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# Quantitative Measurements of the Vinylacetate Content in High Pressure Ethylene Vinylacetate Copolymers

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The pyrolysis-IR spectrometry method, described in a previous paper,<sup>2</sup> is extended to EVA copolymers having a % wt VA content up to 55. The  $3460\text{ cm}^{-1}/2678\text{ cm}^{-1}$  absorption ratio *v.* % wt VA calibration curve for IR measurements, shows a positive deviation from linearity. All results obtained by pyrolysis, IR spectrometry and <sup>1</sup>H-NMR are comparable, showing that each method is equally valid and gives fast, reliable % wt VA values.

## INTRODUCTION

The knowledge of the vinylacetate (VA) content in ethylene vinylacetate (EVA) copolymers is essential to characterize these macromolecules. Several methods to determine the VA content have been described in literature.<sup>1</sup> However, only three techniques will be discussed in this paper, *i.e.*, pyrolysis, IR spectrometry and <sup>1</sup>H-NMR. The choice for these methods was inspired by the need for fast, reliable and easy to obtain quantitative wt % or mol % VA values. Moreover, we intended to broaden the applicability range of the pyrolysis and IR method to high pressure EVA copolymers with a larger than 28 wt % VA, up to 55 wt %. In addition, these results could be checked for their validity with the VA values obtained by <sup>1</sup>H-NMR.

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**EXPERIMENTAL**

The procedure and experimental set-up for pyrolysis, has been described in a previous paper.<sup>2</sup> Fourteen EVA types (Table I) were analyzed for their VA content. The pyrolysis experiment was repeated 10 times for each EVA type in order to determine the reproducibility of the method. First, an IR spectrum was taken of each sample. The combination of the average of 10 pyrolysis wt % VA values and the average of 10  $3460\text{ cm}^{-1}$  VA/ $2678\text{ cm}^{-1}$  CH<sub>2</sub> absorption ratios for each EVA type, allowed the construction of a calibration curve depicted in Figure 1.

ABS. RATIO

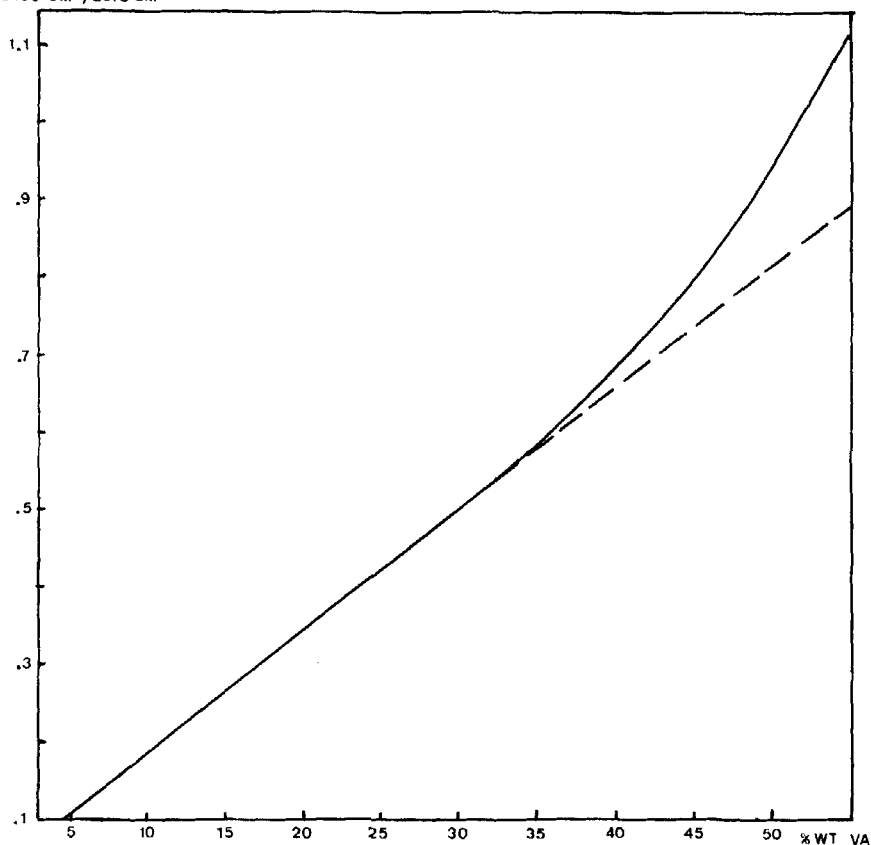
 $3460\text{ CM}^{-1}/2678\text{ CM}^{-1}$ 

FIGURE 1 The calibration curve for quantitative IR measurements of the VA content in EVA copolymers, using the first carbonyl overtone at  $3460\text{ cm}^{-1}$ .

