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APPARENT ACTIVATION ENERGIES OF THE NON-ISOTHERMAL DEGRADATION OF EVA COPOLYMER

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Abstract

When ethylene-vinyl acetate copolymer, EVA, is heated, a two-stage thermal degradation occurs following its melting. The vinyl acetate content of the copolymer was determined to be 43.8% by using TA 2950 and TA 2050 thermogravimetric instruments. TG/FTIR was used to detect the evolved gas. Acetic acid and *trans*-1-R-4-R'-cyclohexane were the main products evolved from EVA in the first and second stage, respectively. The apparent activation energies were determined for both stages by differential methods.

Keywords: activation energy, DSC, ethylene-vinyl acetate copolymer, TG, TG/IR, thermal degradation

Introduction

Ethylene-vinyl acetate copolymer, EVA, is widely used for its softness and pliability. When EVA is subjected to temperature-programmed heating, a two-stage decomposition occurs after melting [1, 2].

Marin *et al.* [3] determined the apparent activation energy E_a associated with the overall deacetylation process by using thermogravimetric analysis. Their studies showed that the E_a value increased with increasing heating rate up to 20°C min^{-1} when samples with VA (vinyl acetate) content between 9% and 20% were used. In addition, the E_a value obtained by means of a multi-curve (Kissinger) method was much higher than that determined by means of single curve (Coats-Redfern, etc.) methods.

The main goal of this research has been to study the two-stage degradation process of EVA by means of thermal and FTIR methods. In order to get an insight into the degradation mechanism, the apparent activation energies were determined.

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Experimental

Apparatus

TG measurements were carried out employing the TA 2050 and TA 2950 thermogravimetric instruments. Temperature calibration was accomplished using indium and aluminum with purity of 99.99%. Mass calibration was done with a standard mass. Nitrogen was used as the purge gas at a flow rate of 50 ml min^{-1}.

A more complete analysis of decomposition processes was obtained by coupling a TA 2050 instrument with a Nicolet Magna-760 FTIR spectrometer. The flow rate of the carrier gas was 50 ml min^{-1}. The spectra were collected through a gas sample cell kept at 200°C. Data acquisition parameters were as follows: detector: DTGS KBr, mirror velocity=0.6329 cm s^{-1}, collection length=2.3 s, resolution=8 cm^{-1}, number of sample scans=8, and number of background scans=32.

A TA 2910 modulated differential scanning calorimeter was used in DSC measurements. The purge gas was also nitrogen at a flow rate of 60 ml min^{-1}. Open sample pans were used without lid.

Sample

The sample of EVA (FLEX), a product of DuPont, was identified by using FTIR. The searching result of its spectrum matches ELVAX 40P (EVA of DuPont) in the Industrial Coatings Library in a score of 97.38%.

The vinyl acetate content of the copolymer was determined by TG. The sample was cut with scalpel to a size of about 1 mm for all measurements. No mass loss could be detected up to 250°C.

Results and discussion

TG/IR Gram-Schmidt reconstruction: acetic acid and trans-1-R-4-R'-cyclohexane

A TG/FTIR coupled simultaneous technique was used. The TG measurements were carried out with 10 mg samples at heating rates of 10 and 20°C min^{-1}. The IR total intensity profile of the evolved gas was recorded in synchronism with the TG/DTG curves. Two peaks at the profile corresponded to two stages of mass loss. The reproducibility of the measurement was good. The peak temperatures t_p at different heating rates for the corresponding measurements are listed in Tables 1 and 3. The IR spectrum of the gas evolved in the first stage was well matched with that of acetic acid in the Nicolet Vapor Phase Library. The match score was as high as 98.37%. Obviously, the mechanism of the first stage is deacetylation from the side chains of the copolymer, ester pyrolysis takes place through a cross-linking, and a polyene structure remains in solid state [1, 2].

