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RESEARCH ARTICLE

Study on Flame Retardancy of Phosphate Reinforced Polyester Fiber

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Abstract

Polyester products are widely used in both civil and industrial applications, because of their good strength, high modulus, good heat resistance, dimensional stability and many other excellent properties [1-3]. Polyester is the largest output in the world and is also the most widely used chemical synthetic fiber, but its flame-retardant properties limits its application. In this study, terephthalic acid (PTA) and ethylene glycol (EG) were used as the basic unit, and 2-carboxylethylphenylphosphonic acid (CEPPA) was used as copolymer flame retardant. We prepared phosphate-containing flame-retardant polypropylene terephthalate co-polyester (FR-PET) [4-8]. The method for adding flame retardant and influence of flame retardant on synthesis process was studied and discussed. We especially analyzed the mass fraction of flame retardant for fire resistance of flame retardant PET copolyester, and the best synthesis process for preparing flame retardant PET copolyester was determined. Fourier infrared spectrometer (FTIR), thermogravimetric analyzer (TGA) and differential scanning calorimetry (DSC) were used to study the structure, elemental composition, thermal properties, thermal stability and flame-retardant properties of copolyesters.

Keywords: Copolymer Flame Retardant; Copolyesters; Phosphate; Polyethylene Terephthalate (PET)

Introduction

In recent decades, with progress of polymer synthesis and processing technology, polyester, nylon and other synthetic fiber materials and their products have been rapidly developed, constantly replacing cotton, metal and other traditional materials, and widely used in every field of daily life and social production. However, textiles and their products belong to flammable and flame spread fast materials, when burning it will produce a lot of heat, smoke, toxic gases, causing secondary damage by high temperature melt drop. These have caused great harm to people, environment and social production. Therefore, flame retardant treatment have attracted widely attention from the whole society through appropriate flame retardant technology can greatly reduce the risk of fire. Flame retardant textiles significantly reduce the speed of fire spread, weaken the release of harmful gas and smoke, and prevent the occurrence of secondary dripping, thus preventing danger to personal safety.

Experimental

Materials

Terephthalic acid (PTA), 2-carboxylethylphenylphosphonic acid (CEPPA), ethylene glycol (EG), TMP (Trimethylolpropane) , toner cobalt acetate, and condensation catalyst Sb_2O_3 were puchase from Aladin company in Shanghai China.

Pre-esterification of CEPPA

PTA and EG were used as basic raw materials, CEPPA was used as flame retardant, flame-retardant polyethylene terephthalate copolyester (FR-PET) with high phosphorus content was prepared [9-12].

CEPPA was measured according to the quantity fractions of flame retardant in the synthesized FR-PET, and a certain amount of EG was measured according to the molar ratio of EG: CEPPA =2:1, EG: PTA=2:1. The material was added to the reaction kettle which was washed and internal temperature was maintained at 150 °C for 3 h. Based on the amount of esterification water yield and temperature in the top of fractionating column to judge whether the pre-esterification was completed.

Synthesis of flame-retardant PET copolyesters

Direct esterification-polycondensation continuous process was used in the synthesis. After completion of pre-esterification, a certain amount of PTA, stabilizer TMP (Trimethylolpropane) , toner cobalt acetate, and condensation catalyst Sb_2O_3 were added into 5 L reactor. The pulping temperature was increased to 230~250 °C for 30 min, and pressure was maintained at 0.1~0.3 MP, and reaction time was 2.5~3.5 h. When the temperature on the top of the fractionating column was increased continuously and then fell to below 100 °C, the esterification water yield was slightly larger than theoretical esterification water yield. This can be judged that the esterification stage was over [13-17]. After esterification stage, the temperature was raised to 260~280 °C, and excess EG was steamed at atmospheric pressure for about 30 min, and then entered the vacuum stage. This stage was divided into two stages: low vacuum stage and high vacuum stage. The low vacuum stage was transition stage from the normal pressure state to the high vacuum state in the kettle, and the low vacuum reached -0.08 MPa. This process was carried out slowly (30~50 min) to prevent the material in the kettle from being sucked out and causing pipe blockage. This stage was not completed until entry the high vacuum stage. The high vacuum degree was less than 100 Pa, and then the condensation polymerization was carried out. The temperature in the kettle was controlled at 275~285 °C during the condensation stage. The speed of stirring motor was constant, and degree of condensation was judged according to the motor power. When it reached a certain value, nitrogen was charged to protect it and reaction was stopped and material was discharged [18-20].

