Determination of the vinyl acetate content in ethylene–vinyl acetate copolymers by thermogravimetric analysis

Zhao Wenwei*, Zhong Xiaoguang, Yu Li, Zhang Yuefang and Sun Jiazhen
Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China
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The dependence of thermal degradation behaviour on vinyl acetate (VA) content of ethylene–vinyl acetate (EVA) copolymers was studied by thermogravimetric analysis (t.g.a.). Among the parameters investigated, the maximum rate of weight loss at the stage of acetic acid evolution was found to have a linear relationship with VA content and to be independent of molecular weight and heating rate. Thus, a new method based on t.g.a. for the prediction of VA content of EVA copolymers is suggested.

(Keywords: copolymers; vinyl acetate; thermogravimetric analysis)

Introduction

Ethylene–vinyl acetate (EVA) copolymers are the most widely used polar copolymers. Their properties are closely related to the contents of ethylene and vinyl acetate (VA). Products with different VA contents are used for different applications; for example, a copolymer with low VA content is usually used as a thermoplastic, and a copolymer with high VA content is generally considered as an oil-resistant elastomer or is used to prepare hot-melt adhesive. Thus, VA content is an important parameter of the copolymer, and needs to be known before the material is put into use.

The thermal degradation behaviour of EVA has been studied by several researchers[1–4], and information such as structural changes, identification of volatile decomposition products, and degradation mechanism has been derived. Isothermal degradation studies indicate that the dominant degradation product from EVA is acetic acid (HAc), while under progressive heating conditions HAc is evolved first, before the main-chain degradation occurs. HAc evolution increases with VA content in both cases[3,4]. The object of this work is to find out the correlation between degradation behaviour and VA content of EVA. A quantitative relationship between the rate of weight loss at specific temperature and VA content will be shown. In contrast to the method based on ^{1}H n.m.r. or i.r. measurements, this may be a more convenient and more reliable method to determine the VA content in EVA copolymers.

Experimental

Some characteristics of the EVA samples are listed in *Table 1*. Samples subjected to thermogravimetric analysis (t.g.a.) were sliced from pellets provided by the producers, with weights varying from 2.0 to 2.5 mg and with irregular shapes. The thermogravimeter used was a TGS-2 Thermal Analyzer (PE Co., USA). The atmosphere was air or nitrogen, as indicated in the text, and heating rates were 5, 10 and 20°C min^{-1}.

Results and discussion

It has been suggested that deacetylation occurs when EVA copolymers are subjected to thermal degradation, and the deacetylation of EVA copolymers has an autocatalytic character, similar to that of poly(vinyl acetate) (PVA)[2,3,5,6]. This argument implies that a possible correlation exists between the thermal degradation behaviour and the VA content of EVA copolymers.

Figure 1 shows the typical t.g. and d.t.g. curves of EVA copolymer. The two peaks on the d.t.g. curve, at about 350 and 460°C, correspond to the evolution of HAc and the main-chain degradation, respectively[4], verifying the general theory of a two-stage process in the thermal degradation of EVA. In this communication, only the first stage, in which the deacetylation reaction is involved, is taken into consideration.

Several parameters derived from t.g. and d.t.g. measurements were carefully analysed. As shown in *Table 2*, the temperature at which deacetylation begins (T_0) varies with the VA content and molecular weight of the sample. The peak maximum (T_{max}) is about 10–20°C higher than that of PVA, depending on the VA content and also perhaps on the block content and sequence length of the VA component, according to McNeill *et al.*[2]. However, the maximum rate of weight loss $(\mathrm{d}W/\mathrm{d}t)_{max}$ and the corresponding percentage weight loss

Table 1 Characteristics of copolymer materials

Sample code	Melt index[a] (g/10 min)	VA content (mol%)	Supplier
LDPE	2	0	Yanshan, China
EVA-1	1.5	14	Tosoh Co., Japan
EVA-2	250	28	Shanghai, China
EVA-3-1	10	30	Shanghai, China
EVA-3-2	30	30	Shanghai, China
EVA-4	25	45	Bayer Co., Germany
EVA-5	5	50	Bayer Co., Germany
PVA	5×10^5 (M_n)	100	This laboratory[7]

[a] At 196°C, 2.16 kg

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* To whom correspondence should be addressed

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W% increase monotonically, while the VA content in the copolymer keeps increasing, in spite of the differences (e.g. in molecular weight and chain structure) between the samples. A plot of VA content *versus* $(dW/dt)_{max}$ (*Figure 2*) revealed a good linear relationship, and the following equation was obtained:

$$\text{VA(mol\%)} = 7.11\ (dW/dt)_{max} - 0.74$$

It was also found that data in the literature[4] fit the equation very well (see also *Figure 2*).

The dependence of deacetylation rate on VA content may be due to the neighbouring-group effects, as suggested by McNeill *et al.*[2]. At low VA levels, the VA units will be isolated, and will eliminate HAc to yield isolated double bonds in the chain. As the VA content rises, VA groups will increasingly appear in sequence. The neighbouring group of VA in the VA sequence can catalyse deacetylation of HAc, and every short sequence of VA units in the copolymers requires its own initiation step. The average sequence length increases with VA content and, consequently, accelerates the rate of deacetylation.

