

## THERMAL DECOMPOSITION OF COPOLYMERS FROM ETHYLENE WITH SOME VINYL DERIVATIVES

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The thermal degradation of ethylene-vinyl acetate (EVA), ethylene-vinyl-3,5-dinitrobenzoate (EVDNB) and ethylene-vinyl alcohol (EVAL) copolymers have been studied using differential thermal analysis (DTA) and thermogravimetry (TG) under isothermal and dynamic conditions in nitrogen. Thermal analysis indicates that EVA copolymers are thermally more stable than EVDNB samples. The degradation of the copolymers considered occurs as an additive degradation of each component polyethylene (PE) and poly(vinyl acetate) (PVA), poly(vinyl-3,5-dinitrobenzoate) (PVDNB) or poly(vinyl alcohol) (PVAL). The apparent activation energy of the decomposition was determined by the Kissinger and Flynn–Wall methods which agree well.

**Keywords:** activation energy, ethylene-vinyl acetate copolymers, ethylene-vinyl alcohol copolymers, ethylene-vinyl-3,5-dinitrobenzoate copolymers, thermal degradation

### Introduction

The thermal degradation behaviour of EVA copolymers has been studied by several researchers [1–10]. Thermal degradation of EVA occurs in two stages, in the first one acetic acid is lost (573–673 K), that is enhanced with increasing in vinyl acetate content [1, 3, 4]. The second step involves random chain scission (703 K) [1]. The mechanism of evolution of acetic acid is based on ester pyrolysis, which takes place through a cross-linking mechanism [11], and the process appears to be autocatalytic [4]. In the second decomposition step butene, ethylene, methane and acetaldehyde are produced [3, 4]. The thermal analysis of some EVAL copolymers with high content of vinyl alcohol has been reported [12] and the apparent kinetic parameters are determined. The thermal degradation of some other polyethylene copolymers, has also been reported [1, 4, 13].

The present study is devoted to comparison of the thermal degradation of EVA copolymers, EVDNB copolymers and EVAL copolymers using TG and DTA, the kinetic parameters are evaluated on the basis of isothermal and dynamic degradation data. FTIR spectroscopy has been used qualitatively to study the structure of the residue produced and elucidate the thermal degradation mechanism.

### Experimental

#### Polymer samples

EVA copolymers (vinyl acetate contents 6, 10 and 14 mol%) were supplied by Repsol-YPF. EVAL copolymers containing 50 mol% vinyl alcohol was supplied by Polysciences, those containing 56 and 73 mol% vinyl alcohol by Aldrich, and those with 6, 10 and 14 mol% vinyl alcohol were obtained by transesterification of EVA copolymers with sodium methoxide as described elsewhere [14]. EVDNB copolymers were prepared by esterification of EVAL copolymers with 3,5-dinitrobenzoyl chloride in a homogeneous medium with N,N'-dimethylpropyleneurea(1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone) (DMPU) as solvent. Experimental details of this synthesis are described elsewhere [14]. Details of the copolymers used in this work are given in Table 1.

#### Thermal analysis

The thermal degradation of the copolymers was studied by thermogravimetric analysis (TG), derivative thermogravimetric analysis (DTG) and differential thermal analysis (DTA) using a Polymer-Laboratories STA-1000 system. All the analysis were carried out with 8–12 mg of samples on platinum pans in nitrogen (28 mL min<sup>-1</sup>).

Thermogravimetric analysis under dynamic conditions was carried out at heating rates of 2, 5, 10 and

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**Table 1** Peak temperatures in DTA thermograms for EVA, EVDNB and EVAL (Heating rate 20 K min<sup>-1</sup>)

