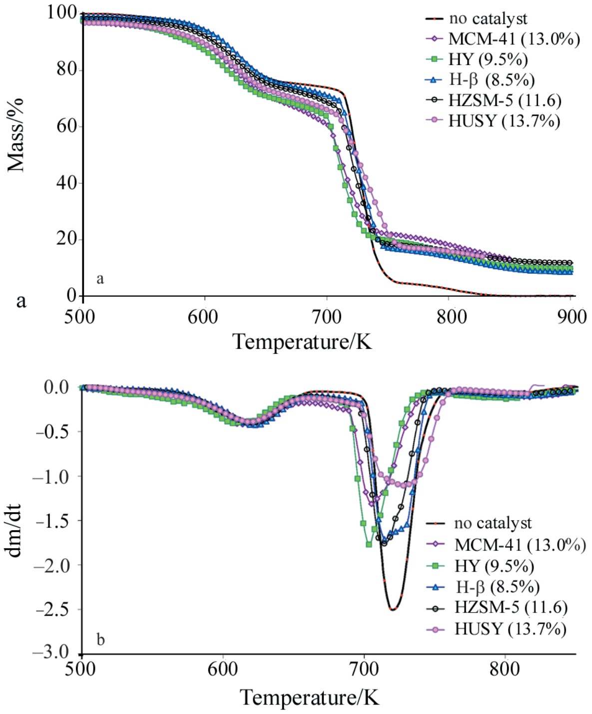

Fig. 7 a – TG and b – DTG curves obtained for different EVA2+catalyst mixtures at 10 K min^{-1}

- Second step (excluding the overlapped peaks): at around 706–723 K. No significant differences have been observed between EVA1 and EVA2 containing systems, but this reaction step occurs at higher temperatures than that observed for the EVA0 containing systems. This fact reflects the decrease of the sensitivity to the action of the catalysts over cracking processes as the VA content of EVA increases [15].
- Third step: at around 725–736 K.
- Fourth step: at around 802–837 K.

As commented previously, despite the increase of the overlapping between the DTG peaks corresponding to the second and third degradation steps, which difficults distinguishing between them, some systems show the existence of the above-mentioned shoulders. However, whereas in the EVA0 containing systems, the main mass loss in the presence of MCM-41, HY and H-β proceeds through the second step, and in the presence of HZSM-5 and HUSY, through the third step, in the range of concentration studied, in some of the EVA1 and EVA2 containing systems, the zeolite concentration may also affect the relative extension of the different types of reactions involved in the oxidative degradation process. As an example, in the presence of HY zeolite, when the catalyst percentage is low, the main mass loss occurs through the second decomposition step, but when the catalyst content is high enough, this tendency clearly changes (Fig. 8), and the third step seems to be more important. This situation has also been observed in the cases of EVA2+HY, EVA1+H-β and EVA1+HUSY.

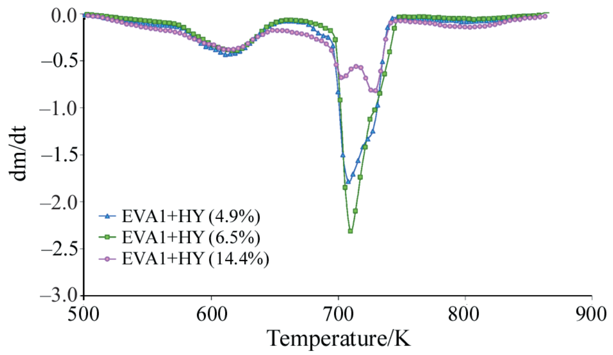

Fig. 8 DTG curves obtained for different EVA1+HY zeolite mixtures at 10 K min^{-1}

A marked increase of the complexity of the process is worth noting, reflected by the appearance of a tail in the range 655–695 K, that appears in some systems (i.e., EVA1+HY, EVA1+HZSM-5, EVA2+MCM-41, EVA2+HZSM-5, EVA2+HUSY), being specially noticeable in the case of EVA1+HZSM-5 (Fig. 6). This effect seems to increase when the zeolite content increases.

Study of the residue formation

The non-volatile residue remaining in the sample holder of the thermobalance when the last decomposition step starts has been directly obtained by reading in the corresponding TG curves, and the amount of residue at this stage has been calculated as follows:

$$\text{residue\%}=\frac{m_{\text{beginning of the last step}}-m_{\text{final residue}}}{m_{\text{initial}}\ \text{of EVA; dry basis}}\cdot 100\%$$

Figure 9 shows the plot of % residue *vs*. the catalyst content obtained for each EVA+catalyst system. This residue represents the low-volatile compounds formed in the preceding reaction steps, which are slowly oxidized at around 800 K, and may be considered, in some way, similar to coke formed in the pyrolysis processes.