FR-PET Melt Spinning

It was important to maximize drying of slices before spinning. On one hand, we removed the water from the slices and improved the crystallinity and softening point of polyester slices. The moisture contained in the slices was easy to vaporize under high temperature, resulting in broken and hairness filament and screw feeding area was easy to produce blocking material. On the other hand, hydrolysis easily occurred in the cut with high temperature melting, which led to significant decrease of polyester molecular weight, thus affecting the fiber quality. After drying, the moisture content of the slices was controlled below 200 ppm.

The POY (partially oriented yarn) was prepared by melting spinning, mixing flame retardant PET copolyester slices, which was composed of high phosphorus content (CEPPA 20wt%) PET and pure PET, until CEPPA was 5wt%, and temperature of each spinning zone was mainly based on melting property, melting point, intrinsic viscosity, and melting of polyester. The number of screw heating zone, comprehensive consideration before decided. The screw of spinning machine was divided into feeding section, compression section and mixing section. And the temperature of the feeding section was too high, otherwise it would lead to the slices softening adhesion, causing blocking, and affecting the spinning. The temperature of spinning box was very important for melt spinning, and its fluctuation affected the spinnability and reel quality of wound wire. The technology of biphenyl gas phase heating was used in the heating cabinet, and minimum temperature was not less than 250 . In the spinning process, the warm melt was connected with a metering pump through a screw head. Metering pump temperature must be close to the cabinet, so it was heated with biphenyl to reduce temperature fluctuations. Comprehensive considering the above requirements, in the spinning process, corresponding spinning temperature was determined, spinning process was smooth, no ring blocking material and winding forming was good [21-23].

Results and Discussion

The flow curves for five melt samples. The shear viscosity of the melt can be described at a wide shear rates in the flow curves. The shear stress of all samples was increased with increased shear rate, and they were typical non-Newtonian fluids. According to its characteristics, it should be classified as pseudoplastic fluid, there was a transient entanglement in the plastic melt that was different from the chemical crosslinking junctions [24-26].

The entanglement was being broken and rebuilt continuously, in a certain condition, the broken and reconstruction will reach dynamic equilibrium, which can be called the transient network system. The dynamics equilibrium was easily affected by external condition, the dynamic equilibrium was changed with change of shear stress. When the shear stress was increased, part of the entanglements were separated, causing decreased concentration of entanglements and apparent viscosity. When shear rate was increased, the stress also increased in the chain segment but was too late to release, resulting in formation of orientation of chain segment in the flow field. The orientation effect of segment reduced the ability of macromolecular chain to transfer momentum between flow layers. Consequently, the drag forces between the flow layers decreased, and apparent viscosity of the polymer decreased consequently. So, the flame retardant copolyesters had typical shear change characteristics of dilute non-Newtonian fluids.

According to the free-linking segment model, the flow of macromolecular chain in flame retardant copolyester melt can be regarded as the total result of transition of molecular chain segment to hole, since viscosity was related to diffusion process for chain segment to the hole, and temperature obviously affected diffusion temperature had a great influence on flow curve for flame retardant copolyester melt. The shear stress of flame retardant copolyester melt decreased with increased temperature at the same shear rate. The movement of the polymer was not whole chain but the local movement of the chain segment. The flow of the polymer melt was a sequential transition similar to the creep of earthworm. So, it was subject to Arrhenius' law, and this law could be used to describe the flow behavior of the polyester.

$$\eta_\alpha = C \cdot \exp\left({}^{\Delta E}\!\big/_{RT} \right) \tag{1}$$

$$\ln \eta_\alpha = \ln C + {}^{\Delta E}\!\big/_{RT} \tag{2}$$

Where η_α was apparent viscosity, C was constant; E was flow-activation energy; R was gas constant, The temperature sensitivity of polymer viscosity can be determined by the flow activation energy of melt. The higher flow activation energy was, the more sensitive was the viscosity to the change of temperature is the $\ln\eta\alpha\text{-}1/T$ curve for sample 4 at different shear rates. It can be seen from the the linear correlation of regression equation for the curve obtained was good. According to the curve slope, the flow activation energy for sample 4 melt was calculated as shown.