Polymer	Ester/ Alcohol/ mol%	Exotherm temperatures/K			Endotherm I temperatures/K			Endotherm II temperatures/K		
		Initial	Peak	Final	Initial	Peak	Final	Initial	Peak	Final
EVA6 <sup>a</sup>	6	–	–	–	565	624 638 <sup>f</sup>	673	673	755 719 <sup>f</sup>	789
EVA10 <sup>a</sup>	10	–	–	–	565	606 636 <sup>f</sup>	683	683	759 789 <sup>f</sup>	799
EVA14 <sup>a</sup>	14	–	–	–	566	604 616 <sup>g</sup> 636 <sup>g</sup>	683	686	750 755 <sup>g</sup> 760 <sup>g</sup> 787 <sup>f</sup>	798
EVDNB6 <sup>b</sup>	6	530	587	637	673	726 <sup>f</sup> 764 785 794	812	–	–	–
EVDNB10 <sup>b</sup>	10	543	615	–	663	738 <sup>h</sup> 764 <sup>h</sup>	–	–	790 <sup>f</sup> 799	824
EVDNB14 <sup>b</sup>	14	530	–	–	929	717	–	–	785	816
EVAL6 <sup>c</sup>	6	–	–	–	–	–	–	703	758	792
EVAL10 <sup>c</sup>	10	–	–	–	626	651	–	703	761	788
EVAL14 <sup>c</sup>	14	–	–	–	626	661	–	–	758	788
EVAL50 <sup>d</sup>	50	–	–	–	573	662	711	–	–	–
EVAL56 <sup>e</sup>	56	–	–	–	616	673	729	–	–	–
EVAL73 <sup>e</sup>	73	–	–	–	597	668	703	–	–	–

<sup>a</sup>Repsol YPF; <sup>b</sup>Esterification; <sup>c</sup>Transesterification; <sup>d</sup>Polysciences; <sup>e</sup>Aldrich; <sup>f</sup>Shoulder; <sup>g</sup>Endotherm split into three peaks;

<sup>h</sup>Endotherm split into two peaks

20 K min<sup>-1</sup> recording the mass loss and the rate of mass loss as a function of temperature. The following characteristics were determined from the thermogravimetric curves: the initial thermal decomposition temperature ( $T_i$ ), the temperature of maximum rate of the first reaction step ( $T_{max}^1$ ), the temperature of maximum rate of the second reaction step ( $T_{max}^2$ ) and the mass loss for the first and the second reaction step ( $W^1$ ,  $W^2$ ).

In isothermal thermogravimetric analysis the sample was heated at 40 K min<sup>-1</sup> until the experimental temperature was reached, taking as zero time the moment at which the temperature of the system was stabilized.

Differential thermal analysis was carried out using a heating rate of 20 K min<sup>-1</sup>.

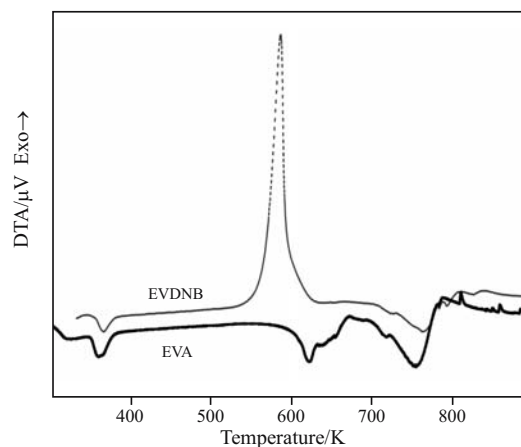
#### Fourier transform infrared spectroscopy

ATR-FTIR spectroscopy was done using a Nicolet Magna 560 spectrometer equipped with an ATR device with zinc selenide (ZnSe) crystal. The spectra were taken as an average of 50 scans at 8 cm<sup>-1</sup> resolution.

## Results and discussion

### Thermal analysis by DTA

DTA curves of EVA, EVDNB and EVAL copolymers are shown in Figs 1 and 2. The peak temperatures for the various thermal effects are given in Table 1.

