Synthesis and Characterization of Polyimide by Aqueous Phase Method

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Abstract:

With water as reaction medium, polyimide powder was prepared from 4, 4'- biphenyl tetracarboxylic acid dianhydride and 4,4'- diamino diphenyl ether.The structure and properties of which were characterized by IR,TGA and DSC. The results showed that the polyimide had excellent thermal and mechanical properties, and its Tg reached 271℃, Td5% reached 577℃, and the tensile strength reached 141MPa, and the bending strength reached 194MPa. In aqueous phase, the filtrate of polyimide can be recycled, and the process is environment-friendly.

Key word: Aqueous polymerization; Synthesis of polyimide

1 Introduction :

As advanced structural materials or functional materials, polyimide with high temperature resistance, friction resistance, corrosion resistance, radiation resistance, oxidation resistance, low density, high mechanical strength, excellent properties and characteristics of the diversity of synthesis and processing way, has a wide range of applications in the aerospace, aviation, microelectronics, mechanical and electrical, instrumentation, chemical and other fields. Currently, the main method of synthesizing polyimides include melt polycondensation method, interfacial polycondensation method and. solution polycondensation. Melt polycondensation method is that polymers was synthesized from monomer, catalyst and molecular weight regulator under the molten state in the reaction kettle. The melt polycondensation method is suitable for the synthesis of thermoplastic polyimide and has certain limitation in application [1, 2]. Interfacial polycondensation reaction is a polycondensation In the vicinity of the interface of two mutually soluble solution with different monomer. Interfacial polymerization is actualyl less in industry application because of high reactive monomer, consumption of a large amount of solvent and the low. utilization rate of equipment [3]. Solution polycondensation is a method in the solvent for chemical actions. Because any diamine or dianhydride compounds are hydrophobic organic compounds, Organic solvent as reaction medium is used in polyimide synthesis by almost all industrial or synthetic polyimide academy ,such as toluene, xylene, acetone, ethanol, petroleum ether etc.. Synthesis method of polyimide solution with a long cycle, high cost and pollution, danger, derived a lot of process from separation and recover of organic solvents and polyimide, which cause time consuming and energy dissipation. Therefore, it is the only way for the development of polyimide to explore environment-friendly and efficient synthesis method in the future.

As the basis of life and carrier, water is the basis for the evolution of life on earth. As the solvent, water can occur a series of biochemical organic reactions and inorganic reactions. Reaction with water as reaction medium has many potential advantages [4] (1) low cost; (2) high safety; (3) high synthesis efficiency; (4) easy to operate; (5) environmental friendly; (6) the possibility of the development of new synthetic methods

In this paper, based on the concept of green chemistry, we have explored the new

technology of synthesis of polyimide in the water phase and achieved success. Synthesis method of polyimide aqueous phase is that reaction such as the monomer and molecular weight regulator generated polyimide powder at certain temperatures in water. Compared with the traditional method of solution, synthesis of polyimide aqueous phase has many advantages: (1) the process is simple, dianhydrides and diamines generated polyimide rather than polyamide acid in the kettle.; (2) saving the cost of the organic solvent; (3)polyimide aqueous phase synthesis technology is environmental and comply with the national industry development strategy. It with no organic solvent in the entire reaction process greatly reduces the harm to the environment because the filtrate can be recycled after filtration.

2. Aqueous phase synthesis of Polyimides

2.1 Raw materials and equipment

1)3, 3 ', 4, 4 '- biphenyl tetracarboxylic acid dianhydride (BPDA), purity≥99%, Shijia Zhuang Haili Fine Chemical Limited Company

2)Phthalic anhydride (PA), analysis of purity, National Medicine Group Chemical Reagent Co., LTD.

3)4, 4 '- diamino diphenyl ether (4, 4' - ODA), purity≥99%,, Dongying City Crown's Insulation Products Co., LTD;

Major equipment:

1)Reaction vessels: GSH - type high pressure reaction kettle, Weihai Xin Hui Chemical Machinery co., LTD

2)Ubbelohde viscometer: Shanghai Long Xxtension Equipment co., LTD.

3)Infrared spectrometer:FTIR - 650, Guangzhou Sawn Scientific Instrument co., LTD.;

4)Differential scanning calorimetry (DSC) analyzer: DSC - 100, Beijing Permanent Scientific Instrument Factory

5)Thermogravimetric analyzer (TGA), TGA - Q500, TA Instrument Company

2.2 synthesis method

The water phase synthesis of polyimide [5].

