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EFFECTS OF ADDING NANO METAL POWDERS ON THERMOOXIDATIVE DEGRADATION OF POLY(ETHYLENE GLYCOL)

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Effects of nano-metal powders (aluminum and nickel) addition on the thermooxidative degradation of binder PEG in air atmosphere from 20 to 350°C were studied by TG/DTA and in-situ FTIR. TG/DTA results showed that the addition of nano-Al slowed down the degradation process of PEG in the early period but accelerated the process in the late period; the addition of nano-Ni made the PEG degradation process begin as soon as melted. The in-situ FTIR results showed that nano-Ni promoted the thermooxidative degradation of PEG in air, and made the degradation process of PEG complete much earlier.

Keywords: *adsorbent catalysis capability, nano-metal powders, poly(ethylene glycol), specific surface area, thermooxidative degradation*

Introduction

Poly(ethylene glycol) (PEG) is a popular polymer that finds a number of applications in packing, cosmetics, pharmaceutical, biotechnology and so on. PEG has also been used as a binder in solid propellants [1, 2]. The non-oxidative thermal degradation of PEG has been widely studied by varied experimental techniques [2–5]. Voorhees *et al.* made PEG samples pyrolyzed in a tube furnace under nitrogen at 450 and 550°C, and identified five major series of pyrolysis products that contained up to 12 monomer units by GC/MS and GC/FTIR [2]. Arisawa and Brill studied flash pyrolysis of PEG at 370–550°C by T-jump/FTIR spectroscopy. They concluded that the major volatile pyrolyzates contained hydroxyl, ‘methyl ether’ and ‘ethyl ether’ end groups [3]. Lattimer carried out the PEG pyrolysis under argon flow in the temperature range 150–325°C. The residue in the pyrolysis tube was analyzed by MALDI/MS and CI/MS after pyrolysis, and eight series of oligomeric pyrolyzates were characterized [4]. Pielichowski and Flejtuch studied the thermal decomposition of PEG under non-oxidative conditions conducted by TG, TG/FTIR and TG/MS. Their experimental results showed that the main decomposition products were ethyl alcohol, methyl alcohol, alkenes, non-cyclic ethers, formaldehyde, acetic aldehyde, ethylene oxide, water, CO and CO_2 [5].

The thermooxidative degradation of PEG or PEG binding with other materials has been also investigated. Most of these works were for the purpose to study the stabilization of PEG exposed in air and to search for the effective measurements of antioxidation [6–9]. For example, Han *et al*. found PEG degraded severely when maintained at 80°C for 1000 h in air, and the degradation could be successfully suppressed by adding MBMTBP as an antioxidant [7]. Chen *et al*. found that PEG with high molecular mass readily underwent degradation during preparation of composites, which was due to oxidative attack at low temperature (60°C). Precautions against oxidative attack were therefore recommended to avoid decomposition while preparing PEG-clay nanocomposites [9].

Nanometer-sized metal powders can improve the characteristics of propellants evidently even with low content. The effects of nano-metal powders on the thermal or combustion properties of the oxidizers of propellants have been widely studied and reported [10–16]. However, few people paid their attention to the effects of nano-metal powders on the thermal degradation of propellant binders in inert atmosphere or in air. As the oxidizers decompose and produce oxygen in the thermal decomposing or burning process of actual propellants, the researches about thermal degradation of binder PEG in oxygenous atmosphere are of much importance and significance. In the present work, TG/DTA and in-situ FTIR were employed to study the effects of addition of nano-metal powders, nano-Al and nano-Ni, on the thermooxidative degradation of binder PEG in air.

Experimental

Samples

Poly(ethylene glycol) with average molecular mass of 2000 was supplied by Sinopharm Chemical Reagent Co. Ltd., Shanghai, China, and the melting

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point is about 45°C. Nano-Al and nano-Ni powders are supplied by Shengtai Nano Co. Ltd., Jilin, China, and the average grain sizes are 83 and 68 nm, respectively.

Mixtures of nano-metal powders and PEG were prepared by mechanical mixing. The mixing process was roughly as following: the pure PEG (solid state at room temperature) was heated to melt by water-bash; the nano-metal powders were added into the regularly stirred melted PEG; the temperature of water-bash was set to decrease quickly after the needed amount of nano-metal powder was added and uniformly dispersed; the mixture was stored in a sealed container as soon as it concreted. The samples of PEG and nano-metal powders mixtures (PEG/Al and PEG/Ni) with mass ratio of 10:1 were prepared.

