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Isoconversional kinetics of degradation of polyvinylpyrrolidone used as a matrix for ammonium nitrate stabilization

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ABSTRACT

Thermogravimetric analyzer (TGA) has been applied to measure the kinetics of the thermal degradation of virgin polyvinylpyrrolidone (PVP) and a phase stabilized PVP–ammonium nitrate (AN) material. The PVP–AN samples have been prepared by using 20 wt.% of AN and PVP of three different molecular weights. Virgin PVP undergoes a major mass loss in the region 380–550 °C leaving a small amount of nonvolatile residue. The application of an advanced isoconversional method to the respective degradation process demonstrates that its effective activation energy increases from ~70 kJ mol^{-1} to a plateau value at 250–300 kJ mol^{-1}, which is independent of the molecular weight. The PVP–AN materials lose spontaneously ~20% of their mass on heating above the glass transition temperature of the PVP matrix (160–180 °C). After the escape of AN, the remaining PVP matrix degrades in the same temperature region as virgin PVP, however, the effective activation energy of this degradation is ~150–200 kJ mol^{-1}.

1. Introduction

Polyvinylpyrrolidone (PVP) is a polymer, having a number of pharmaceutical, cosmetic, and medicinal applications. Since none of these applications involves the use of high temperatures, the thermal degradation of PVP has not been well studied, especially compared to other polymers. To our knowledge, there has been only one study [1] devoted specifically to the mechanism and kinetics of the thermal degradation of PVP. Our interest in the process has been inspired by a novel material that presents a solid solution of ammonium nitrate (AN) in a PVP matrix [2]. Because of a large dipole moment of pyrrolidone groups, the PVP matrix is capable of holding the ammonium and nitrate ions separately form each other that provides an effective solution to the problem of phase and thermal stabilization of AN, the material which is notorious for being a cause of numerous catastrophic expositions. PVP can dissolve up to ~30 wt.% of AN so that the resulting PVP–AN material does not demonstrate any of the four solid–solid phase transition of AN that normally occur at −17, 32, 84, and 125 °C [3]. Once the material is heated above the glass transition temperature of the PVP matrix (160–180 °C), AN quickly escapes to the gas phase. Basic characteristics of the PVP–AN material have been discussed in our communication [2]. One of the applications of this material could be as a propellant. From this standpoint, AN and PVP would respectively provide an oxidant and a fuel. The rate of the propellant combustion would largely be determined by the degradation kinetics of the PVP matrix remained after AN has escaped from it. Although the mass loss from the PVP–AN material observed right above the glass transition suggests [2] that it loses only AN, the remained PVP matrix appears damaged so that its degradation kinetics can be expected to differ from that of virgin PVP. The present paper compares the thermal degradation kinetics of matrix and virgin PVP of different molecular weights in terms of the effective activation energies of the respective processes. The focus is placed on the application of isoconversional analysis [4] that yields the effective activation energy as a function of conversion. Although the activation energy is not the only parameter that affects the process kinetics, obtaining a conversion dependence of the activation energy is usually adequate for solving a number of practical problems [4]. It should, in particular, be noted that the activation energy of the thermal decomposition of a burning material is the parameter that defines the temperature dependence of the linear burn rate in various combustion models [5–7].

2. Experimental

PVP–AN samples were prepared in the form of thin films containing 20 wt.% of AN. PVP (Acros Organics) had molecular weights