2.3 characterization analysis

2.3.1 inherent viscosity test: Ubbelohde viscometer, concentrated sulfuric acid as solvent, test temperature for (50 ± 1) ℃;

2.3.2 IR test: the FTIR - 650 meter, thin film thickness around 25 um, scanning range from 4000 to 400 cm - 1;

2.3.3 DSC analysis: DSC analyzer, under nitrogen atmosphere, the heating rate of 10 ℃ / min, temperature range from 25 to 400 ℃;

2.3.4 TGA analysis: the TGA - Q500 meter, under nitrogen atmosphere, the heating rate of 10 ℃ / min, temperature range from 25 to 800 ℃;

2.4 **pressing mould**

(1) powder molding:380 ℃/30min /150 Mpa

(2) heat treatment process: 380 ℃/8h

3. Results and discussion

3.1, structure characterization

1.synthesis of polyimide

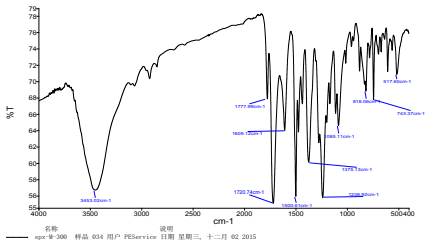

Figure 1 - ODPA / 4, 4 - ODA PI

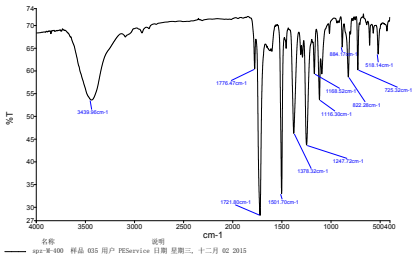

figure 2 - PMDA / 4, 4 - ODA PI

From figure 1 and figure 2,It shows that peaks near 1780 cm^{-1} (respectively, 1775cm^{-1}, 1771 cm^{-1}, 1778 cm^{-1}, 1776 cm^{-1}) and near 1720 cm^{-1} (respectively, 1720 cm^{-1}, 1720 cm^{-1}, 1721 cm^{-1}, 1720 cm^{-1}) is respectively asymmetry and symmetry vibration reduction peak of the imide C = O, peak near 738 cm^{-1} (respectively, 729 cm^{-1}, 738 cm^{-1}, 725 cm^{-1}, 743 cm^{-1}) is for C = O bending vibration peak, peak near 1381 cm^{-1} (respectively, 1377 cm^{-1}, 1378 cm^{-1}, 1378 cm^{-1}, 1375 cm^{-1}) Is C - N stretching vibration peak , peak around 1500 cm^{-1} (respectively, 1500 cm^{-1}, 1503 cm^{-1}, 1501 cm^{-1}, 1500 cm^{-1})is for benzene stretching vibration peak, which indicate polymer main chain structure is polyimide.

(1) IR spectrum

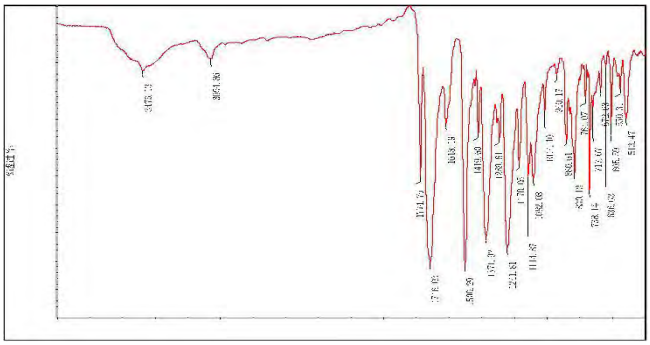

Figure 3 IR spectrum

As can be seen from the first chart,1771 cm^{-1} and 1715cm^{-1} is respectively asymmetry and symmetry vibration reduction peak of the imide C = O,738 cm^{-1} for C = O bending vibration peak, 1381 cm^{-1} Is C - N stretching vibration peak , 1501 cm^{-1} for benzene stretching vibration peak, which indicate Polymer main chain structure is polyimide.

(2) DSC

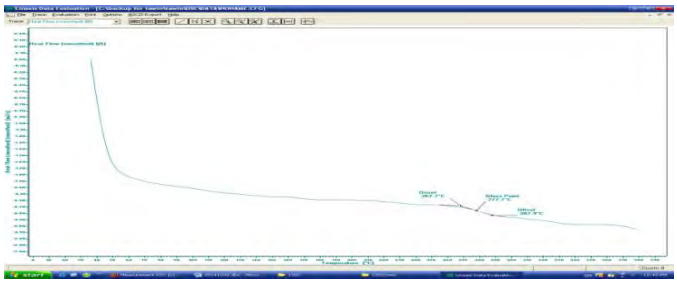

Figure 4 DSC figure of the products

As can be seen By the figure 4,it appear obvious heat absorption phenomenon from 267 ℃ to 287 ℃, which shall be the products of the glass transition area. Since then, the DSC curve goes flat, which shows that the polymer is amorphous.