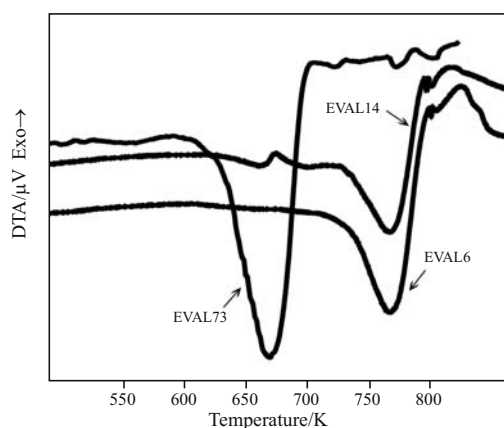


**Fig. 1** DTA curves of EVA6 and EVDNB6 copolymers. Heating rate 20 K min<sup>-1</sup>

**Table 2** Characteristics of thermal degradation of EVA, EVDNB and EVAL. Heating rate, 20 K min<sup>-1</sup>

Polymer	Ester/Alcohol		$T_i$ /K	$T_{max}^1$ /K	$W^1$ /%	$T_{max}^2$ /K	$W^2$ /%	Residue/%	Char/%
	mol%	mass%							
EVA6	6	16	582	644	13	755	87	0	0
EVA10	10	25	573	637	20	757	80	0	0
EVA14	14	33	581	641	23	750	74	3	2
EVDNB6	6	35	527	590	17	765	65	18	14
EVDNB10	10	49	526	577	39	760	36	25	19
EVDNB14	14	58	528	573	66	751	12	26	22
EVAL6	6	9	623	760	100	–	–	0	0
EVAL10	10	15	643	761	95	–	–	5	5
EVAL14	14	20	638	760	98	–	–	2	2
EVAL50	50	61	573	663	82	743	16	1	1
EVAL56	56	67	610	673	80	743	8	1	1
EVAL73	73	81	605	673	80	743	8	0	0

$T_i$ : initial thermal decomposition temperature,  $T_{max}^1$ : temperature of maximum rate of the first reaction step,  $W^1$ : mass loss for the first reaction step,  $T_{max}^2$ : temperature of maximum rate of the second reaction step,  $W^2$ : mass loss for the second reaction step

**Fig. 2** DTA curves of EVAL copolymers. Heating rate 20 K min<sup>-1</sup>

For EVA copolymers, the endotherm in the temperature range 563–673 K corresponds to the evolution of acetic acid, and the endotherm in the temperature range 673–798 K corresponds to the main chain degradation [1]. As can be seen the two thermal decomposition processes occur at similar temperatures for all the samples, regardless of the amount of VA.

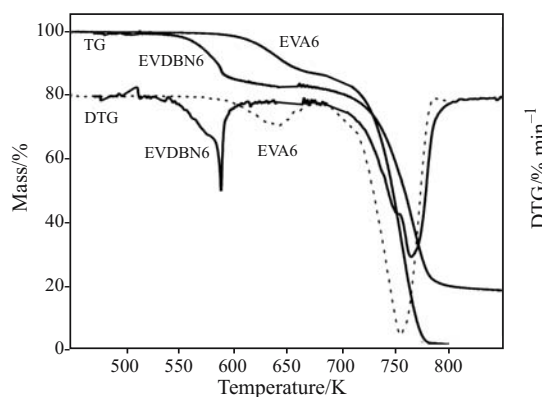
In the case of EVDNB copolymers, DTA traces show an exotherm, and an endotherm. DTA curve of the copolymer with 6 mol% VDNB shows an exotherm with a maximum at 587 K and an endotherm with a maximum at 764 K. For EVDNB copolymers with 10 mol% VDNB or higher, DTA curves show the exotherm, a fast liberation of heat, with a maximum at 573 K and two endotherms. The lower thermal stability of EVDNB copolymers is apparent.

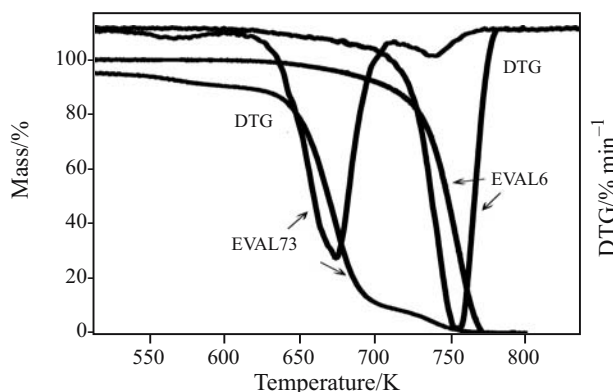
For EVAL copolymers, the endotherm in the temperature range 573–723 K corresponds to the vinyl

alcohol component, while the endotherm observed in the temperature range 703–788 K corresponds to the ethylene component.

