



## Analysis Method

# Novel analytical method for determination of contents of backbone and terminal/branch vinyl acetate groups of poly(ethylene-co-vinyl acetate) using deacetylation reaction



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## ABSTRACT

Vinyl acetate (VA) groups in poly(ethylene-co-vinyl acetate) (EVA) exist in backbone, terminal, and branch positions. The VA moieties were converted to carbon-carbon double bonds ( $\sim\text{CH}=\text{CH}\sim$ ) by deacetylation reaction. By deacetylation, the backbone VA group was converted to 1,4-unit ( $\sim\text{CH}_2\text{CH}=\text{CHCH}_2\sim$ ) while the terminal and branch ones were converted to 1,2-unit ( $\sim\text{CH}=\text{CH}_2$ ). A novel analytical method for determination of ratio of backbone and terminal/branch VA contents was developed using off-line pyrolysis and transmission-Fourier transform infrared spectroscopy (FTIR). The analytical method included sample preparation of deacetylated EVA coated on NaCl window for transmission-FTIR analysis and calculation of backbone and terminal/branch VA contents using quantitative analysis of 1,4- and 1,2-units of the deacetylated EVA. Influence of deacetylation conditions (pyrolysis temperatures and times) on degree of deacetylation and other side reactions was also investigated, and proper deacetylation condition was suggested. From the experimental results, proper off-line pyrolysis condition of EVA coated on NaCl window was 300 °C for 60–80 min. The novel analytical method was reliable with the experimental error of below 5%.

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## 1. Introduction

Poly(ethylene-co-vinyl acetate) (EVA) is a copolymer of ethylene (E) and vinyl acetate (VA), and its properties usually depend on the VA content [1–3]. In general, VA content of EVA is determined using infrared spectroscopy (IR), nuclear magnetic resonance spectroscopy (NMR), and thermogravimetric analysis (TGA) [4–12]. According to the ASTM D5594-98(2012) [7], the VA content can be obtained using a calibration curve of the peak height ratio of  $609\text{ cm}^{-1}/2019\text{ cm}^{-1}$ ,  $1029\text{ cm}^{-1}/2019\text{ cm}^{-1}$ , or  $609\text{ cm}^{-1}/1465\text{ cm}^{-1}$ . However, this method does not serve sufficiently correlated calibration curve and reliable reference EVAs have to be required for the calibration curve. NMR analysis of EVA gives information of  $\text{CH}_3$ ,  $\text{CH}_2$ , and  $\text{CH}$  groups and the VA content can be determined using peak intensity ratios of  $\text{CH}_3$ ,  $\text{CH}_2$ , and  $\text{CH}$  [6,8,12]. For TGA, the VA content can be determined using weight loss by deacetylation [9,12].

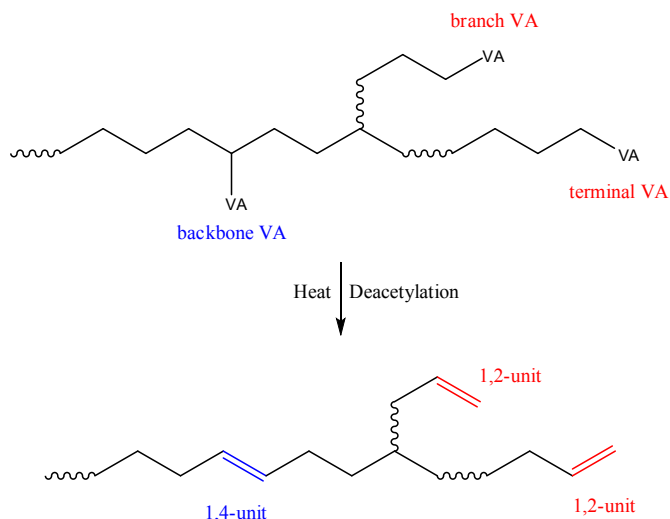
Monomer sequence and terminal group type of a copolymer

wholly affect the polymer's properties [13–17]. Su et al. studied analysis of the sequence distribution of crystalline EVA using high-resolution NMR and reported that most of the VA segments are isolated in the main chain and three kinds of sequence distributions of VA–VA head to tail, VA–E–VA head to tail, and VA–E–E–VA head to tail existed in the EVA copolymers with higher VA content [18]. However, there is no report about analytical method for determination of the VA types such as backbone, terminal, and branch VAs. In this study, analytical method for determination of the backbone and terminal/branch VAs using deacetylation reaction and transmission-Fourier transform IR (FTIR). When EVA is deacetylated, carbon-carbon double bond ( $\sim\text{CH}=\text{CH}\sim$ ) can be formed in the position of VA unit. By deacetylation, the backbone VA unit could be converted to 1,4-unit ( $\sim\text{CH}_2\text{CH}=\text{CHCH}_2\sim$ ) while the terminal and branch VA units could be converted to 1,2-unit ( $\sim\text{CH}=\text{CH}_2$ ) as shown in Scheme 1.

In the previous work, we prepared EVA film by solution casting on aluminum foil, and analyzed C=C bond of deacetylated EVA using attenuated total reflectance-FTIR (ATR-FTIR) [19]. In general, ATR-FTIR is a good technique for qualitative analysis to observe functional groups of organic materials but it is not proper for quantitative analysis. Transmission-FTIR is a good technique for

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**Scheme 1.** Formation of carbon-carbon double bonds ( $\sim\text{C}=\text{C}\sim$ ) by deacetylation of EVA.