3.2 thermal propertoes

TGA

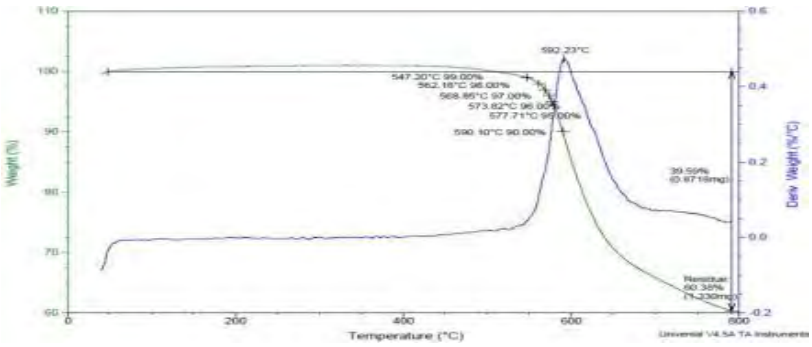

Figure 5 TGA curves

As can be seen by the figure 5, the thermal weight loss roughly range from 400 ℃ to 800 ℃, the decomposition rate of maximum temperature is 592.23 ℃, which corresponding thermal weight loss percentage is 39.59%. the temperature corresponding weightlessness 1% is 547.20 ℃, and the temperature corresponding weightlessness 2% is 562.18 ℃, the temperature corresponding loss of weight 3% is 568.85 ℃, the temperature corresponding loss of weight 4% is 573.82 ℃, the temperature corresponding loss of weight 5% is 577.71 ℃, the temperature corresponding loss of weight 10% is 590.10 ℃.Therefore, the water phase synthesis of polyimide with good thermal stability.

3.3 properties comparison

Test Item		**Units**	**PI-1**	**PI-2**	**Test Method**
Density		g/cm^3	1.41	1.39	ASTM D792-2008
Rockwell hardness（R）		M Scale	128	114	ASTM D785-2008
Tensile strength		MPa	141	116	ASTM D638-2010
Tensile Elongation		%	7.7	5.0	
Flexural strength		MPa	194	161	ASTM D790-2010
Flexural modulus		MPa	4.3	4.2	
Izod impact strength	notch	J/m	157	74.5	ASTM D256-2010
	unnotch	J/m	1299	919	ASTM D4812-2010
Tg		℃	298	294	ASTM E1640
$Td_{5\%}$		℃	580	548	
CTE(23-80℃)		1/℃	3.25×10^{-5}	3.62×10^{-5}	ASTM E-233
dielectric strength		MV/m	17.2	18	ASTM

(2mm thickness)				D149-2009
Volume resistivity	Ω cm	3.5×10^{15}	1.8×10^{16}	ASTM D257-2007

PI-1 means polyimide with the water phase synthesis process

PI-2 means polyimide with solution methods

4. recycling and reuse of wastewater

4.1 Characterization

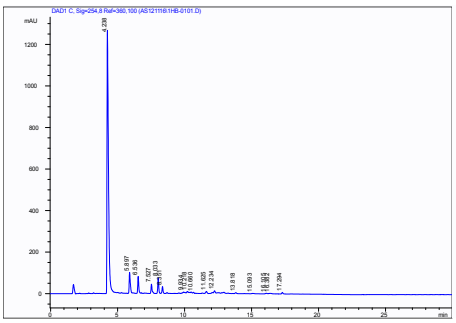

figure 6

figure 7

It shows from figure 6 and figure 7 that the molecular weight of main product in the filtrate is 330. According to the formula, the main products is tetra carboxylic acid biphenyl. Residue in filtrate is 66 mg/l，which is about 0.2% of total anhydride.

4.2 influence about recycling of wastewater

cycle index	reaction medium	inherent viscosity（ml/g）	bulk density（g/cm^3）
0	Distilled water	1.00	0.099
1	filtrate	0.99	0.097
2	filtrate	1.05	0.10
3	filtrate	1.02	0.12
4	filtrate	1.02	0.10
5	filtrate	1.00	0.10
6	filtrate	0.97	0.98
Average		1.02	0.099
maximum		1.05	0.12
minimum		0.99	0.097

The table shows that product with circulating water as reaction medium is stable。 the average viscosity of products is 1.02 and products conform to the technical requirements with the range of 0.1. The average density of products is 0.12 and products conform to the technical requirements with the range of 0.03.

5. Conclusion

(1), the polyimide was synthesized successfully in the water phase and Its comprehensive performance

has reached the performance of the solution method.

(2) aqueous synthesis technology of polyimide can be suitable for general two and two amine anhydride

(3)Water as reactive medium can be recycled which reduces the cost of the synthesis of Polyimide and reduces pollution.

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