

Kinetic Analysis of Thermal Degradation in Poly(ethylene–vinyl alcohol) Copolymers

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ABSTRACT: Thermal analysis of EVOH copolymers with different ethylene content, were performed by TGA/DTGA under dynamic conditions. Apparent kinetic parameters were determined using different classical kinetic approaches. The apparent activation energy values obtained confirm that thermal stability of EVOH increases with eth-

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INTRODUCTION

Ethylene–vinyl alcohol copolymers (EVOH) are widely used in practical applications due to their excellent oxygen barrier properties, processability, and thermal stability.¹ Besides the studies concerning barrier properties, rheological behavior, and mechanical properties, understanding their thermal stability and thermal degradation behavior is of great importance from the processing and recycling point of view. Usually, to decrease the viscosity of the semicrystalline polymers to facilitate processing, the temperature of extruders and/or injection machines is increased. It is evident that, to predict the degree of degradation of such materials under processing conditions, the thermal degradation kinetic must be understood.

Thermal degradation of poly vinyl alcohol (PVOH), has been extensively reported in the literature.^{2–4} Below 300°C, the major degradation product reported is water, produced by elimination of the hydroxyl side group.² Recently, Holland and Hay³ reported that thermal degradation mechanism of PVOH in the molten state consists of water elimination and chain scission, via a six-member transition state, leading to the formation of volatile products, such as saturated and unsaturated aldehydes and ketones.⁴ However, and despite the fact that thermal stability of PVOH increases by the presence of ethylene cocomponent, there is a lack of information concerning the kinetic

parameters involved in the thermal degradation process of EVOH copolymers.

The aim of the present work was to find a simple expression of the thermal degradation kinetics of poly(vinyl alcohol) copolymers with different ethylene content, to understand the influence of the ethylene content in the degradation process.

EXPERIMENTAL

Materials and methods

Poly(ethylene–vinyl alcohol) (EVOH) copolymers with three different molar ethylene contents: 32, 38, and 44% (EVOH 32, EVOH 38, EVOH 44), were purchased from Sigma-Aldrich S.A.

Dynamic thermogravimetric analysis (TGA) was performed with a Shimadzu TGA-DTGA instrument. Dynamic experiments were run from 298 to 1273 K at heating rates in the range of 5 to 25 K/min. TG/DTG tests were carried out under nitrogen atmosphere (20 mL/min) to prevent any thermoxidative degradation.

THEORETICAL BACKGROUND

Traditionally, TGA is used to obtain kinetic information from thermal decomposition of polymers. Despite some drawbacks, dynamic TGA is still widely used to estimate kinetic parameters, mainly the apparent activation energy.¹¹ Kinetic studies are based on the general equation:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

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where k is the kinetic constant and $f(\alpha)$ is a function of the conversion, and α is the degree of conversion or fractional mass loss defined as:

$$\alpha = \frac{(m_t - m_0)}{(m_0 - m_f)} \quad (2)$$

where m_t is the mass at any degradation time, m_0 is the initial mass and m_f is the final mass at the end of the degradation process.

The temperature dependence of the kinetic constant can be expressed according to the following Arrhenius-type equation:

$$K(T) = A \exp\left(\frac{-E_a}{RT}\right) \quad (3)$$

where E_a is the apparent activation energy ($\text{kJ} \cdot \text{mol}^{-1}$), A is a preexponential factor (min^{-1}), R is the gas constant, and T is the temperature (K). For polymer degradation, it is assumed that the rate of conversion is proportional to the concentration of material that has to react (12):

$$f(\alpha) = (1 - \alpha)^n \quad (4)$$

where, n is the apparent reaction order.

The combination of eqs. (1)–(4) gives the following relationship:

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

For dynamic experiments, the heating rate, $\beta = dT/dt$ must be considered. Thus, eq. (5) become:

$$\frac{d\alpha}{(1 - \alpha)^n} = \frac{A}{\beta} \exp\left(\frac{-E_a}{RT}\right) dT \quad (6)$$

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. Among all linear forms of eq. (5), the methods of Kissinger,⁵ Friedman,⁶ Flynn-Wall,⁷ Horowitz-Metzger,⁸ Osawa,⁹ and Van Krevelen¹⁰ are the most used.

