

Thermogravimetric analysis of ethylene–vinyl acetate copolymers with Fourier transform infrared analysis of the pyrolysis products

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Abstract

Ethylene–vinyl acetate (EVAc) copolymers were examined using thermogravimetric analysis (TGA). The method permitted rapid and reproducible determination of the vinyl acetate content of the copolymer. The weight loss profile for low density polyethylene, i.e., ethylene–vinyl acetate with a 0% vinyl acetate content, showed a single-step decomposition from 460 to 560°C that accounts for 100% of the observed weight loss of the sample. The heating of ethylene–vinyl acetate with vinyl acetate contents from 9 to 40% resulted in a two-step decomposition in the ranges 360–450°C and 450–550°C. A TGA–Fourier transform infrared spectrometer (FTIR) coupled system permitted the identification of the pyrolytic products in the effluent gas as acetic acid for the first-step product, and a mixture of 1-butene, carbon dioxide, ethylene, methane, and carbon monoxide.

INTRODUCTION

Ethylene–vinyl acetate (Fig. 1) is safe, bio-compatible and stable to heat. It is employed as the rate-controlling membrane in drug delivery devices for the intraocular release of pilocarpine [1], the intrauterine release of progesterone [2] and the transdermal delivery of nitroglycerin [3] and estradiol [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, while thermal decomposition does not begin until 350°C. The 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

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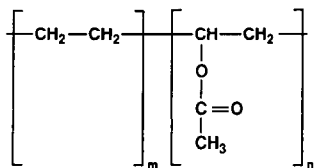


Fig. 1. Ethylene-vinyl acetate comonomer unit.

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 objectives of this work were to determine the vinyl acetate content of the EVAc copolymers using thermogravimetric analysis (TGA), to identify qualitatively the pyrolytic degradation products with a TGA-FTIR coupled system, and to examine the susceptibility of the vinyl acetate ester linkage to proton- or hydroxide-catalyzed cleavage.

MATERIALS AND METHODS

Materials

Low density polyethylene (ALATHON 20[®]) and ethylene-vinyl acetate (ELVAX[®]) copolymers were generously provided by the Polymer Products Department of E.I. du Pont de Nemours & Company, Inc., Wilmington, Delaware and were washed serially with ethanol prior to use. All other reagents were of analytical grade.

Thermal analysis

Thermogravimetric analysis (Perkin-Elmer 7 Series Thermal Analysis System, Norwalk, CT) was employed to determine the vinyl acetate content in the copolymers. Samples typically ranging from 10 to 20 mg were placed in a platinum pan, lowered into a furnace and heated under a dry stream of nitrogen. The samples were heated at 40°C min⁻¹ from 25 to 650°C. The heating rate was validated, using rates as low as 2°C min⁻¹ with the ethylene-vinyl acetate containing 40% vinyl acetate; no differences were seen in the onset, rate or extent of decomposition. Qualitative identification of the decomposition products was made using a Fourier transform IR spectrometer coupled directly to the TGA effluent (5SX FTIR spectrometer, Nicolet Instruments, Cincinnati, OH; Thermogravimetric Analyzer, E.I. Du Pont de Nemours, Wilmington, DE). The TGA heating rate was 10°C min⁻¹. The effluent gas passed directly from the furnace to the cell of the spectrometer and was scanned at a rate of 1 scan sec⁻¹.

Ethylene–vinyl acetate aqueous stability

To determine the aqueous stability of ethylene–vinyl acetate, the copolymer was incubated with phosphate buffer (0.1 M, pH 2.4 and $\mu = 0.25$) and NaOH (0.1 N, pH 12.6 and $\mu = 0.25$) at 37°C and the vinyl acetate content was determined by TGA.

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 vinyl acetate content. The decomposition profiles for low density polyethylene, i.e., ethylene–vinyl acetate with a 0% vinyl acetate content and ethylene–vinyl acetate with a 40% vinyl acetate content, are given in Fig. 2.

Low density polyethylene shows a single-step degradation from 460 to 560°C that accounts for 100% of the observed weight loss of the sample. The heating of ethylene–vinyl acetate with a 40% vinyl acetate content results in a two-step decomposition from 360 to 450°C, and from 450 to 550°C. The initial loss reflects directly the vinyl acetate content which can be calculated by determining the inflection point of the derivative thermogram for the first step and multiplying this percentage by the ratio of the molecular weight of the vinyl acetate monomer to the molecular weight of acetic acid. Initially, experiments were conducted to validate the heating rate. Table 1 shows that the same results were obtained with heating rates of 2, 10, 20, and 40°C min⁻¹; consequently a heating rate of 40°C min⁻¹ was used for all determinations. The thermal analyses of the vinyl acetate contents in the

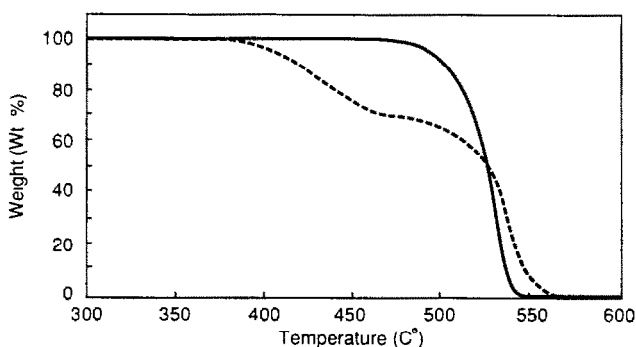


Fig. 2. Percent weight loss vs. temperature for the thermal decomposition of low density polyethylene (—) and ethylene–vinyl acetate with a 40% vinyl acetate content (- - - - -).

