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Coupled DTA–TGA–FT-IR investigation of pyrolytic decomposition of EVA, PVC and cellulose

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Abstract

The behavior of individual polymers (EVA, PS, PVC and cellulose) was investigated under pyrolysis at different heating rates. A kinetic model is proposed for the weight loss and compared with the experimental results and the kinetic parameters were determined and compared with the available published data. IR spectrometric analysis was used to follow the evolution of the gaseous pyrolysis products versus the temperature. Analysis of online FT-IR spectra confirmed the initial loss of acetic acid for EVA and one HCl for PVC.

Keywords: DTA; TGA; Polymer

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1. Introduction

The thermal degradation of widely used polymers or biopolymers (EVA, PE, PP, PS, PVC, PET, cellulose, lignin, etc.) has been described in the literature. The pyrolysis of these polymers has been studied in detail and many published articles describe the mechanism and rate of decomposition. Waste pyrolysis could be a clean alternative to incineration because this process combines material recovery with energy production and minimizes the ultimate residues. In Europe there is currently rising interest in biomethanization, pyrolysis and vitrification processes as alternatives to incineration. The objective of our research is to investigate the degradation under pyrolysis conditions of binary mixtures of polymers in which one of the components is EVA. In order to better understand the process in these mixtures, we first investigated the behavior of individual polymers: EVA, PS, PVC and cellulose. This investigation is the subject of this paper. The innovative aspect of these results is the use of a thermobalance connected to an FT-IR spectrometer via a heated line allowing continuous recording of the IR spectra with identification of the evolved gas.

EVA (ethylene vinyl acetate) with different percentages of vinyl acetate (VA) is very extensively used, especially in the production of cables, piping, adhesive tape, etc. Ethylene vinyl acetate copolymers represent the largest volume segment of the ethylene copolymer market. Their properties depend on the VA content: products ranging from 2 to 40% VA are marketed for different purposes. An extensive bibliography [1–19] is available on the degradation of EVA and the estimated kinetic parameters of the process. Basically, the thermal degradation of EVA copolymers is a two-step process. The first step, occurring in the temperature range from 300 to 400 °C, consists in the elimination of one acetic acid molecule, leading to the formation of an ethylene structure on the rest of the carbon chain instead of the previous carbonyl function group. For this reaction, the radical mechanism and ionic elimination have been proposed [15]. PEA (poly[ethylene-*co*-(acetylene)]), formed in the first stage, begins to decompose into smaller chains by the mechanism of the random splitting of the carbon skeleton. This second stage occurs around 425 °C [16] or 470 °C [17]. The decomposition of the acetoxy groups is favored by the tendency to form a six-ring transition state (via a hydrogen bond with active methylene

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groups). The activated complex decomposes thermally, eliminating the acetic acid [18].

The thermal degradation of PS is a radical chain mechanism, where initiation, propagation and termination reactions are the relevant reaction classes. Two types of initiation reactions can be identified [3]. It has been shown that styrene is the primary PS decomposition product [20]. Various kinetic models have been proposed in the literature. Marcilla and Beltran [19] analyzed two types of models, and concluded that the best models are those that involve the formation of an intermediate species, with gases generated in two stages. They also chose this model for the degradation of EVA.

The thermal degradation of PVC has been the subject of numerous investigations and various kinetic models have been proposed in the literature [21–27,32,33] to quantitatively describe the chemical reactions that take place during PVC pyrolysis. It is generally considered a two- or three-step process (depending on the authors) in which the first step is the loss of one HCl molecule by a free radical mechanism beginning at about 200 °C and resulting in the formation of polyene in competition with the formation of a cross-linked structure involving different chain radicals. The second and third steps are parallel reactions, occurring in the range 350–520 °C. Cracking of some carbon–carbon bonds of the previous polyene structures occurs where monocyclic and polycyclic aromatics compounds like benzene, toluene and naphthalene derivatives obtained by cyclization of the conjugated olefin intermediate structures are formed rather than aliphatic structures.

