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Anti-static Agent Containing Zinc Oxide and its Modification for PA6 Fiber

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A new anti-static agent was synthesized from zinc oxide-adipic acid-polyethylene glycol and caprolactam by three-step reactions. The antistatic agent (called poly(ether ester amide zinc oxide) or PEEAZ) was analyzed by IR and DSC. The results showed that zinc oxide existed in the main chain of PEEAZ. The glass temperature and melt temperature of poly(ether ester amide zinc oxide) (referred to as PEEAZ in the following) decreased with increasing poly(ether ester zinc oxide) increasing in PEEAZ. Antistatic PA6 fiber was obtained by adding PEEAZ 2–8% (wt/wt) to PA6 during blend spinning. The specific resistance and the static half-value period of PA6 fiber was less than $10^9 \Omega \cdot cm$ and 60 sec, respectively. Excellent antistatic property remained after being washed 30 times.

Keywords poly(ether ester amide zinc oxide), antistatic fiber, PA6

Introduction

Polyamides are important members of the plastics family. It was the first synthetic fiber to achieve industrial importance. Today, polyamide fiber has a significant growth rate (growth rate is around 6% and total output in the word was 4200 kt in 2004) in filaments, staple fiber, etc. (1). Because polyamide fiber accumulates static charge easily, its application is limited. Research on improving polyamide antistatic properties has received much attention. The conventional antistatic products are fabricated by adding an anti-static agent and using conductive fillers like carbon black, conductive metal fibers and metal powders to enhance their effective anti-static properties. The products described above have the advantages of being low-cost and having high-conductivity; however, the products have the disadvantages of being poor in color. In order to obtain a white fiber, composite fiber spinning process is adopted. For example, Unitika Ltd. (2) has produced a sheath/core-type conjugate fiber composed of a core of component A, a polyamide resin containing titanium oxide micro-particles surface-

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coated with stannic oxide and a sheath of component B, a different polyamide resin. This method can improve poor color, but must use expensive and complex composite spinning equipment. A compound with the functional group of ethylene glycol, such as polyoxyalkylene glycol or polyethylene oxide (PEO), is added as an anti-static agent to provide the products with the original resin color (3). However, the drawbacks are that cost is high and the resistance of such products to water-washing is poor. Avoiding the drawbacks of the conventional anti-static material described above, a new anti-static agent (called PEEAZ in the following) was synthesized from zinc oxide-adipic acid-polyethylene glycol and caprolactam by three-step reactions. Adding this anti-static agent to polyamide 6, anti-static fiber can be obtained and it has excellent water-washing resistance properties.

Experimental

Materials

Zinc oxide was obtained from the Shenyang Reagent Factory, adipic acid from the Beijing Chemical Factory, polyethylene glycol 10000 from the Shanghai Chemical Reagent Factory, caprolactam was obtained from the Zhejiang Juhua Group Corporation, and PA6 from BASF.

Methods

Zinc oxide and adipic acid were mixed with a mole ratio of zinc oxide to adipic acid equal 1:2. The mixture was heated to react for 1 h at 30 to 40°C and formed adipic acid zinc with two −COOH groups at the ends (called AZ in following):

$$ZnO + 2HOOC(CH_2)_4COOH \longrightarrow HOOC(CH_2)_4COOZnOOC(CH_2)_4COOH + H_2O$$

AZ was washed in water three times in order to remove unreacted adipic acid. AZ and polyethylene glycol 10000 were mixed with a mole ratio of AZ to polyethylene glycol 10000 equal 1:1 and reacted for 3 h at 150 to 160°C to give poly(ether ester zinc oxide) (called PEEZ in following).

$$HOOC(CH_2)_4COOZnOOC(CH_2)_4COOH + HO(CH_2CH_2O)_nCH_2CH_2OH \longrightarrow$$
$$HOOC(CH_2)_4COOZnOOC(CH_2)_4COO(CH_2CH_2O)_nCH_2CH_2OH + H_2O$$

PEEZ, caprolactam and catalyst were then mixed in a reactor and polymerized for 6–8 h at 230°C to 240°C. Finally, the final product (poly(ether ester amide zinc oxide) (called PEEAZ in the following)) was discharged from the lower outlet and was rapidly cooled by cooling water. Then, the solidified product was cut into granules by a cutting machine to obtain the PEEAZ.

