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EVALUATION OF KINETIC PARAMETERS OF THE THERMAL DECOMPOSITION OF POLYETHYLENE-VINYL ACETATE GRAFT COPOLYMERS

D. MUNTEANU and SONIA TURCU

Research Laboratory, Petrochemical Works "Solventul", Timişoara. Research Laboratory, Petrochemical Works, Piteşti, Romania

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The thermal decomposition of the polyethylene-vinyl acetate graft copolymers was studied by thermogravimetry (nonisothermal conditions, constant heating rate of 4°/min). Between 275 and 350° the thermal decomposition is due to the splitting of the acetoxy groups of the grafted chains and the elimination of acetic acid. The reaction order, activation energy and frequency factor were computed by means of the Coats-Redfern and Fuoss methods. The activation energy and frequency factor values obtained with the two methods agree well and they do not depend on the grafted vinyl acetate content (2.6—17.6%).

In earlier papers [1—4], the themal decomposition of polyethylene-vinyl acetate graft copolymers and ethylene-vinyl acetate random copolymers was studied. The present paper deals with the computation of the kinetic parameters (i.e. reaction order, activation energy and frequency factor) of the thermal decomposition of polyethylene-vinyl acetate graft copolymers. Nonisothermal thermogravimetric data, and the Coats-Redfern and Fuoss method are used.

Experimental

A series of polyethylene-vinyl acetate graft copolymers are studied by thermogravimetry (TG). They have a grafted vinyl acetate content (%VAgr.) of 2.6—17.6%, determined by chemical analysis [5] and IR spectroscopy [6]. The graft copolymers have been obtained by means of the melt grafting method. The vinyl acetate, and the dissolved peroxide initiator, are injected in the barrel of a twin-screw extruder (Werner-Pfleiderer ZSK 53 L/v) fed with low-density polyethylene. The poly(vinyl acetate) homopolymer formed in the grafting reaction is eliminated by selective precipitation [1, 7, 8].

The Mettler 810 thermobalance with Pt—Pt/Rh (10% Rh) thermocouple wires was used. The thermal decomposition of the graft copolymers was carried out in inert medium (8 l/h N_2) at a constant heating rate (4°/min), using samples of about 100 mg.

The TG curves of graft copolymers with different %VAgr. are shown in Fig. 1. They have a similar pattern. Although the initial temperature is 250°, the weight loss is relatively low up to 300°. In the 300—350° interval, the decomposition suddenly increases, and accordingly so does the weight loss: the higher %VAgr., the greater the loss. At about 350° there is an inflection point, so that in the next interval, up to 400°, the weight loss is low (the TG curve exhibits a plateau). After 400° the weight loss suddenly increases, due to hydrocarbon chain splitting.

We proved earlier [2, 3] that in the initial temperature range, i.e. up to 350°, the thermal decomposition is due to the splitting of the acetoxy groups of the grafted chains and the elimination of acetic acid. Since the weight loss is proportional to %VAgr., a quantitative method for their determination could be elaborated [2]. The DTG curves show that the decomposition rate of the acetoxy groups has a maximum at 300°. At 350° (the inflection point of the TG curves) the splitting of the acetoxy groups is practically completed.

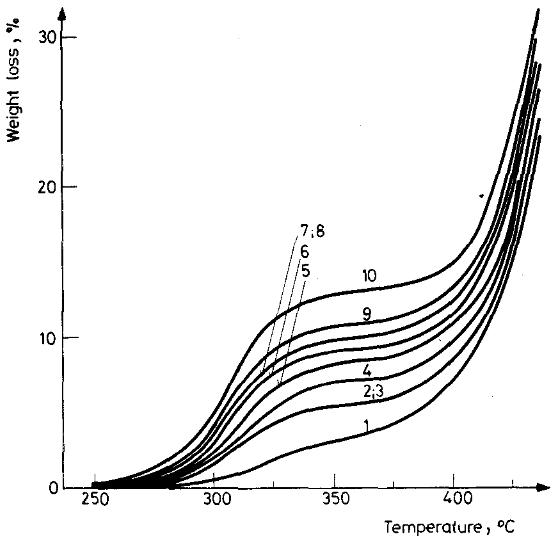
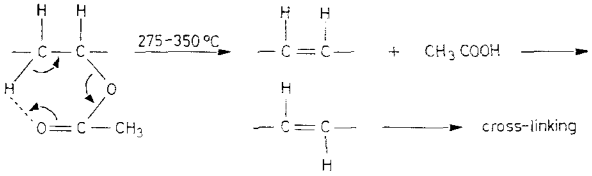


