Determination of Vinyl Acetate (VA) Content of Ethylene-vinyl Acetate (EVA) Copolymers in Thick Films by Infrared Spectroscopy

N. U. JAMROZ
Department of Chemistry, Quaid-I-Azam University, Islamabad-45320, Pakistan

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Summary: The infrared spectroscopic method was applied for the determination of vinyl acetate (VA) content in thick films of ethylene-vinyl acetate (EVA) copolymers. From spectral analysis, the A_{3460}/A_{3610} ratio was used for quantitative determination. This technical measurement is simple, quick, does not require a complicated sample preparation method and also does not need a tedious calculation procedure for the exact determination of vinyl acetate (VA) content. The overall procedure, thus adopted, presents an excellent resemblance with different practically applied methods.

Introduction

The ethylene-vinyl acetate (EVA) copolymer has vast industrial applications which is due to its' dynamic and stable physico-chemical properties and this makes EVA distinguishable over different other co-polymeric products [1-3]. The most important characteristic is the distribution of VA content with respect to ethylene-vinyl acetate (EVA) copolymer depending upon which different applied products are constituted [4-6]. Apart from the molecular mass distribution, the major properties of EVA copolymers are determined by their VA contents. The molecular mass is determined by the conditions of polymerization and VA content by the ratio of monomers [7-9]. In order to determine the structural evidences of polymeric or co-polymeric materials, VA contents are primarily determined followed by the evaluation of overall molecular masses [9-13]. The VA units are randomly distributed along the EVA chain [14-17]. Depending upon the ratio of EVA/VA contents, a number of quality products can be manufactured e.g, in the commercial products, the VA contents range from 5 to 40m/m% whereby usually giving rise to a rubber like shape for the overall product [8-17]. The copolymers containing ≥5m/m% VA contents are used for the production of thin films with intermediate rubber elasticity. With the increase of VA content from 6 to 12m/m%, the films of improved weather resistance can be obtained. EVA with having 15--18m/m% VA content is often used for the preparation of coextruded poly-propylene (PP) and poly-ethylene (PE) films with good heat resistance. The VA content of EVA used for the production of adhesives rarely exceeds 30m/m%.

A number of methods exist for VA determinations [9-13] of particular interest in IR techniques [18]. However, the present study deals with a comfortable and reliable procedure for the determination of VA contents in EVA copolymers with the exception of following advantages:

- The spectral interpretations are simple and do not include long calculations,
- The ratio A_{3460}/A_{3610} becomes a standard for various other VA contents upon various EVA compositions which specifically invites for further investigations. Thus, a huge data upon various other polymers or copolymers and the impact of VA contents upon them can easily be interpreted.

Results and Discussion

The determination of VA content becomes obvious depending upon the infrared spectrum of EVA as can be seen in Fig.1. This spectrum shows that characteristic absorbances of some bands assigned to VA contents or units are 1740 cm^{-1}, 1240 cm^{-1}, 1020 cm^{-1} and, 610 cm^{-1} and can be related to absorbances of ethylene groups as 2920 cm^{-1}, 2850 cm^{-1}, 1470 cm^{-1} and 720 cm^{-1}. In this regard, Koopmans has already given a comprehensive survey of all such possibilities and has also discussed various practical difficulties in the use of infrared spectroscopy [14-17]. The EVA spectrum, as shown in Fig.1, was recorded on a very thin film having concentration as 15–20 μm

