

Kinetic Features of the Nonisothermal Oxidative Degradation of Ethylene Vinyl Acetate Copolymers

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ABSTRACT: Thermogravimetric analysis was used for a comparative investigation of the thermooxidative decomposition of ethylene vinyl acetate (EVA) copolymers with different vinyl acetate (VA) group contents. There were two

stages of mass loss in this process. It was revealed that the apparent activation energies were correlated with the content of VA groups in the EVA copolymers. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 1958–1961, 2004

INTRODUCTION

We investigated industrial ethylene vinyl acetate (EVA), which was prepared by the combined polymerization of ethylene with vinyl acetate (VA) in mass under high pressure. The EVA is broadly utilized in industry, because it has a variety of useful properties. The content of VA groups changed different properties of EVA. The augmentation of VA groups in EVA decreased hardness, heat resistance, and crystallinity but increased density, elasticity, transparency, and adhesion.

EVA is used for manufacturing different articles and for details of technical application, in glue composition, as a pack-material, in medicine, and so on.

In this work, we studied the thermooxidative EVA (Orgsintez, Kazan, Russia) decomposition by thermogravimetric analysis. Experiments were conducted in air on an MOM-Q-1500 D instrument (Hungary) at a heating rate of 10°C/min at an interval of 20–600°C. The initial weight of the samples was 100 mg, and the mass loss (ΔW) was determined.

RESULTS AND DISCUSSION

A detailed review of thermooxidative EVA decomposition was made in the study in¹. In most cases, thermal EVA decomposition has been studied *in vacuo* or in inert surroundings. The kinetic characteristics of these processes have been listed in some articles. However, information on the kinetic characteristics of thermooxidative EVA decomposition in a high-temperature range has not been reported.

Because the absorption of oxygen during the thermal oxidation of EVA (200°C) is described by S-like curve and is retarded by antioxidants,² this process has a radical chain mechanism.

EVA copolymers containing up to 30 mass % VA consist of blocks, which are built by 20 or more ethylene units and some VA units.¹ Therefore, the initiation of EVA thermal oxidation was carried out as VA and ethylene blocks.

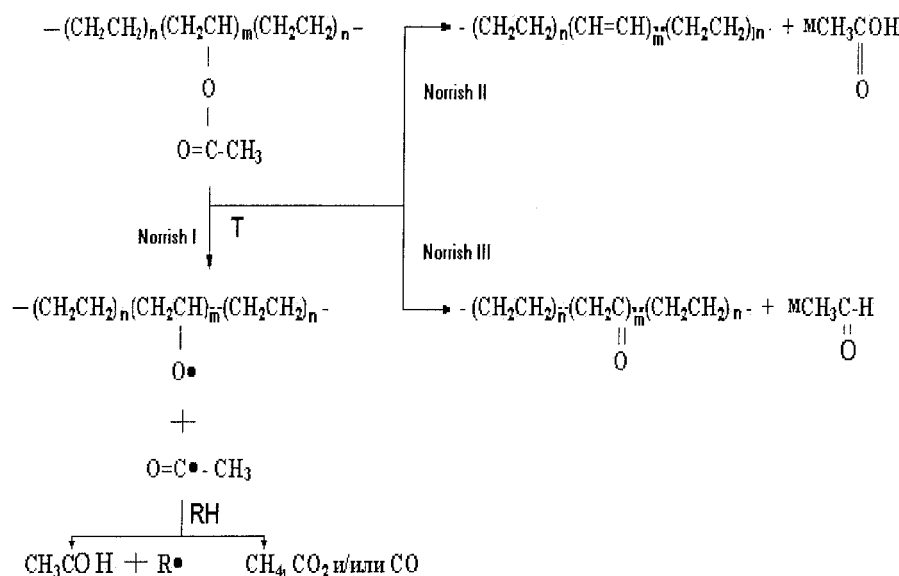
The following scheme for that mechanism was given in ref. 1:

Products, produced by the reaction of II type, may be also formed when the initiation of EVA thermal oxidation is beginning on ethylene groups.² Oxidation occurs as an intramolecular process. The kinetic chain develops a side ethylene block and retards on a carbon atom, which is bound with a VA group:

The thermodecomposition of EVA containing 43.8% VA groups was investigated by thermogravimetric analysis in inert surroundings at heating rates of 5–40°C/min.³ There were two stages of EVA thermodecomposition. The initial part concluded at 380–390°C. The main product in that reaction stage was acetic acid. Regardless of the heating rates, the average weight loss (ΔW) for the first stage of 11 runs was about 30% of the initial sample mass. The thermogravimetric curve was processed with the Coats–Redfern integral method.⁴ The initial part of the thermogravimetric curve for the first stage indicated an induced period of nonisothermal decomposition. The upward trend of the last part overlapped with the beginning of the second degradation stage, which had another activation energy (E_a). These two parts of the curves were neglected in the data processing.

The experimental thermogravimetric curve transformed as $\log[-\ln(1 - \alpha)/T^2]$ versus T^{-1} , where α is the reaction fraction. This implied that the thermal EVA degradation was a first-order reaction.⁵ The

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Scheme 1

slopes obtained from the principal part of ΔW gave the $E_a = (2.303 R \times \text{Slope})$ where R is universal gas constant.