Fig. 1. TG curves of graft copolymers (N_2, 8 l/h, 4°/min). 1 – 2.6%; 2 – 4.8%; 3 – 4.9%; 4 – 6.5%; 5 – 7.6%; 6 – 8.3%; 7 – 8.7%; 8 – 8.9%; 9 – 13.0%; 10 – 17.6%

Our previous results [3], obtained by TG, pyrolysis gas chromatography and IR spectroscopy, allowed us to propose the following reaction mechanism. In the grafted chains, the decomposition of the acetoxy groups is favoured by the tendency to form (via a hydrogen-bond with the active methylene group) a six-membered ring transition state. The activated complex decomposes thermally, eliminating the acetic acid. The double-bonds formed in the grafted chains have a "trans" configuration at the end of decomposition and favour the cross-linking process [3]:



Results and discussion

TG may be used to evaluate the kinetic parameters of a solid-state reaction only when the sample changes in weight during a chemical reaction (absorption or elimination of volatile components). The thermal decomposition of the graft copolymers is a solid thermal decomposition, with the elimination of a volatile compound (CH_3COOH in our case) according to reaction (1):

$$aA_{(s)} \rightarrow bB_{(s)} + cC_{(g)} . \tag{1}$$

The sample weight decreases and the weight loss increases with the rise of the temperature (Fig. 1).

There are several methods for the evaluation of the kinetic parameters using TG. Both isothermal and nonisothermal methods may be used, the latter having certain advantages: the possibility of identifying the different reaction stages in the solid-gas system, and the need for one determination per sample. The present paper applied the Coats–Redfern [9] and Fuoss [10] methods, which use TG curves obtained under the conditions of nonisothermal decomposition.

The Coats–Redfern method [9] considers that in reaction (1) the rate of dissappearance of A may be expressed by:

$$\mathrm{d}\alpha/\mathrm{d}t = k(1 - \alpha)^n \tag{2}$$

where:

α is the fraction of A decomposed at time t ($\alpha = 1 - w_t/w_0$);
w_t is the sample weight at time t;
w_0 is the initial sample weight;
n is the order of reaction;
k is the rate constant, given by:

$$k = Ze^{-E/RT} \tag{3}$$

Z is the frequency factor (statistical or preexponential factor) (min^{-1});
E is the activation energy of the reaction (KJ/mol);
R is the gas constant;
T is the absolute reaction temperature (K).

At constant heating rate a, (degree/min):

$$a = \mathrm{d}T/\mathrm{d}t . \tag{4}$$

By combining Eqs (2), (3) and (4), rearranging and integrating, we have:

$$\int_0^\alpha d\alpha/(1-\alpha)^n = A/a \int_0^T e^{-E/RT} dT. \tag{5}$$

The left-hand side of Eq. (5) has two different solutions, depending on the value of n, namely:

$$\frac{1-(1-\alpha)^{1-n}}{1-n} \quad \text{for} \quad n \neq 1, \quad \text{and}$$

$$\frac{-\log(1-\alpha)}{T^2} \quad \text{for} \quad n = 1.$$

In both cases, the right-hand side of Eq. (5) has the solution

$$ZRT^2/aE(1-2RT/E)e^{-E/RT}.$$

After taking log's, the following equations are obtained:

$$\log\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \log ZR/aE(1-2RT/E) - E/2.3RT \text{ for } n \neq 1, \text{ and} \tag{6}$$

$$\log\left[-\frac{\log(1-\alpha)}{T^2}\right] = \log ZR/aE(1-2RT/E) - E/2.3RT \text{ for } n = 1 \tag{7}$$

In the thermal decomposition of polymers, E/RT is greater than 20, and accordingly $2RT/E \ll 1$. Thus $\log ZR/aE(1-2RT/E)$ is practically constant, and plots of

$$\log\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] \quad vs. \quad 1/T(n \neq 1) \tag{8}$$

and

$$\log\left[-\frac{\log(1-\alpha)}{T^2}\right] \quad vs. \quad 1/T(n = 1) \tag{9}$$

respectively, result in a straight line with slope $-E/2.3RT$ for the correctly chosen value of n.