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8,000, 58,000, and 1,300,000 g mol^{-1}. The respective samples are denoted 8K, 58K, and 1.3M. AN (99.9% purity) was purchased from ACRŌS Organics. The PVP–AN films were prepared by combining the appropriate masses of AN and a polymer to bring the total mass to 0.5 g. The PVP–AN mixture was then dissolved in methanol, cast in 15 ml aluminum pans and allowed to dry overnight under vacuum. The temperature dependent mass loss during thermal degradation was monitored by thermogravimetric analyzer (TGA.) The TGA measurements were performed on a TGA/SDTA 851^e manufactured by Mettler–Toledo. For TGA measurements, nonisothermal heating programs with an isothermal drying step were employed. The temperature was ramped from 25 to 115 °C at 5 °C min^{-1}, and held at 115 °C for 20 min in order to drive off any absorbed water or residual solvent. The heating program then continued to 550 °C at the following heating rates: 2, 5, 7, 9, 11, 13, and 15 °C min^{-1}. The data obtained from this second nonisothermal ramp of TGA measurements were subjected to isoconversional kinetic analysis, which, as discussed in a recent review paper [4] provides a very effective approach to exploring complex kinetics in polymeric materials.

The activation energy, E_α, as a function of the extent of conversion, α, was determined using the advanced isoconversional method developed by Vyazovkin [8,9]. The method allows one determine the E_α dependence from a set of n experimental runs performed under different temperature programs, $T_i(t)$. Then the effective activation energy is determined at any particular value of α by finding E_α, which minimizes the function:

$$\Phi(E_\alpha) = \sum_{i=1}^{n}\sum_{j\neq i}^{n} \frac{J[E_\alpha, T_i(t_\alpha)]}{J[E_\alpha, T_j(t_\alpha)]} \tag{1}$$

where:

$$J[E_\alpha, T_i(t_\alpha)] \equiv \int_{t_{\alpha-\Delta\alpha}}^{t_\alpha} \exp\left[\frac{-E_\alpha}{RT_i(t)}\right] \mathrm{d}t \tag{2}$$

In Eq. (2), α varies from $\Delta\alpha$ to $1-\Delta\alpha$ with a step $\Delta\alpha$, typically chosen to be 0.02. The integral, J, is evaluated numerically by using the trapezoid rule. The minimization procedure is repeated for each value of α to find the dependence of the activation energy on the extent of conversion. The mean relative error of the E_α values determined in this study was within 15% in accordance with the results [10] of the earlier analysis of the method. In addition to the ability of treating data obtained under arbitrary temperature programs, the advanced isoconversional method offers another important advantage over the frequently used isoconversional methods of Flynn and Wall [11] and Ozawa [12]. This advantage originates from performing integration over small time segments [Eq. (2)] that allows for eliminating a systematic error [9] occurring in the Flynn and Wall and Ozawa methods when E_α varies significantly with α.

3. Results and discussion

Fig. 1 provides representative TGA data of the thermal degradation of neat PVP of different molecular weights. It is seen that the initial degradation temperature decreases with decreasing of the molecular weight. In the case of the low molecular weight sample (8K), the mass loss on initial degradation is close to 10%, whereas the two other samples experience significantly smaller mass losses in this stage. A major mass loss takes place in the temperature range 380–500 °C in all three samples. In that range, degradation does not demonstrate any significant dependence of the molecular weight of PVP. During this degradation step almost all PVP converts to gaseous products leaving ∼4–5% of a nonvolatile residue.

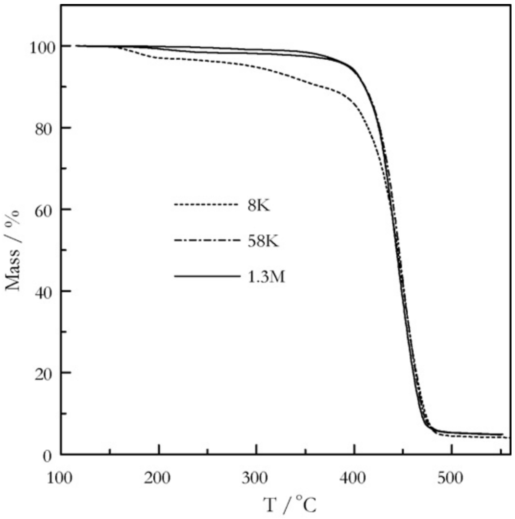

Fig. 1. TGA data for the thermal degradation of virgin PVP of different molecular weights at 15 °C min^{-1}.