We also accepted the Coats-Redfern integral method and the assumption of first-order reaction in our investigation of thermooxidative EVA decomposition.

A typical thermogravimetric curve for the nonisothermal oxidative EVA decomposition is presented in Figure 1. The two-stage process of degradation was observed for all of the EVA samples with different VA group contents. The first stage was completed at about 380°C and the next proceeded in the interval 380–510°C. The initial and transitional ranges of the curve were neglected because of the previously mentioned reasons. The plot of $\log [-\ln(1 - \alpha)/T^2]$ versus T^{-1} for typical thermogravimetric data at a heating rate of 10°C/min is shown in Figure 2. It is clear from Figure 2 that the nonisothermal oxidative EVA degradation proceeded by two consecutive mechanisms with different apparent E_a values. It was characteristic that the apparent E_a of the low-temperature stage decreased, but the high-temperature stage increased if the number of VA groups in the EVA copolymer were increased.

The interdependency calculation values of the apparent E_a for the two stages of the thermooxidative EVA decomposition and VA group content is shown in Figures 3 and 4, respectively.

These dependencies are described by following correlative linear equations:

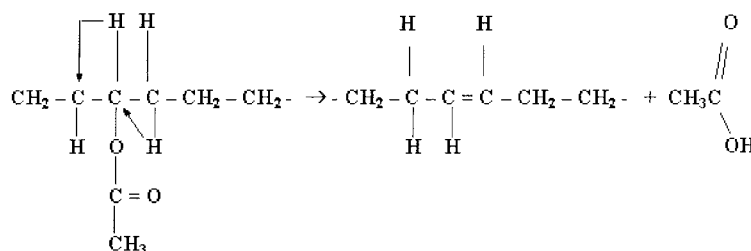
$$E_{a1} = -2.06[\text{VA}\%] + 191.0 \text{ kJ/mol} \quad (k = 0.98) \quad (1)$$

$$E_{a2} = 4.02[\text{VA}\%] + 136.1 \text{ kJ/mol} \quad (k = 0.84) \quad (2)$$

where [VA%] is the VA group content in the sample (mass %) and k is the correlative coefficient.

In the first-stage process, if the VA group content increased, the EVA thermooxidative stability decreased. This phenomenon was connected both to the extension of the VA block dimension and the catalytic action of educed acetic acid. The values we obtained for the apparent E_a 's of the thermooxidative EVA decomposition were considerably lower than those obtained for the thermal decomposition *in vacuo* or in inert surroundings.³

The net structures probably formed under macro-radical recombination in the process of thermooxidative EVA decomposition.



Scheme 2

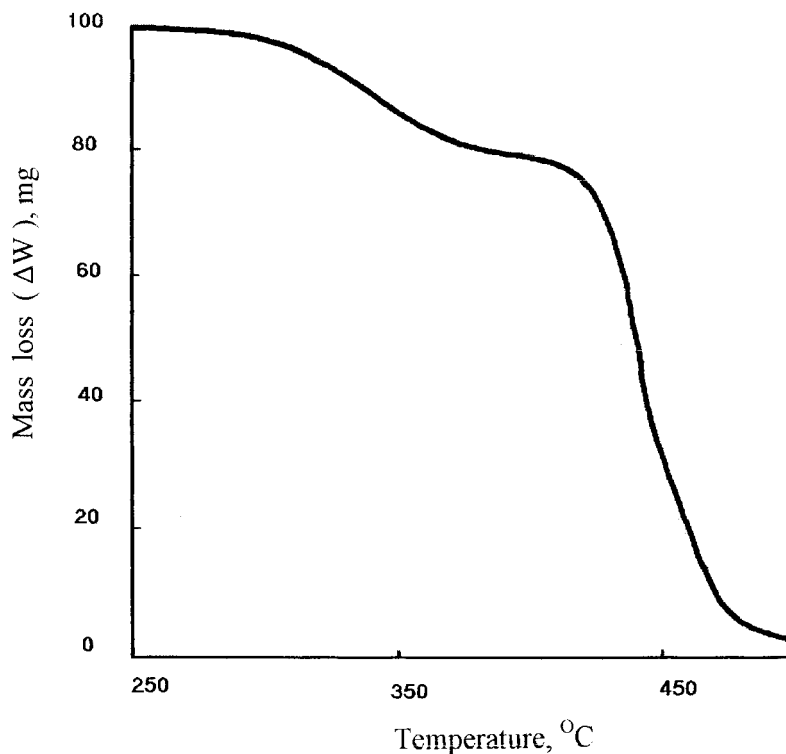


Figure 1 ΔW (TG) curve of the thermooxidative EVA decomposition with a VA group content of 26 mass %.