TABLE 1

Thermal decomposition of ethylene–vinyl acetate: effect of heating rate

Labeled vinyl acetate content (% w/w)	Heating rate ($^{\circ}\text{C min}^{-1}$)	Observed vinyl acetate content (% w/w) ^a
9	10	9.49 \pm 0.09
9	40	9.29 \pm 0.09
25	20	25.5 \pm 0.6
25	40	25.7 \pm 0.4
40	2	42.1 \pm 0.2
40	40	42.3 \pm 0.2

^a Mean \pm standard deviation ($n = 5$).

TABLE 2

Thermal decomposition of ethylene–vinyl acetate

Labeled vinyl acetate content (% w/w)	Observed weight loss (% w/w) ^a	Observed vinyl acetate content (% w/w) ^a
0	0	0
9	6.48 \pm 0.07	9.29 \pm 0.09
18	12.5 \pm 0.1	18.0 \pm 0.1
25	17.9 \pm 0.3	25.7 \pm 0.4
33	23.0 \pm 0.2	33.0 \pm 0.2
40	29.5 \pm 0.2	42.3 \pm 0.2

^a Mean \pm standard deviation ($n = 5$).

copolymer were in excellent agreement with the labeled values, except for the 40% EVAc which deviated by 5% (Table 2).

Subsequently, the Fourier-transform infrared spectrometer in tandem with the TGA was used to verify the composition of the effluent gas. 1-Butene, ethylene, methane, and carbon monoxide were observed in all samples. The ethylene–vinyl acetate also produced acetic acid during the first-step transition from 350 to 460 $^{\circ}\text{C}$, as a product of the thermal elimination from the vinyl acetate component of the copolymer.

Ethylene–vinyl acetate aqueous stability

The ethylene–vinyl acetate also showed no instability after incubation with phosphate buffer (0.1 M, pH 2.4) and NaOH (0.1 N, pH 12.6) at 37 $^{\circ}\text{C}$ for 15 days (Fig. 3).

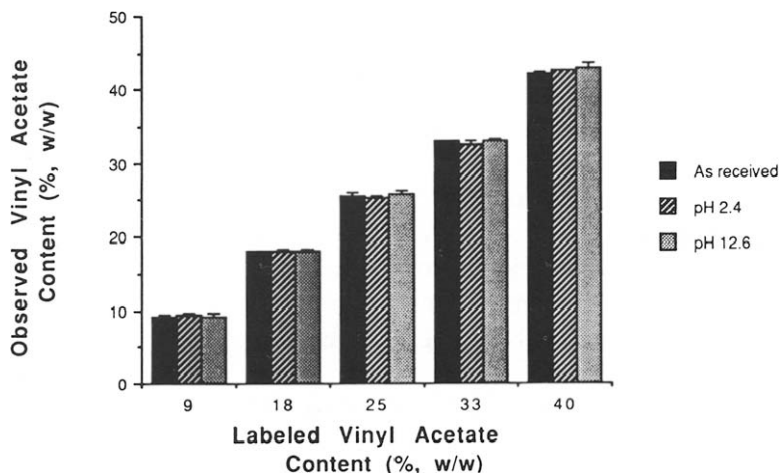


Fig. 3. Mean vinyl acetate content \pm standard deviation ($n = 5$) vs. time for the aqueous stability of ethylene-vinyl acetate copolymers with different vinyl acetate content as a function of pH after 15 days at 37°C.

DISCUSSION

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

The TGA-FTIR coupled system permitted qualitative identification of the decomposition products with minimal sample processing. The major

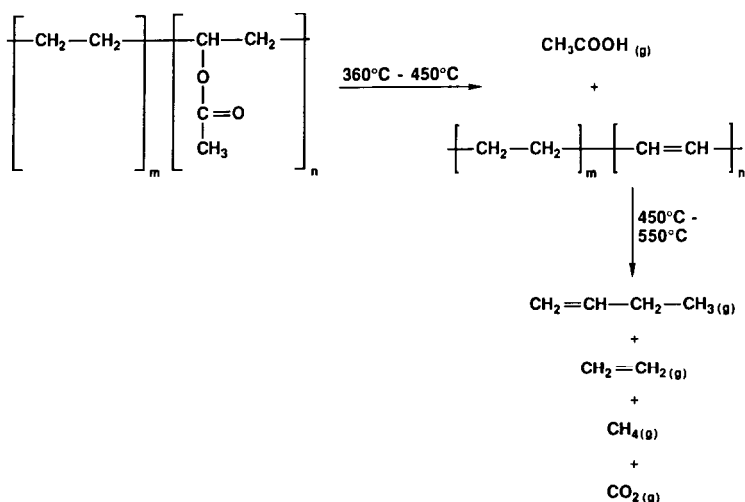


Fig. 4. Ethylene-vinyl acetate pyrolysis mechanism.

pyrolysis product from low density polyethylene was 1-butene with the effluent also containing ethylene, methane and carbon dioxide. Acetic acid was evolved during the first step in the two-step decomposition of EVAc, with the second step evolving 1-butene, ethylene, methane and carbon dioxide. Those observations are consistent with previous work that employed a liquid nitrogen condensation system with subsequent mass spectrometry [7]. A pyrolytic scheme for the EVAc copolymer can be envisioned where elimination of the acetic acid occurs from 360 to 450°C and then subsequent decomposition of the remaining copolymeric chain takes place from 450°C to 550°C producing 1-butene, ethylene, methane and carbon dioxide (Fig. 4).

The copolymeric ester bond was found to be resistant to both proton- and hydroxide-ion-catalyzed cleavage, thus providing further support that charged molecules do not enter the EVAc copolymers [8].

ACKNOWLEDGEMENTS

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