Equations (6) and (7) may be applied using a simple graphical technique. For reaction (1), $n = 0$, 1/2, 2/3 or 1 may be justified theoretically [9]. Using $n = 0$, 1/2 and 2/3 in expression (8), and $n = 1$ in expression (9), one can observe for which value of n a straight line results, the reaction order being easily estimated. The method which allows the determination of both n and E [11] is more complicated.

Figure 2 shows the plots (8) and (9) for a graft copolymer sample with 8.3%VAgr. A straight line is obtained only for $n = 1$. The same results have been obtained for all samples investigated here. Thus, one concludes that in the thermal decomposition of the acetoxy groups, all the unsplit groups have the same decomposition probability during the reaction.

Once the reaction order $n = 1$ is established, the corresponding Eq. (7) may be used in the temperature range 275–350° (acetoxy group splitting) to compute E from the slope of the straight line, and Z from the intercept.

We used the Fuoss method [10] for evaluation of the kinetic parameters of the thermal decomposition of the polyethylene-vinyl acetate graft copolymers too. The method takes into consideration the active weight of the sample which undergoes thermal decomposition, and therefore only the sample fraction which is able to participate in the thermal decomposition:

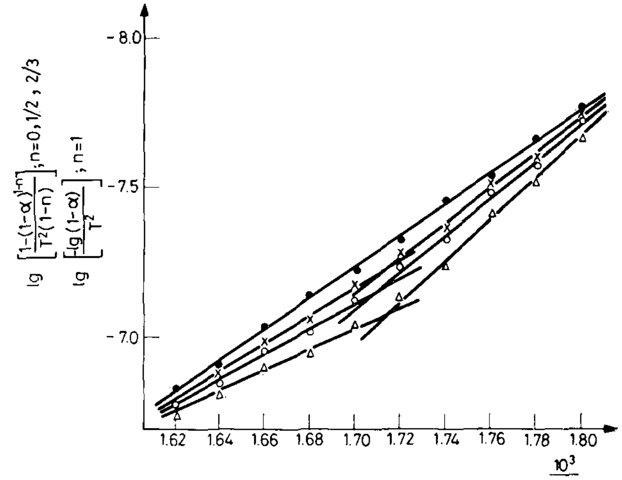


Fig. 2. Coats-Redfern method (graft copolymer sample with 8.3 %VAgr.). × $n = 0$; ● $n = 1$; ○ $n = 1/2$; △ $n = 2/3$

$$w = w_t - w_f \tag{10}$$

where:

w is the active weight of the sample;
w_t is the sample weight at time t; and

w_f is the final weight of the sample (at the end of the studied decomposition interval).

It is assumed that the active weight of the sample submitted to thermal decomposition reacts according to first-order kinetics, so that

$$-\mathrm{d}w/\mathrm{d}t = Zwe^{-E/RT} \tag{11}$$

and the temperature (T) changes linearly with time: $T = T_0 + at$, because the heating rate (a) of the sample is constant. Multiplying Eq. (11) by $\mathrm{d}t/\mathrm{d}T = 1/a$, it is transformed into the equation for the slope of the TG curve (12):

$$dw/dT = -(Zw/a)e^{-E/RT}. \tag{12}$$

By differentation of Eq. (12), one gets

$$d^2w/dT^2 = -(Z/a)e^{-E/RT}(dw/dt + wE/RT^2). \tag{13}$$

If the TG curve has an inflection point, at that point $d^2w/dT^2 = 0$. From this condition the activation energy (14) is computed:

$$E = -(RT_i/w_i)(dw/dT)_i \tag{14}$$

where:

T_i is the temperature at the inflection point;
w_i is the active weight of the sample at the inflection point; and
$(dw/dT)_i$ is the slope of the TG curve at the inflection point.