Table 1 Mass loss, activation energy E_a and peak temperature t_p of the first stage

Heating rate β/°C min^{-1}	TG			DSC	
	mass loss/%	E_a*/kJ mol^{-1}	t_p(DTG)/°C	E_a*/kJ mol^{-1}	t_p/°C
5	30.52	169	344.1	115	338.1
10	30.62	174	354.2	131	347.3
15	30.59	176	360.6	153	358.0
20	30.65	175	364.4	143	363.0
30	30.72	174	369.0		
40	30.60	174	373.8		
Kissinger		221 kJ mol^{-1}		162 kJ mol–1	

* F1/Coats-Redfern integral method

It is interesting to find that the main product evolved in the second stage was *trans*-1-hexyl-4-tetradecylcyclohexane at a correlation match higher than 98.5%, or *trans*-1-dodecyl-4-octylcyclohexane higher than 95.4%. If the limitation of the Nicolet Vapor Phase Library and the similarity of the IR spectra of long chain analogues are taken into account, *trans*-1-R-4-R'-cyclohexane should be a more reasonable formula for describing the main component, which probably consists of some of the analogues, in the gas evolved in the second stage. The general formula can be explained by the rearrangement of the *trans*-poly-ene chain after the deacetylation [1]. The high match score suggests that the composition of the evolved gas is relatively uniform. Thus, the thermal degradation must be controlled by a single mechanism. This point might be useful in studies on other polymers.

In principle there should be some other smaller molecules and fragments other than acetic acid and *trans*-1-R-4-R'-cyclohexanes co-existing in the evolved gas. When low concentrations of smaller molecules, such as methane, ketenes, aldehydes, are to be detected or identified, gas chromatography or TG/MS are considered more effective [4].

Vinyl acetate content of the copolymer

In the first stage, acetic acid is lost quantitatively [1]. The vinyl acetate content of EVA can be calculated by the following equation [1, 5]:

$$\mathrm{VA\%} = \text{mass loss in the first stage}\times\frac{M_{\text{vinyl acetate}}}{M_{\text{aceticacid}}} = \Delta W_1\%\times 1.43 \qquad (1)$$

A high-resolution TA 2950 thermogravimetric instrument was used. The resolution was set on +4 (sample mass 19.969 mg) and +5 (sample mass 18.591 mg) at a heating rate of 10°C min^{-1}. A 30.88% mass loss was determined in the first stage. All the other TG experiments were run by using TA 2050 instrument. The experiments at heating rates ranging from 5 to 40°C $\min^{-1}$ gave good TG curves. Part of the results is shown in Table 1. The average of $\Delta W_1\%$ of 11 runs was $(30.62\pm0.10)\%$. This was in good agreement with the result obtained by high-resolution TG. 30.62% was taken as the amount of acetic acid released in deacetylation, the VA content of the EVA copolymer should, therefore, be 43.8% according to Eq. (1).

Activation energy of the first thermal degradation stage

Three methods were used to evaluate the activation energy for the first thermal degradation stage.

The Coats-Redfern integral method applied to TG curves

The TG curve for the first stage was processed using the Coats-Redfern integral method. Marin *et al.* made a plot of $\log[(-1/T^2)\ln(1-\alpha)]$ *vs.* T^{-1}. This implied that F1 (viz. Avrami-Erofeev equation, n=1) was taken as the mechanism function, assuming that the thermal degradation was a first-order reaction [3]. This assumption was also accepted in this work. The plot of $\log[-\ln(1-\alpha)/T^2]$ *vs.* T^{-1} for typical TG data at a heating rate of 10°C $\min^{-1}$ is shown as curve *a* in Fig. 1. The curve, which looks like a very flat 'W', covers the range of the reaction fraction α from 1 to 99% for the first stage. The initial part of the curve indicates the induced period of the non-isothermal decomposition; the upward trend of the last part overlaps with the beginning of the second degradation stage, which has a higher activation energy. These two parts of the curves were neglected in the data processing. The slopes obtained from the principal part of the mass loss give the

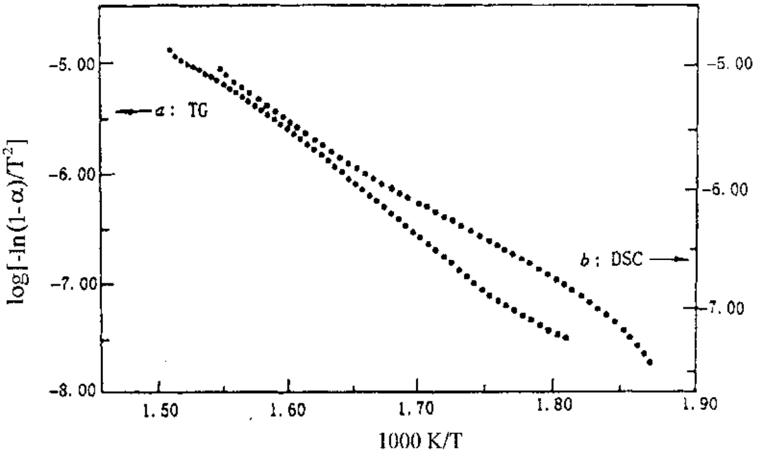

Fig. 1 The Coats-Redfern method applied to the first degradation stage of EVA at β=10°C $\min^{-1}$

