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Poly(ethylene-*co*-vinyl alcohol-*co*-vinyl mercaptoacetate) (EVALSH)-determination of the vinyl mercaptoacetate content by thermogravimetric analysis and FTIR spectroscopy

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Summary

A quantitative method for the determination of vinyl mercaptoacetate (VMA) in poly(ethylene-co-vinyl alcohol-co-vinyl mercaptoacetate) (EVALSH) based on Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA) was developed. A plot of relative absorbance values (A_{1736} / A_{720}) versus esterification degree in EVALSH samples determined by TGA analysis revealed a good linear relationship.

Introduction

Functional polymers have been employed as reactive compatibilizers in several polymer blends (1). Their synthesis are normally performed by polymerization or copolymerization of functional monomers or by modification of some commercial polymers. The last method is technologically more attractive because it does not involve special polymerization techniques and special functionalized monomers. Ethylene - vinyl acetate (EVA) copolymers constitute a versatile class of commercial polar copolymers. Their properties and application are strongly dependent on the vinyl acetate content. In addition, the acetate groups along the backbone can be easily transformed into other functional groups by using well-known organic reactions. The classical example of such EVA modification is the hydrolysis which gives rise to another important commercial copolymer, poly(ethylene-co-vinyl alcohol) (EVOH) (2).

Recently we have employed the simple esterification reaction to introduce mercapto groups along the EVOH backbone (3). By heating a toluene solution of EVOH with mercaptoacetic acid, a new class of functionalized copolymer was developed. This material, namely poly(ethylene-co-vinyl alcohol-co-vinyl mercaptoacetate) (EVALSH) was prepared with different mercapto contents and employed for the synthesis of graft copolymers (3-5). In addition, the mercapto-modified EVOH was also employed as reactive compatibilizing agent for natural rubber/EVA (6-7) and nylon-6/LDPE (7) polymer blends. Both in graft copolymerization and reactive compatibilization, the SH content is an important parameter to be taken into account. The evaluation of esterification degree has been performed either by acid-base or iodometric titration of non reacted mercaptoacetic acid, which remains in the washing layer after precipitation of the polymeric material into methanol. This procedure is not recommended when a great amount of copolymer has to be modified. In addition, the determination of SH content in

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the copolymer by iodometry is not reproducible due to the insolubility of the copolymer at room temperature.

Thermogravimetric analysis (TGA) is often employed to determine the vinyl acetate content in EVA copolymers (8-9). Its efficiency was recently confirmed in CTA laboratories in Brazil (10). The amount of acetic acid evolved is related to the vinyl acetate (VA) content in these copolymers. Assuming similar thermal degradation behavior for vinyl mercaptoacetate (VMA) in EVALSH copolymers, the same procedure should be employed for VMA content determination.

Therefore, we would like to describe in this work a quantitative method for determination of VMA content in such copolymers based on thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FTIR).

Experimental

Ethylene - vinyl acetate copolymer (EVA) (vinyl acetate = 18.6 wt-%; melt flow index = 0.7g/10min at 150°C) used was kindly supplied by Petroquímica Triunfo S. A., Brazil. EVA samples were completely hydrolyzed and the corresponding EVOH submitted to esterification with mercaptoacetic acid (MAA), according to literature (3).

TGA analyses were carried out in a 951 Thermogravimetric Analyzer fitted with a 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 4cm^{-1}; gain 1; 4000 to 500 cm^{-1}; 40 scans). The samples were analyzed by potassium bromide (KBr) technique.

Results and discussion

Determination of vinyl mercaptoacetate content in EVALSH by TGA

Figure 1 shows the non-isothermal thermogravimetric (TGA) curves of EVA (VA=18.6 wt-%), hydrolyzed EVA (EVOH) and EVALSH, obtained by esterification of EVOH with MAA. The structures of the copolymers are illustrated in Figure 2.