The Kissinger method assumes that kinetic parameters are not dependent on the heating rate. Calculations are based on the point for the maximum degradation rate (T_m) and evaluated from the first derivative of the mass loss curve. The following expression was proposed:

$$\frac{E\beta}{RT_m^2} = An(1 - \alpha)^{n-1} \exp\left(\frac{-E_a}{RT}\right) \quad (7)$$

Kissinger also assumes that reaction order is equal or very near to the unity, thus, from eq. (7):

$$\frac{d\left(\ln \frac{\beta}{T_m^2}\right)}{d\left(\frac{1}{T_m}\right)} = \left(\frac{-E_a}{R}\right) \quad (8)$$

Friedman⁶ provides an approximation to eq. (5). In this model, the decomposition rate ($d\alpha/dt$) for a given conversion (α), is determined using different heating rates, β . The following logarithmic differential equation is obtained:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln A + n \ln(1 - \alpha) - \frac{E_a}{RT} \quad (9)$$

Equation (9) can be used to estimate E_a from the slope of iso-conversional plots, $\ln(d\alpha/dT)$ vs. $1/T$. The reaction order can be obtained by plotting the ordinate as a function of $(1 - \alpha)$.

Based on TG/DTG curves performed at different heating rates, Flynn and Wall method express the eq. (5) as:

$$\frac{-d(\ln \beta)}{d\frac{1}{T}} = -0.457 \frac{E_a}{R} \quad (10)$$

The apparent activation energy can be obtained by plotting $d(\ln \beta)$ against $d(1/T)$. Flynn and Wall method makes no assumption about the reaction order in the calculation of the activation energy.

Kinetic parameters can be also determined from the standard TGA trace by using integral methods. By integration of the eq. (5) and introducing the initial condition of $\alpha = 0$ at $T = T_0$, the following expression is obtained:

$$F = \int_0^\alpha \frac{d\alpha}{(1 - \alpha)^n} = \frac{A}{\beta} \int_{T_0}^T \exp\left(\frac{-E_a}{RT}\right) dT \quad (11)$$

The differences between the various techniques employing integral methods lie in their approach to solving the above integral equation.

Horowitz-Metzger⁸ derived the following expression by using a series of approximations and simplifications, and assuming a pseudofirst-order kinetics:

$$\ln(1 - \alpha) = -\exp\left(\frac{-E_a \theta}{RT_s^2}\right) \quad (12)$$

where T_s is the temperature at which $1/(1 - \alpha) = 1/\exp(E_a \theta / RT_s^2) = 0.368$ and $\theta = T - T_s$. By plotting

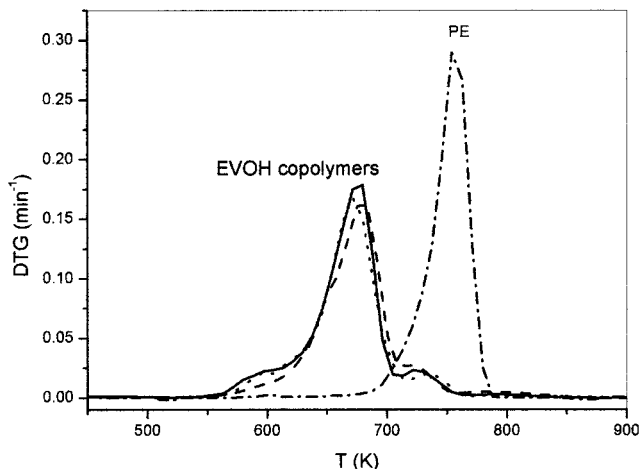


Figure 1 TGA curves obtained at 10 K/min for EVOH with different ethylene content: (—)EVOH 32, (---)EVOH 38, (····)EVOH 44 For comparing purposes, DTG curves for pure PE (- · - · - ·), is also included.

In $(\ln(1-\alpha))$ against temperature, the activation energy is taken from the slope.