E_a (=2.303 R×slope) values shown in Table 1. The data are quite close and the mean value of E_a of the deacetylation is (173.7±2.4) kJ mol^{-1}. Although Marin *et al.* reported that E_a increased with increasing heating rate under their experimental conditions, the results of the present work seem to be independent of heating rate.

The Coats-Redfern integral method applied to DSC curves

In order to purge the evolved gas and maintain fresh reaction circumstances, a sample pan without lid was used in DSC runs. The measurement stopped as soon as the second stage started. It should be pointed out that the mass and composition change gradually and continuously in the course of thermal degradation, the baseline is shifted in the exothermic direction as the heat capacity changes. This leads to some difficulty in measuring the area of the endothermic effect and the reaction fraction α. Nevertheless, α, $d\alpha/dt$ or $d\alpha/dT$ at T can be obtained on the basis of a sigmoidal baseline method by using Program General V4.1. (TA Instruments). Similarly to the TG data, a plot of $\log[-\ln(1-\alpha)/T]$ *vs.* T^{-1} is shown in Fig. 1, curve b. Undoubtedly, the change in enthalpy is different from that in mass. It is questionable whether the method can be applied to DSC results. However, the activation energies were calculated with longer portions of the initial parts of the curves omitted than in TG. The mean value of E_a shown in Table 1 is (135.5±16.4) kJ mol^{-1}. Obviously, the high standard deviation comes from the shift of the baseline and from the sigmoidal baseline taken.

Kissinger's multi-curve method applied to DTG and DSC curves

Kissinger's multi-curve method was originally developed for analysis of DTA patterns. The peak temperature t_p varies with the heating rate if the mechanism of the reaction and the experimental conditions other than the heating rate are maintained fixed. The slope of the $\ln(\beta/T_p^2)$ *vs.* T_p^{-1} plot is equal to $-E_a/R$ [6, 7]. In the present work this method was applied to both DTG and DSC analyses.

The six TG curves, whose heating rate β and t_p data are given in Table 1, gave a result of E_a=221 kJ mol^{-1}, with a correlation coefficient r=0.9983, while four DSC curves gave E_a=162 kJ mol^{-1} and r=0.9878. It is to be expected that the correlation coefficient of the latter is relatively low. The shift of the baseline affects not only the integration of the area but also the position of t_p. Since the endothermic signal is offset by the shift of baseline in the exothermic direction, the peak recorded appears at a lower temperature before the real peak temperature is attained. Although the program made a correction, the difference between the mathematical model and thermal behaviour still exists. This results in an uncertainty of t_p, which depends on the heating rate and the operation conditions leading to a low r value.

Both DTG and DSC gave a similar trend, namely that E_a obtained by Kissinger's method were about 25% higher than that by the Coats-Redfern method. Marin *et al.* [3] reported the same tendency but to a greater extent (about 80%).

Ozawa's multi-curve method applied to DTG curves

Since E_a is not dependent on the heating rate as discussed above, the mechanism of non-isothermal decomposition can be assumed to be unchanged throughout the entire stage. Therefore, Ozawa's multi-curve method [8] is also suitable to check the variation of the activation energy with the reaction fraction α.