Methods

The thermal analysis was performed on a PerkinElmer, Diamond TG/DTA instrument. The experimental conditions were: sample mass, about 5 mg; heating rate=10°C min^{-1}; air atmosphere, flow rate=80 mL min^{-1}; open α-Al_2O_3 pan. In-situ Fourier transform infrared spectroscopy (In-situ FTIR) spectra were recorded by a Nicolet MAGNA-IR 750 spectrometer with the spectral range of 4000–500 cm^{-1} in air atmosphere.

Results and discussion

TG/DTA experiments

The TG/DTA experiments were carried out to study the mass loss process and the thermal behaviors of the PEG from room temperature to 350°C in air atmosphere. The TG-DTG curves for the pure PEG (p-PEG), PEG/Ni and PEG/Al are showed in Fig. 1. The TG-DTG data are listed in Table 1. The data inside the parentheses are the corresponding maximum rate of mass loss.

The TG data show that the beginning temperature of mass loss T_O for PEG/Al is almost the same as the one for *p*-PEG, but its ending temperature of mass loss T_E is 12°C later than that of p-PEG. For PEG/Ni, its T_O is 6°C earlier than that of p-PEG, while the ending temperatures for PEG/Ni and p-PEG are the same 286°C. The DTG data show that the temperatures of maximum rate of mass loss T_M for all the three samples are close to ending temperatures T_E, especially for PEG/Al. This indicates that the mass loss is accelerated through the degradation process of PEG for all the three samples, and there is a prominent autoxidative degradation process that may occur when most polymers are exposed in air. This autooxidative degradation has the characteristics of autocatalytic reaction, so the degradation of PEG is an accelerated process and the rate of mass loss increased continually as the TG-DTG curves display [17].

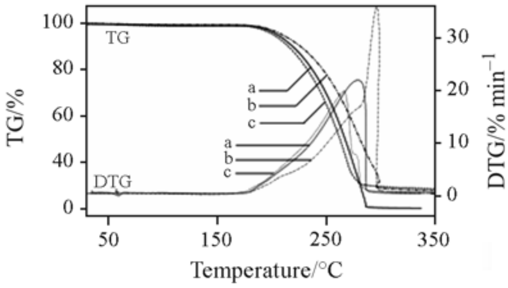

Fig. 1 TG-DTG curves of a – *p*-PEG, b – PEG/Al and c – PEG/Ni

Table 1 TG-DTG data of *p*-PEG, PEG/Al and PEG/Ni

Sample	T_O/°C	T_E/°C	T_M/°C
p-PEG	182	286	279 (22% min^{-1})
PEG/Al	183	298	295 (36% min^{-1})
PEG/Ni	176	286	265 (20% min^{-1})

The DTA curves and data are showed in Fig. 2 and Table 2, respectively. The strong heat releasing of the thermooxidative degradation of the three samples all begin around 160°C, lower than the temperature of mass loss beginning by about 20°C. These results show that the thermooxidative degradation of PEG has occurred much earlier than the mass loss. The heat releasing before mass loss is due to the forming of α-hydroperoxide. When exposed in the air, PEG, like other polymer, is likely attacked by oxygen to form α-hydroperoxide. This peroxide is expected to be thermally labile and its decomposition is considered to be one of the important propagating approaches of the degradation process [7, 17].

The DTA curves show that the addition of nano-Al slows down the thermooxidative degradation

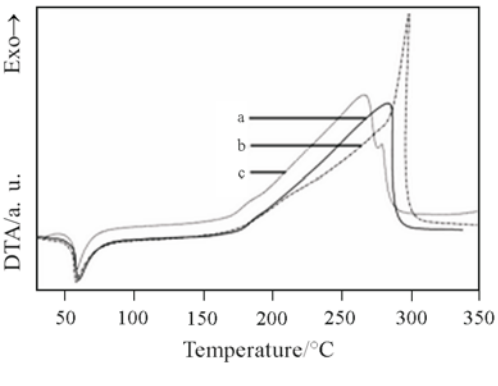

Fig. 2 DTA curves of a – p-PEG, b – PEG/Al and c – PEG/Ni

Table 2 DTA data of *p*-PEG, PEG/Al and PEG/Ni

Sample	T_O/°C	T_E/°C	T_M/°C
p-PEG	163	301	282
PEG/Al	161	315	298
PEG/Ni	1596	300	265