#### Thermal analysis by dynamic TG and DTG

Figure 3 shows thermogravimetric and differential thermogravimetric curves of the EVA and EVDNB copolymers, obtained at 20 K min<sup>-1</sup> in nitrogen. The results indicate that for EVA copolymers no residue remains at the end of the cycle and that the overall degradation process can be considered as two-step process. First, acetic acid is evolved from the acetate, followed by the second step which corresponds to the main chain degradation [1]. In the case of EVA6 thermal degradation starts at about 583 K and continues up to 673 K with 13% mass loss, whereas the decomposition process of EVDNB6 starts at 528 K and continues up to 673 K with 17% mass loss. Table 2 shows

**Fig. 3** TG and DTG curves of EVA6 and EVDNB6. Heating rate 20 K min<sup>-1</sup>



**Fig. 4** TG and DTG curves of EVAL copolymers. Heating rate  $20 \text{ K min}^{-1}$

the corresponding initial thermal decomposition temperature and peak temperatures for the first mass loss ( $T_i, T_{\max}^1$ ), corresponding to the elimination of the VA units from the polymer chains in the case of EVA copolymers, and the peak temperature for the second mass loss ( $T_{\max}^2$ ). It can be seen that increasing the content of VDNB in the copolymers the  $T_{\max}$  values decrease gradually. When the VDNB content of the copolymer is 10 mol%, the fast mass loss takes place and during this step an increase in the sample temperature is observed. From Table 2 can be seen that the stability towards mass loss decreases as the proportion of VA or VDNB in the copolymer increases. Table 2 also shows the amount of residue for the reaction found at the cessation of the rapid loss in sample mass. The results indicate an increase in the amount of residue with increasing proportions of VDNB, while in the case of EVA copolymers the residue is absent. The char found at 873 K is negligible for EVA copolymers, while for EVDNB copolymers increases as the VDNB content increases. Figure 4 represents the TG and DTG curves obtained for EVAL copolymers with different alcohol content, obtained at  $20 \text{ K min}^{-1}$ . The degradation of EVAL copolymers with low content of vinyl alcohol (6–14 mol%) takes place in one step in the temperature range 623–783 K, which can be attributed to the ethylene component. The decomposition of EVAL copolymers with high content of vinyl alcohol (50–73 mol%) takes place in two steps. In the first stage, temperature range 603–723 K, the most decomposition of the polymer takes place and can be attributed to the major component, vinyl alcohol. The second step, observed at higher temperatures, can be attributed to the ethylene component. The stability towards mass loss decreases as the proportion of VAL in the copolymer increases.

#### Calculation of kinetic parameters

Thermogravimetry is a method widely used for determination of kinetics of degradation of polymers

[5, 15]. A reaction rate may be defined as the derivative of conversion. For thermogravimetric measurements, conversion may be defined as:

$$\alpha = \frac{(m_0 - m)}{(m_0 - m_f)} \quad (1)$$

where  $m_0$ ,  $m$  and  $m_f$  are the initial, actual, and final masses of the sample, respectively. The rate of conversion in a dynamic TG experiment at constant heating rate can be expressed as:

$$\frac{d\alpha}{dt} = B \frac{d\alpha}{dT} = k(T)f(\alpha) \quad (2)$$

where  $B$  is the heating rate,  $B = dT/dt$ ,  $k(T)$  is the rate constant, and  $f(\alpha)$  is the conversional functional relationship.

For polymer degradation, it is assumed that the rate of conversion is proportional of the concentration of nondegraded material:

$$f(\alpha) = (1 - \alpha)^n \quad (3)$$

where  $n$  is the apparent reaction order.

Arrhenius expression, which describes the temperature dependence of the rate constant,  $k(T)$ , may be expressed as:

$$k(T) = A \exp\left(-\frac{E}{RT}\right) \quad (4)$$

where  $E$  is the apparent activation energy,  $A$  is the preexponential factor,  $R$  is the gas constant and  $T$  the absolute temperature.

Combining Eqs (1) through (4), the following relation may be derived:

$$\frac{d\alpha}{dt} = B \frac{d\alpha}{dT} = A(1 - \alpha)^n \exp\left(-\frac{E}{RT}\right) \quad (5)$$

The differential Eq. (5), is usually manipulated until a straight line can be obtained and the kinetic parameters are predicted from the slope and ordinate values.

In the present study two different non isothermal methods, the Kissinger [16] and Flynn–Wall [17] methods, are used for the computation of the kinetic parameters. Kissinger uses the temperature at which the rate of mass loss is at maximum ( $T_{\max}$ ) from which the kinetic parameters are obtained, and assumes that these parameters are independent of  $B$ . Since the maximum rate occurs when  $d(d\alpha/dt)/dt$  is zero, differentiation of Eq. (5) with respect to time and setting the resulting expression equal to zero gives:

$$\frac{BE}{RT_{\max}^2} = An(1 - \alpha_{\max})^{n-1} \exp\left(-\frac{E}{RT_{\max}}\right) \quad (6)$$

where  $\alpha_{\max}$  is the conversion at  $T_{\max}$ .

