Study on Synthesis and Dissolving Characteristics of Water-soluble Polyester

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Abstract: Water-soluble polyester has become an indispensable industrial material in the field of chemical fibers, but the production efficiency in industrial production is not high, and there is no big patent breakthrough in experimental research. The experimental reaction rate of water-soluble polyester was studied by changing the amount of SIPM in the experiment. By changing the concentration of sodium hydroxide, the factors affecting the base deweighting rate of water-soluble polyester were explored. The experimental results show that the esterification rate decreases with the increase of the amount of SIPM. This problem can be solved by reducing the reaction residual pressure and prolonging the experimental reaction time. In order to increase the base deweighting rate rate of polyester, the concentration of sodium hydroxide and the reaction temperature can be increased.

1. Research background

1.1 Literature review

Polyester has unique biocompatibility and biodegradability. Petrochemical materials are widely used as raw materials in polyester products. Water-soluble polyesters are usually prepared by esterification and polycondensation. For example, new water-soluble polyesters are prepared by using methylene succinic acid, 1,4-butanediol and sodium succinic acid-2-methylsulfonate as raw materials. The chemical properties of water-soluble polyesters are usually measured by hydrogen spectroscopy and infrared spectroscopy. By changing the experimental conditions, the different changes of the properties of polyesters under different conditions are tested. After adjusting the proportion of raw materials, the optimum synthetic conditions of the polyester are esterification reaction temperature 180 C, polycondensation reaction temperature 160 C, pressure 0.1 MPa, reaction time 5 hours and 2.5 hours respectively (Liu, 2019). The properties of water-soluble polyesters are affected by the proportion of raw materials. In a certain range, the water-solubility of WSPET can be improved by increasing the dosage of ethylene adipate and polyethylene glycol, dissolving time and temperature in a certain range (Wu, Wu and Li, 2000). When water-soluble polyester is prepared by adding m-dibenzoic acid or other modified components in the polycondensation reaction, the study of modified polyester shows that its fibre separation and spinnability are improved (Tang and Sun, 2004). In the study of the properties of water-soluble polymers after CO polycondensation of isophthalic acid, glycol and dimethyl-5-sulfonate (SIPM), it was found that the increase of the last substance in the separation chain would enhance the water solubility of the polymers. The solubility of water-soluble polyesters varies greatly even in the same solvent due to the different samples in the solvent (Ying and Wu, 1998).

1.2 Purpose of research

At present, dissolvable component materials are urgently needed in the field of chemical fibers. They are mainly used in composite spinning. Water-soluble polyesters have been found to be suitable for the development and production of this material because the fibers can be separated by water. Water-soluble polyester can be used as superfine composite fibers to produce superfine composite fibers with good hygroscopicity and soft handle. This soluble fiber can improve the antistatic and hygroscopicity of the product very well, so it will also be mixed with other common

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raw materials in industrial production. With the increasing awareness of environmental protection, high-tech and soluble polyester technology has attracted worldwide attention. Germany, Japan, the United States and other countries have obtained patents in water-soluble polyester research. Many universities in China have also launched research and development of this product. China is investing more and more in this field. It is of great significance to study the synthesis and solubility of water-soluble polyesters. The purpose of this paper is to understand more about the factors affecting the synthesis and solubility of water-soluble polyesters, so as to provide solutions for industrial production.

2. Experiment

2.1 Synthesis of water-soluble polyester

Main raw materials of the experiment: according to the classification of chemical raw materials, there are industrial grade isophthalic acid, antimony trioxide, glycol, polyethylene glycol, zinc acetate, sodium acetate, cobalt acetate, etc.; fiber grade is dimethyl terephthalate; polymer dimethyl isophthalic acid-5-sulfonate sodium; general polyester chips (Cheng and Tu, 2009).

The main equipments needed are: infrared spectrometer, melting point instrument, gel permeation chromatograph, nuclear magnetic resonance spectrometer, X ray diffraction analyzer, etc. (Yu et al, 2013).

Polymerization process: First of all, esterification reaction, taking diethylene glycol condensate, dimethyl terephthalate, 1,2 propylene glycol and other raw materials in the same molar number, mixing, placed in four-mouthful flasks, then adding a small amount of catalyst, heating, and other substances show a melting state, start stirring. The temperature was maintained at 160 C for the first hour, then gradually heated to 190 C within 5 hours until no methanol was released. Diols need to be collected in the polycondensation reaction, and the reaction temperature is slowly raised to 200 C, then the temperature is kept warm for one hour and the pressure is gradually raised to 0.1 atmospheric pressure. At this time, in order to ensure the stable outflow of ethanol, the temperature should be gradually raised. At the later stage of the experiment, a large number of bubbles were generated and the liquid viscosity was enhanced. After a certain amount of diol was collected, the experiment was stopped.

2.2 Evaluation of solubility of water-soluble polyester

The water-soluble polyester samples obtained from the above experiments were dried in a dryer to a constant weight state. The samples were placed in three-mouth flasks, and distilled water was added to mix 25% of the dispersed liquid. Heat and stir to dissolve completely, then drop to room temperature. The mechanical impurities appearing in the liquid are removed, and the precipitation of the solution can be observed when it is placed at room temperature for a long time, which can be observed until the solution is stable.