Table 2 E_a obtained by using Program TGAKin V4.0 from 6 TG curves

α (full TG curves)		α (in specific stage)	E_a/kJ mol^{-1}	log$A$/min^{-1}
0.031	the first stage	0.10	259	21.2
0.061		0.20	255	20.8
0.092		0.30	251	20.3
0.122		0.40	249	20.0
0.153		0.50	245	19.6
0.184		0.60	241	19.2
0.214		0.70	237	18.7
0.245		0.80	234	18.4
0.276		0.90	232	18.1
0.376	the second stage	0.10	407	29.8
0.445		0.20	408	29.4
0.514		0.30	442	31.6
0.584		0.40	440	31.3
0.653		0.50	437	30.9
0.722		0.60	433	30.5
0.792		0.70	427	30.0
0.861		0.80	415	29.1
0.931		0.90	400	28.0

The data processing was done with the TG decomposition kinetics data analysis program TGAKin V4.0 (TA Instruments). From the six TG curves E_a and log$A$ at some given α are listed in Table 2. It can be seen that E_a decreases with increasing α, and hence with increasing T. On the other hand, the slightly convex form of the main part of curve *a* in Fig. 1 also illustrates the descending slope within the range of $1.75\cdot10^{-3}$ K^{-1} to $1.55\cdot10^{-3}$ K^{-1} (about 300 to 370°C). So E_a should decrease in the same direction. The relationship between E_a and T, however, can usually be expressed by some equations, such as [9],

$$E_a \approx \Delta H^{\ddagger} + RT \quad \text{or} \quad E_a \approx E + mRT \tag{2}$$

If the diffusion and departure of the molecules of acetic acid become more and more difficult during the course of reaction as the reaction advances from the surface into the centre of the solid sample, E_a should increase with increasing reaction fraction α. The fact that the change is just the opposite, can be explained by the catalytic effect of the acetic acid evolved.

The meaning of the compensation effect between E_a and $\log A$ is still in dispute, thus no further discussion is offered of the data mentioned above. However, the data in Table 2 are fitted by the linear least-squares method for reference as follows:

$$\log(A/\text{min}^{-1}) = 0.114E_a \text{ mol kJ}^{-1} - 8.20 \tag{3}$$

The lower results obtained from DSC data will be discussed later together with the studies of other polymers.

Activation energy of the second thermal degradation stage

The residue of the first stage degrades and gasifies further due to chain scission. The second degradation stage is completed at about 550°C. The IR library search for the evolved gas of this stage gives very high and almost fixed match score. It implies that the reaction keeps an unchanged mechanism. Therefore, kinetic analysis for this stage is meaningful.

Determination of the mechanism function by single curve methods and evaluation of E_a

The Coats-Redfern integral equation [10] and the differential equation of Achar *et al.* [11] have frequently been applied to process the data of single TG curves. Only mechanisms that give close values of the kinetic parameters in both integral and differential methods can be considered as probable reaction mechanisms. Take $g(\alpha)$ and $f(\alpha)$ as the general forms of the integral and differential mechanisms, respectively, the Coats-Redfern integral and the Achar differential equations can be expressed as Eqs (4) and (5), respectively.

$$\ln\frac{g(\alpha)}{T^2} = \ln\frac{AR}{\beta E_a} - \frac{E_a}{RT} \tag{4}$$

$$\ln\frac{\mathrm{d}\alpha/\mathrm{d}t}{f(\alpha)} = \ln A - \frac{E_a}{RT} \tag{5}$$

The relationship between $g(\alpha)$ and $f(\alpha)$ is defined by

$$f(\alpha)=\frac{\mathrm{d}\alpha}{\mathrm{d}g(\alpha)} \tag{6}$$

In the present work, thirty commonly used mechanism functions [12–14] have been tried by using Eqs (5) and (6). The plots of $\log[g(\alpha)/T^2]$ or $\log[(\mathrm{d}\alpha/\mathrm{d}t)/f(\alpha)]$ *vs.* T^{-1} were prepared. Slopes, intercepts, the linear correlation coefficients, and thus, E_a(=–2.303R×slope), A or log$A$, can be obtained. As examples, only two out of the thirty mechanisms are shown in Fig. 2. As discussed for the first stage, only the principal part of a curve is taken to be fitted by linear least-squares method. It is easy to conclude that mechanism D3 is much more suitable than F1. E_a can be evaluated from curve a, but the curvature of the middle part of curve b is too large to estimate the linear parameters. Therefore, the values given in the column under 'F1/C-R' in Table 3 are substantially invalid. Some other mechanisms among the thirty gave parabolas or strange curves, which are not shown in Fig. 2.