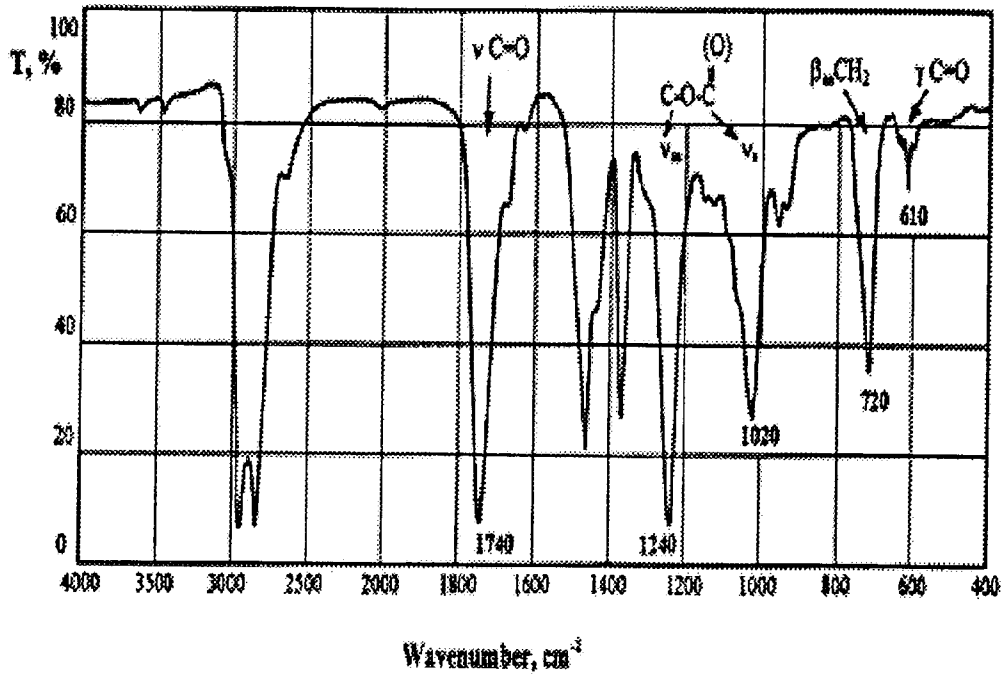

Fig.1. IR spectrum of a thin (20 μm) EVA film.

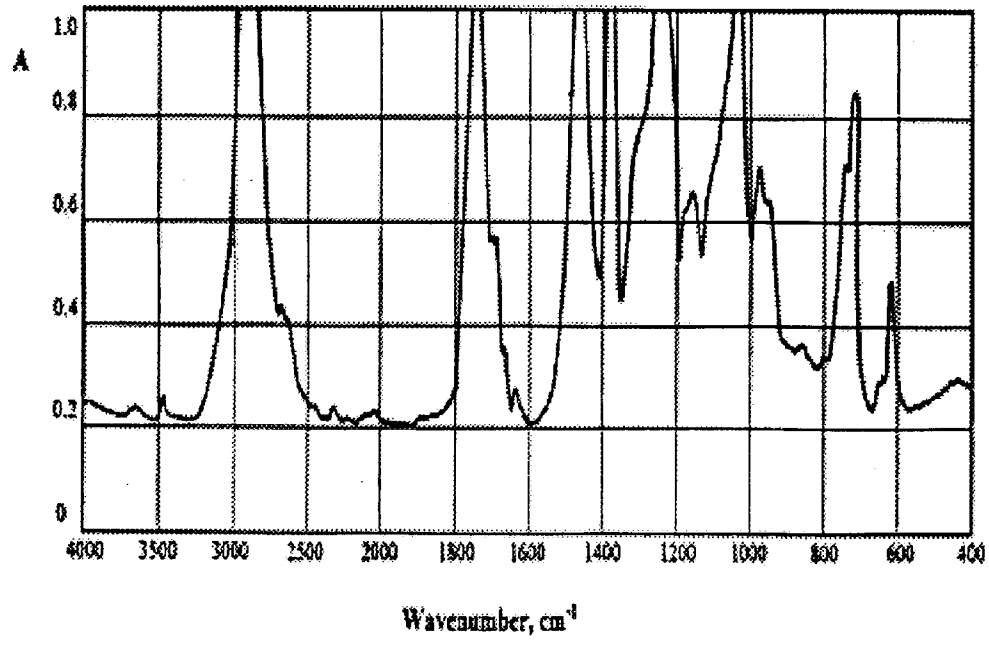

Fig.2. IR spectrum of a 100 μm thick EVA film.

which was prepared by casting from chloroform. The bands at 2920 cm^{-1}, 2850 cm^{-1}, 1740 cm^{-1} and 1240 cm^{-1} cannot be used for quantitative determinations because of the distortion of these bands. In case of thicker films, these above mentioned bands are less suitable for the determination of VA content as the thickness of a commercial product is generally 90–100 μm. Fig.2 shows the spectrum of a 90 μm thick commercial film in which all the bands are distorted. The thinner EVA films furnish non-distorted bands which are more suitable or reliable for infrared spectroscopic measurements [18].

It is known that the vibration at 3460 cm^{-1} is a characteristic overtone band, double frequency of the carbonyl group, of VA units [18]. Koopmans has used 3460 cm^{-1}/2678 cm^{-1} absorption ratio to determine the VA content [14-17]. In order to avoid the over-crowding of results in this paper, such an observed spectrum section of this range has not been included. However, based upon EVA spectra, the band at 2678 cm^{-1} was specified as the standard value on the band found at 2700-3000 cm^{-1} as the C–H stretching vibrations on the baseline of this band is very steep. Because of this, it can be accepted that the method is uncertain. It can be shown that the vibration at 3610 cm^{-1} is related to the ethylene units as can be seen in Fig.3. It is assumed as a combination band of the vibration at 720 cm^{-1} frequency as a rocking vibration in the plane of ethylene units. In the spectrum of EVA, the above mentioned two bands can be distinguished well as given in Fig.4. In the case of 100–1000 μm thick EVA films, the method can be used without further sample preparation. It can be seen in Fig.4 that 3610 cm^{-1} band is not an isolated band. Therefore, the absorbance ratios in Table.1 are integrated absorbance values, designating the baselines between 3720–3540 cm^{-1} and 3540–3300 cm^{-1}. The method is similar to the NIR (Near Infrared Spectroscopy) technique where overtone and combination bands are used for quantitative measurements. However, the procedure presented here does not require a NIR spectrophotometer [14-17]. Nominal VA content of some commercial products available and calculated integrated absorbance ratios are listed in Table.1.