process of PEG in the early period but accelerates it in the late period. When nano-metal powders are mixed with other substances, their interface provides additional reactive location [13]. So there are two different interfaces in the samples after nano-metal powders are added: one is the interface between the PEG and air, which is on the sample surface, and the other one is the interface between the PEG and the metal nano powders, which is inside the sample. These two interfaces are the main locations where the degradation of PEG takes place. The degradation of PEG on the sample surface is an exothermic oxidative process, while the degradation of PEG inside the sample is an endothermic pyrolysis process. Because of the large specific surface area of nano-Al (21.6 m^2 g^{-1}), a large number of PEG in the interface between the PEG and nano-Al degraded. The pyrolysis of PEG inside the PEG/Al leads to heat absorption, so that the whole amount of exothermic heat decreases and the degradation process is delayed. As a result, the TG and DTA curves of PEG/Al are smoother than that of the *p*-PEG in the early period. In the late period, the PEG which separated the pyrolysis products from air in the early period has degraded, so that the pyrolysis products can enter into air and reacted with the oxygen. The oxidation of these pyrolysis products releases a great deal of energy, and this greatly enhances the degradation of PEG. So the slopes of TG and DTA curves of PEG/Al become large suddenly in the late period.

The effects of nano-Ni addition on the thermooxidative degradation of PEG are rather different from that of nano-Al. The DTA curves show that the PEG/Ni begins to release heat slightly after melting, and this thermal process does not complete when the mass loss ends. The DTA curves of the p-PEG and the PEG/Al, however, do not show any similar thermal behavior. This thermal behavior is related to the adsorptive catalysis of nano-Ni. Nickel, like other transition metals, has good capability of catalysis [18, 19]. There are many adsorption centers in the surface of nickel, especially the nano-Ni. Lots of nano nickel powders are exposed in the air and they adsorb both atmospheric molecules and the gas products of the thermooxidative degradation of PEG. These adsorbed molecules react with each other on the nano-Ni surface and released heat.

The pyrolysis behavior also occurs inside the PEG/Ni like the PEG/Al, and the small exothermic peak around 278°C is due to the oxidation of the pyrolysis products. But the specific surface area of nano-Ni (6.6 m^2 g^{-1}) is much smaller than that of nano-Al, so that the amount of heat released is much less than that of PEG/Al as the DTA curves show.

In-situ FTIR experiments

In-situ FTIR was used to analyze the condensed residues of the samples in the thermooxidative degradation process of PEG. The FTIR spectra with 10 main absorption peaks marked at 20°C are showed in Fig. 3. The FTIR spectra of p-PEG accords commendably with that given in reference [5]. The assignments of these peaks are listed in Table 3 [5, 20].

The behaviors of PEG degradation during the preparing processes of three samples can be known by observing the FTIR spectra in Fig. 3. The FTIR spec-

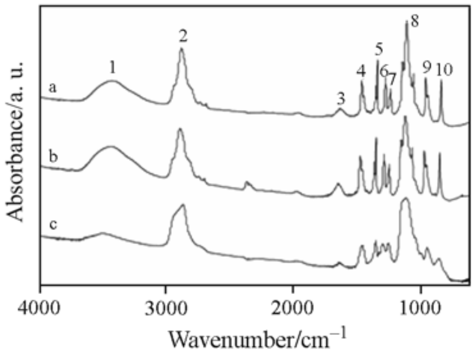

Fig. 3 FTIR spectra of a – p-PEG, b – PEG/Al and c – PEG/Ni at 20°C

Table 3 Assignments of FTIR spectra absorption peaks at 20°C

Peak No.	Wavenumber/ cm^{-1}	Assignments
1	3430	OH stretching
2	2890	CH_2 stretching
3	1650	CH bending
4	1470	CH_2 bending
5	1340	OH bending, CH_2 formation
6	1280	CH_2 formation
7	1240	CH_2 formation
8	1120	C–O stretching, C–C stretching
9	964	CH_2 bending, CH_2 formation
10	843	C–O stretching, C–C stretching, CH_2 bending

tra show that there are no visible differences between the p-PEG and the PEG/Al except a little enhancement in OH group absorption peak (peak 1, around 3430 cm^{-1}). This difference may be due to the slight disaggregation of PEG in the mixing process, resulting in producing PEG oligomers with OH group. But no evident degradation of PEG happened as the FTIR spectra show.