Osawa's method,⁹ which is essentially the same as the Flynn and Wall,⁷ represents a relatively simple method for determining activation energies directly from weight loss against temperature data obtained at several heating rates. Essentially, the technique assumes that A , $(1-\alpha)^n$, and E_a are independent of T , and that A and E_a are independent of α wherein the variables given in eq. (11) may be separated and integrated to give the following expression in the logarithmic form:

$$\log F(\alpha) = \log\left(\frac{AE_a}{R}\right) - \log \beta + \log p\left(\frac{E_a}{RT}\right) \quad (13)$$

Using Doyle's approximation for the integral, valid for $E_a/RT > 20$, then $\log p(E_a/RT)$ may be expressed as:

$$\log p\left(\frac{E_a}{RT}\right) \cong -2.315 - 0.4567 \frac{E_a}{RT} \quad (14)$$

Thus, eq. (13) now becomes:

TABLE I
Temperatures at the Maximum Degradation Rate (T_{max}) for Different EVOH and PE Obtained at Different Heating Rates

Heating rate (K/min)	T_{max} (K)			
	EVOH 32	EVOH 38	EVOH 44	PE
5	638	654	659	733
10	664	678	682	753
15	673	483	689	764
20	680	689	694	771
25	695	702	708	778

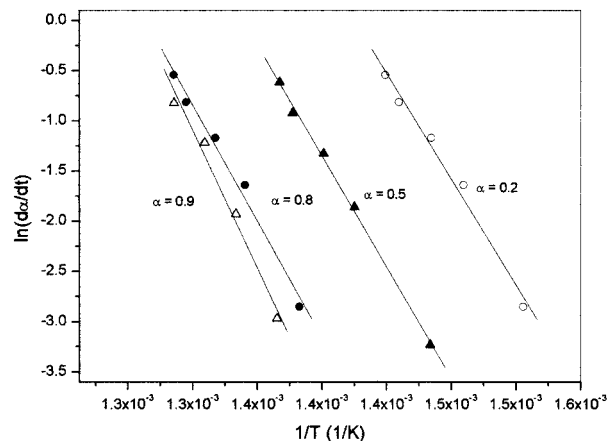


Figure 2 Friedman plots for EVOH 32 for iso-conversion: ○ $\alpha = 0.2$, ▲ $\alpha = 0.5$, ● $\alpha = 0.8$, △ $\alpha = 0.9$.

$$\log F(\alpha) = \log\left(\frac{AE_a}{R}\right) - \log \beta - 2.315 - 0.4567 \frac{E_a}{RT} \quad (15)$$

The apparent activation energy can be obtained from a plot of $\log \beta$ against $1/T$ for a fixed degree of conversion because the slope of such line is given by $-0.4567.E_a/R$. In addition, a value of $\log A$ can be found from the intercept on the $\log \beta$ axis.

Van Krevelen¹⁰ provides an approximation to the integral, resulting in the following expression.

$$\left[\ln\left(\frac{1}{1-\alpha}\right) - 1 \right] = \ln \left[\frac{A}{\beta} \left(\frac{0.368}{T_m}\right)^{E_a/RT} \frac{1}{\frac{E_a}{RT_m} + 1} \right] + \left(\frac{E_a}{RT_m} + 1\right) \ln T \quad (16)$$

According to this method, at a fixed temperature, T_m , a maximum rate can be measured and $0.9 T_m < T < 1.1 T_m$. Thus, by plotting $\ln [1/(1-\alpha)]$ against $\ln T$, a

TABLE II
Kinetic Parameters Obtained from the Iso-Conversional Friedman Plots

Material	E_a (kJ/mol)	Reaction order	0.1 < α < 0.80	
			$\log A$ (min ⁻¹)	Correlation coefficient (r)
EVOH 32	140.1 ± 8.2	1.20	11.9	0.991
EVOH 38	149.2 ± 11.1	1.22	12.8	0.990
EVOH 44	157.8 ± 10.3	1.17	13.0	0.990
0.89 < α < 0.96				
EVOH 32	168.4 ± 2.8	1.12	3.6	0.992
EVOH 38	171.3 ± 1.1	1.14	3.8	0.992
EVOH 44	177.8 ± 10.3	1.07	4.3	0.992

TABLE III
Calculated First-Order Activation Energies by Kissinger Method (r = Correlation Coefficient)

Material	$0.1 < \alpha < 0.80$		$0.89 < \alpha < 0.96$	
	E_a (kJ/mol)	r	E_a (kJ/mol)	r
EVOH 32	123.3	0.993	158.2	0.998
EVOH 38	134.6	0.992	159.4	0.992
EVOH 44	156.4	0.991	161.3	0.991

straight line is obtained and the slope and intercept permit the determination of the activation energies and preexponential factor, A .

