Preparation and Properties of a Kind of Hydrophilic Polyimide Film with Quaternary Ammonium Salt Structure

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Abstract: We synthesized a polyamide acid by copolycondensation reaction using diphenyl ether tetraacid dianhydride (ODPA) as the dianhydride monomer, diaminodiphenyl ether (ODA) and N-methyl-2,2-diaminodiethylamine (diethylamine) as the diamine monomer. Then the polymer with side-linked branch sulfonate structure was synthesized, and the structure of quaternary ammonium salt was added to the polyamide acid. A hydrophilic PI film was prepared by coating and thermal imidization process. The main influence factors in the formation process of hydrophilic PI film were discussed, then its hydrophilic properties and thermal properties were tested. The results show that diethylamine can react with lactone in the PI molecular chain in the DMAc system. The introduction of quaternary ammonium salt significantly improves the hydrophilic properties of the polyimide film surface, the water contact angle of the film dried at 130°C is 58.065°. Above 140°C, breakage and decomposition of the -N+SO3- structure bond will occur, and the hydrophilic property will decrease.

1. Introduction

In recent years, membrane water treatment technology has been widely used in sewage treatment due to its advantages of good separation effect, low operating energy consumption, low environmental pollution, and significant environmental benefits and economic value in research and practical applications and other water treatment fields[1-2]. Polyimide polymers refer to a series of polymers containing amide segments (-CONH-). Its outstanding features are high mechanical strength and good chemical stability, which are suitable for the production of separation membranes that require high mechanical strength[3]. However, the water wettability of ordinary polyimide membranes is insufficient, which will affect the separation efficiency. Therefore, it is necessary to improve its hydrophilic properties while ensuring good mechanical properties. Zwitterionic compound materials with super antifouling ability have attracted people's attention, and they are gradually used as antifouling materials[4-7]. Representative zwitterionic polymers include phosphate betaines (such as dodecyl dimethyl hydroxypropyl phosphobetaine) and sulfobetaines (such as methacryloyl ethyl sulfobetaine) And carboxybetaines (such as carboxybetaine methyl methacrylate), etal[8]. Gu J[9] used TPA-NMe2, BAPBS, ODA and ODPA to synthesize a zwitterionic polyimide. The polyimide ultrafiltration membrane was prepared and the polyimide ultrafiltration membrane was improved. In addition to the excellent mechanical properties and chemical stability of PI films, the hydrophilic polyimide film containing quaternary ammonium salt structure, due to its unique structure of grafted...
quaternary ammonium salt, makes the surface of the prepared film have a good hydrophilic properties can take into account both mechanical properties and hydrophilicity. Therefore, the research and development of hydrophilic polyimide films containing quaternary ammonium salts are of great significance in anti-fouling and hydrophilic aspects.

2. Materials and Methods

2.1. materials
Diphenyl ether tetraacid dianhydride (ODPA): molecular formula C\textsubscript{16}H\textsubscript{6}O\textsubscript{7}, molecular weight 310, Sinopharm Chemical Reagent Co., Ltd., analytical grade; 4,4′-diaminodiphenyl ether (ODA): molecular formula C\textsubscript{12}H\textsubscript{12}N\textsubscript{2}O, molecular weight 200.24, Sinopharm Chemical Reagent Co., Ltd., analytical pure; N,N-dimethylacetamide (DMAc): molecular formula C\textsubscript{4}H\textsubscript{9}NO, molecular weight 87.12, Sinopharm Chemical Reagent Co., Ltd., analytical pure; N-methyl-2,2-diaminodiethylamine (Hereinafter referred to as diethylamine), the molecular formula is C\textsubscript{5}H\textsubscript{15}N\textsubscript{3}, the molecular weight is 117.19, Sinopharm Chemical Reagent Co., Ltd., analytical pure; 1,3-propane sulfone: the molecular formula is C\textsubscript{3}H\textsubscript{6}O\textsubscript{3}S, the molecular weight is 122.14, Sinopharm Chemical Reagent Co., Ltd., analytical pure.