3. Results and discussions

3.1 Water-soluble polyester synthesis

3.1.1 Ester exchange reaction dynamics

Water-soluble polyester can be synthesized by transesterification and post-polycondensation. This method means that the ester group is first divided into two steps for transesterification, and the reaction activity is the same, reaching reversible equilibrium under certain conditions. In our experiments, we need to make the reaction go forward, so we need to change the reaction conditions. The reaction conditions can be carried out in three directions: increasing the concentration of reactants, increasing the experimental temperature or separating by-products. The by-product methanol in this experiment was detected, and the reaction process was investigated according to the ratio of theoretical mass to actual mass of methanol. The experimental data analysis showed that the conversion of methyl ester group was linear with time, and the conversion increased with time.

By calculating the reaction rate with the linear regression equation, different transesterification rates can be obtained after changing the original experimental conditions. It was found that sodium dimethyl isophthalate-5-sulfonate used in the raw material could reduce the reaction rate in the experiment. Therefore, in order to complete the esterification reaction, the reaction time should be prolonged properly in the synthesis process of water-soluble polyester.

3.1.2 Effect of reaction residual pressure on molecular mass of target products

The formation of water-soluble polyester is reversible. Therefore, lower residual pressure can promote the positive reaction, facilitate the separation of ethylene glycol from the product, thereby improving the production efficiency of the product. The viscosity properties of the product are negatively correlated with the residual pressure in the reaction system, i. e. the reaction residual pressure decreases and the product viscosity increases. According to Polyester Polymerization Degree Formula

$Xn = \frac{K}{nW} \bullet \frac{1}{2}$, Xn represents the degree of polymerization of polyester, nW eepresents the molar fraction of small molecule products,Reaction Equilibrium Coefficient K value 0.43, It can be seen from the formula that the degree of polymerization of the product can not be improved without removing the by-products of small molecules in the reaction process. Because of the small equilibrium coefficient in the reaction, it is necessary to control the vacuum degree well in the experiment, and the high vacuum condition is needed in the experiment to obtain the water-soluble polyester with the degree of polymerization greater than 100.

3.1.3 Effect of SIPM dosage on experiment

By studying the effect of SIPM dosage on the experiment, it was found that the amount of raw material was negatively correlated with the molecular weight of water-soluble polymer under the same conditions. Because when SIPM enters macromolecule, it will increase the interaction force between macromolecule and increase the polymer viscosity under the influence of strong polar sulfonic acid group contained in SIPM itself. Because the movement of macromolecule is limited, the effective collision probability between molecule and molecule decreases, which leads to the decrease of reaction rate. At the same time, it is more difficult to separate the by-product glycol with the increase of viscosity. Ultimately, the production efficiency of water-soluble polymer is reduced.

3.2 Solubility of Water-soluble Polyester

1) Relationship between Solubility and Dissolution Temperature and Time

The base deweighting rate rate of polyester with 4% NaOH solution increased with time by changing the temperature conditions and at 70, 80 and 90 ~C. Finally, the base deweighting rate rate increases with the increase of temperature. Alkali hydrolysis is a double diffusion process. Reactors in solution diffuse to the surface of slices and also to the edges of crystalline and non-crystalline regions. The products in the experiment diffuse from the crystalline edge to the solution. Accelerating the diffusion rate of reactants and products can increase the experimental reaction rate. The higher the reaction temperature, the higher the reaction coefficient, the higher the hydroxyl permeability and the stronger the exercise ability. In the experiment, the mobility of macromolecule will be enhanced with the increase of temperature. The hydroxyl radical will pass through the instantaneous gap between the molecules and enter the slice to participate in the reaction smoothly, so that the yield of the product will increase rapidly. It can be seen from the table that the base deweighting rate rate increases with time at the beginning of the reaction. After the reaction lasted 60 minutes, the effect of reaction time on the base deweighting rate rate hardly increased. This is because the concentration of hydroxyl radicals in the reaction system decreases with the prolongation of reaction time. The effect of temperature on the experiment is that the higher the temperature, the shorter the time for the reaction rate to reach its maximum.

2) The relationship between the concentration of sodium hydroxide and its solubility

In order to study the effect of sodium hydroxide concentration on the base deweighting rate rate of polyester, the increase of base deweighting rate rate of polyester was studied by changing the alkali content in the reaction under the same reaction conditions. The mass fractions of sodium hydroxide used in the experiment are 1%, 3%, 4% and 5% respectively. The experimental results show that the base deweighting rate rate of polyester increases with the increase of the mass fraction of sodium hydroxide. This is due to the increase of the concentration of hydroxide ion in sodium hydroxide, which enlarges the attack probability of carbonyl carbon. Increasing the probability of intermediate formation in the experiment will promote the experiment to move towards the forward hydrolysis process.

4. Conclusion

The synthesis rate of water-soluble polyester will decrease with the increase of SIPM. The area where the reaction rate of water-soluble polyester decreased markedly was that the mass fraction of SIPM was in the range of 8% - 12%. Moreover, the increase of SIPM will decrease the molecular weight of the product. Therefore, in order to ensure the complete reaction, the reaction time should be extended appropriately. At the same time, the molecular weight of the product can be increased by reducing the reaction residual pressure. In the test of base deweighting rate rate, increasing the concentration of sodium hydroxide and the temperature of base deweighting rate can promote the increase of base deweighting rate rate.

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