RESULTS AND DISCUSSION

Thermal degradation of different EVOH was analyzed by TG/DTG experiments. Figure 1 represents the DTG curves obtained for EVOH with different ethylene content, and measured at 10 K/min. The curves show two main peaks, corresponding to the maximum degradation rate (T_{\max}), of each component. The first peak, at temperatures in the range of 660 K to 680 K (at 10 K/min), can be attributed to the major component, PVOH. The second peak, observed at higher temperatures, can be attributed to the ethylene cocomponent. Table I shows EVOH and polyethylene T_{\max} values determined at different heating rates. Even if the shape of the mass loss curves does not change and exhibit the same starting temperature of decomposition, the maximum degradation rate is slightly shifted to higher values as the heating rate increases. This behavior may be attributed to heat transfer problems between the sample and the instrument.¹¹

It is important to note that DTG curves of both components are partially overlapped in a conversion range (Fig. 1). As a consequence, thermal degradation

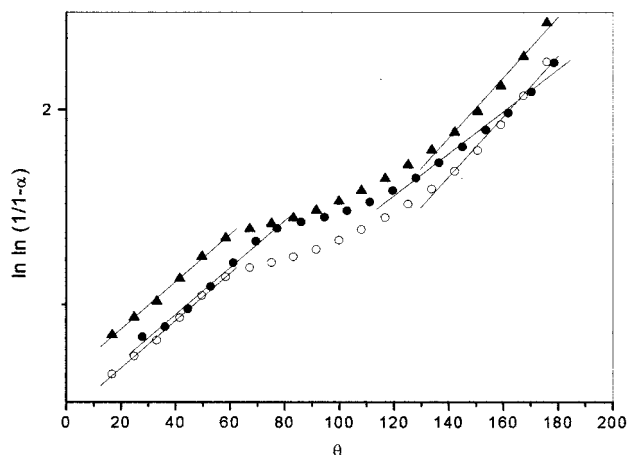


Figure 3 Application of Horowitz-Metzger's method to experimental data obtained at a heating rate of 10 K/min for different EVOH: ○ EVOH 32, ● EVOH 38, ▲ EVOH 44.

TABLE IV
Calculated First-Order Activation Energies in Degradation of EVOH According to the Horowitz-Metzger Method (r = Correlation Coefficient)

Heating rate (K/min)	$0.1 < \alpha < 0.80$					
	EVOH 32		EVOH 38		EVOH 44	
	E_a (kJ/mol)	r	E_a (kJ/mol)	r	E_a (kJ/mol)	r
5	178.0	0.899	180.8	0.988	186.9	0.998
10	171.3	0.993	175.9	0.998	177.0	0.956
15	151.8	0.999	162.2	0.994	177.3	0.998
20	162.3	0.992	167.4	0.998	184.0	0.996
25	156.5	0.996	174.2	0.996	175.6	0.995
	$0.89 < \alpha < 0.96$					
5	172.2	0.992	174.2	0.983	176.6	0.992
10	173.4	0.993	176.3	0.996	179.2	0.986
15	165.3	0.997	168.4	0.996	182.3	0.992
20	168.7	0.997	169.1	0.993	184.1	0.985
25	173.6	0.996	173.8	0.996	178.4	0.994

of one component may be affected by the presence of the other. The effect of ethylene content on PVOH degradation process can be examined from Table I. For a given heating rate, the temperature at the maximum degradation rate of PVOH is shifted to higher values as ethylene content increases, whereas T_{\max} values for ethylene cocomponent are almost unchanged. It should be remarked that an increase in T_{\max} is associated with an improvement in thermal stability. Therefore, polyethylene acts as a thermal stabilizer of EVOH in EVOH copolymers.