In order to enhance the crystallinity and remove water, the PEEAZ granules were held at 60°C for 1h under vacuum, and then the temperature was raised to 130°C and kept for 8 h. Likewise, PA6 was at 80°C for 2 h and 130°C for 8 h. PEEAZ and PA6 were mixed and then fed to the extruder. The extruded polymer mixture jet emerging from the spinnerette holes was drawn and simultaneously quenched with cool air. The filaments solidified and were eventually collected by a take-up reel with a speed of 400 m/min. The filaments then were drawn 3.5 times at 70°C.

Materials Characterization

Fourier transform infrared (FTIR) analysis: AZ and PEEAZ were characterized using a Spectrum 1-B Perkin-Elmer FTIR spectrometer. The finely powdered dilute dispersions of solid materials in potassium bromide were analyzed in the form of pressed discs.

Differential Scan Calorimetry (DSC)

AZ, PEEZ and PEEAZ were examined to study the thermal parameters of the systems (type DSC-821, Mettler Toledo Star^e System) such as glass transition temperature (T_g), melting point (T_m) and crystallization temperature (T_c). Samples packed in aluminium pans were heated from $-$ 40°C to 260°C, at a heating rate of 10°C/min, then cooled at the same rate down to 30°C.

The Fiber's Specific Resistances

The fiber's specific resistances were measured with a fiber specific resistance tester (type YG321, Changzou Textile Instrument Factory). 15 grams of fiber were placed in the tester box at 20 $\pm$ 1°C, relative humidity 65 $\pm$ 5%, and the resistance tested. The specific resistance was calculated according to the following formula:

$$R_s = \frac{Rbhf}{l}$$

where R_s is the specific resistance/Ω cm; R is the tested resistance/Ω; b is the pole plate length (=8 cm); h is the pole plate height (=6 cm); l is the distance between the two pole plates (=4 cm)and f is the degree of filling (=0.27).

Half-Value Period of Static Charges

Half-value period of static charges is the time for the voltage to reduce to zero. The fibers were rubbed on a rubber sheet 15 times and the time of reduction of voltage tested using a static potentiometer (type DWJ-81, Shanghai Electron Instrument Factory).

Results and Discussion

Fourier Transform Infrared (FTIR) Analysis

The FTIR spectra were analyzed in terms of the appearance and disappearance of characteristic bands of the main chemical groups. Figure 1 shows the characteristic OH stretching band due to the carboxylic group (COOH) at 2951.85–2670.64 cm^{-1}, suggesting that COOH existed in AZ. The presence of the band at 1535.13 cm^{-1}, related to the salt carboxyl group COO, suggests that zinc oxide was reacted with adipic acid and the adipic acid metallic salt was produced. The band at 3415.54 cm^{-1} was attributed to intermolecular hydrogen bonds.

Comparing Figure 1 for AZ and Figure 2 for PEEAZ, significant modification was noted. Figure 2 shows the characteristic stretching band C=O due to the amido bond (–CONH) at 1638.01 and 1618.04 cm^{-1}. Bands appeared at 620 cm^{-1} and 3414 cm^{-1}, due to N-H bending and stretching vibration, respectively. The band at 1113.36 cm^{-1} was attributed to the ether bond (C–O–C) stretching vibration. The presence of a smaller band at 1535.13 cm^{-1}, related to the salt carboxyl group COO^-, suggested that