The destruction of the polymeric chains occurred in the second part of thermooxidative EVA decomposition. A higher VA group content in the EVA molecule resulted in the production of more branched second

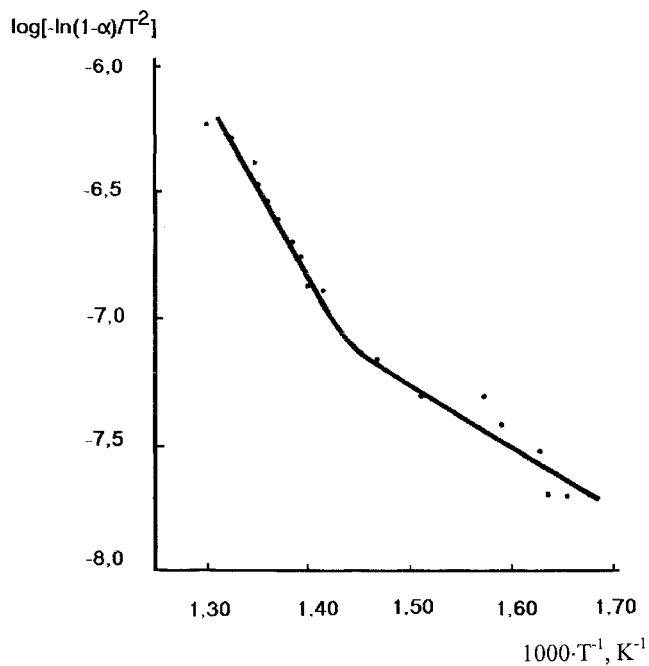


Figure 2 Transformed thermogravimetric curve for EVA with a VA group content of 26 mass %.

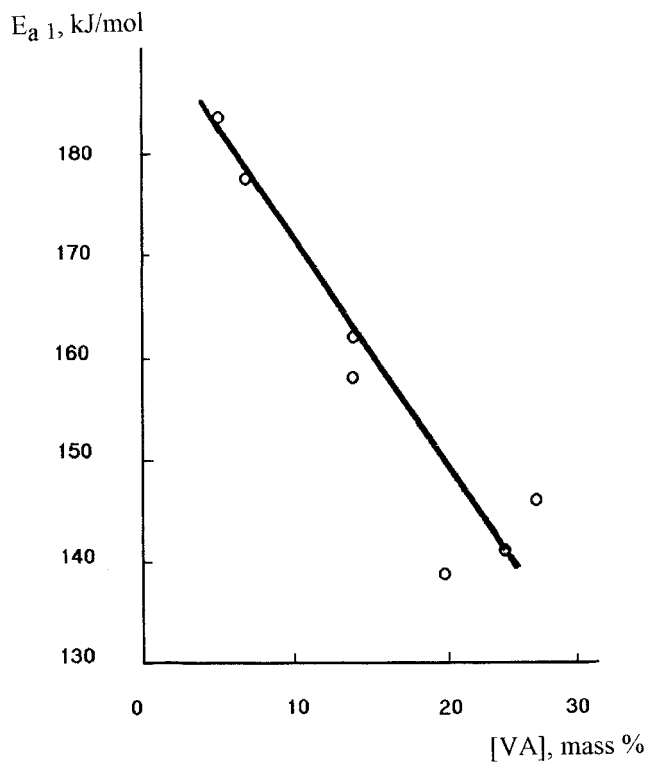


Figure 3 Influence of VA group content on the apparent E_a for the first stage of EVA decomposition.

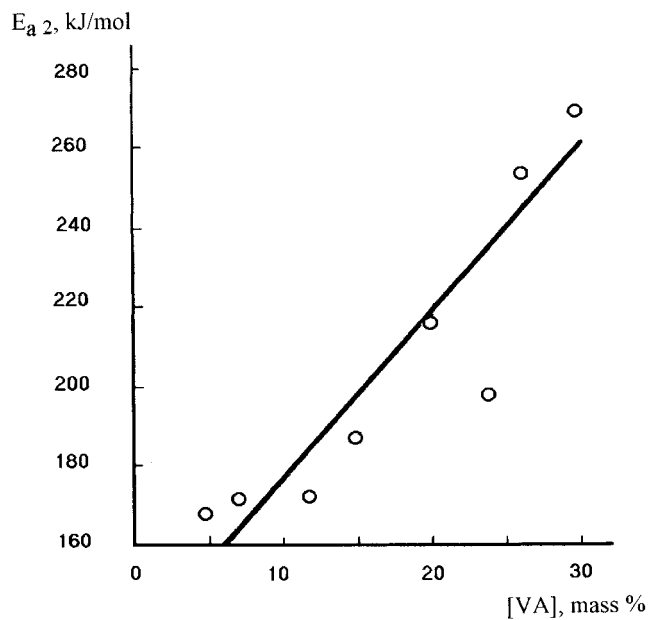


Figure 4 Influence of VA group content on the apparent E_a for the second stage of EVA decomposition.

oxidation products in the initial reaction stage. Therefore, the apparent E_a of the thermooxidative EVA decomposition in the secondary stage was greater than those in the first stage of the decomposition. The correlative eq. (2) agreed with the supposed interpretation of a two-stage passage of thermooxidative EVA decomposition.

Later, we will study the intermediate and final reaction products. This will permit us to examine the thermooxidative EVA decomposition mechanism in detail.

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