2.2. Characterizations
HD2015W electric stirrer; KQ5200E ultrasonic instrument; Byko-Drive automatic film coating machine; automatic Ubbelohde viscometer: Shanghai Korda Scientific Instruments Co., Ltd., capillary inner diameter 0.64mm; gel chromatography (GPC, Agilent 50, USA) Company); Fourier Transform Infrared Spectrometer: Model Cary630; Differential Scanning Calorimeter: Model NETZSCH DSC404; Contact Angle Tester: Model JGW-360A.

2.3. Methods
Weigh a certain amount of ODA, diethylamine and were dissolved in the DMAc solvent. After it was completely dissolved, added a certain amount of ODPA in batches. The reaction was stirred at room temperature, and the stirring for 4 hours after the feeding was completed to obtain a yellow, viscous, clear and transparent polyamic acid (PAA) solution. Weigh 1,3-propane sulfone in the same amount as diethylamine and added it to the above PAA solution, stirred and reacted for 4h at room temperature, and graft the hydrophilic SO\textsuperscript{3}-functional group to the polyamide amide with a quaternary ammonium salt structure. After the PAA solution was filtered, the film was coated on a clean glass plate with an automatic film coater, and the film thickness can be controlled within 10-30μm. The film was thermally imidized in an oven using a stepped heating method. After it was naturally cooled to room temperature, it was soaked and separated in a clean water phase to obtain a light yellow transparent film. After the oven was dried, the structure was characterized and the performance was analyzed and tested.

The molecular weight of PAA was characterized by gel permeation chromatography (GPC); the structure of PI film was characterized by Fourier transform infrared spectroscopy (FTIR); the thermal performance of the film was measured by differential scanning calorimeter (DSC); static contact angle tester test Its hydrophilicity.

3. Results and discussion

3.1. The effect of raw material ratio on the viscosity of polyamic acid
The test was carried out with the ratio (molar ratio) of diamine and dianhydride 1:1, 1:1.01, 1:1.02, 1:1.03, and 1:1.04. Table 1 shows the intrinsic viscosity values of PAA with different raw material ratios measured by an automatic Ubbelohde viscometer.
Table 1: Intrinsic viscosity values $[\eta]$ of PAA

| Number | 1   | 2   | 3   | 4   | 5   |
|--------|-----|-----|-----|-----|-----|
| $[\eta]$ | 0.32450 | 0.33790 | 0.38905 | 0.35574 | 0.33937 |

From the data in Table 1, it can be seen that the solution viscosity was the largest when the ratio was 1:1.02, and there is also obvious pole climbing phenomenon in the experiment. The reason for using a slight excess of dianhydride is that there was a trace amount of water in the reaction system, which converts part of the reactant dianhydride into an inactive acid; if the dianhydride was excessively large, the viscosity of the PAA solution obtained would also decrease, and the excess dianhydride would also interacted. The amide of PAA undergoes anhydrolysis reaction to obtain an oligomer with terminal anhydride groups; if the diamine was excessive, an aminate reaction will also occurred to obtain an oligomer with terminal amino groups. In addition to the benzene ring in the structure of the diphenyl ether type PAA, it also contained a C-O bond. The internal rotation of the C-O bond was easier than that of the C-C bond. Therefore, the flexibility of the main chain was better than that of polyamic acid with only a benzene ring structure in the main chain.

3.2. The effect of diamine ratio on polyamic acid

Diethylamine was a compound with a double-terminal amino structure, which replaced part of ODA and became part of the PAA main chain. The reactivity of aliphatic structure of diethylamine and dianhydride monomer was significantly higher than that of ODA, and it would also have a great impact on the stability of PAA molecules. In the experiment, three PAA systems with ODA:diethylamine molar ratios of 9:1, 8:2, and 5:5 were synthesized, and the stability of the PAA system was analyzed when different amounts of diethylamine were added.