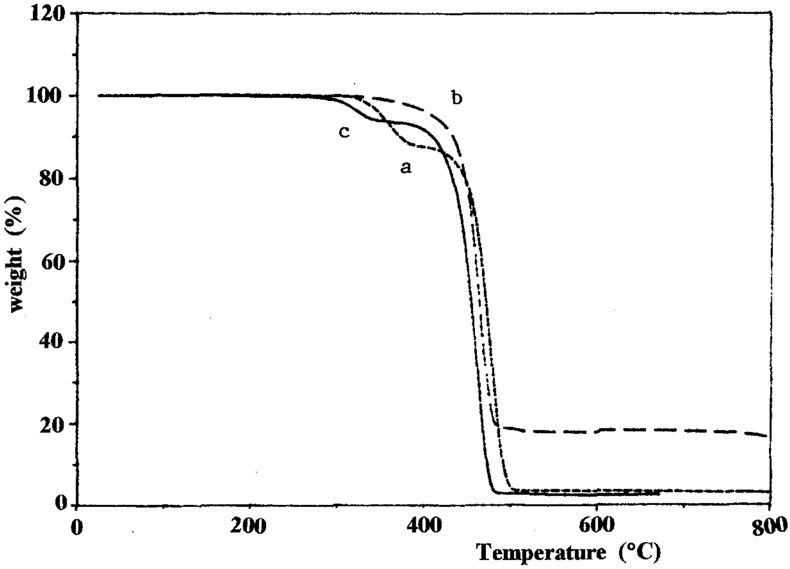

Fig.1. Nonisothermal thermogravimetric curves of (a) EVA, (b) EVOH and (c) EVALSH.

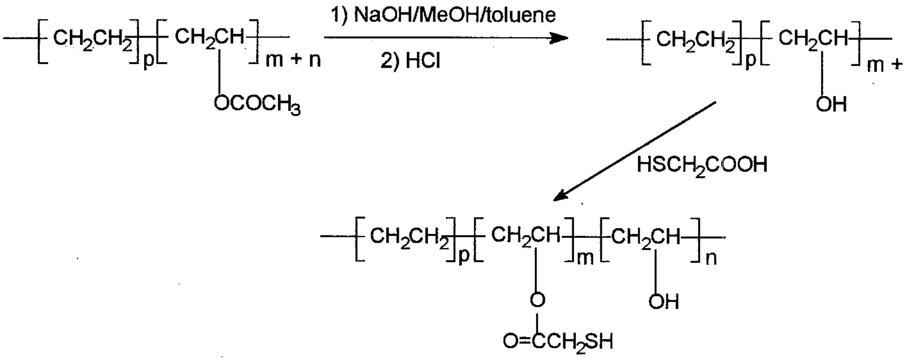

Fig.2. Scheme for EVALSH synthesis

As shown in Figure 1, EVA presents two degradation steps, as expected. The first one starts at 300°C and corresponds to acetic acid elimination. The onset degradation temperature of the second step is 400°C and is related to main chain degradation. The thermal degradation of EVOH takes place in one step and starts at 380°C. The incorporation of MAA in the EVOH backbone results in EVALSH whose degradation occurs in two steps, as in the case of EVA. The onset temperatures of both stages are lower than that of the EVA sample (270 and 370°C, respectively). Since EVOH does not degrade until 380°C, the first step degradation in EVALSH is attributed to mercaptoacetic acid evolution. These preliminary results prompted us to develop a systematic analytical method based on TGA to quantify MAA incorporation into the EVOH backbone.