The flow activation energy for melt sample 4 decreased significantly with increased shear rate. The flow activation energy was determined by the resistance of flow unit during transition. This was determined by the structure of macromolecular chains. The destruction degree for the network structure formed by the entanglement of macromolecular chains was low with relatively low shear rate, and the activities of the chain segments were blocked greatly, which led to a larger activation energy of the flow. When the shear rate was increased, the tendency of entanglement for the network structure was much greater than the tendency of reconstruction, and the resistance of the macromolecular chain segments decreased, leading to decreased flow activation energy. The flow activation energy for flame retardant copolyester melt decreased with increased shear rate, indicating that, the effect of temperature on viscosity of flame retardant copolyester melt decreased obviously at higher shear rate. Therefore, flame retardant copolyesters were suitable to higher extrusion speed, because it required lower temperature control.

Flame retardant mechanism for phosphorus system

Phosphorus flame retardants have condensation flame retardant and gas flame retardant, there were two main flame retardant modes of condensed phase: carbonization mode and coating mode. Phosphorus flame retardants decomposed into phosphoric acid or anhydride with high temperature. These were strong dehydrating agents that promoted dehydration, crosslinking and carbonization of oxygen-containing polymers, forming a tight and non-combustible coke layer, and reducing the escape of combustible gas. The coke layer can isolate the contact between the internal polymer and oxygen, resulting in combustion asphyxia, while the coke layer formed a heat insulation layer of the polymer and outside heat transfer was isolated, thus slowing down the thermal decomposition reaction. With high heat, the phosphate was further dehydrated and polymerized into polyphosphate. The polyphosphoric acid was a glassy melt that coated the surface of the polymer to form a coating that prevented oxygen contact and release of volatile split products. Another flame-retardant mechanism for phosphorus series flame retardant was vapor phase flame retardant mechanism. Phosphorus flame retardants can be decomposed into small molecules, such as $PO\cdot$, $P\cdot$, PO_2 and HPO_2 , with high temperature which can effectively reduce the amount of hydrogen and hydroxyl radicals around the flame area and terminate the combustion chain reaction, thus playing the effect of vapor phase flame retardant [27].

In the testing process, after adding 5wt% flame retardant, the flame retardant copolyester showed fluidity at a relatively low temperature, and the melting index of flame retardant copolyester showed a sharp increase in small temperature range. The melting index of flame retardant copolyesters under the same conditions (temperature 255 ℃, load 2.16 kg) is shown. With increased flame retardant, the melting index for different proportions of flame retardant copolyesters also showed significant differences and increased significantly (the melting index MI reached maximum of 78.78 when the flame retardant sample was 20wt%). The phenomena is as follows: the structure of polyester macromolecule chain was destroyed after the block copolymerization for flame retardant CEPPA. With increased flame retardant, the melting point of flame retardant copolyester decreased gradually, and probability of macromolecule chain segment entanglement decreased. There was a certain amount of small molecule oligomer in the flame retardant copolyester at the same time, and its content increased with increased flame retardant and difficulty of copolymerization.

The infrared spectrum for flame retardant PET and RE-PET are shown 3041.17 cm^{-1} corresponded to stretching vibration peak O-H for carboxyl；1717.16 cm^{-1} corresponded to the stretching vibration peak for C=O；2309.71 cm^{-1} corresponded to the stretching vibration peak for O-H in the -POOH；1143.57 cm^{-1}、1122.161 cm^{-1} corresponded to the stretching vibration peak for P=O；The stretching vibration peak for P=O in the RE-PET moved from the original 1143.57 cm^{-1} and 1122.16 cm^{-1} to a low wave number 1099.16 cm^{-1} 1122.16 cm^{-1} because of some chemical reaction. This indicates that the small molecular monomer for the flame retardant CEPPA had indeed been copolymerized into the PET macromolecular chain [28].

The surface topography for fibrous was evaluated using a scanning electron microscopy (SEM, Zeiss SIGMA 500 Germany). Samples were sputter-coated with a thin gold layer (Eiko IB3, Tokyo, Japan) and the obtained SEM images were employed to estimate the average fiber surface amorphous. It can be seen that, the surface morphology of FR-PET was coarser than the surface of pure PET, meaning that the pure PET polymerized the flame retardant successfully.