Kinetic parameters were predicted from the dynamic TG/DTG data. EVOH thermal degradation may be viewed as a composite degradation process of the two different cocomponents. Consequently, kinetic parameters should be predicted taking into ac-

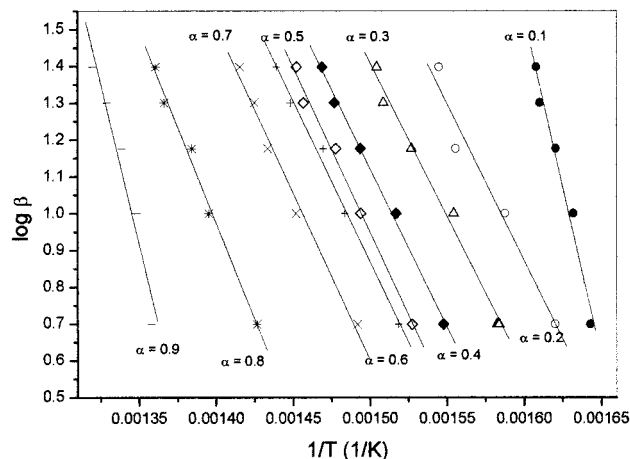


Figure 4 Application of Osawa's method to EVOH 32: ● $\alpha = 0.1$, ○ $\alpha = 0.2$, △ $\alpha = 0.3$, ◆ $\alpha = 0.5$, + $\alpha = 0.6$, × $\alpha = 0.7$, * $\alpha = 0.8$, - $\alpha = 0.9$.

TABLE V
Apparent Activation Energies Determined by Ozawa's Method (r = Correlation Coefficient)

Conversion (α)	EVOH 32			EVOH 38			EVOH 44		
	E_a (kJ/mol)	$\log A$ (min^{-1})	r	E_a (kJ/mol)	$\log A$ (min^{-1})	r	E_a (kJ/mol)	$\log A$ (min^{-1})	r
0.1	101.9	8.20	0.983	334.9	28.69	0.988	139.4	11.23	0.979
0.2	139.6	11.00	0.994	197.9	16.10	0.962	153.4	12.04	0.976
0.3	124.4	9.53	0.997	151.7	11.96	0.993	157.5	12.14	0.995
0.4	135.7	10.33	0.996	150.1	11.78	0.992	162.9	12.42	0.998
0.5	142.9	10.80	0.989	156.5	12.06	0.998	167.4	12.66	0.999
0.6	136.7	10.23	0.999	161.6	12.44	0.996	172.3	12.93	0.999
0.7	138.6	10.27	0.987	159.2	12.02	0.996	178.8	13.31	0.998
0.8	155.2	11.43	0.989	163.7	12.24	0.994	176.9	13.08	0.992
0.9	192.7	4.64	0.9841	200.5	3.58	0.9951	211.6	3.17	0.9994

count a multistep process. This approach was used to predict kinetic parameters for copolymers, such as the ethylene-vinylacetate copolymer (EVA).^{13,14}

The range of conversion for each step was determined based on TG/DTG curves obtained at the lower heating rate analyzed (5 K/min). The first step, associated with PVOH decomposition, was in the range of $0.1 < \alpha < 0.80$. The second step, was found in the range of $0.89 < \alpha < 0.96$ and was assigned to polyethylene.

The differential method of Friedman was applied to EVOH copolymers. As an example, Figure 2 presents the iso-conversional Friedman plots obtained for EVOH 32. The predicted apparent activation energy associated with PVOH decomposition ($0.1 < \alpha < 0.8$), was 148 kJ/mol. Activation energy does not change drastically with conversion (as can be concluded from the slopes in Fig. 2). This result indicates that degradation mechanism of PVOH remains unchanged throughout the whole process, and could be attributed to the cleavage of linkages with similar bond energies. For conversions $\alpha > 0.8$, associated with polyethylene chain decomposition, the apparent activation energy increases to an average value of 168 kJ/mol. Table II

summarizes the apparent activation energies values, reaction order, and preexponential factors, obtained for both steps and for all the EVOH analyzed. Activation energies for the first stage increase with ethylene content. These results are in agreement with those previously observed from the values of T_{max} in TG/DTG experiments (Table I). The reaction order, determined from the intercept, was near the unity for both processes.

