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Thermal degradation of poly(vinyl chloride)/poly(ethylene oxide) blends: Thermogravimetric analysis

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ABSTRACT

Thermal stability of poly(vinyl chloride)/poly(ethylene oxide) (PVC/PEO) blends has been investigated by thermogravimetric analysis (TGA) in dynamic and isothermal heating regime. PVC/PEO blends were prepared by hot-melt extrusion (HME). According to TG analysis, PEO decomposes in one stage, while PVC and PVC/PEO blends in two degradation stages. In order to evaluate the effect of PEO content on the thermal stability of PVC/PEO blends, different criteria were used. It was found that thermal stability of PVC/PEO blends depends on the blend composition. The interactions of blends components with their degradation products were confirmed. By using multiple heating rate kinetics the activation energies of the PVC/PEO blends thermal degradation were calculated by isoconversional integral Flynn–Wall–Ozawa and differential Friedman method. According to dependence of activation energy on degree of conversion the complexity of degradation processes was determined.

1. Introduction

The blends of poly(vinyl chloride) (PVC) and poly(ethylene oxide) (PEO) were extensively studied in the past two decades. The characteristics of these blends were described on the basis of the results obtained from various experimental techniques such as X-ray scattering techniques, chromatography, dilute solution viscosimetry, various spectroscopic and microscopic techniques, dynamic mechanical analysis, differential scanning calorimetry and molecular simulations [1–16]. The miscibility of PVC and PEO was proved and explained as result of donor–acceptor interactions between chlorine atoms of PVC, as a weak acceptor species and oxygen atoms of PEO, as a donor species [6,11]. In spite of that explanation, there is a lack of compliance if the positive interactions of PEO and PVC concern a full or partial range of blend compositions. Moreover, S. M. S. Neiro et al. [6] have emphasized that interactions of PVC and PEO depend on the molecular weight of PEO and miscibility could be expected in the blends where low molecular weight polymer is used. In the above-mentioned studies PVC/PEO blends were prepared by solution casting technique. Considering that materials are usually melt-processed, the samples in this work were prepared by extrusion, technique commonly used in plastic industry. During hot-melt extrusion, polymers are subjected to mechanical, thermal and oxidative degradation [17,18]. The degradation processes occur not only during production and processing of polymeric materials but also during the process of waste disposal, the final stage of their life cycle. Hence, a good knowledge of thermal characteristics and stability of the polymer is very important. Thermal analysis techniques have demonstrated to be very appropriate and reliable methodologies to monitor and control the influence of degradation phenomena on polymeric materials. Many authors have investigated the thermal properties of PVC [19] and PEO [20], respectively, but there is no information on the thermal degradation properties of PVC/PEO blends.

Due to its applicability in the macroscopic scale, the modelling of the thermal decomposition processes in inert or reactive conditions has been broadly applied by using isoconversional and non-isoconversional methods proposed by different authors [21]. According to P. Budrugeac [22] and S. Vyazovkin [23] the correct kinetic analysis of non-isothermal data corresponding to a heterogeneous process can be only performed by making use of the experimental data recorded at several heating rates. These data enabled application of the model-free methods in assessing the activation energy dependence on the degree of conversion that can be correlated with the investigated process mechanism. Thermal degradation of polymers and polymer blends is a heterogeneous process in which a set of chemical reactions and physical processes proceed with an overall rate. Therefore, the activation energy

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calculated by isoconversional method is called apparent activation energy. The activation energy of complex process, like polymer degradation is, is not parameter describing the degradation process by itself, without preexponential factor A and algebraic function $f(\alpha)$. The global reaction kinetic is completely specified by these three pieces of information usually called the "kinetic triplet". For a complex process of the polymeric material degradation, dependence of apparent activation energy on degree of conversion could be expected and used to draw some mechanistic conclusions. Since the thermal methods of analysis do not provide information about mechanism of the polymer thermal degradation, Vyazovkin [24] consider that would be reasonable to replace the term "mechanism" to a more confined one "kinetic scheme". The latter may be defined as a sequence of those stages which affect a change in a physical property being measured by thermal analysis technique, for example, a mass of sample. Hence, in this work the isoconversional integral Flynn–Wall–Ozawa (FWO) and differential Friedman (FR) methods were applied in order to determine dependence of apparent activation energy on conversion and, consequently, the kinetic scheme of thermal degradation process of PVC/PEO blends.

The aim of this work was to study the interactions of PVC, PEO and their degradation products in a full range of blend compositions by thermogravimetric analysis.

2. Experimental

2.1. Materials

The powders of PEO (M_v = 100,000) and PVC (M_v = 86,000) were purchased from Sigma–Aldrich and Solvin, respectively. PVC/PEO blends of different compositions (100/0, 80/20, 60/40, 50/50, 40/60, 20/80 and 0/100) were prepared by mixing polymer powders in a laboratory extruder (Dynisco, Qualitest, North America) at 160 °C and screw speed 180 rpm. The samples were hot-pressed after extrusion at 120 °C for 30 s. In order to prevent thermal degradation of PVC during the sample preparation 2 wt.% Ca/Zn stabilizer (Reapack B-NT/7060) was added.