Kissinger also assumes that the product  $n(1 - \alpha_{\max})^{n-1}$  is not only independent of  $B$ , but is equal

**Table 3** Values of apparent activation energies and their confidence intervals (at a level of confidence of 95%) for the various stages of thermal degradation of EVA, EVDNB and EVAL copolymers under dynamic conditions

Polymer	Ester/ Alcohol/ mol%	$\alpha/\%$	$K^a$		$F-W^a$	
			$E/\text{kJ mol}^{-1}$	$\log A/\text{min}^{-1}$	$E/\text{kJ mol}^{-1}$	Confidence interval for $E$
EVA6	6	0–12	166	14.63	183.8	180.9–186.7
		45–100	265	19.54	232.6	231–234.2
EVDNB6	6	0–12	119	11.61	147.8	144.5–150.1
		45–85	240	17.56	253.9	249–256.8
EVAL6	6	0–100	254	17.65	254.9	251–258.8
EVAL14	14	0–100	235	17.31	229.4	224.3–234.5
EVAL56	56	10–80	145	12.11	167.2	164.5–169.9
		85–98	214	16.18		
EVAL73	73	10–80	174	13.35	168.3	166–170.6
		85–98	308	25.29		

<sup>a</sup> $K$ : Kissinger's method;  $F-W$ : Flynn–Wall's method

or very near to the unity. Substituting this value in Eq. (6) and differentiating, neglecting small quantities, then the following expression is obtained:

$$\frac{d\left(\ln\frac{B}{T_{\max}^2}\right)}{d\left(\frac{1}{T_{\max}}\right)} = -\frac{E}{R} \quad (7)$$

Therefore a plot of  $\ln(B/T_{\max}^2)$  vs.  $1/T_{\max}$  gives the apparent activation energy for each degradation step.

Flynn and Wall expressed the Eq. (5) as:

$$-\frac{d\log B}{d\frac{1}{T_{\alpha}}} = 0.457\frac{E}{R} \quad (8)$$

where  $T_{\alpha}$  is the temperature for an isoconversion level. The apparent activation energy  $E$  can be obtained from the slope of isoconversional plots of  $\log B$  vs.  $1/T_{\alpha}$ . This method provides activation energies as a function of conversion without any assumption about the reaction order. If the determined activation energy is the same for the various values of  $\alpha$ , the existence of a single-step reaction can be concluded with certainty. On the contrary, a change in  $E$  with increasing degree of conversion is an indication of a complex reaction mechanism.

The kinetic parameters were calculated from the TG and DTG curves, using the Eqs (7) and (8). The Kissinger method allows calculation of activation energy from one point (maximum on DTG curve) at several heating rates. The method of Flynn–Wall requires several curves at different heating rates.  $E$  was calculated from the slope of the plots of Eq. (8)

( $\log B$  vs.  $1/T_{\alpha}$ ) at various degrees of conversion to test the constancy with respect to conversion.

The values of  $E$  determined by the above mentioned methods together with their confidence intervals (at a level of confidence of 95%) are given in Table 3, for EVA, EVDNB and EVAL copolymers. This parameter has been evaluated using the method of least squares for all the methods. The preexponential factor has been calculated at the maximum of reaction rate by Eq. (6) for each step of degradation, assuming that  $n(1-\alpha_{\max})^{n-1}$  is equal or very near to the unity.

It can be seen from Table 3 that two distinct apparent activation energy values can be reported for the thermal degradation of ethylene vinyl ester copolymers. Activation energy does not change for conversions up to 0.12 and between 0.45 and 1, indicating that the degradation in each region takes place through the cleavage of linkages with similar bond energies. These results are consistent with the two degradation steps reflected in TG and DTG

**Table 4** Initial rates,  $d\alpha/dt$ , and activation energies obtained from the initial reaction rates in isothermal experiments