The function of the A_{3460}/A_{3610} ratio plotted against VA content of EVA films is a convex hyperbola as can be seen in Fig.5. This fact is understandable that the calibration graphs using

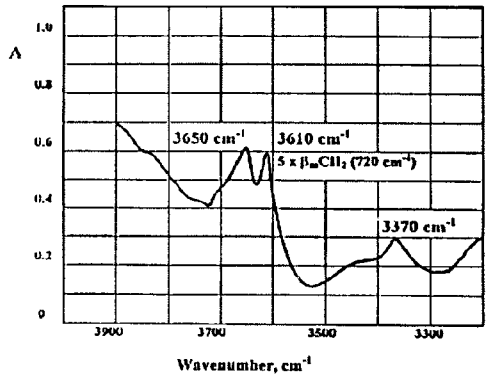

Fig.3. A section of the IR spectrum of LDPE.

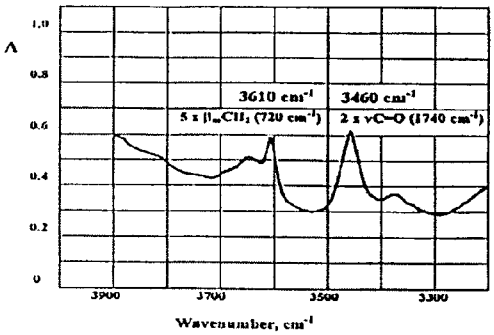

Fig.4. A section of the IR spectrum of EVA.

Table-1:Nominal vinyl acetate (VA) contents and measuring results of the commercial ethylene-vinyl acetate (EVA) films

Commercial Name	Given vinyl acetate (VA) contents (m/m%)	A_{3460}/A_{3610}
Escorene LD 361 ID	4	0.51
Lupolen 3510 K	13	2.09
Lupolen DX 3910	18	3.38
Greenflex MH 40	18	3.41
H3 GR 24	18	3.42
Escorene 60119	18	3.39
Evathene 24-03	24	5.21

absorbance ratios may be curved due to the fact that as the concentration of one component is increasing the other is decreasing. There were four products available having nominal VA content of 18 m/m% which proved accuracy of technique, presented above, because all four points (18 m/m%) fit the

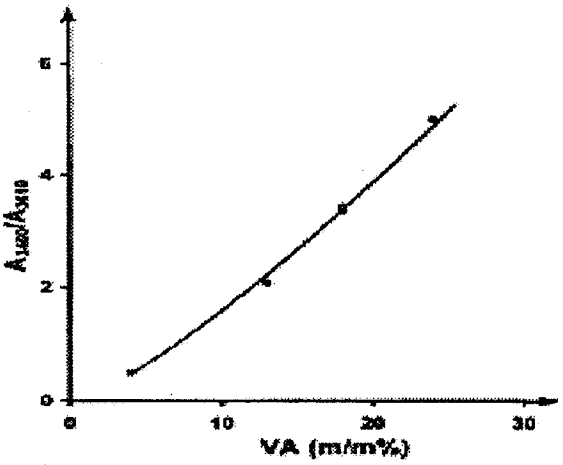

Fig.5. A_{3460}/A_{3610} as a function of the VA content.

calibration curve and standard deviation is also small. The reported IR method is very simple, quick and does not require tedious sample manipulation or special instrumentation. It is suitable for measurements and for the control of VA content in commercial EVA films.

Experimental

Measurements

Spectra were recorded on a Perkin-Elmer 783-IR spectrophotometer. The scan time was 3.0 minutes for each spectrum. The other particulars of the measurements are as follows:

- Sample: 100–120 μm-thick foils
- Range: 3900–3200 cm^{-1}
- Evaluation: base-line correction method
- Ordinate expansion: 5×
- Concentration range: 2–24 m/m%

Preparation of foils.

The simplest way to prepare thin foils is by calendering and pressing at an appropriate temperature. Because of these difficulties of sample preparation and measurements, a simple technique was developed for the determination of VA content in thick, commercial EVA films (~ 100μm) without special preparation.

Acknowledgement

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