Cellulose is the most widely studied substance in the field of wood and biomass. The kinetics of cellulose pyrolysis have been extensively investigated by numerous researchers and many kinetic schemes have been proposed [28–32,26]. Despite the research effort, however, the various mechanisms are not fully known. The degradation of cellulose consists of a complex set of reactions. Font et al. showed that the modified Kilzer–Broido (KBM) model of kinetic thermal decomposition of cellulose yields the best results, and that with all models that take the activation of cellulose into account (with the formation of anhydrocellulose in the first step) the agreement between experimental and calculated values increases.

2. Experimental

2.1. Materials

All samples in the present study (EVA, PS, PVC and cellulose) were pure polymers from Aldrich Chemical Company. EVA samples with 12, 25 and 40% VA content weighing between 20 and 40 mg were used to investigate the pyrolysis of EVA.

2.2. Thermogravimetric and online FT-IR analysis

The samples were placed in the platinum crucible of the thermobalance. Heating rates ranging from 1 to 30 °C min^{-1} were applied (1, 2, 5, 7, 10, 15, 20 and 30 °C min^{-1} for PS; 5, 7, 10, 15, 20 and 30 °C min^{-1} for EVA; 5, 10, 20 and 30 °C min^{-1} for PVC; 10 and 30 °C min^{-1} for cellulose) and duplicate runs were carried out at all heating rates. Pyrolysis was carried out in N_2 atmosphere, with the gas flow maintained at 27 $\mathrm{cm}^3\,\mathrm{min}^{-1}$. The data measured are the mass loss and temperature, the curve were obtained in % of mass loss versus temperature and the apparatus calculate the curve DTG which means d(% mass loss)/d*t*. A Setaram model TGA 92-16 thermobalance was connected to the FT-IR spectrophotometer by means of a heated line to allow continuous recordings of the IR spectra corresponding to the evolved gases. The spectrophotometer was a Perkin-Elmer System 2000 equipped with a gas cell and a DTGS detector. The heated line and gas-cell were temperature-regulated and maintained at 250 °C to prevent unwanted condensation and guarantee the most quantitative transfer possible of gaseous decomposition products and high detection sensitivity. The evolved gases were continuously recorded with TimeBase®. The Gram–Schmidt Fourier transform provides the corresponding spectra for each time interval. FT-IR spectra were recorded for wave numbers ranging from 4000 to 400 cm^{-1} with a spectral resolution of 8 cm^{-1}. Throughout experiment the spectrophotometer recorded the spectra corresponding to the evolved gases in a 2–4 s interval (depending on the heating rate). Spectrum analysis was performed with the KnowItAll® analytical system.

3. Results and discussion

For all the TGA analysis curves the initial and final decomposition temperatures were variable, and the temperature increased with the heating rate, as expected.

3.1. Analysis of results for EVA and PS

3.1.1. Interpretation of experimental curves

The following experimental data were recorded: weight loss percentages, temperatures of DTG peaks observed and DTG value.

3.1.1.1. EVA. The TGA curves for EVA copolymers with different weight percentages of VA are all of similar shape. Two weight losses were observed. Although the initial temperature was 250 °C, the weight loss was relatively minor up to 300 °C. The decomposition rate suddenly increased between 300 and 350 °C. The higher the percentage of vinyl acetate, the greater the first weight loss. At about 350 °C, the curve shows an inflection point with a shoulder extending to 400 °C, corresponding to a slight weight loss (a plateau on the TGA curve). Above 400 °C the weight loss sharply increases again. It

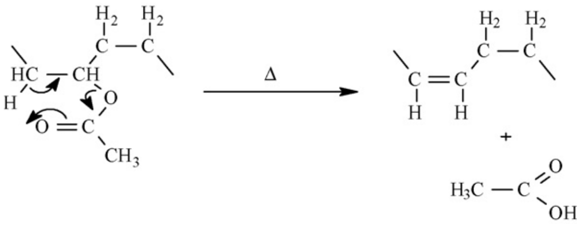

Fig. 1. Thermal degradation mechanism of EVA (step 1): release of an acetic acid molecule.