The flame retardant CEPPA should be pre-esterified and then added into the reaction system to improve its thermal stability and meet the conditions for copolyester synthesis process. With increased flame retardant, the glass transition temperature (Tg) and melting temperature (Tm) of copolyesters also decreased, while the cold crystallization temperature (Tc) increased. The temperature with maximum decomposition rate was increased, and mass retention rate in 600 also increased significantly, but decreased slightly when the CEPPA was 20wt%. The flame-retardant properties for FR-PET were also improved. FR-PE melt was pseudoplastic fluid. With increased flame retardant monomer content, the non-Newtonian index increased gradually and the spinning temperature was adjusted to lower temperature.

According to the TG test results shown the decomposition temperature for polyester increased at first and then decreased with increased CEPPA and initial decomposition temperatures of 15wt% and 20wt% FR-PET were lower than pure PET. The maximum decomposition rate was increased significantly when the CEPPA was 15wt%. The maximum residual amount reached 19.44wt% but decreased slightly when the CEPPA was 20wt%. Because the P-C bond energy in flame retardant polyester was relatively lower than others, and it was easier to break and degrade at high temperature, the P-C bond decomposed and formed a coke layer that prevented heat transfer. Therefore, the maximum decomposition temperature increased after adding flame retardant, and the char formation rate was effectively improved, so the retention rate at 600 was also improved. When the content of flame retardant was relatively low, the decomposition of P-C bond formed a coke layer, which hampered the heat transfer and played a delaying role in the further thermal decomposition, so that at first decomposition temperature increased when the mass fraction was 5% and 10%. However, with further increase of flame retardant, the thermal decomposition of P-C at fracture began to play a leading role. Therefore, the mass fraction 15% and 20% FR-PET initial decomposition rate and initial decomposition temperature were lower than pure PET.

Stress-strain curves and related data of five kinds of fibers spun with same conditions can be seen. The addition of flame retardant caused decreased breaking strength of the fiber, because polyester macromolecular regularity was destroyed in the copolymerization by flame retardant monomer. The crystallization degree for the molecules was also destroyed, resulting in decreased crystallinity and fracture strength. But the elongation at break point increased also. These were the result for the flame retardant was more uniform dispersed in the mixture.

LOI (limiting oxygen index) is a minimum oxygen content mixed with nitrogen at which a specimen no longer burns. It was measured with an oxygen index combustibility tester (Yasuda Seiki Seisakusho, Japan) according to ISO 4589:2000 (determination of burning behavior by oxygen index) as the following equation (3):

$$LOI = \frac{V(O_2)}{V(N_2) + V(O_2)} \times 100 \tag{3}$$

Where $V(O_2)$ and $V(N_2)$ are the volume fractions of oxygen and nitrogen gases in the mixed gas environment respectively.

As shown, the limit oxygen index of conventional PET was only 23.4%. When the flame retardant CEPPA was copolymerized, the limit oxygen index of flame retardant copolyester increased sharply (the mass fraction of flame retardant 5%). The limit oxygen index LOI of flame retardant copolyester was 30.3%, and increased with increased flame retardant. When the mass fraction of flame retardant was 20%, the limit oxygen index of flame retardant copolyester reached 40.5%. However, it can be seen from the limit oxygen index of flame retardant copolyesters increased with increased flame retardant was not a simply linear, but in a curve of decreasing curvature. The limit oxygen index of flame retardant copolyester with 15% flame retardant was very similar to the flame retardant copolyester with 20% flame retardant, and the difference was less than 3%.

Conclusion

The basic synthesis process, structure and properties of FR-PET copolyester were studied in this study, and the following conclusions are drawn as follows; After pre-esterification, the flame retardant CEPPA was added into the reaction system, which formed the esterification substance to improve its thermal stability. The method for pre-esterification effectively improved the temperature of decomposition, in order to avoid being decomposed in the high temperature processing, and it was also helpful for appropriately raising the reaction temperature to speed up the reaction rate. Infrared spectrum test proved the existence of P element in flame retardant copolyesters and small flame-retardant molecules were indeed copolymerized into PET macromolecular chain. The thermal and flame-retardant properties of flame retardant copolyesters were analyzed by TG and LOI. The results showed that, with increased flame-retardant content, the flame retardant copolyester Tg, Tm, decreased, but Tc increased. The thermal degradation temperature first increased and then decreased with increased flame-retardant mass fraction, and the final carbon residue increased. After adding a small amount of flame retardant, the limit oxygen index of flame retardant copolyester increased sharply. When the mass fraction over 15% the limit oxygen index of flame retardant copolyester did not have obvious change.

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