The FTIR spectra of PEG/Ni, however, are much different from that of p-PEG and PEG/Al. The main differences between the FTIR spectra of PEG/Ni and that of the p-PEG are as following: (1) peak 1 (3430 cm^{-1}) weakened observably; (2) the profile of peak 2 (2890 cm^{-1}) changed markedly; (3) two shoulder peaks on peak 8 (1120 cm^{-1}) disappeared; (4) other peaks all weakened more or less. These differences above show that considerable degradation of PEG has taken place in the PEG/Ni preparing process. This confirms that the melting PEG degraded when mixed with nano-Ni due to the good catalysis capability of nano-Ni.

The FTIR spectra of *p*-PEG, PEG/Ni and PEG/Al at 20, 150, 200, 250, 270, 300°C are showed in Figs 4–6.

The FTIR spectra of *p*-PEG at 150°C show that peak 1 and the peaks involved with CH_2 weaken observably, and the two should peaks on peak 8 disappeared as the FTIR spectra of PEG/Ni display at 20°C in Fig. 3. These two should peaks are considered to be involved with CH_2 [5]. But peak 8, which only involves with C–O and C–C in the PEG backbone, does not weaken observably in intensity. All these results above show that OH group has been severely oxidized and PEG has been attacked by the oxygen in air and resulted in forming of α-hydroperoxide [7] at 150°C, but the PEG backbone does not cleavage much at the same time.

The differences among the FTIR spectra of *p*-PEG at 150, 200, 250 and 270°C are not evident, the main peaks only slightly weakened from 150 to 270°C. There is a small peak around 1730 cm^{-1} in the FTIR spectra of the p-PEG 250°C. This peak is involved with C=O, which is considered to be the one of the main groups of the thermooxidative degradation of PEG in air [7–8]. The peak around 2350 cm^{-1} is involved with carbon dioxide, but there is no credible evidence to determinant whether it is the product of PEG degradation or comes from the air.