Polymer	Ester/ mol%	$T/\text{K}$	$\frac{d\alpha}{dt}$ $10^4/\text{min}^{-1}$	$E/\text{kJ mol}^{-1}$
EVA6	6	543	4	129.7
		553	6	
		563	10	
		573	18	
EVDNB6	6	488	2	178.3
		498	5	
		508	11	
		518	26	

curves shown in Fig. 3. The activation energy of the first stage ( $\alpha < 0.12$ ) of EVA may be assumed to be between 166–187 kJ mol<sup>-1</sup>, while that of the second stage ( $\alpha > 0.45$ ) is between 231–265 kJ mol<sup>-1</sup>. The values obtained for the activation energy are similar to those reported by Munteanu and Turcu [2], Nam and Seferis [5]. For EVDNB copolymer the activation energy of the first stage ( $\alpha < 0.12$ ) is between 119–150 kJ mol<sup>-1</sup>, and that of the second stage ( $0.45 < \alpha < 0.85$ ) is between 240–257 kJ mol<sup>-1</sup>. In the transition region between the two stages ( $0.12 < \alpha < 0.45$ ) the value of activation energy is not constant for both kind of copolymers. This result agrees with the results reported in the literature [5]. This may be due to the fact that the EVA copolymer is a block copolymer of PE and PVA. The main mass loss of each block will take place in different temperatures ranges but in some region of temperature or conversion the two blocks may degrade simultaneously. This region may be  $0.12 < \alpha < 0.45$ , where the  $E$  values change with conversion. When comparing the result obtained for EVA and for EVDNB, the activation energy of the first stage is lower for EVDNB copolymer, while that of the second step is similar for both copolymers.

For EVDNB copolymers, when the copolymer composition is 10 mol% VDNB or higher the fast mass loss took place, and during this step it was observed that the sample temperature exceeded that dictated by the temperature programme. For these copolymers it was impossible to determine the kinetic parameters from TG and DTG curves. A similar behaviour was observed in the pyrolysis of other polymers containing nitroaromatic side groups [18, 19].

A values obtained by the Kissinger method agree well with those reported by Nam and Seferis [5]. For EVAL copolymers the activation energy and the preexponential factor of the stage attributed to the decomposition of the ethylene component is similar to that obtained for the second step of EVA and EVDNB copolymers. The activation energy of the stage attributed to the degradation of the vinyl alcohol component is between 145–174 kJ mol<sup>-1</sup>, that value and  $A$  value are similar to those reported by Alvarez *et al.* [12].

#### *Isothermal degradation*

The thermogravimetric behaviour of EVA and EVDNB copolymers under isothermal conditions was studied in the temperature interval 488–573 K.

The initial rates of degradation (expressed as the fraction,  $\alpha$ , of the sample decomposed per min) obtained from the resulting degree of conversion *vs.* time curves are presented in Table 4. The apparent activation energy values for the beginning of the

reaction, evaluated from the Arrhenius plot, are reported in Table 4.

The apparent activation energy at different degrees of conversion was also evaluated in the following way: if the rate of decomposition process,  $d\alpha/dt$ , can be expressed as a function of two variables, temperature ( $T$ ) and conversion ( $\alpha$ ), using general formulation [15]

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (9)$$

and its integrated form is

$$F(\alpha) = k(T)t \quad (10)$$

where

$$F(\alpha) = \int_0^\alpha \frac{1}{f(\alpha)} d\alpha \quad (11)$$

The value of  $F(\alpha)$  for a given value of  $\alpha$  does not depend on temperature, since  $k$  depends on temperature according to the Arrhenius relationship, Eq. (10) can be rewritten in the form:

$$F(\alpha) = A \exp(-E/RT)t \quad (12)$$

or

$$\exp(E/RT)F(\alpha)/A = t \quad (13)$$

and therefore

$$E/RT + \ln[F(\alpha)] - \ln A = \ln t \quad (14)$$

where  $E$  is the apparent activation energy,  $A$  is the preexponential factor and  $R$  the gas constant. For a constant value of conversions  $\alpha$ ,  $\ln F(\alpha)$  is constant and  $E$  can be determined from the slope of  $\ln t$  *vs.*  $1/T$ , without assuming the kinetic function.

Using Eq. (14), plots of the time necessary to reach a certain degree of conversion *vs.* the inverse of temperature were drawn and  $E$  values obtained from the slopes of the lines are listed in Table 5 for the conversion interval studied.