Therefore, EVALSH copolymers with different VMA content were obtained by performing the esterification with excess of MAA and withdrawing aliquots at regular time intervals. The reaction conditions and copolymer composition are indicated in Table I. The percentage of MAA incorporation was determined from TGA analysis whose partial thermograms concerning the first degradation step are illustrated in Figure 3, for some EVALSH samples. The weight loss until 370°C corresponds to MAA evolved (Δm_1) and increases with the VMA content. Since each mol of vinyl mercaptoacetate yields one mol of MAA, thus Δm_1 multiplied by 1.28 gives the VMA content by weight. As indicated in the experimental part, the EVA employed contains 18.6 wt-% of vinyl acetate which corresponds to 2.16 mmol VA/g. After hydrolysis, there is a decrease of weight of polymeric material, as a consequence of the difference between the molecular weight of $-CH_2CH(OCOCH_3)-$ (MW = 86) and $-CH_2CH(OH)-$ (MW = 44) units. Thus, a totally hydrolyzed EVA results an EVOH with 2.38 mmol OH/g.

To calculate the extent of esterification, the number of incorporated MAA should be related to the OH number initially present in EVOH. The esterification results in an increasing of polymer weight, which corresponds to the difference between the molecular weight of $-CH_2CH(OH)-$ (MW = 44) and $-CH_2CH(OCOCH_2SH)-$ (MW = 118) groups. Thus, the weight increase per mol of incorporated MAA is expressed as follows:

$$\Delta x = [SH] \cdot \Delta_{MW}$$

where [SH] is the number of incorporated MAA per gram obtained by TGA and Δ_{MW} is the difference between the molecular weight of vinyl mercaptoacetate and vinyl alcohol units ($\Delta_{MW} = 74$).

The extent of esterification indicated in Table I was then calculated as follows:

$$\text{esterification degree} = \frac{[SH]\cdot(1+\Delta x)}{[OH]_o} \times 100$$

where [SH] is determined from TGA; $(1 + \Delta x)$ is the weight of polymer after MAA incorporation and $[OH]_o$ is the initial OH concentration in EVOH, which corresponds to 2.38 mmol OH/g.

By Figure 3 it is also noted that MAA evolution begins at lower temperatures as the vinyl mercaptoacetate content increases. This behavior was also observed in EVA thermal degradation (8) and may be attributed to neighboring groups effects, where the mercaptoacetate leaving group accelerates the leaving of other mercaptoacetate units.

Table 1. Reaction conditions for EVALSH synthesis [a]

sample code	time (hr.)	Δm_1 [b] (wt-%)	VMA content[c] (wt-%)	VMA content [d] (mmol/g)	Esterification degree [d] (mol-%)
A1	5.0	2.51±0.17	3.22±0.21	0.273	11.57±0.88
A2	8.5	4.05±0.29	5.18±0.37	0.439	19.04±1.55
A3	12.5	5.55±0.11	7.11±0.15	0.602	26.33±0.61
A4	16.0	6.36±0.20	8.14±0.25	0.690	30.47±1.06
A5	19.5	7.87±0.38	10.07±0.50	0.853	37.96±2.05
A6	22.0	8.17±0.10	10.46±0.13	0.886	39.67±0.53
A7	26.0	8.50±0.20	10.88±0.26	0.922	41.29±1.09
A8	30.0	9.54±0.33	12.22±0.42	1.035	46.57±1.76
A9	33.5	10.96±0.50	14.03±0.65	1.188	54.40±2.71
A10	37.0	11.13±0.25	14.25±0.32	1.207	55.39±1.35
A11	43.0	12.63±0.10	16.16±0.12	1.369	63.40±0.52
A12	56.0	14.2±0.20	18.24±0.26	1.546	72.60±1.07

a) EVOH = 15g (0.036 mol OH); MAA = 15g (0.163 mol); temp. = 110°C; toluene = 300ml.
b) Δm_1 = weight of MAA evolved, obtained by TGA.
c) VMA = $\Delta m_1 \times 1.28$
d) VMA = VMA (wt-%) $\div (118 \times 100)$

Quantitative analysis of EVALSH by FTIR

The FTIR spectra of EVOH and EVALSH samples with different VMA contents are shown in Figure 4. An increase in the intensity of the carbonyl absorption at 1736cm^{-1} associated with the decrease of OH absorption intensity at 3800-3500 cm^{-1} is observed as the mercaptoacetic acid incorporation increases. These features confirm esterification and may be a suitable analytical method to quantify the VMA content in EVALSH.