It is generally believed that the sample size and geometry will affect the rate of weight loss in the thermolysis of polymers if it is controlled by the rate of diffusion. In our experiments, the sample size was as small as possible in order to eliminate this effect.

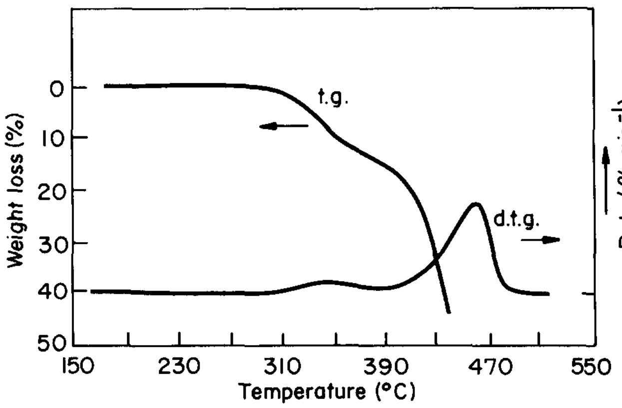

Figure 1 T.g. and d.t.g. curves of EVA copolymer with 14 mol% VA (atmosphere: N_2; heating rate: 10°C min^{-1})

Table 2 T_o, T_{max}, $(dW/dt)_{max}$ and *W*% data of various samples (heating rate 10°C min^{-1} under N_2)

Sample code	T_o (°C)	T_{max} (°C)	$(dW/dt)_{max}$ (% min^{-1})	*W* (%)
LDPE	260	–	–	–
EVA-1	280	350	2.22	8.0
EVA-2	236	346	4.00	18.0
EVA-3-1	256	346	4.25	19.0
EVA-4	250	344	6.40	25.5
EVA-5	232	342	7.25	27.0
PVA	230	330	14.70	52.5

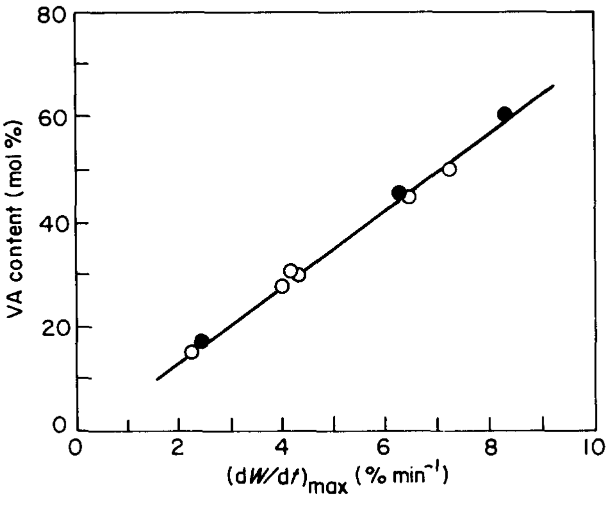

Figure 2 Plot of VA content *versus* $(dW/dt)_{max}$: ○, this work; ●, ref. 4

Table 3 Data on $(dW/dt)_{max}$ for samples of different molecular weight and under different experimental conditions

Sample code	Molecular weight (MI)	VA content (mol%)	Heating rate (°C min^{-1})	Atmosphere	$(dW/dt)_{max}$ (% min^{-1})
EVA-3-1	10	30	10	N_2	4.25
EVA-3-2	30	30	10	N_2	4.20
EVA[a]	≤5	45	10	N_2	6.31
EVA-4	25	45	10	N_2	6.40
EVA-3-1	10	30	5	N_2	4.25
EVA-3-1	10	30	10	N_2	4.25
EVA-3-1	10	30	20	N_2	4.20
EVA-5	5	50	5	N_2	7.50
EVA-5	5	50	10	N_2	7.25
EVA-5	5	50	20	N_2	7.50
EVA-1	1.5	14	10	N_2	2.22
EVA-1	1.5	14	10	air	3.10
EVA-3-1	10	30	10	N_2	4.25
EVA-3-1	10	30	10	air	4.50
EVA-4	25	45	10	N_2	6.40
EVA-4	25	45	10	air	6.61

[a] Data in ref. 4

The dependence of $(\mathrm{d}W/\mathrm{d}t)_{\max}$ on molecular weight was further analysed. Although the available sample was limited, the results given in *Table 3* indicate that the value of $(\mathrm{d}W/\mathrm{d}t)_{\max}$ is independent of sample molecular weight. The data listed in *Table 3* also demonstrate the effect of experimental conditions, such as atmosphere and heating rate, on the value of $(\mathrm{d}W/\mathrm{d}t)_{\max}$. It can be seen that $(\mathrm{d}W/\mathrm{d}t)_{\max}$ maintains an almost constant value when different heating rates are used, but a small increase was observed when degraded in air.

Under a specific atmosphere, $(\mathrm{d}W/\mathrm{d}t)_{\max}$ is linearly related to VA content, in spite of the differences in molecular weight and chain structure between the copolymers and the heating rate used in the experiments; the value of $(\mathrm{d}W/\mathrm{d}t)_{\max}$ can be obtained from the peak on the first stage of the t.g.a. curve. We therefore conclude that a new method has been developed for determining the composition of EVA copolymers by thermal degradation analysis. Further detailed investigations, on the effects of sample size, geometry and additives, are in progress.

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