The IR measurements were made on thin foils ( $50 \pm 20 \mu\text{m}$ ) with a Beckman 4240 spectrometer. Of quantitative interest were the  $3460 \text{ cm}^{-1}$  (first overtone carbonyl stretching), the  $1020 \text{ cm}^{-1}$  (ester bending) and the  $610 \text{ cm}^{-1}$  (ester wagging) band. The drawing of the baseline as well as the operating conditions have been presented in a previous paper.<sup>2</sup> In addition to the IR spectra used for establishing the calibration curve in Figure 1, newly prepared thin foils were used to determine the reproducibility of most IR measurements.

The  $^1\text{H-NMR}$  spectra were recorded on a JEOL PS-100 spectrometer operating at 100 MHz. The spectra were measured at elevated temperature ( $100^\circ\text{C}$ ) for 5% w/v  $\text{C}_2\text{Cl}_4$  solutions with cyclosilane as an internal standard. The chemical shift values were converted to the tetramethylsilane (TMS) scale using:  $\delta_{\text{TMS}} = \delta_{\text{cyclosilane}} - 0.327 \text{ ppm}$ . Quantitative data were obtained by the ratio method using the integration of the 1.92 ppm  $\text{CH}_3(\text{VA})$  and 1.26 ppm  $(\text{CH}_2)_n$  peak for EVA type 3, and the 4.77 ppm  $\text{CH}(\text{VA})$  and 1.26 ppm  $(\text{CH}_2)_n$  peak for all other copolymers examined (Figure 2) (Table II).

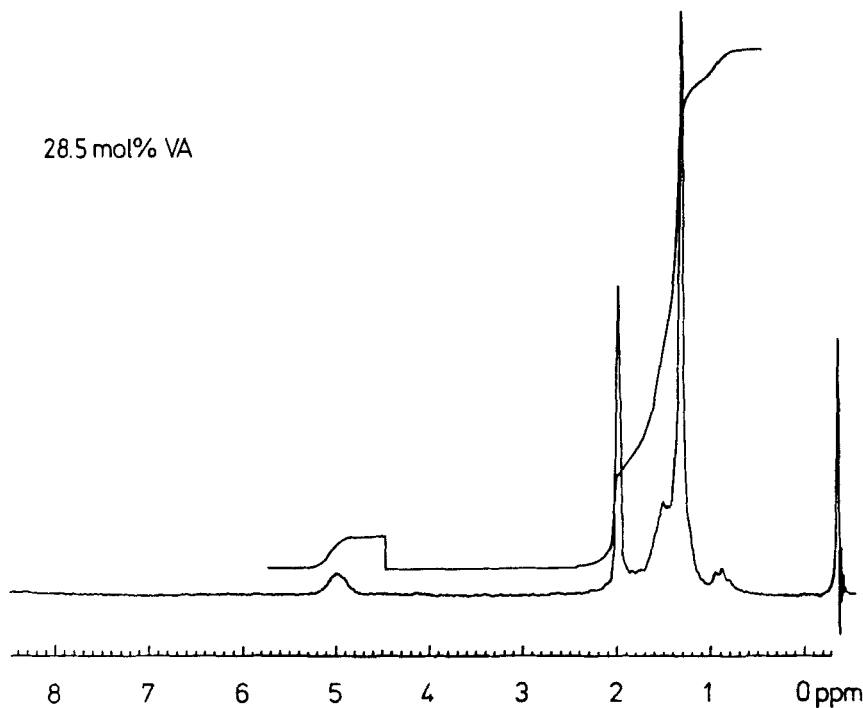


FIGURE 2 A typical  $^1\text{H-NMR}$  spectrum of an EVA copolymer.

## RESULTS AND DISCUSSION

All wt % VA values obtained by the different techniques are summarized in Table I. The pyrolysis VA results are the average of 10 experiments and are presented together with their standard deviation  $S$  ( $S = (\sum_i(x_i - \bar{x})^2/N - 1)^{1/2}$ ). The average maximum error is 0.4 wt % VA.

The IR  $3460\text{ cm}^{-1}$  values were obtained using the calibration curve in Figure 1. The  $1020\text{ cm}^{-1}$  and  $610\text{ cm}^{-1}$  VA results were measured using the respective calibration curves presented in a previous paper.<sup>2</sup> The standard deviations for the results of both other VA bands were not studied in detail, because their quantitative value was limited. The  $1020\text{ cm}^{-1}$  band is only valid for EVA types having a low VA content (<25 wt %). In this range the VA values, as presented in Table I, showed good correspondence with those obtained by pyrolysis and  $3460\text{ cm}^{-1}$  IR analysis. A higher than 25 wt % VA content gave, using the thin foil method, too intense a band. The wt % VA values obtained through the  $610\text{ cm}^{-1}$  band showed, compared to pyrolysis and  $3460\text{ cm}^{-1}$  IR analysis, a progressively lower VA content. This deviation can be attributed to the unisolated character of the  $610\text{ cm}^{-1}$  band which makes the proper choice of a baseline difficult.