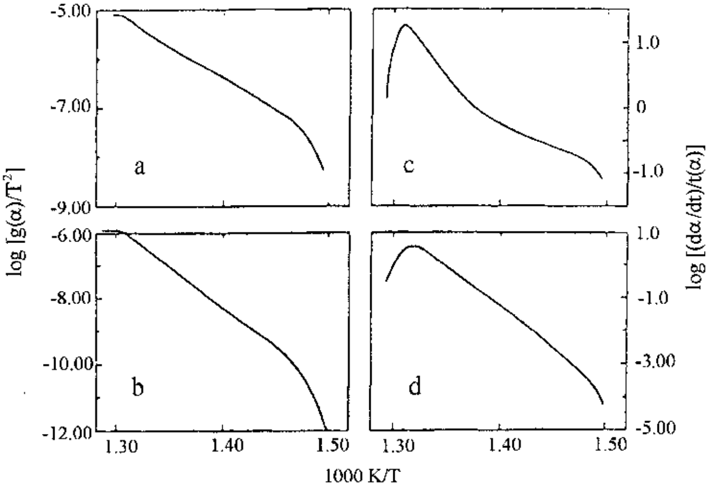

Fig. 2 The Coats-Redfern and the Achar method using F1 and D3 as mechanism functions applied to the second thermal degradation stage of EVA at $\beta=10^{\circ}\mathrm{C\ min^{-1}}$; a: F1/Coats-Redfern; b: F1/Achar; c: D3/Coats-Redfern; d: D3/Achar

On the other hand, D3 gives relatively good curves. E_a values evaluated from curves c and d are listed in Table 3. The data also seem to be independent of the heating rate. The mean values are (473.3±5.5) kJ mol^{-1} and (477.7±4.1) kJ mol^{-1} for the integral and differential methods, respectively. These two results are in good agreement with each other and relatively close to those obtained from the multicurve methods which are presented below.

The mechanism of D3 (or called Jander equation) is three-dimensional diffusion, its equations are:

$$g(\alpha) = [1-(1-\alpha)^{1/3}]^2 \tag{7}$$

$$f(\alpha) = \frac{3(1-\alpha)^{2/3}}{2\left[1-(1-\alpha)^{1/3}\right]} \tag{8}$$

This mechanism seems to be a more reasonable model for a degradation, leading to complete gasification.

Ozawa's and Kissinger's multi-curve methods applied to TG/DTG curves

As in the data processing of the first stage, E_a and log$A$ for the second stage are listed in the lower part of Table 2. It can be observed that the E_a value first increases and then decreases with increasing fraction α. The average is about 420 kJ mol^{-1}.

Table 3 Activation energy E_a and peak temperature T_p of the second stage

Heating rate β/°C min^{-1}	E_a/kJ mol^{-1}			T_p(DTG)/ °C
	F1/C-R*	D3/C-R**	D3/A***	
5	261	479	479	463.0
10	261	471	477	469.8
15	267	467	473	474.5
20	264	481	479	478.1
30	257	471	474	482.4
40	256	471	484	484.1
Kissinger		430 kJ mol^{-1}		

* F1/C-R: F1/Coats-Redfern integral method

** D3/C-R: D3/Coats-Redfern integral method

*** D3/A: D3/Achar differential method

The T_p of six DTG curves are listed in Table 3. Kissinger's method gives a result of 430 kJ mol^{-1}, r=0.9958. This is in good agreement with that resulted by Ozawa's method.

The activation energy of the second stage obtained from multi-curve methods is about 10% lower than that from single curve methods. It is contrary to the case in the first stage.

Conclusions

The thermal degradation of EVA was found to occur in two stages. The main products in the evolved gas, identified by TG/IR, were acetic acid and *trans*-1-R-4-R'-cyclohexane in the first and second stage, respectively.

The apparent activation energies of both stages were determined from the TG curve. The E_a values determined for a sample with VA content of 43.8% showed that they were independent of the heating rate when calculated using a single-curve method. F1 (Avrami-Erofeev equation) and D3 (Jander equation) were taken as the mechanism functions in the first and the second stages, respectively. Multi-curve methods were applied to TG/DTG curves.

DSC curves were also used to estimate the activation energy for the first stage.

In the first thermal degradation stage, E_a values obtained by the multi-curve methods were higher than those resulted by the single curve methods, but it was quite the contrary in the second stage.

The process of the non-isothermal degradation of EVA can be described as follows: an induction period occurs first and then a relatively stable degradation goes on while acetic acid is evolved, two thermal degradations overlap and the sample completely decomposes at last.

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