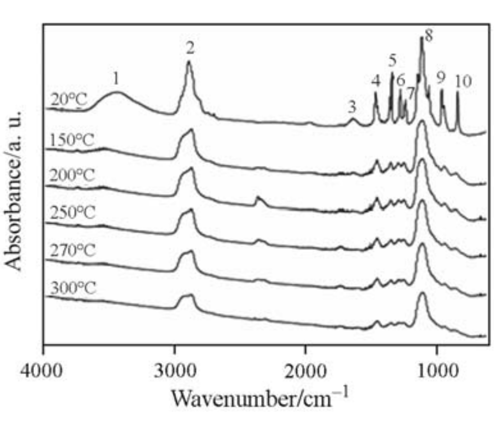

Fig. 4 FTIR spectra of p-PEG from 20 to 300°C

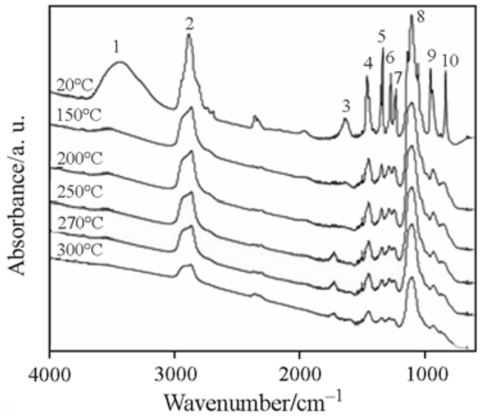

Fig. 5 FTIR spectra of PEG/Al from 20 to 300°C

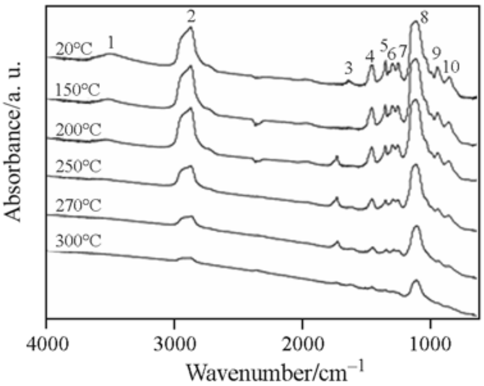

Fig. 6 FTIR spectra of PEG/Ni from 20 to 300°C

Almost all the peaks weaken evidently at 300°C, what may prove that the oxidation and the backbone cleavage of PEG become much more sever. The disappearing of the peak involving C=O group shows that the products containing C=O group, like other degradation products that produced in the anterior period, has decomposed to the low-molecular mass products and escaped from the sample surface. But the thermooxidative degradation process of PEG does not complete at 300°C because the intensity of many main peak are still considerable, especially the peak 2 and the peak 8. No evidence of FTIR spectra of p-PEG from 150 to 300°C show the existence of peaks which are different from that of the FTIR spectra at 20°C except the peak involving C=O group. Other functional groups of possible products of PEG thermooxidative degradation in air were not detected because these volatile products were created on the sample surface and immediately escaped into the air [5].

The FTIR spectra of PEG/Al show that the thermooxidative degradation process of the PEG in the PEG/Al in air is very like that of p-PEG. The peak involving in C=O group around 1730 cm^{-1} weakened at 300°C but not disappeared like the FTIR spectra of p-PEG. This may confirm that the pyrolysis of PEG occurs inside the PEG/Al and the pyrolysis products are oxidized later, which results in the producing of C=O group.

The FTIR spectra of PEG/Ni show that there are many differences in the thermooxidative degradation process of PEG in air between PEG/Ni and the p-PEG. The dominating differences are as following: (1) The main peaks obviously weakened from 250°C while the *p*-PEG from 300°C; (2) The existence of the peak at 1730 cm^{-1} involving C=O group began at 200°C while the p-PEG at 250°C; (3) The main peaks except peak 8 have almost disappeared before 300°C while many main peaks in the FTIR spectra of p-PEG are still considerable. These differences confirm that the nano-Ni has notable effects on the thermooxidative degradation of PEG in air, and PEG may complete the degradation process much earlier than the PEG in the *p*-PEG. The effects are apparently relative to the good catalysis capability of nano-Ni. The catalysis of nano-Ni makes the degradation of PEG in the PEG/Ni begin and reach its maximum much earlier as the TG/DTA data show. In the process of the thermooxidative degradation of PEG in air, many gas molecules are adsorbed on the surface of the nano-Ni and react with each other. These reactions catalyzed by nano-Ni promote the thermooxidative degradation of PEG in air.

Other functional groups of possible products of thermooxidative degradation of PEG except C=O were not detected by the FTIR spectra for the reasons mentioned above, so more information about the effects of the nano metal powders on the products of the thermooxidative degradation of PEG in air were unknown.

Conclusions

Effects of addition of nano-Al and nano-Ni on the thermooxidative degradation of PEG in air atmosphere under 350°C were studied by TG/DTA and in-situ FTIR. The experimental results showed that nano-Al and nano-Ni had evident effects on the thermooxidative degradation process of PEG. The addition of nano-Al can slow down the degradation process of PEG in the early period but accelerated the process in the late period because of the large specific surface area of nano-Al. The addition of nano-Ni made the PEG degradation process began as soon as melted and made the thermooxidative degradation process of PEG complete much earlier than that of the *p*-PEG due to the good adsorbent catalysis capability of nano-Ni. Aldehyde group was detected by the FTIR spectra, but other reported possible functional groups of the thermooxidative degradation of PEG were not found because these volatile products are created on the surface of the samples and immediately escape into the air.

Nomenclature

DTA	differential thermal analysis
DTG	derivative thermogravimetry
FTIR	Fourier transform infrared spectroscopy
nano-Al	nanometer-sized Al powders
nano-Ni	nanometer-sized Ni powders
PEG	poly(ethylene glycol)
PEG/Al	mixtures of nano-Al powders and PEG sample
PEG/Ni	mixtures of nano-Ni powders and PEG sample
p-PEG	pure PEG sample
TG	thermogravimetry
T_E	end temperature of mass loss or heat release of the thermooxidative degradation
T_M	the temperature that maximal rate of mass loss or heat release occur
T_O	onset temperature of mass loss or heat release of the thermooxidative degradation

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