

# Pyrolysis behaviors of deacetylated poly(ethylene-co-vinyl acetate) depending on pyrolysis temperature

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## ABSTRACT

Pyrolysis behaviors of poly(ethylene-co-vinyl acetate) (EVA) depending on pyrolysis temperature were investigated. EVA was pre-pyrolyzed at 400 °C to remove acetic acid before main pyrolysis. The deacetylated EVA was pyrolyzed at 550–800 °C and variations of the major pyrolysis products with the pyrolysis temperature were examined. The major pyrolysis products were alkanes, alkenes, alkadienes, and cyclic compounds including aromatic species. Most of the major pyrolysis products increased as the pyrolysis temperature increased except for the alkanes. Relative abundances of the alkadienes and aromatic compounds were notably increased by increasing the pyrolysis temperature. By increasing the pyrolysis temperature, relative intensity ratios of butadiene/1-butene and styrene/1-butene linearly increased whereas those of cycloheptadiene (or vinylcyclopentene)/1-butene and vinylcyclohexene/1-butene linearly decreased. From Arrhenius plots for the principal pyrolysis products, relative activation energies for the formations of butadiene, cycloheptadiene (or vinylcyclopentene), vinylcyclohexene, and styrene were obtained. Pyrolysis behaviors of the deacetylated EVA were explained by formation mechanisms including ethylene-vinyl acetate heterosequence and dehydrogenation reactions.

## 1. Introduction

Properties and applications of poly(ethylene-co-vinyl acetate) (EVA) is depending on the vinyl acetate (VA) content [1–3]. General analysis techniques for determination of the VA content of EVA are infrared spectroscopy (IR), nuclear magnetic resonance spectroscopy (NMR), and thermogravimetric analysis (TGA) [4–11]. Pyrolysis techniques have been applied for characterization of polymers including EVA [12–23]. Costache et al. analyzed large pyrolysis products (over C8 species) of EVAs and reported that the major pyrolysis products were composed of  $\alpha,\omega$ -alkadienes, 1-alkenes, and alkanes [15].

Pyrolysis temperature is very important because kinds and relative abundances of pyrolysis products of polymeric materials depend on the pyrolysis temperature [18,19,21]. For poly(ethylene-co-propylene) (EPM), relative abundances of C7-species pyrolysis products formed from the ethylene-propylene heterosequences decreased as the pyrolysis temperature increased [18]. For ethylene-propylene-diene terpolymer (EPDM), by increasing the pyrolysis temperature relative abundances of benzene and toluene increased whereas that of 4-ethylidene-1-cyclopentene decreased [19]. For styrene-butadiene rubber (SBR), relative abundances of 3-phenylcyclopentene and 4-phenylcyclohexene formed from the styrene-1,2-unit heterosequence decreased

with increasing the pyrolysis temperature [21]. Activation energies for formations of pyrolysis products can be obtained using Arrhenius plot of  $\ln k$  vs  $1/T$ , where  $k$  is the relative abundance ratio of pyrolysis products and  $T$  is the absolute temperature [24].

Acetic acid is the most abundant species of the pyrolysis products formed from EVA and its broad peak prevents separation of other pyrolysis products. In our previous study, pre-pyrolysis step was introduced to eliminate the broad acetic acid peak of EVA and analytical conditions for separation of the pyrolysis products were established [25]. In the present work, variations of pyrolysis products formed from EVA with the pyrolysis temperature were investigated. Activation energies for the formations of principal pyrolysis products of EVA were obtained using Arrhenius plots and relative favorabilities to form the pyrolysis products were examined. Plausible mechanisms to form the principal pyrolysis products were also suggested.

## 2. Experimental

EVA (VA content 25 wt%) was purchased from Aldrich Co. (USA). Pyrolysis-gas chromatograph/mass spectrometer (Py-GC/MS) was conducted with a CDS Pyroprobe 1500 heated filament pyrolyzer (Chemical Data System, Oxford, USA) coupled to an Agilent 6890 gas

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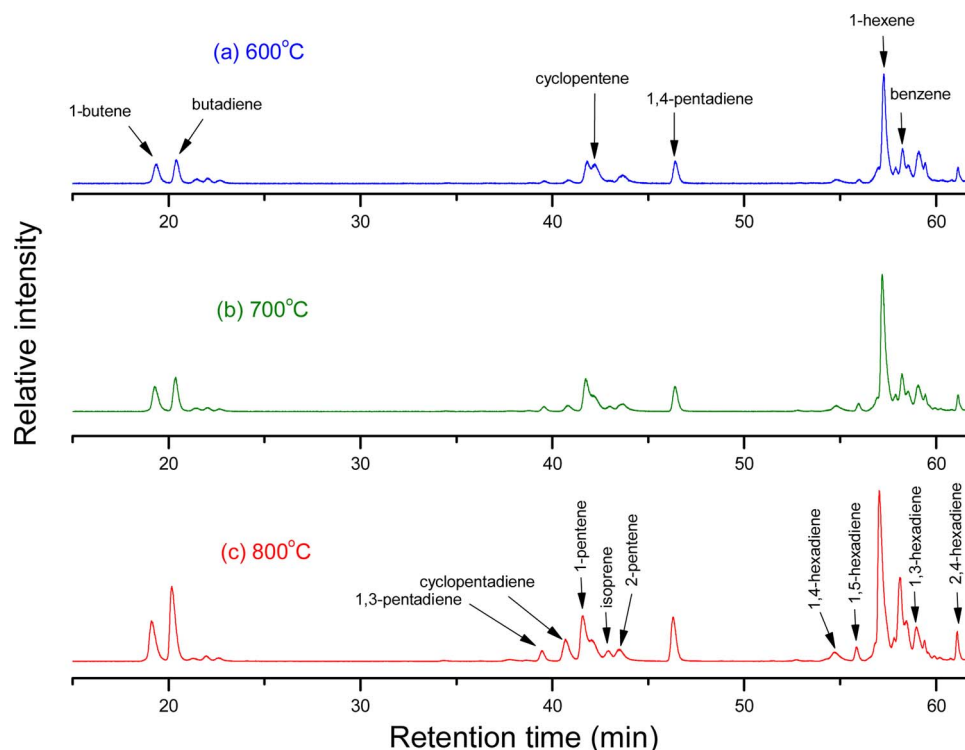