As can be seen in Fig. 9a, the residue oxidized in the fourth decomposition step of the oxidative degradation of EVA0 in the presence of MCM-41, HY and H-β increases as the catalyst content increases, being higher in the presence of H-β zeolite, whereas HZSM-5 and HUSY zeolites do not noticeably modify the amount of non-volatile residue. A relatively similar behaviour has been observed in the oxidative degradation of EVA1 and EVA2 (Figs 9b and c). In the case of EVA1 (Fig. 9b), the effect of the catalyst, increasing the amount of non-volatile residue at the beginning of the fourth reaction step, is only noticeable when the catalyst content is higher than 10 mass/mass%. In this case, the increase of the residue is also more favoured by MCM-41, HY and H-β but contrarily to the EVA0 case, besides HZSM-5 and HUSY increases enough the residue formation. In the case of EVA2 (Fig. 9c), when the catalyst content is lower than 15 mass/mass%, the behaviour is similar to the above-mentioned for EVA1, with a noticeable effect of HZSM-5 and a negligible effect of HUSY. The effect of HUSY zeolite only appears above 15 mass/mass%, and the influence of HUSY on the non-volatile residue amount increases noticeably as the catalyst content increases, reaching values similar to HUSY above 30 mass/mass%. Finally, in some cases, it seems that a kind of saturating effect may appear, and from certain zeolite content, no increase of the non-volatile residue is observed. In the range of composition studied for each system, this behaviour is clearly showed by EVA0+HUSY and EVA2+HY systems.

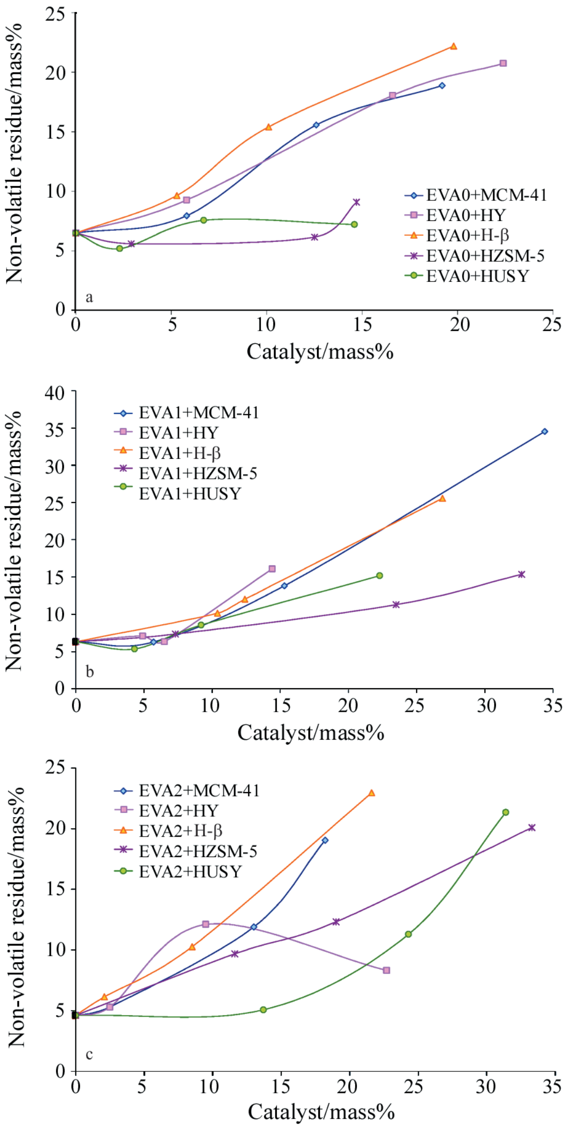

Fig. 9 Non-volatile residue amount formed at the beginning of the fourth decomposition step *vs*. catalyst content in the EVA+catalyst mixtures. a – EVA0, b – EVA1 and c – EVA2

Conclusions

In this work, a study of the oxidative degradation of EVA copolymers has been carried out and the effect of the presence and concentration of five catalysts have been analyzed. The results obtained show the existence of a complex process which involves at least four main decomposition steps, each of them also involving different types of reactions. The presence of MCM-41, HY and H-β does not seem to affect the overall degradation temperature, despite the temperature of maximum reaction rate for the second decomposition step being slightly displaced towards lower temperature, probably due to the existence of the reactions with low O_2 consumption, which are similar to the reactions occurring during the pyrolysis process, and thus which may be affected by the presence of the acid active sites of the solid. Contrarily, the presence of HZSM-5 and HUSY zeolites seems to displace the third stage of the oxidative degradation process towards higher temperatures. Moreover, the relative importance of the second and third decomposition step, as well as the extension of the reactions involved in the oxidative pyrolysis depend on the nature and concentration of the catalyst mixed with the EVA sample.

Finally, the results obtained in this work show that the residue oxidized in the fourth decomposition step of the oxidative degradation of EVA in the presence of MCM-41, HY and H-β increases as the catalyst content increases. The effect of the presence of HZSM-5 and HUSY zeolites seems to be more dependent on the EVA characteristics, and do not noticeably modify the amount of non-volatile residue in the case of EVA0. In some cases, a kind of saturating effect may appear, and from certain zeolite, no increase of the non-volatile residue is observed.

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