During the synthesis process, it was discovered that the dianhydride added to the reaction system would react quickly with diethylamine first, and a white turbid gel would be formed, and a viscous gel would be formed on the wall of the reactor. As the input of dianhydride increased, the viscous colloid will gradually disappeared, and the system appeared light yellow, clear and transparent. This was because the segments of diethylamine and dianhydride and the segments of ODA and dianhydride form the entire PAA polymer molecule, which was successfully polymerized into the main chain structure of the polymer.

When the added amount of diethylamine increased, the difficulty for viscous colloids to enter the PAA main chain increased. When the molar ratio of ODA:diethylamine was 8:2, the viscosity of the PAA system would be significantly reduced, although at the end of the reaction, the film can be formed after amine, but the brittleness was obvious, and the flexibility was very low, indicating that too many aliphatic segments in the PI chain greatly reduced the mechanical properties. When the molar ratio of ODA:diethylamine was 5:5, a homogeneous polyamic acid system can no longer be formed, a good polymer high molecular weight chain cannot be formed, the viscosity of the system was low, and a complete thermal imidization cannot be formed. After being left for several days, the system separated phases and appeared white turbidity. Therefore, we choose the molar ratio of ODA and diethylamine to be 9:1 for polymerization reaction with ODPA, and then add propanesultone equimolar with diethylamine for quaternary ammonium salt reaction, so that the side chain of the polymer molecule introduce SO$_3^-$hydrophilic group. Figure 1 shows a gel permeation chromatogram of the molecular weight of PAA obtained by the polymerization reaction.
The results show that when the molar ratio is 9:1, the peak molecular weight, number average molecular weight, weight average molecular weight and molecular weight distribution of PAA tested by gel permeation chromatography are: \( M_p : 491038 \); \( M_n : 694956 \); \( M_w : 1030865 \); \( d = 1.48 \).

3.3. Analysis of membrane structure
The temperature stability of the quaternary ammonium salt structure in the system can be analyzed by infrared spectroscopy. Figure 2 shows the infrared spectra of PI films with different heating temperatures.

Among the curves (a) and (b) of Figure 2, sharp C-H characteristic peaks appear at wave numbers of 2922 cm\(^{-1}\) and 2853 cm\(^{-1}\), which are caused by CH\(_3\) and CH\(_2\) introduced by diethylamine. The curves (c) and (d) have no peaks here, which was due to the complete decomposition of diethylamine at 280°C. It shows that diethylamine can normally polymerize into the PAA molecular chain, and it can also react with lactone in the DMAc system under PAA state. Curve (a) shows an obvious stretching vibration peak at 1208 cm\(^{-1}\), which was the stretching vibration peak of the quaternary ammonium salt. The peak heights of curves (b) and (c) here were weakened, indicating that as the temperature increases, the quaternary ammonium salt will partially decompose, indicating that the quaternary ammonium salt was an unstable chemical structure, and the chemical bond cannot be The stable existence caused the decomposition of the quaternary amine salt, and will also decomposed the N-CH\(_3\) of diethylamine, so the peak at 1208 cm\(^{-1}\) in curve (d) basically disappeared, and in curve (e), it was replaced by a sharp peak shape appears at 1227 cm\(^{-1}\), which was a characteristic peak of the imine ring.
It can be seen from the infrared chart that the quaternary ammonium salt was still decomposed, after the film adding the lactone was dried at 140°C. When the system was at 130°C, the quaternary ammonium salt still existed and may be partially decomposed. The quaternary ammonium salt structure of lactone and ethylenediamine was heat-resistant and unstable, and will completely decomposed and break at about 140°C.

3.4. Thermal stability analysis of quaternary ammonium salt structure
First, the film material was dried, and then the thermal stability of the film was tested by differential scanning calorimetry (DSC). The membrane material tested under N2 protection, the heating rate is 10°C/min, and the testing range is 0-800°C. The DSC curves at different heating rates are shown in Fig. 3, and Fig. 4 is an enlarged view of 100-500°C in Fig. 3.