It should be noted, however, that the analytical use of the  $3460\text{ cm}^{-1}$  band is limited to pure EVA resins. Interference of OH and NH groups is feasible

TABLE I

The wt % VA values of fourteen EVA types determined by pyrolysis, IR spectrometry and  $^1\text{H-NMR}$ . The pyrolysis and  $3460\text{ cm}^{-1}$  IR VA values are each the average of 10 sample measurements. The standard deviations  $S$  are mentioned. The  $^1\text{H-NMR}$  results are obtained by using the ratio method which allowed the determination of  $S$ , assuming a 2% integrating error

EVA type	Pyrolysis		IR spectrometry				$^1\text{H-NMR}$	
	wt % VA	$S$	wt % VA $3460\text{ cm}^{-1}$	$S$	$1020\text{ cm}^{-1}$	$610\text{ cm}^{-1}$	wt % VA	$S$
1	6.69	0.06	6.9	0.1	—	—	—	—
2	9.5	0.1	9.1	0.1	—	—	—	—
3	9.9	0.4	9.5	—	9.5	7.3	8.5	0.2
4	14.0	0.3	14.0	0.4	13.4	11.1	—	—
5	20.5	0.5	20.6	0.2	19.6	16.5	—	—
6	28.4	0.4	28.3	0.3	—	—	—	—
7	29.5	0.1	29.4	—	—	24.9	30.0	0.5
8	28.2	0.1	29.7	—	—	—	27.6	0.5
9	30.8	0.4	30.8	0.3	—	—	—	—
10	40.3	0.3	40.4	0.4	—	—	—	—
11	41.3	0.2	41.0	1.1	—	36.7	40.8	0.7
12	48.3	0.1	48.3	0.2	—	—	—	—
13	55.0	0.2	—	—	—	—	53.7	1.2
14	84.6	0.3	—	—	—	—	84.6	1.3

TABLE II  
Spectral assignments for ethylene vinylacetate copolymers

Chemical shift <sup>a</sup> ppm	Proton <sup>b</sup>
0.75	—CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>3</sub>
1.26	—CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub>
1.47	—CH <sub>2</sub> —CH(OOCCH <sub>3</sub> )—CH <sub>2</sub> —CH <sub>2</sub>
1.72	—CH <sub>2</sub> —CH(OOCCH <sub>3</sub> )—CH <sub>2</sub> —CH(OOCCH <sub>3</sub> )
1.92	—CH <sub>2</sub> —CH(OOCCH <sub>3</sub> )—CH <sub>2</sub> —CH <sub>2</sub>
4.77	—CH <sub>2</sub> —CH(OOCCH <sub>3</sub> )—CH <sub>2</sub> —CH <sub>2</sub>

<sup>a</sup> Chemical shifts will respect to tetramethylsilane standard.

<sup>b</sup> Proton of interest is underlined.

whenever high concentrations of additives are present. The  $1742\text{ cm}^{-1}$  C=O band cannot be used when IR measurements are made on thin foils. The carbonyl absorption is too intense. The choice of the  $2678\text{ cm}^{-1}$  CH<sub>2</sub> reference band proved to yield the best possible wt % VA results. Its validity was checked using ratio measurements of the  $3460\text{ cm}^{-1}$  absorption *v.* sample thickness.

Examining Table I and Figure 1 further, reveals two additional features: (1) an average maximum error of 0.6 wt % VA is present in the VA values obtained using the  $3460\text{ cm}^{-1}$  IR band, and (2) the  $3460\text{ cm}^{-1}/2678\text{ cm}^{-1}$  absorption ratio *v.* wt% VA curve does not remain linear above 33 wt% VA. This second feature can mainly be attributed to the choice of the  $2678\text{ cm}^{-1}$  CH<sub>2</sub> band as reference. On considering the mol % VA and mol % E (ethylene), it becomes clear that the number of CH<sub>2</sub> decreases with increasing VA content. However the replacement of one E by one VA unit leaves one CH<sub>2</sub> untouched. Therefore, as the CH<sub>2</sub> number effect will be small at the beginning with low VA content values, the calibration curve shows first a linear behavior. Later at approximately 15 mol % of 33 wt % VA, the decreasing CH<sub>2</sub> number will produce a distinct positive deviation from linearity. This effect becomes clear on considering Figure 3. Here the ordinate scale represents the VA/CH<sub>2</sub> number ratio (mol % VA/200 – mol % VA) and the abscissa scale the mol % VA. At  $\pm 15$  mol % VA the positive deviation is obvious.