**Table 5** Isothermal TG of EVA and EVDNB copolymers in nitrogen atmosphere. Apparent activation energies on the temperature interval studied obtained at various degrees of conversion

Polymer	Ester/ mol%	$T/K$	$\alpha/\%$	$E/\text{kJ mol}^{-1}$
EVA6	6	543–573	5–10	151.8
EVDNB6	6	488–518	5–10	163.9

#### *Infrared spectra of residual products*

The degraded EVDNB samples at 548–553 K, were studied at different stages by infrared spectrometry.

EVDNB at low extents of degradation (10% mass loss) yields a brown residue insoluble in normal solvents for undegraded EVDNB. At extents of degradation higher than 10% mass loss, a black tar is obtained.

The infrared analysis of EVDNB (14 mol%, 58 mass%) at different degrees of degradation leads to the following observations.

For undegraded EVDNB, absorption bands related to C–H stretching at 3000–2840  $\text{cm}^{-1}$  (alkanes), C=O stretching at 1730  $\text{cm}^{-1}$  (aromatic ester), and  $\text{NO}_2$  antisymmetric and symmetric stretching at 1548 and 1343  $\text{cm}^{-1}$ , respectively are observed. The brown residue produced at low extents of degradation (10% mass loss) contains the same infrared bands that the undegraded copolymer (3000–2840, 1730, 1548 and 1343  $\text{cm}^{-1}$ ), and two shoulders at 1700  $\text{cm}^{-1}$  (C=O stretching, acid) and 1230  $\text{cm}^{-1}$  (C–O stretching, acid). The residue after 25% mass loss contains new bands in the 3300–2500  $\text{cm}^{-1}$  region (O–H stretching, acid), at 1700  $\text{cm}^{-1}$  (C=O stretching, acid), at 1600  $\text{cm}^{-1}$  due to double bonds (C=C stretching) along the carbon backbone, at 1440  $\text{cm}^{-1}$  (C–O–H bending, acid), at 1230  $\text{cm}^{-1}$  (C–O stretching, acid), the bands due to  $\text{NO}_2$  stretching at 1548 and 1343  $\text{cm}^{-1}$  are present, while the band at 1730  $\text{cm}^{-1}$  (aromatic ester) is absent, suggesting the total elimination of the dinitrobenzoate groups at this low extent of degradation and the formation of acid group, with subsequent formation of double bonds [20]. In the IR spectra of the residue after 35% mass loss a new broad band appears at 1810  $\text{cm}^{-1}$  (vinyl and vinylidene groups), and another band at 900  $\text{cm}^{-1}$  (alkenes C–H stretching, and vinylidene structures), while those due to the acid and nitro groups appear attenuated. The formation of vinyl and vinylidene groups are connected with main chain cleavage of low density polyethylene (LDPE) [21]. When the mass loss has reached 60% the band in the 3300–2500  $\text{cm}^{-1}$  region disappears.

## Conclusions

The thermal decomposition of EVA, EVDNB and EVAL copolymers has been examined by DTA and by isothermal and dynamic TG experiments in nitrogen. The results have shown that EVDNB copolymers are less thermally stable compared to EVA copolymers, and EVAL copolymers are the most stable copolymers. The mass loss of EVA, EVDNB and EVAL copolymers is accomplished in two stages. The two stages are connected with different degradation mechanisms, the first stage has been attributed to the polyvinyl ester or polyvinyl alcohol decomposition, followed by decomposition of polyethylene. The activation energies have been determined by the Kissinger method using the maximum rate temper-

ature and with isoconversional method of Flynn–Wall for all values of  $\alpha$ . The apparent activation energies estimated by the two different methods are consistent. Comparing the dependence of activation energy on the  $\alpha$  value, two regions of  $E$  values have been identified. This constitutes a clear indication that the kinetic description of thermal decomposition can be accomplished through two different mechanisms, and this conclusion is consistent with the results of DTA, TG and DTG analysis. In EVA copolymers first acetic acid is evolved from the acetate, followed by the main chain degradation. FTIR studies of thermal degradation of EVDNB have shown complete loss of the ester functionality with formation of dinitrobenzoic acid and the concurrent formation of conjugated dienes, followed by the formation of vinyl and vinylidene unsaturations associated with the main chain cleavage. The thermal decomposition of EVDNB leaves char residue, and has been found to increase in amount with increasing VDNB content, while in the thermal decomposition of EVA and EVAL copolymers the residue is absent, suggesting that the degraded products from EVDNB copolymers are less volatile probably due to crosslinking.

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