Once E is determined Eq. (14), Z may be obtained from Eq. (12) as:

$$Z = (-a/w_i)(dw/dT)_i e^{-E/RT}. \tag{15}$$

The method may be applied to graft copolymers, because (i) it was established that $n = 1$, (ii) the heating rate is $a = 4°/\text{min} = \text{constant}$, and (iii) the TG curve possesses an inflection point (see Fig. 1).

Figure 3 and Table 1 illustrate the computational approach for a graft copolymer sample (8.3%VAgr). The TG curve shows the dependence on temperature

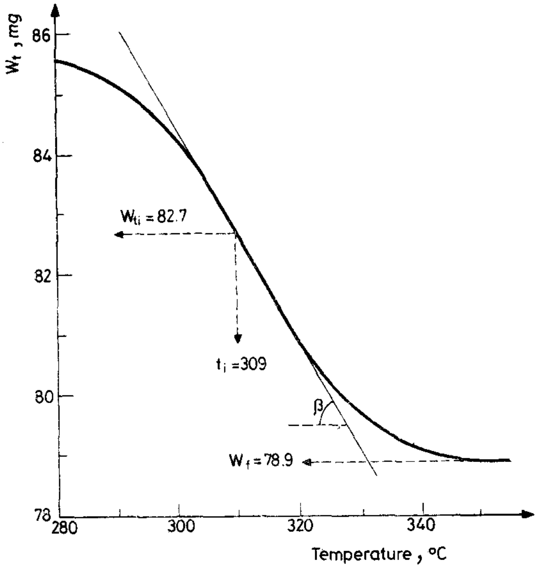


Fig. 3. Fuoss method (graft copolymer sample with 8.3%VAgr.) $w_i = w_{ti} - w_f = 82.7 - 78.9 = 3.8$; $T_i = 581$; $\left(\frac{dw}{(dT)}\right)_i = \text{tg}\beta = 0.195$; $E_a = 143.7$ kJ/mol; $Z = 1.8 \cdot 10^{12}$ min^{-1}

Table 1

The Fuoss method: calculation of E and Z

Graft copolymer		T_i, °C	w_{ti}, mg	w_f, mg	w_i, mg	$\left(\frac{dw}{dt}\right)_i$	E, KJ/mol	Z, min^{-1}
Type	%VAgr.							
1	2.6	589	82.4	80.9	1.5	−0.069	137.9	3.3 10^{11}
2	4.8	588	82.4	80.3	2.1	−0.098	133.8	1.5 10^{11}
3	4.9	588	110.4	107.6	2.8	−0.136	139.2	4.8 10^{11}
4	6.5	588	71.0	68.2	2.4	−0.110	129.6	9.3 10^{11}
5	7.6	587	121.1	117.9	4.2	−0.207	140.8	7.2 10^{11}
6	8.3	581	82.7	78.9	3.8	−0.195	143.8	1.8 10^{12}
7	8.7	585	111.7	106.6	5.1	−0.240	133.8	1.7 10^{11}
8	8.9	588	79.0	75.8	3.2	−0.156	140.8	6.3 10^{11}
9	13.0	579	89.8	85.1	4.7	−0.263	155.9	2.6 10^{13}
10	17.6	581	120.0	126.1	6.1	−0.333	152.9	1.3 10^{12}

of the sample weight (w_t). The position of the inflection point is specified, determining its coordinates. i.e. the temperature (T_i) and the sample weight (w_{ti}). The active weight of the sample at the inflection point (w_i) was determined according to relationship (10), subtracting from the sample weight at the inflection point (w_{ti}) the final weight of the sample (w_f). w_f represents the sample weight when acetoxy group splitting is completed, and it is determined from the TG curve. From the same curve the slope at the inflection point, $(dw/dT)_i$, was determined. The values of E and Z are determined by means of Eqs (14) and (15), the values at the inflection point of the temperature, sample active weight and slope being known. Table 1 illustrates the computational approach to E and Z for the series of graft copolymers studied here.

Table 2 shows the E and Z values obtained by means of the Coats–Redfern and Fuoss methods, the agreement between the two methods being quite good.