The application of the advanced isoconversional method to the TGA data on degradation of PVP of different molecular weights results in obtaining the E_α dependencies shown in Fig. 2. In general, all three samples show a similar trend in variation of the effective activation energy. At the beginning of degradation, the values of E_α are small (∼70 kJ mol^{-1}) as frequently found in degradation of many polymers [4]. The lower values are typically attributed to the process of initiation on various defects of the polymer chain or so-called weak links such as head-to-head, hydroperoxy, and peroxy structures. Further, progress of degradation is accompanied by an increase in E_α that reaches a plateau at E_α around 250–300 kJ mol^{-1}. Within the existing error bars (Fig. 2), the plateau values do not appear to depend significantly on the molecular weight of PVP. However, the transition from the initial low to the high plateau values of E_α is clearly molecular weight dependent. In the 8K sample the plateau value is reached above α ∼0.15, whereas in the 58K and 1.3M samples this occurs at α ∼0.35 and ∼0.45, respectively. The fact that the transition occurs slower in the higher molecular weight samples suggests that the contribution of the initiation process increases with the molecular weight of PVP.

It is noteworthy that Peniche et al. [1], who applied the Ozawa method to the thermal degradation of PVP reported that the E_α values remain practically constant (240–250 kJ mol^{-1}) in the α range 0.1–0.8. The reported value is obviously in agreement with our

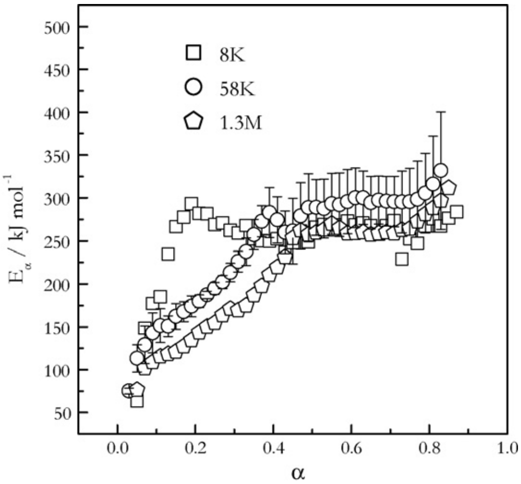

Fig. 2. Dependencies of the effective activation energy on conversion for the thermal degradation of virgin PVP of different molecular weights.

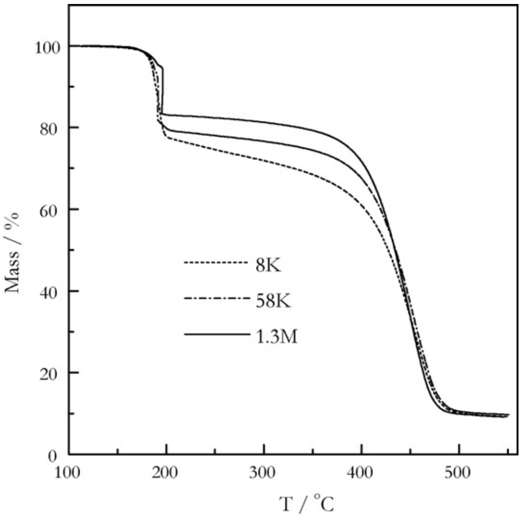

Fig. 3. TGA data for the thermal degradation of PVP–AN materials based on PVP of different molecular weight at 15 °C min^{-1}.

