Polymer Bulletin 41, 61–67 (1998)

Polymer Bulletin

Determination of the vinyl mercaptoacetate content in poly(ethylene-*co*-vinyl acetate-*co*-vinyl mercaptoacetate) (EVASH) by TGA analysis and FTIR spectroscopy

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Received: 14 July 1997/Revised version: 29 April 1998/Accepted: 5 May 1998

SUMMARY

A new method has been developed for determining the esterification degree (ED) of EVASH copolymers by Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA). A plot of absorbance values (A_{1736} - A_{720}) versus ED in EVASH samples determined by TGA analysis revealed a good linear relationship.

INTRODUCTION

The synthesis and characterization of functional polymers employed as reactive compatiblizers in several polymer blends are important researches developed in the Instituto de Macromoléculas (IMA) and CTA laboratories in Brazil (1-5). Poly(ethylene-*co*-vinyl alcohol-*co*-vinyl mercaptoacetate) (EVALSH) was employed in graft copolymerization of methyl methacrylate (2-3). EVALSH copolymers were also effective in the reactive compatibilization of natural rubber-EVA (4-5) and nylon-polyethlene blends (6-7). Recently we have developed an analytical method based on TGA and FTIR for the determination of vinyl mercaptoacetate (VMA) in EVALSH (8).

Now we have developed a new class of functionalized copolymers. These materials, namely poly(ethylene-*co*-vinyl acetate-*co*-vinyl mercaptoacetate) (EVASH), were prepared by direct reaction of mercptoacetic acid (MAA) with ethylene - vinyl acetate (EVA) copolymers (9). The presence of a little EVASH in polypropylene (PP) fibers increased the elastic modulus, indicating reinforcing of these functional polymers (10). The presence of SH groups along the EVA backbone may enhance the adhesive properties of this compound. Therefore, methods for the determination of this group in EVASH copolymers point to a useful way to study the properties of their blends.

TGA and FTIR were effective in the determination of VMA in EVALSH (8), however, it should not be employed to EVASH copolymers without adaptations due to several factors: the degradation of VA and VMA occurs simultaneously; the carbonyl absorptions of the VA and VMA groups are observed at the same wavenumber. Thus, it is necessary to find alternative techniques for these methods for determining the ED of EVASH.

Therefore, we describe a quantitative method for the determination of VMA content in such copolymers based on TGA/FTIR method used for EVALSH with new adaptations.

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EXPERIMENTAL

Ethylene - vinyl acetate copolymer (EVA) (vinyl acetate = 18.6 wt-%; melt flow index = 0.7 g/10 min at 150°C), EVA (vinyl acetate = 28 wt-%; melt flow index = 6.4 g/10 min at 80°C) and EVA (vinyl acetate = 40 wt-%; melt flow index = 0.78 g/10 min at 80°C) used kindly supplied by Petroquimica Triunfo S.A., and Politeno S.A., Brazil. EVA 18 samples were completely hydrolyzed and the corresponding EVOH submitted to esterification with MAA, according to literature (1). EVASH samples were prepared by direct reaction of MAA (9) with EVA 18, EVA 28 and EVA 40. The reaction conditions and copolymer composition are discussed in this reference (9).

TGA analyses were carried out in a 951 Thermogravimetric Analyser fitted with Du Pont TA-9900 in nitrogen atmosphere (flow rate = 100 ml/min) at a heating rate of 10°C/min, from room temperature to 400°C. FTIR analyses were performed with a 1750 Perkin-Elmer spectrometer (resolution 4 cm^{-1}; gain 1; 4000 to 500 cm^{-1}; 40 scans). The samples were analyzed by the potassium bromide (KBr) technique.

RESULTS AND DISCUSSION

Characterization of EVASH by TGA

The structure of EVASH is ilustrated in Figure 1.