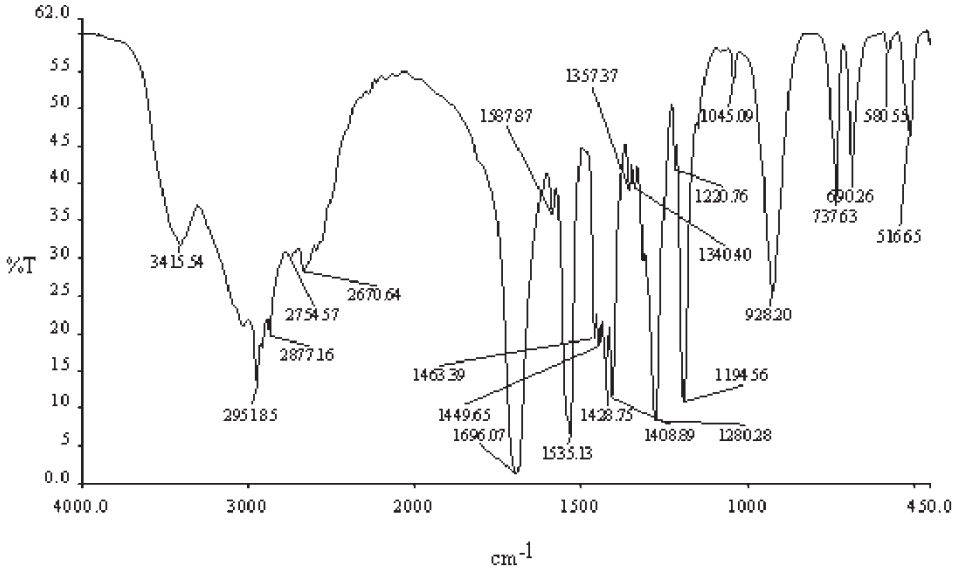

Figure 1. FTIR spectrum of AZ.

the content of salt carboxyl in PEEAZ was lower than in AZ. All this information showed that PEEAZ was a copolymer containing a metallic salt.

Differential Scanning Calorimetry (DSC) Analysis

Typical DSC traces of PEEAZ containing 5%, 10%, 15%, and 20% PEEZ are shown in Figure 3; the corresponding thermal parameters was presented in Table 1. The analyzed

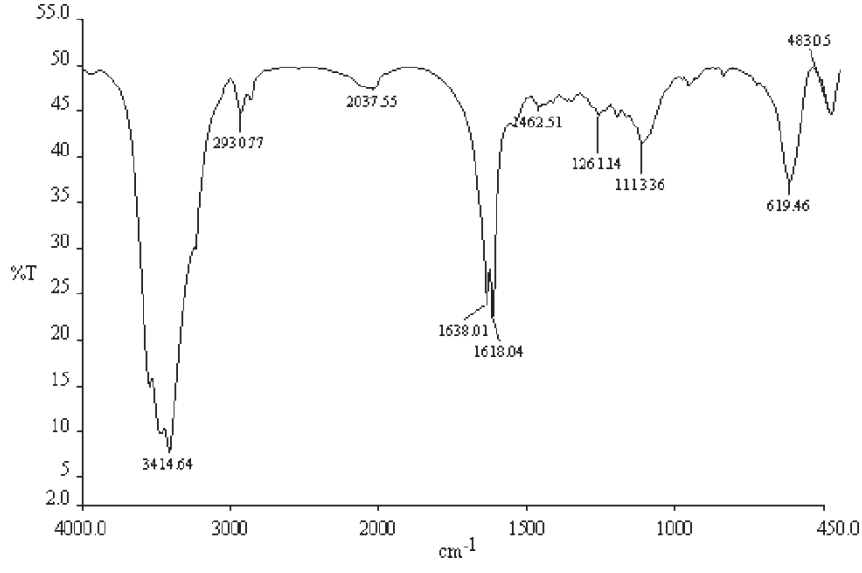

Figure 2. FTIR spectrum of PEEAZ.

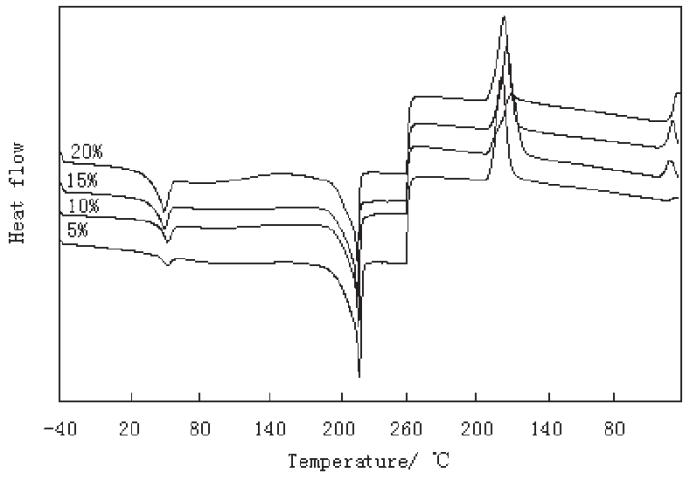

Figure 3. The DSC of PEEAZ with different PEEZ concentration.

parameters, such as T_g, T_c, ΔH_c, T_m, and ΔH_m varied with the PEEZ content. The T_g of PEEZA decreased gradually with an increasing amount of PEEZ, while the melting point (T_m) decreased slightly with an increasing PEEZ content. This behavior can be attributed to introducing ether bonds (in the mers of polyethylene glycol) in the large molecules that improved the molecular flexibility and increased mobility of the molecules. The lowest crystallization temperature (T_c) and crystal enthalpy (ΔH_c) was observed at a concentration of 10%. This can be due to the opposite effects of three aspects. First, plasticization by flexible chain of PEEZ made the crystallization easier. Second, introducing polyethylene glycol in the large molecules damaged the regularity of the large molecules and made crystallization more difficult. Third, intramolecular and intermolecular hydrogen bonds increasingly inhibited crystallization.