As shown in Fig.3, the most obvious exothermic peak is around 600°C, which is the decomposition peak of PI. The enlarged Fig.4 clearly shows that there was an obvious peak at 140-180°C, and the highest point was at 176°C. In addition to the PI decomposition peak in Fig3, another peak in Fig 4 was around 390°C, which may be the cause of the breakage of the main chain of diethylamine.

The thermal imine process is an important step that affects the performance of PI, and the imidization temperature is an important factor in the reaction process of PAA to PI. Generally speaking, the strength of PI increases as the molecular weight of PAA increases, that is, high molecular weight PAA is a prerequisite for obtaining PI with excellent mechanical properties. However, due to the decomposition of diethylamine and quaternary ammonium salt, for the hydrophilicity of the film, the high temperature thermal imidization process of PAA cannot be simply considered, but the factors of both mechanical properties and hydrophilic properties must be integrated. Therefore, during the imidization reaction, attention should be paid to uniform coating film, temperature control, retention of quaternary ammonium salt structure, and holding time.

3.5. Hydrophilicity test of membrane
The hydrophilicity of the membrane surface is characterized by the size of the static contact angle. The smaller the contact angle, the better the hydrophilicity. In this experiment, the static contact angle of
the film surface was measured by the JGW-360A contact angle tester at room temperature. Ensure that the surface of the film was dry before testing; the size of the water droplet for each test was 2 µL; the average value of five points for each sample tested.

Table 2 shows the static contact angle test values of the film after drying at 280°C, 140°C, 130°C, and 100°C.

| Temperature (°C) | 280  | 140  | 130  | 100  |
|------------------|------|------|------|------|
| Left             | 69.12| 65.93| 59.96| 58.35|
| Right            | 68.65| 65.12| 59.39| 57.78|
| Average          | 68.885| 65.525| 59.675| 58.065|

The calculated average value of the film at 280°C is 68.885°. With the same test method and calculation method, the average contact angle of the water contact angle of the PAA system film after adding lactone is calculated at a drying temperature of 100°C is 58.065°. It shows that the quaternary ammonium salt structure introduced into the PAA main chain after the addition of lactone significantly reduced the contact angle, thereby effectively improving the hydrophilicity of the film.

Next, the test calculated the average contact angle of the water contact angle of the film of the PAA system after adding the lactone at a drying temperature of 140°C is 65.525°. This shows that at 140°C, the introduced lactone disappeared, that was, the quaternary ammonium salt structure was decomposed, the contact angle increased, and the hydrophilicity decreased. This conclusion also corresponded to the infrared spectrum.

Finally, the test calculated the average contact angle of the film of the PAA system was 59.675° after adding the lactone when the drying temperature is 130°C. It shows that at 130°C, the quaternary ammonium salt structure has been partially decomposed. Although the quaternary ammonium salt structure was partially decomposed, the film still had a certain degree of hydrophilicity. Based on the previous infrared spectra, it can be concluded that the imidization temperature of the system was appropriate at 130°C.

4. Conclusions
(1) Using ODPA as the dianhydride monomer, ODA and N-methyl-2,2-diaminoethanol as the diamine monomer, using the characteristic quaternary ammonium salt reaction of diethylamine and propane sultone, successfully grafted SO₃⁻ groups on the side of the polymer.

(2) The surface of PI film containing quaternary ammonium salt structure had good hydrophilicity, and the static water contact angle was significantly reduced. The contact angle is 58.065° of the film.
dried at 130°C, indicating that hydrophilic groups were introduced into the PI molecular structure. It can significantly improve the hydrophilic properties of PI membranes.

(3) The stability of the quaternary ammonium salt structure was insufficient, and its heat-resistant temperature was low. Comprehensive analysis of infrared spectroscopy and DSC showed that it began to decompose at about 140°C, which was not conducive to the high temperature imidization of PI films. The route of grafting hydrophilic functional groups with quaternary ammonium salt after the completion of imidization of the PI film can be considered.

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