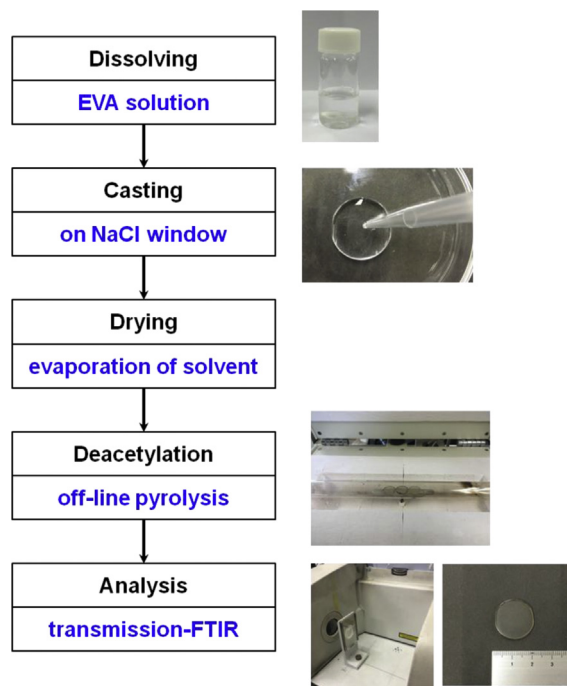
quantitative analysis of polymeric materials in one spectrum [7,12,20–25]. In the present work, analytical method for determination of backbone and terminal/branch VA contents was developed. The analytical method included sample preparation of deacetylated EVA coated on NaCl window for transmission-FTIR analysis and calculation of backbone and terminal/branch VA contents using quantitative analysis of 1,2- and 1,4-units of the deacetylated EVA. Influence of deacetylation conditions (pyrolysis temperatures and times) on degree of deacetylation and other side reactions was also investigated, and optimal deacetylation condition was suggested.

## 2. Experimental

EVA was supplied from Hanhwa Co. (Korea). Chloroform was purchased from Aldrich Co. (USA). NaCl window (2 cm diameter and 2 mm thickness) was purchased from Edmund Optics Co. (USA). Off-line pyrolysis apparatus (Sojung Measuring Instrument Co. of Korea) is composed of furnace (1.4 kW, 40 cm length, 3.6 mm diameter) and quartz tube (60 cm length and 2.8 mm outer diameter).

Preparation process of deacetylated EVA for transmission-FTIR analysis was described in Fig. 1. About 0.4 g of raw EVA was thoroughly dissolved in 5 mL of chloroform. 0.2 mL of the EVA solution was casted on NaCl window and was dried for 1 h at room temperature and for 1 h in 60 °C vacuum oven. The EVA coated on NaCl window was placed in the quartz tube and pyrolyzed. Thickness of the EVA film coated on NaCl window was about 0.3 mm. The pyrolysis conditions were 300 °C/30 min, 300 °C/60 min, 300 °C/90 min, 350 °C/30 min, and 350 °C/60 min. Pyrolysis was performed under inert atmosphere of  $\text{N}_2$  gas. The off-line pyrolysis temperature was raised from 50 °C to the target temperature, and then after deacetylation the temperature was cooled down to 50 °C and the deacetylated sample was taken out from the quartz tube. The deacetylated EVA was analyzed using transmission-FTIR.

Transmission-FTIR analysis was carried out using a PerkinElmer spectrum100 FTIR (USA) and number of scans was 30. The 1,2-unit and *trans*-1,4-unit contents were determined according to the ISO 21561:2005. TGA analysis was carried out using a thermogravimetric analyzer (TGA/DSC1 star system of Mettler Toledo Co.). The heating rate was 10 °C/min. Approximately 10 mg of the sample



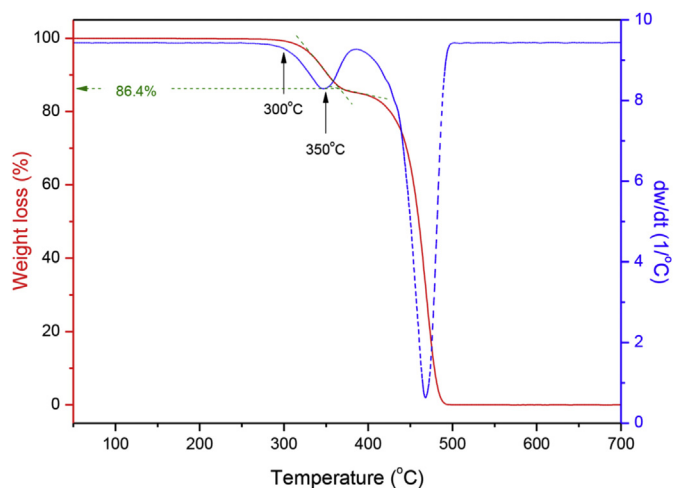
**Fig. 1.** Experimental process for analysis of deacetylated EVA using transmission-FTIR.

was heated from 50 to 700 °C under a continuous  $\text{N}_2$  flow at 50 mL/min.

## 3. Results and discussion

Pyrolysis temperatures for deacetylation of EVA were set based on the TGA results. Fig. 2 shows the TG and DTG curves of EVA. As shown in Fig. 2, the deacetylation was started around 300 °C and the peak temperature was around 350 °C. Off-line deacetylation temperature of 300 °C was selected for slow deacetylation reaction to prevent unexpected side reactions, while that of 350 °C was selected for fast deacetylation reaction.

Fig. 3 shows transmission-FTIR spectra of raw EVA and EVAs deacetylated at 350 °C. In the transmission-FTIR spectrum of raw



**Fig. 2.** TG and DTD curves of EVA.

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