The Kissinger method was also used for determining kinetic parameters. The fact that this method assumes that the reaction order is equal or near the unity may be overlooked, in agreement with the reaction order predicted by Friedman method. Table III summarizes the apparent activation energies determined for both steps. PVOH activation energy increases with ethylene content, from 123 to 156 kJ/mol. The apparent activation energy for polyethylene was almost constant (158 to 161 kJ/mol).

The integral method of Horowitz-Metzger was also applied to determine the kinetic parameters. Figure 3 shows a typical plot for EVOH 32. Horowitz-Metzger plots allow identification of different stages of decom-

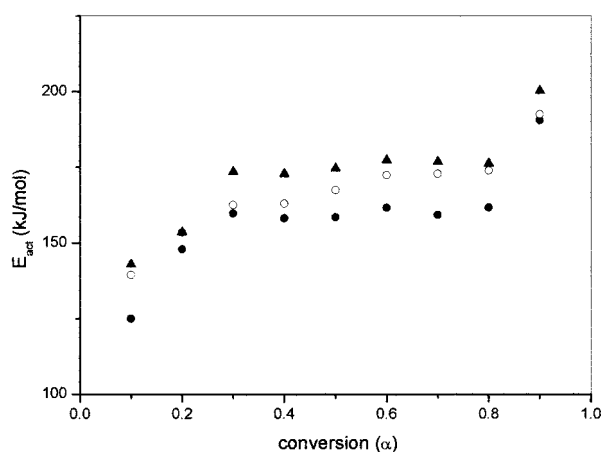


Figure 5 Activation energy as a function of the conversion for Ozawa's method: \circ EVOH 32, \bullet EVOH 38, \blacktriangle EVOH 44.

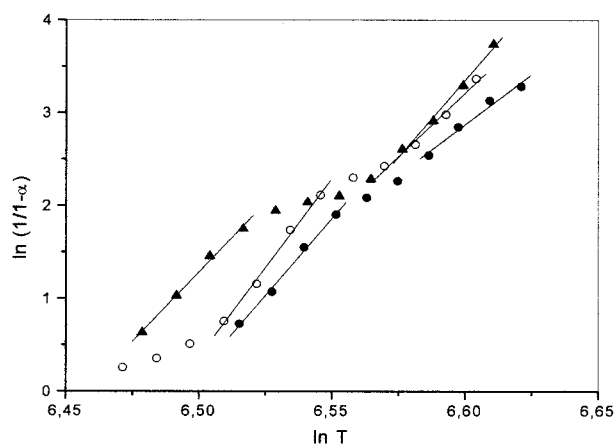


Figure 6 Application of Van Krevelen's method to the experimental data obtained at 10 K/min for the three EVOH: \circ EVOH 32, \bullet EVOH 38, \blacktriangle EVOH 44.

TABLE VI
Kinetic Parameters Determined by Van Krevelen Method (r = Correlation Coefficient)

Heating rate (K/min)	0.1 < α < 0.8					
	EVOH 32		EVOH 38		EVOH 44	
	E_a (kJ/mol)	r	E_a (kJ/mol)	r	E_a (kJ/mol)	r
5	142.3	0.983	149.3	0.984	178.5	0.951
10	139.7	0.994	144.0	0.995	149.9	0.965
15	140.7	0.984	144.2	0.997	159.8	0.974
20	142.7	0.994	148.5	0.998	165.9	0.995
25	141.4	0.962	145.2	0.932	153.0	0.960
0.89 < α < 0.96						
5	170.4	0.981	171.3	0.993	180.3	0.971
10	168.6	0.992	174.2	0.995	179.7	0.982
15	172.1	0.994	174.8	0.989	179.9	0.991
20	173.4	0.989	178.6	0.993	185.4	0.983
25	171.2	0.973	175.7	0.961	183.0	0.992

position at one heating rate. Similar plots were obtained for all the EVOH copolymers analyzed employing all the heating rates proposed. The results are summarized in the Table IV. It is possible to calculate the average activation energy for all the heating rates and all the EVOH analyzed: 164 ± 14 kJ/mol for EVOH 32; 178 ± 16 kJ/mol for EVOH 38, and 188 ± 13 kJ/mol for EVOH 44. The values obtained by applying Horowitz-Metzger are slightly higher than those predicted by using the previous methods.