The <sup>1</sup>H-NMR results are also represented in Table I, together with their standard deviation *S*. This *S* value was calculated assuming a 2% integration error. A comparison of these VA values with pyrolysis and  $3460\text{ cm}^{-1}$  IR results shows a very good conformity for all EVA types. The maximum deviations for these results are  $-0.5$  and  $+1.3$  wt % VA.

Consequently it can be concluded that each method is equally valid for fast and reliable quantitative VA determinations of high pressure EVA copo-

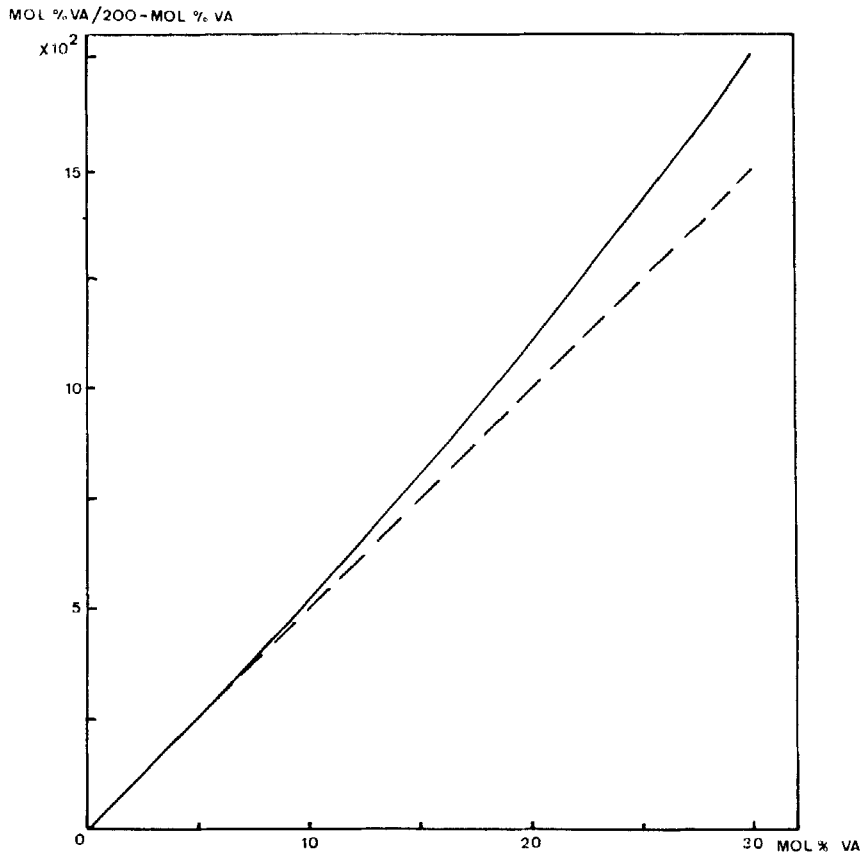


FIGURE 3 The mol % VA/(200 - mol % VA) ratio *v.* mol % VA curve. Explains the non-linear  $3460\text{ cm}^{-1}$  calibration curve represented in Figure 1.

lymers having a VA content up to 55 wt % VA. The  $^1\text{H-NMR}$  determinations take about 10 minutes once the solutions are prepared which is slightly less than the 15 minutes necessary for the IR measurements. The pyrolysis method takes about 30 minutes once the base and acid solutions are prepared and the pyrolysis device is set.

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### References

1. O. Aydin, B. V. Kaczmar and R. C. Schultz, *Angew. Makrom. Chem.* **24**, 1971 (1972).  
R. C. Schultz and O. Aydin, *J. Polym. Sci., Appl. Polym. Symp.* **50**, 497 (1975).

- A. Streitwieser and C. H. Heathcock, *Introduction to Organic Chemistry* (McMillan, N.Y., 1976), p. 35.
- E. M. Barrall, R. S. Porter and J. F. Johnson, *Anal. Chem.* **35**, 73 (1963).
- J. Chiu, *Anal. Chem.* **40**, 1516 (1968).
- R. Disselhoff, *Mitt. Deutsches Kunststoff Inst. Darmstadt* no 12, July (1972).
2. R. J. Koopmans, R. Van der Linden and E. F. Vansant, *J. Adhesion* **11**, 191 (1980).