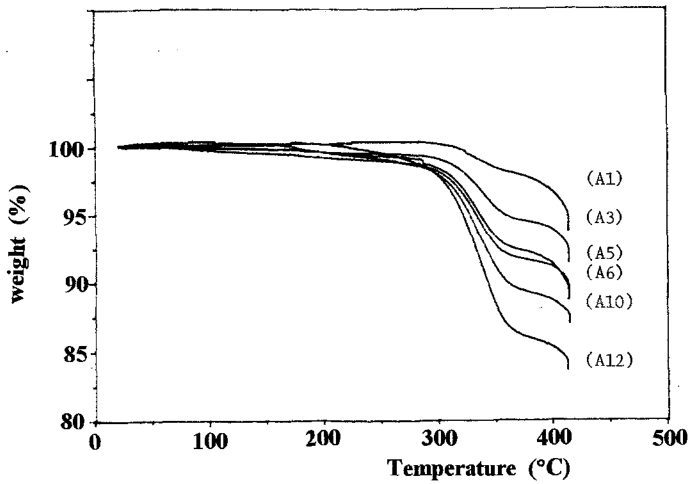

Fig.3. Nonisothermal thermograms of EVALSH with different VMA content (sample characteristics indicated in Table 1)

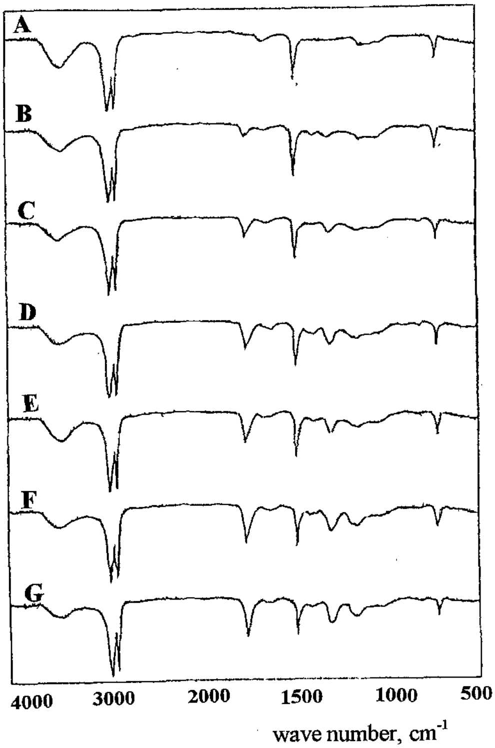

Fig.4. Overlaid FTIR spectra of (A) EVOH (B) A1, (C) A3, (D) A5, (E) A6, (F) A10 AND (G) A12 EVALSH samples (EVALSH characteristics related to sample codes are indicated in Table 1)

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 for thickness correction of specimens, because it is not influenced by esterification. The baseline points at 1840.3 cm^{-1} and 766.5 .cm^{-1} were established in calculations of absorbance values for carbonyl absorption at 1736 cm^{-1} and methylene absorption at 720 cm^{-1}.

Table 2 presents the A_{1736}/A_{720} ratio as a function of esterification degree, obtained by TGA. The absorbance values represent the median (μ) of five analyses. According to Horak (11), μ is recommended when working with a low number of experiments. The standard deviation, $\hat{\sigma}_{\mu}$, of the median absorbance are calculated as follows:

$$\hat{\sigma}_{\mu} = \hat{\sigma} / \sqrt{n}$$

where $\hat{\sigma}$ is the assessed standard deviation of the basic set and is a quantitative measurement of the precision for each individual measurement; n is the number of experiments.

