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Thermogravimetric analysis of ethylene–vinyl acetate copolymer with dynamic heating rates

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Abstract

Ethylene–vinyl acetate (EVAc) copolymer with a vinyl acetate content of 40% was examined using thermogravimetric analysis with dynamic heating rate control. The method permitted determination of the vinyl acetate content of the copolymer and maximized the resolution of the two step weight loss profile by varying the heating rate in response to the weight loss. The weight loss profile resulted in a two step decomposition that varied in onset and completion as a function of the variable heating rate process. The resolution from a derivative profile of the two step weight loss was improved from 1.45 at a constant heating rate of 40°C min^{-1} to 3.89 with the dynamic heating rate.

INTRODUCTION

Ethylene–vinyl acetate (EVAc; Fig. 1) is safe, biocompatible and heat stable. It is employed as the rate controlling membrane in drug delivery devices for several pharmaceuticals [1–4]. A unique advantage that ethylene–vinyl acetate provides is its heat stability, which makes the copolymer very amenable to processing. Softening occurs between 40 and 80°C, depending on the vinyl acetate content, but thermal decomposition does not begin until 320°C. This temperature difference provides a large margin of safety for manufacturing processes.

Previously, infrared spectrometry was used to characterize the vinyl acetate content of the intact EVAc copolymer by comparing the intensity of the C–H and C–O stretch bands [5]. The oxidative stability of ethylene–vinyl acetate copolymers has also been examined using thermogravimetric analysis [6]. The vinyl acetate content measured by TGA, the qualitative identification of the pyrolytic degradation products with a TGA–FTIR system and the susceptibility of the vinyl acetate ester linkage to proton or hydroxide catalyzed cleavage have been presented [7].

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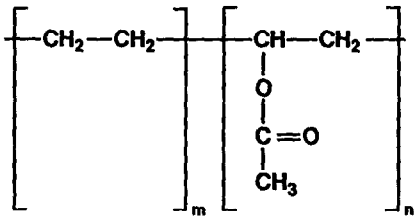

Fig. 1. Ethylene–vinyl acetate comonomer unit.

The utilization of dynamic heating has been previously reported as a means to improve resolution [8–10]. The objective of this work was to evaluate the effect of a dynamic heating system that utilizes computer controlled algorithms [11, 12] on the resolution of the two step decomposition profile of EVAc.

MATERIALS AND METHODS

Materials

Ethylene–vinyl acetate (ELVAX®) copolymers were generously provided by the Polymer Business of E.I. Du Pont de Nemours & Company, Inc., Wilmington, DE and were washed serially with ethanol prior to use.

Thermal analysis

Thermogravimetric analysis (TGA 2950 Thermogravimetric Analyzer, TA Instruments, New Castle, DE) was employed to determine the vinyl acetate content in the copolymers. Samples typically ranging from 3.6 to 16 mg were placed into a platinum pan, lowered into a furance and heated under a dry stream of nitrogen. The samples were heated initially at 40°C min^{-1} from 200 to 550°C. Subsequent analyses employed one of eight dynamic heating modes (Hi-Res™ TGA, TA Instruments, New Castle, DE).

RESULTS

Thermal analysis

The thermal instability of ethylene–vinyl acetate copolymers at temperatures in excess of the normal processing range, 150–200°C, was utilized for the determination of the resolution of the two step decomposition profile of EVAc. The decomposition profiles for ethylene–vinyl acetate with a 40% vinyl acetate content as a function of the heating mode are given in Fig. 2. The initial loss directly reflects the vinyl acetate content, which can be calculated from the product of the weight loss and