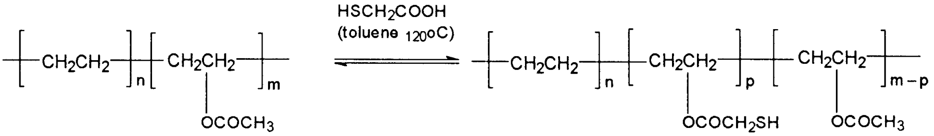

Fig.1. Scheme for EVASH synthesis

As shown in the previous paper (9), in the TGA analysis of EVALSH, the MAA evolution begins at a slightly lower temperature than the acetic acid (HAc) elimination in EVA. These preliminary results suggested the possibility that the two groups could be separated by TGA analysis. However, as shown in the non-isothermal TGA curve of EVASH (Figure 2), the degradation of VA and VMA occurs simultaneously. According to Wenwei (11), the neighbouring group VA in the VA sequence can catalyse deacetylation of HAc. Then, it is reasonable to surmise that VMA evolution also accelerates VA elimination, so the two groups, VA and VMA, are evolued simultaneously.

Quantitative analysis of EVASH by FTIR

The FTIR spectrum of EVASH is shown in Figure 3. The absorptions are similar to those observed for EVA copolymer due to the presence of the ethylene chain (Figure 1). In addition, the C=O and COOC groups present in VA and VMA show absorptions at the same wanenumbers, 1736 cm^{-1} and 1240 cm^{-1}, respectively (12); the SH absorption is characteristically weak and may go undectected in the spectra of thin films (13).