$$\hat{\sigma} = K_R \cdot R$$

where K_R is the coefficient for the calculation of the average standard deviation from the variation range (for five experiments, $K_R = 0.430$); and R is the difference between the largest and smallest element ($X_n - X_1$). $\hat{\sigma}_{\mu}$ is an evaluation of the precision of this median, that is, an evaluation of the result obtained from the treatment of a finite set of measurements which are repeated under completely identical conditions.
The relative error for each sample analyzed was determined as follows:

$$\text{relative error (\%)} = \left(\hat{\sigma}_{\mu} / \mu \right) \times 100$$

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

sample code	esterification degree (mol-%)	A_{1736}/A_{720}	standard deviation ($\hat{\sigma}_{\mu}$)	relative error (%)
A1	11.57	0.441	0.006	1.36
A2	19.04	0.704	0.011	1.56
A3	26.33	0.909	0.022	2.40
A4	30.47	1.119	0.017	1.52
A5	37.96	1.281	0.025	1.95
A6	39.67	1.390	0.017	1.22
A7	41.29	1.492	0.019	1.27
A8	46.57	1.714	0.016	0.93
A9	54.40	1.868	0.050	2.68
A10	55.39	1.946	0.014	0.72
A11	63.40	2.043	0.038	1.86
A12	72.60	2.331	0.044	1.89

Figure 5 shows the plot of A_{1736}/A_{720} versus esterification degree; evidently a good linear relationship is obtained. From the calibration curve taken by FTIR analysis, the following relationship is proposed:

$$y = 0.126 + 0.032x$$

where y is the median relative absorbance (A_{1736}/A_{720}) and x is the esterification degree in EVALSH samples.

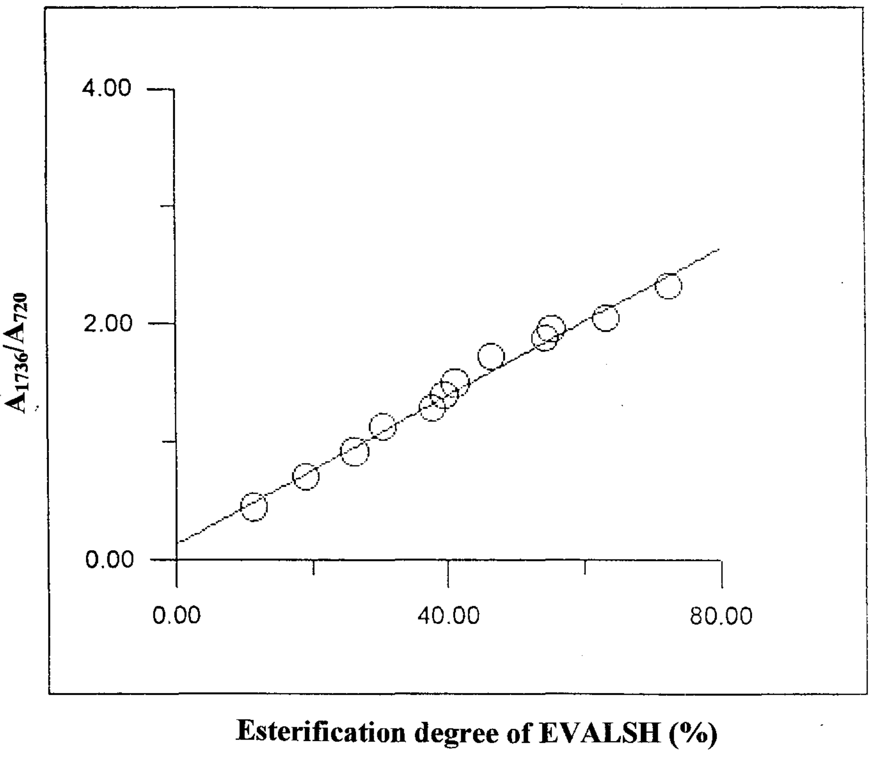

Fig.5. Plot of relative absorbance (A_{1736}/A_{720}) versus esterification degree of EVALSH samples, determined by TGA.

Conclusions

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

Acknowledgments

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