Table 2

The values of E and Z determined by the Coats-Redfern (C–R) and Fuoss (F) methods

Graft copolymer		E, kJ/mol		Z, min^{-1}	
Type	%VAgr.	C–R	F	C–R	F
1	2.6	135.8	137.9	1.6 10^{11}	3.3 10^{11}
2	4.8	125.4	133.8	4.4 10^{11}	1.5 10^{11}
3	4.9	140.0	139.2	9.9 10^{10}	4.8 10^{11}
4	6.5	125.8	131.7	3.7 10^{11}	9.3 10^{10}
5	7.6	136.7	140.8	7.6 10^{11}	7.2 10^{11}
6	8.3	140.0	143.8	1.8 10^{10}	1.8 10^{12}
7	8.7	131.2	133.8	2.6 10^{11}	1.7 10^{11}
8	8.9	139.2	140.9	1.5 10^{11}	6.3 10^{11}
9	13.0	160.9	155.9	2.1 10^{12}	3.6 10^{13}
10	17.6	152.6	152.9	4.1 10^{11}	1.3 10^{12}

The values of E and Z do not depend on %VAgr. E, Z and n, previously computed, allowed the calculation of the rate constant. For different values of the temperature in the range 275–350°, the rate of the acetoxy group splitting reaction was calculated, and it was concluded that for all the graft copolymers the rate has a maximum at about 300°. This result is fully confirmed by the DTG curves; they also have a maximum at about 300°.

Conclusions

1. The thermal decomposition of the polyethylene-vinyl acetate graft copolymers (2.6–17.6%VAgr.) was studied under nonisothermal conditions, i.e. a constant heating rate of 4°/min. By means of the Coats–Redfern and Fuoss methods, the kinetic parameters of the acetoxy group splitting reaction were computed.
2. We found that the reaction order is 1, and accordingly all the unsplit acetoxy groups have the same decomposition probability during the reaction (i.e. 275–350°).
3. The values of the activation energy and frequency factor, calculated by means of the mentioned methods agree well, and they do not depend on the copolymer grafted VA content.

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Résumé — On a étudié par thermogravimétrie (en conditions non isothermes, avec une vitesse de chauffage constante de 4°/min), la décomposition thermique de copolymères greffés — polyéthylène-acétate vinylique. Entre 275 et 350° la décomposition thermique est due au départ des groupes acétoxy des chaînes greffées et à l'élimination de l'acide acétique. On a calculé l'ordre de réaction, l'énergie d'activation et le facteur de fréquence à l'aide des méthodes Coats-Redfern et Fuoss. Les valeurs de l'énergie d'activation et du facteur de fréquence obtenues avec les deux méthodes sont en bon accord et ne dépendent pas de la teneur en acétate vinylique greffé (2.6–17.6%).

Zusammenfassung — Die thermische Zersetzung der Polyäthylen-Vinylacetat Pfropfkopolymeren wurde durch Thermogravimetrie (nicht-isotherme Bedingungen, konstante Aufheizgeschwindigkeit von 4°/min) untersucht. Zwischen 275 und 350° wird die thermische Zersetzung durch das Abspalten der Azetoxy-Gruppen der aufgepfropften Ketten und durch die Eliminierung der Essigsäure verursacht. Die Reaktionsordnung, die Aktivierungsenergie und der Frequenzfaktor wurden mit Hilfe der Coats-Redfern- und Fuoss-Methoden berechnet. Die mit den beiden Methoden erhaltenen Werte der Aktivierungsenergie und des Frequenzfaktors stimmen gut überein und sind nicht von dem Gehalt an aufgepfropften Vinylazetat abhängig (2.6–17.6%).

Резюме — Изучено термическое разложение полиэтилен-винилацетат привитые кополимеров с помощью термогравиметрии (неизотермические условия, постоянная скорость нагрева — 4° с мин.). Мемду 274 и 350° термическое разложение обусловлено расщеплением ацетоксигрупп привитого цепей и выделением уксусной кислоты. С помощью методов Коутся—Рэдферна и Фьюсса вычислены порядок реакции, энергия активации и частотный фактор. Значения энергии активации и частотного фактора, вычисленные этими двумя методами, хорошо согласуются между собой и не зависят от содержания привитого винилацетата (2.6—17.6%).