Osawa's method is essentially the same as Flynn and Wall,⁷ and represents a simple method to determine activation energies from TG curves. Iso-conversional plots for EVOH 32 are shown in the Figure 4, while the calculated apparent activation energies and $\log A$ are given in Table V. Activation energies are almost invariable with the conversion in the range of $0.2 < \alpha < 0.8$, as can be concluded from Figure 5. This result agrees with that obtained by applying Friedman method.

Van Krevelen's method was applied to the different EVOH copolymers. Figure 6 shows the results obtained for a heating rate of 10 K/min. The activation energies predicted for both stages are summarized in

the Table VI. Average energy values are in the same range than those obtained by the Friedman, Kissinger, and Osawa methods.

To compare the results obtained from the analytical treatment of the experimental data, Table VII summarizes the predicted values of activation energy for all the EVOH studied. It is easy to conclude that there is no great variation in the predicted energy values, either using differential or integral kinetic methods. The Horowitz-Metzger method predicts values slightly higher than the other methods. Friedman and Osawa make no assumption about the reaction order, and are applicable to all points of the TG curve. The Friedman method has the additional advantage of predicting the reaction order, which were near 1 for both stages. Kissinger's method uses only one point (T_{max}), and assumes a kinetic of pseudofirst order. Based on the analysis of Table VII, the Kissinger method is able to predict values in close agreement with those obtained by Osawa, Van Krevelen, and Friedman.

The activation energy values were almost invariable with the conversion, within each stage of the degradation process. Thus, the assumption of two independent processes (with independent E_a values) during EVOH thermal decomposition is a good approach for predicting kinetic parameters. However, it must be taken into account that decomposition curves of both components are partially overlapped, with a transition region in the conversion range of $0.8 < \alpha < 0.89$. Thus, there is a conversion region in which both components degrade simultaneously. As a consequence, the thermal stability of each component may be influenced by the presence of the other. Based on the analysis of the apparent activation energy values (Table VII), it is easy to note that the thermal stability of PVOH ($0.1 < \alpha < 0.80$), increased with ethylene content. This result is consistent with the shift observed in the temperature at the maximum degradation rate in DTG curves. Therefore, polyethylene acts as thermal stabilizer of poly(vinyl alcohol) in poly(ethylene-polyvinyl alcohol) copolymers.

TABLE VII
Summary of the Average Apparent Activation Energies (kJ/mol) for Each Stage of the Thermal Degradation of EVOH with Different Ethylene Content

Method	EVOH 32		EVOH 38		EVOH 44	
	0.1 < α < 0.80	0.89 < α < 0.96	0.1 < α < 0.80	0.89 < α < 0.96	0.1 < α < 0.80	0.89 < α < 0.96
Kissinger	123.3	158.2	134.6	159.4	156.4	161.3
Friedman	140.1	168.4	149.2	171.3	157.8	177.8
Horowitz-Metzger	164.0	170.6	168.0	172.4	178.0	180.1
Osawa	134.4	192.7	157.1	200.5	166.7	211.6
Van Krevelen	141.4	171.1	146.2	174.9	161.4	181.7

CONCLUSIONS

The effect of ethylene content on the thermal degradation of ethylene–vinyl alcohol copolymers has been analyzed using dynamic TG experiments. EVOH thermal degradation was considered as a composite degradation process of the two different cocomponents, depending on the whole conversion range. Based on the experimental findings, each stage of weight loss was analyzed by using different classical kinetic models for predicting apparent activation energies and reaction orders associated with each step of the degradation process.

The thermal degradation kinetics parameters obtained are consistent with the shift observed in the temperature at the maximum degradation rate in DTG curves. It was found that the polyethylene acts as a thermal stabilizer of poly(vinyl alcohol) in poly(ethylene–polyvinyl alcohol) copolymers.

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