Resistances and Static Half-Value of Blending Fiber

The resistances and static half-value period ($t_{1/2}$) of the PA6 fiber containing 6% PEEAZ which contained 5, 10, 15, and 20% PEEZ are shown in Figure 4. The resistance and static half-value period of the blended fiber decreased with an increasing PEEZ concentration in PEEAZ. At PEEZ concentration over 15%, the resistances approached a plateau (less then $5 \times 10^8 \Omega \cdot \text{cm}$).

Table 1
Thermal analysis (DSC) of PEEAZ containing various contents of PEEZ

PEEZ content/%	T_g/°C	T_c/°C	ΔH_c/j · g^{-1}	T_m/°C	ΔH_m/j · g^{-1}
5	42	179	72.33	218.45	−76.21
10	36	170	61.75	217.53	−68.12
15	33	174	64.31	216.41	−69.97
20	30	177	67.17	216.93	−70.20
100	—	39	187.29	63.55	−204.9

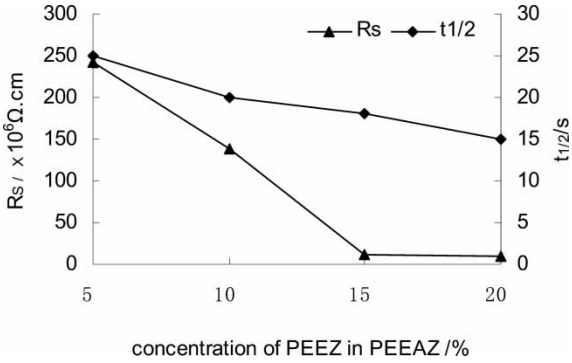

Figure 4. R_S and $t_{1/2}$ of PA6 blended fiber.

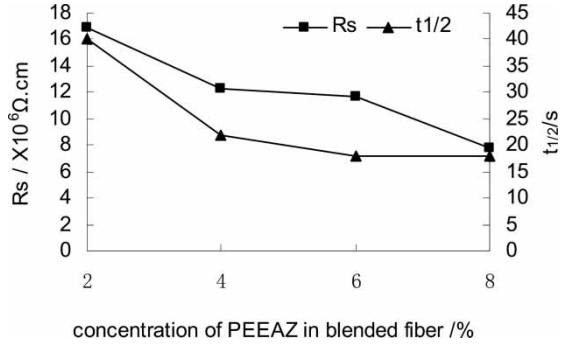

Figure 5. R_s and $t_{1/2}$ of PA6 blended fiber.

The resistances and static half-value periods decreased with an increasing of PEEAZ concentration in PA6 (Figure 5). This is due to the introduction of hydrophilic ether bonds and metal ions in PEEAZ.

In all cases, the resistances and static half-value period of the PA6 composite fiber were less than $2 \times 10^7\ \Omega \cdot \mathrm{cm}$, and 60 sec, respectively. This suggests that PEEAZ with PEEZ 15% provided excellent antistatic properties. After water–washing the above fiber 30 times at 20°C, the resistances of all fibers mentioned above were less than $10^9\ \Omega \cdot \mathrm{cm}$. This indicates that PEEAZ possessed good water-washing resistance.

Conclusions

PEEAZ was a copolymer containing a metallic salt. The glass transition temperature (T_g) and melting point (T_m) of PEEAZ decreased with an increasing amount of PEEZ. Crystallization temperature (T_c) and crystallinity (ΔH_c) were the lowest when the PEEZ concentration was 10%. PEEAZ was a good anti-static agent, and the resistances and static half-value period of the PA6 composite fiber containing PEEAZ decreased with an increasing of PEEZ concentration in PEEAZ and PEEAZ in the

fiber, respectively. After water-washing 30 times, the anti-static property of the fiber was still good.

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