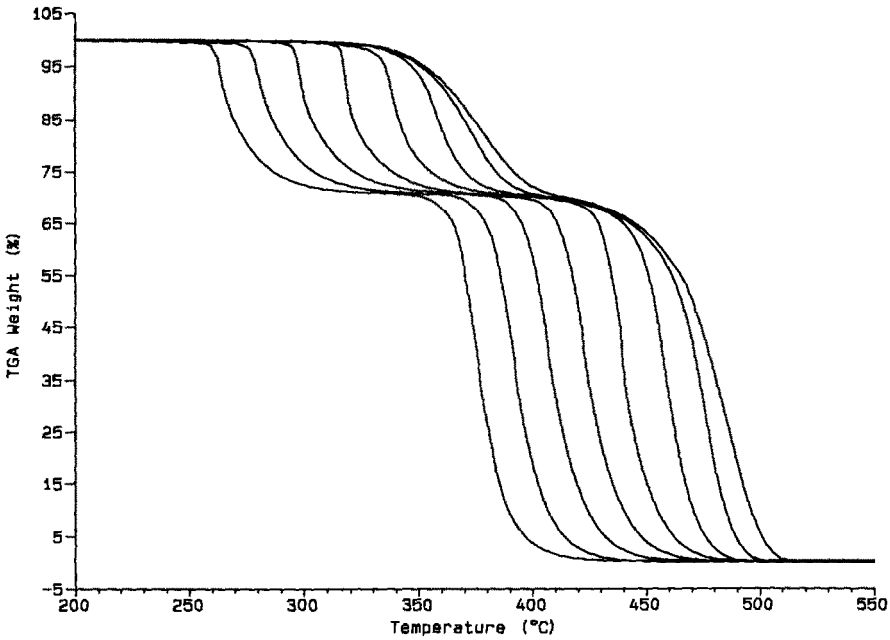

Fig. 2. Percent weight vs. temperature for the thermal decomposition of ethylene–vinyl acetate with a 40% vinyl acetate content as a function of heating mode. The high resolution modes 1–8 are presented from right to left.

the ratio of the molecular weight of the vinyl acetate monomer to the molecular weight of acetic acid. Table 1 shows that the same results were obtained with a "traditional" rate of 40°C min^{-1} and each of the eight dynamic modes. Thermal analyses of the vinyl acetate content in the copolymer gave results in excellent agreement with the labeled value (Table 1).

TABLE 1

Thermal decomposition of ethylene–vinyl acetate

Heating mode	Observed weight loss[a] (wt%)	Vinyl acetate content[a] (wt%)
Traditional	29.0 ± 0.4	41.6 ± 0.6
Hi-Res 1	29.0 ± 0.4	41.5 ± 0.6
Hi-Res 2	28.9 ± 0.2	41.5 ± 0.2
Hi-Res 3	28.7 ± 0.2	41.1 ± 0.3
Hi-Res 4	28.4 ± 0.3	40.6 ± 0.4
Hi-Res 5	29.0 ± 0.7	41.6 ± 0.9
Hi-Res 6	28.6 ± 0.2	41.0 ± 0.2
Hi-Res 7	28.6 ± 0.4	41.0 ± 0.6
Hi-Res 8	28.3 ± 0.1	40.6 ± 0.2

[a] Mean ± standard deviation ($n = 3$).

TABLE 2

Thermal decomposition of ethylene–vinyl acetate

Heating mode	Resolution[a]	Minimum heating rate (°C min^{-1})	Analysis time (min)	Standard analysis time (min)
Traditional	1.45 ± 0.05	40	8.5	8.5
Hi-Res 1	1.52 ± 0.07	25	10	22
Hi-Res 2	1.86 ± 0.1	10	13	55
Hi-Res 3	2.67 ± 0.02	2.5	20	220
Hi-Res 4	3.46 ± 0.2	1.0	43	550
Hi-Res 5	3.68 ± 0.3	0.4	120	1400
Hi-Res 6	3.89 ± 0.4	0.1	340	5500
Hi-Res 7	3.44 ± 0.2	0.03	1100	18000
Hi-Res 8	3.46 ± 0.1	0.02	3700	28000

[a] Mean ± standard deviation ($n = 3$).

The resolution between the two weight loss steps was determined from the derivative profile by standard methods [13]. The resolution, minimum heating rate, analysis time and the analysis time to reach the same resolution from standard TGA are summarized in Table 2.

DISCUSSION

Thermogravimetric analysis of the ethylene–vinyl acetate copolymer provides a rapid and sensitive method for determination of the vinyl acetate content in the copolymer. Results of the thermogravimetric analyses of the vinyl acetate contents in the EVAc copolymers were in excellent agreement with the labeled values.

The Hi-Res dynamic heating mode provided a mechanism to increase the resolution from 1.5 to 3.5 with a corresponding increase in analysis time. However, the run times were substantially less (one-half to one-sixteenth the time) than would have been permitted with a traditional TGA method. The methods were quite reproducible with a average coefficient of variation of 1.03%. Overall, the technique provides a powerful tool for optimizing resolution in thermogravimetric analysis. However, additional quantitative studies are needed to further the current empirical understanding of the magnitude of the effect of changing the dynamic heating mode on the resolution.

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