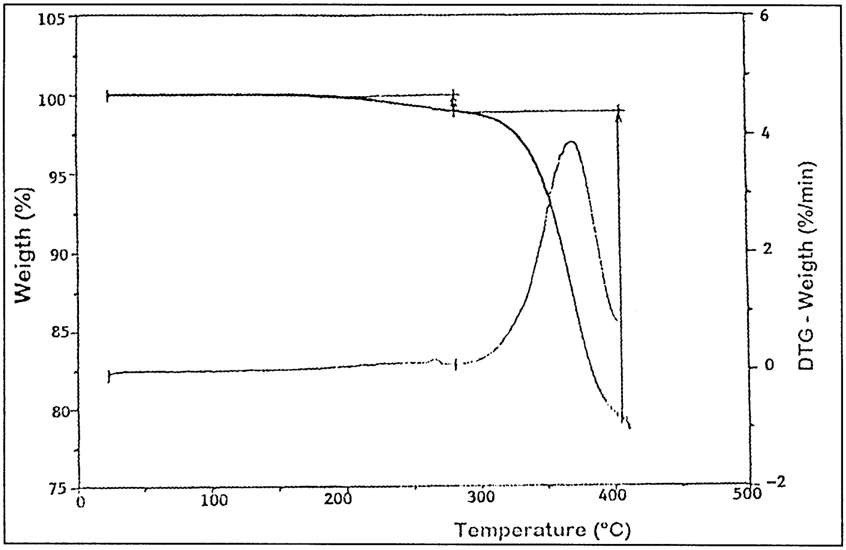

Fig. 2. Nonisothermal thermogravimetric curve of EVASH

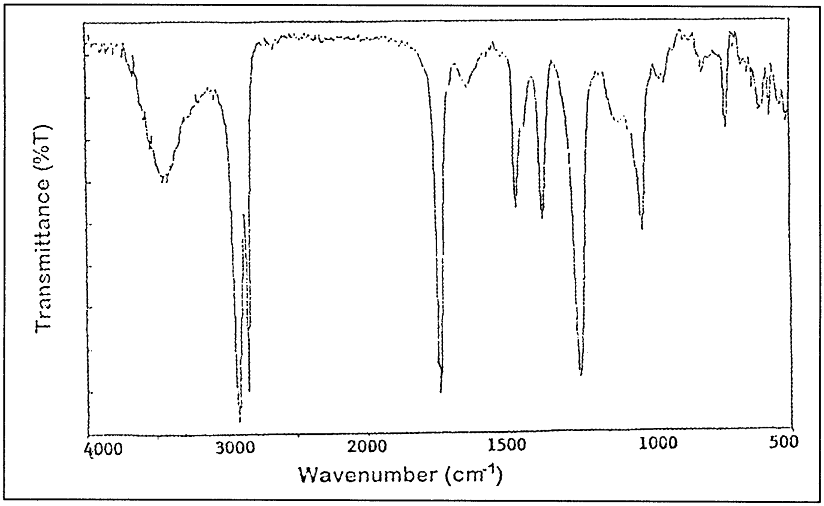

Fig. 3. FTIR spectrum of EVASH

According to Smith (12), in cases of overlapping bands, the absorbance at a particular wavelength is given by the sum of absorbances of each absorbing species at that wavelength. In practice, analytical bands can often be chosen such that interference from the other constituents is negligible or relatively constant for one or more components. Analysis is greatly simplified since the concentration of this constituent can be calculated first, and corrections found from graphs or tables can be applied to the other absorbances.

Thus, by doing the calculation in the proper sequence, one can carry out the entire computation by subtraction of correction and avoid the more tedious algebraic and approximation methods (12).

Thus, for quantitative analysis, the absorbance values at 1736 cm^{-1} were related to those corresponding to the methylene (CH_2) absorption at 720 cm^{-1}. The absorption at 720 cm^{-1} assigned to the polyethylene chain, was chosen as the reference band as used previously (8) for thickness correction. SH concentrations can be known by calibration curve taken by FTIR and TGA analyses of EVALSH, since that to calculate the extent of esterification, the number of MAA incorporated should be related to the VA content initially present in EVA. Thus, these preliminary data prompted us to use the absorption at 720 cm^{-1} as the correction term and developed a systematic analytical method to quantify MAA incorporation into the EVA backbone.

Table 1 presents A_{1736}/A_{720} as a function of ED, obtained by TGA, the calibration curve for the determination of SH concentrations. The aborbance values represent the median (μ) of five analyses. The standard deviation, σ_μ, (14) of the median absorbance and relative error were calculated as in the pevious paper (8).

Table 1. FTIR data of EVALSH samples with different VMA contents

Sample code (run)	ED * (mol- %)	A_{1736}/A_{720}	Standard deviation (σ_μ)	Relative error (%)
A1	13.46	0.441	0.006	1.36
A2	21.70	0.704	0.011	1.56
A3	29.76	0.909	0.022	2.40
A4	34.09	1.119	0.017	1.52
A5	42.15	1.281	0.025	1.95
A6	43.77	1.390	0.017	1.22
A7	45.53	1.492	0.019	1.27
A8	51.14	1.714	0.016	0.93
A9	58.72	1.868	0.050	2.68
A10	59.64	1.946	0.014	0.72
A11	67.65	2.043	0.038	1.86
A12	76.33	2.331	0.044	1.89

* (%VMA/23.89) x 100

The weight loss in a sample with 100% of esterification can be calculated assuming tha all VA units initially present in the EVA are replaced by VMA units. As the VA content was 18.6 wt-%, 100g of EVA would yield 106.99g of EVALSH (25.55 VMA and 81.38g ethylene). Thus the VMA content in a totally esterified sample would be 23.89%. Thus, the ED of EVALSH samples can be calculated dividing the VMA content obtained by TGA analysis by 23.89 and multiplying by 100.

From the calibration curve (Table 1) taken by FTIR/TGA analysis, the following relationship is proposed:

$$\mathbf{y = 0.05 + 0.03\,x}$$

where *y* is the median relative absorbance (A_{1736}/A_{720}) versus ED of EVALSH samples.

To calculate the extent of esterification of EVASH, according to the proposed, method FTIR the median absorbance (A_{1736} - A_{720}) should be related to the calibration curve. Thus, Table 2 shows the ED of EVASH.