Fig. 1. Py-GC/MS chromatograms (C4 – C6 species pyrolysis products) of deacetylated EVA pyrolyzed at 600 °C (a), 700 °C (b), and 800 °C (c).

chromatograph equipped with a 5973 mass spectrometer of Agilent Technology Inc. (USA). An HP-PLLOT/Q column (15 m length, 0.32 mm inner diameter, 20  $\mu$ m layer thickness column, Agilent Technology Inc.) was used for separation of the pyrolysis products. Pre-pyrolysis (deacetylation) step at 400 °C for 10 min was performed to remove acetic acid. Main pyrolysis temperatures were 550, 600, 650, 700, 750, and 800 °C.

The analysis conditions were as follows: pyrolysis time, 10 s; GC injector temperature, 250 °C; split ratio, 1: 20; carrier gas, helium (flow rate, 1.5 mL/min); the interface temperature of GC to MS, 250 °C. The GC oven temperature was programmed from 50 °C to 80 °C at a rate of 1 °C/min, to 130 °C at a rate of 2 °C/min, and then to 250 °C at a rate of 5 °C/min (held for 17 min). The electron ionization (electron energy 70 eV) was used to ionize the separated pyrolysis products. The MS source temperature was 230 °C. Activation energies for the formations of pyrolysis products were obtained using Arrhenius plots of  $\ln k$  vs  $1/T$ , where  $k$  is the intensity ratio of pyrolysis product relative to 1-butene and  $T$  is the absolute pyrolysis temperature [24].

### 3. Results and discussion

Py-GC/MS chromatograms at 600, 700, and 800 °C of deacetylated EVAs were separately displayed in the ranges of C4–C6 and C7–C10 species as shown in Figs. 1 and 2, respectively, to show variations of the pyrolysis products with the pyrolysis temperature in detail. Major peaks of the pyrolysis products were identified based on the mass library and by interpreting the mass spectra. The peak at 66.38 min could be assigned to cycloheptadiene or vinylcyclopentene. Mass spectrum of the peak at 66.38 min was shown in Fig. 3. It is difficult to differentiate between the mass spectra of cycloheptadiene and vinylcyclopentene. Major pyrolysis products of deacetylated EVA were *n*-alkanes, 1-alkenes,  $\alpha,\omega$ -alkadienes, cycloalkenes, cycloalkadienes, and aromatic compounds. The principal pyrolysis products were marked in the Py-

GC/MS chromatograms. The major *n*-alkane pyrolysis products were  $\text{CH}_3(\text{CH}_2)_n\text{CH}_3$  ( $n = 5-8$ ), while the major 1-alkene pyrolysis products were  $\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_n\text{CH}_3$  ( $n = 1-7$ ). Like the 1-alkene pyrolysis products, the major  $\alpha,\omega$ -alkadiene pyrolysis products of  $\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_n\text{CH}=\text{CH}_2$  ( $n = 0-6$ ) were also observed but 1,7-heptadiene ( $n = 3$ ) was detected by trace amount. In addition to the  $\alpha,\omega$ -alkadienes, other alkadienes were also detected. For pentadienes, not only 1,4-pentadiene but also 1,3-pentadiene were observed. Besides 1,5-hexadiene, other three hexadienes of 1,4-hexadiene, 1,3-hexadiene, and 2,4-hexadiene were also observed. The major cycloalkadiene pyrolysis products were cyclopentadiene and cycloheptadiene, and vinylcyclohexene and vinylcyclopentene were observed as the cycloalkene pyrolysis products. The major aromatic pyrolysis products were benzene, toluene, ethyl benzene, xylene, and styrene.

Most of the pyrolysis products increased as the pyrolysis temperature increased. By increasing the pyrolysis temperature, relative abundances of the alkadiene species increased whereas those of the alkane species notably decreased. This indicates that formation of the alkadienes needs much more energy than formation of the alkanes. Relative intensities of the aromatic compounds also increased with increase in the pyrolysis temperature. This also means that formation of the aromatic compounds requires more energy. In order to investigate variations of the relative abundances of major pyrolysis products with the pyrolysis temperature in detail, intensity ratios of the major pyrolysis products were plotted as a function of the pyrolysis temperature by employing 1-butene as the reference. Of the intensity ratio variations of major pyrolysis products, the variations of butadiene/1-butene, cycloheptadiene (or vinylcyclopentene)/1-butene, styrene/1-butene, and vinylcyclohexene/1-butene showed specific trends as shown in Figs. 4–7, respectively. Since cycloheptadiene (or vinylcyclopentene), styrene, and vinylcyclohexene at 550 °C were observed by trace amounts, their data at 550 °C were not included.

The intensity ratios of butadiene/1-butene and styrene/1-butene

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