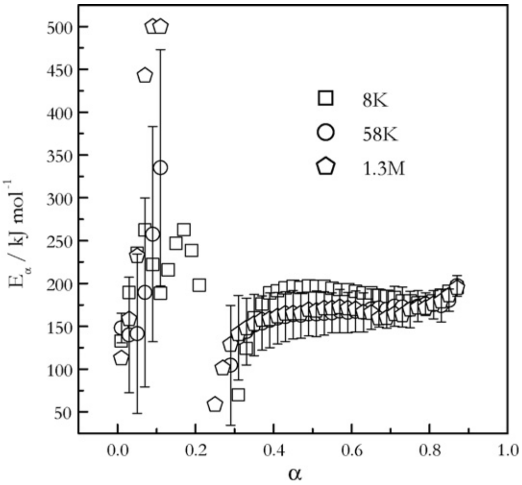

Fig. 4. Dependencies of the effective activation energy on conversion for the thermal degradation of PVP–AN materials based on PVP of different molecular weights.

plateau values. However, Peniche et al did not report any increase in E_α for the initial stages of degradation. This could partially be due to the aforementioned systematic error [9] in the Ozawa method as well as due to the use of a low molecular weight sample. Note that the molecular weight of PVP was not reported in their paper.

TGA data on the thermal degradation of PVP–AN materials are shown in Fig. 3. It is seen that the materials having the PVP matrix of different molecular weight show similar degradation behavior. They reveal a mass loss of ∼20% above ∼160 °C, i.e., above the glass transition temperature of the PVP matrix. Note that under similar experimental conditions neat AN starts to decompose at a markedly lower temperature, ∼120 °C [13]. There is some slight increase in the temperature of the 20% mass loss with increasing the molecular weight of the PVP matrix. The effect is consistent with an increase in the glass transition temperature of PVP with increasing its molecular weight. The mass loss appears somewhat larger in the materials using lower molecular weight PVP. This suggests that the lower molecular weight PVP may produce some volatile products as a result of a chemical reaction with nitric acid formed via proton transfer from ammonium to nitrate ion. After losing AN, the PVP matrices degrade slowly until reaching ∼380 °C, which is the initial degradation temperature of virgin PVP (see Fig. 1). Above this temperature, the residual PVP matrix loses almost all its mass leaving a small amount of nonvolatile residue. This degradation step appears to be similar to that observed for virgin PVP.

The application of the advanced isoconversional method to the mass loss data on degradation of the PVP–AN materials reveals E_α dependencies that are displayed in Fig. 4. The initial part of the dependencies ($\alpha < 0.25$) represents the process of releasing AN from the PVP matrix. The process occurs very quickly with a large exothermic effect [2] that causes significant self-heating of the sample. This effect is noticeable in the TGA traces of the 58K and 1.3M samples (Fig. 3). The rate of the process does not show any systematic dependence on the heating rate. As a result the E_α values show a huge scatter. Once this process is finished, the remaining matrix PVP undergoes regular degradation that is represented by the effective activation energies in the range 150–200 kJ mol^{-1}. Within the error bars, the E_α values do not show any significant dependence on the molecular weight of PVP. By comparing the plateau values of E_α for virgin PVP (Fig. 2) and for remaining matrix PVP (Fig. 4) one can clearly see that the latter are ∼100 kJ mol^{-1} lower than the former. It means that during release of AN the PVP matrix undergoes a damage that significantly affects it degradation kinetics that, however, was not obvious from inspection of the mass loss data (Fig. 3). A significant decrease in the effective activation energy of the thermal degradation would definitely affects the linear burn rate [5–7] of the respective propellant, most likely making it faster but less sensitive to temperature variations.

4. Conclusions

The results of the present study suggest that the thermal degradation of virgin PVP is initiated by a low activation energy (∼70 kJ mol^{-1}) process followed by a steady-state degradation characterized by an effective activation energy 250–300 kJ mol^{-1}. The latter process appears to be independent of the molecular weight of PVP, whereas the contribution of the initiation process increases with increasing the molecular weight. In PVP–AN material, the PVP matrix remained after release of AN undergoes a significant damage that causes the effective activation energy of the degradation process to decrease by ∼100 kJ mol^{-1}. The effect would be of relevance for propellant applications of the PVP–AN material.

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