2.2. Thermogravimetric analysis

Thermogravimetric measurements of the PVC/PEO blends were conducted by using PerkinElmer Pyris 1 TGA thermobalance at the heating rates of 2.5, 5, 10 and 20 °C min^{-1} in a temperature range 50–650 °C under a steady flow of nitrogen (20 cm^3 min^{-1}). Samples weighing approximately 10 mg for the analysis were used. To evaluate the thermal stability of the investigated polymers different criteria can be used. From TG and DTG curves the following characteristics were determined: the onset temperature (T_{onset}), the temperature at 5% mass loss ($T_{5\%}$), the temperature at the maximum degradation rate (T_{max}), the maximum degradation rate (R_{max}), the conversion at the maximum degradation rate of (α_{max}), the final mass (m_f) and the mass loss (Δm) for the corresponding degradation steps. Isothermal thermogravimetric measurements were proceeded at 240 °C by heating the sample from the start (50 °C) to the selected degradation temperature and then held at 240 °C for 120 min.

3. Results and discussion

3.1. Thermogravimetric analysis

The dynamic thermogravimetric curves (mass vs. degradation temperature), and corresponding derivative thermogravimetric (DTG) curves (mass loss rate vs. temperature) of PVC/PEO blends obtained at 2.5 °C min^{-1} are shown in Figs. 1 and 2, respectively.

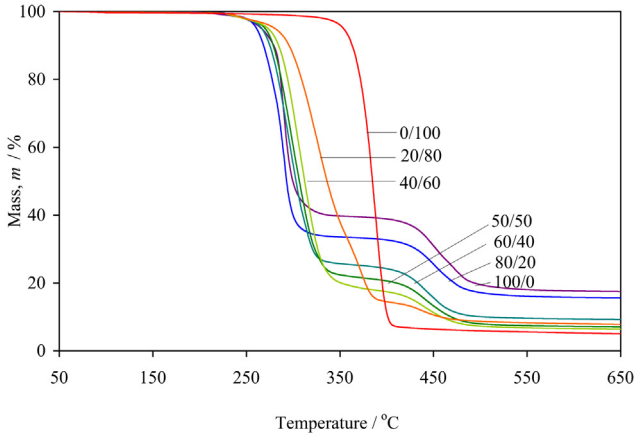

Fig. 1. TG curves of PVC/PEO blends thermal degradation at heating rate of 2.5 °C min^{-1}.

Collected data from TG/DTG curves (tabulated in Table 1) were used to assess the effect of PEO content on the degradation pattern of PVC. A two-stage degradation pattern is seen in the case of PVC. The first stage begins at 280 °C (T_{onset}) and ends at 375 °C with a peak temperature at 291 °C (T_{max}). This corresponds to a weight loss of 60.5%, which is slightly greater than the stoichiometric amount of HCl contained in PVC (cca 56%). The second stage of degradation begins at 422 °C (T_{onset}) and ends at 600 °C with a peak temperature of 453 °C (T_{max}). The total weight loss at this stage is found to be 82.5%. In addition, S. Moulay [25] has exposed that PVC degradation takes place in a three successive stages: (1) HCl formation occurred in the first two stages within 220–370 °C; this two-stage HCl production would indicate that the PVC is actually made of head-to-head and head-to-tail units, (2) benzene was exclusively produced in the first stage (220–290 °C) in parallel with HCl, and (3) the remaining aromatics were developed in the last stage (beyond 370 °C).

PEO exhibits only a single stage degradation that occurs between 367 (T_{onset}) and 450 °C. The peak temperature is observed at 388 °C and the weight loss at the end of this stage is found to be 95%. PEO degradation proceeds by the random chain scission of C–O bonds [26]. Moreover, main decomposition products are ethyl alcohol, methyl alcohol, alkenes, non-cyclic ethers (ethoxymethane, ethoxyethane and methoxymethane), formaldehyde, acetic aldehyde, ethylene oxide, water, CO and CO_2 [20].

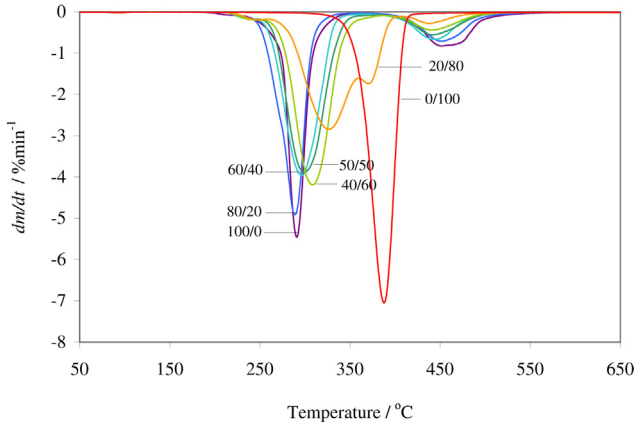

Fig. 2. DTG curves of PVC/PEO blends thermal degradation at heating rate of 2.5 °C min^{-1}.