Table 2. FTIR data of EVASH samples with different VMA contents

Sample code (VA in EVA/run Ax)	ED (mol-%)	A_{1736} - A_{720}	Standard deviation (σ_{μ})	Relative error (%)
18/A1	23.66	0.760	0.017	2.20
18/A2	21.40	0.693	0.044	5,70
18/A3	24.90	0.798	0.049	6.30
18/A4	22.30	0.720	0.028	3.80
18/A5	23.53	0.756	0.020	2.90
18/A6	24.13	0.774	0.034	3.87
18/A7	22.67	0.730	0.030	4.11
28/A8	38.50	1.204	0.010	0.84
28/A9	42.70	1.332	0.060	4.60
28/A10	40.00	1.250	0.090	6.40
28/A11	40.36	1.261	0.034	2.38
40/A12	48.73	1.512	0.078	5.20
40/A13	47.70	1.481	0.081	6.07

Figure 4 shows the plot of A_{1736} - A_{720} versus ED. A good linear relationship is obtained and the same calibration curve is proposed. This relationship can be applied to determination of ED of EVALSH and EVASH with different VMA contents and of EVA with several VA contents, EVA 18, EVA 28 and EVA 40. (Figure 5; Table 1 and Table 2-FTIR/TGA data).

To confirm the FTIR/TGA data the EVASH sample obtained in run 8 (28/A8) was submitted to SH titration. This method involves a reaction of a weighed polymer sample with a standard iodine solution in the presence of a known amount of a low molecular weight mercapto compound, according to the following expression:

$$\mathbf{{}_2R - SH + I_2 \rightarrow R - S - S - R + {}_2HI}$$

The excess of iodine is then back-titrated with a standardized sodium thiosulfate solution to determine the amount of the SH group in the copolymer. From this method, 38.8 mol-% for ED was obtained which agrees with the value obtained by FTIR/TGA (38.5 mol-%) (Table 2). In addition, the good linear relationship shown by Figure .5 also indicates that this FTIR/TGA method for determining the ED is reliable and that the amount of the functional group along the EVA backbone is not so high as that one achieved by esterification of the hydrolyzed EVA with MAA, previously reported (8).

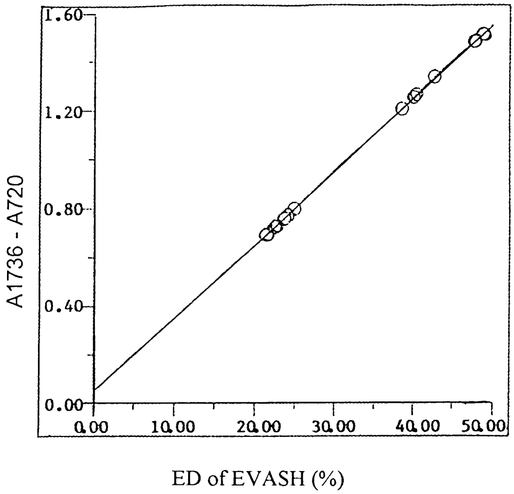

Fig. 4. Plot of absorbance A_{1736} - A_{720} versus ED of EVASH samples, determined by TGA.

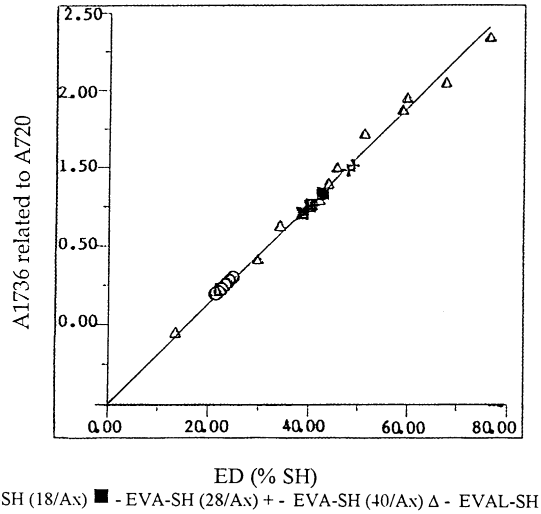

Fig. 5. FTIR/TGA data for detemining the ED of mercapto-modified EVA copolymers (VA in EVA/run Ax).

CONCLUSIONS

A new method has been developed for determining the ED of EVASH copolymers by FTIR and TGA. A good linear relationship was obtained.

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