

Synthesis of Polyimides in Non-polar Solvents

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Aromatic polyimides are widely used in aerospace, transportation, and microelectronic industries due to their excellent thermal stability, good chemical resistance, as well as high mechanical and electrical properties.

In the prior art, polyimide is generally synthesized using dianhydride and diamine as monomers, firstly by performing low-temperature polycondensation on dianhydride and diamine in an aprotic polar solvent such as N,N-dimethyl acetamide, N,N-dimethyl formamide, N-methyl pyrrolidone, to obtain soluble polyamic acid; using the polyamic acid solution to form a film or spinning the polyamic acid solution, followed by heating to about 300°C to obtain a polyimide film or polyimide fibers by cyclodehydration^[1]; or adding acetic anhydride and a tertiary amine catalyst to the polyamic acid solution to obtain a polyimide solution or a polyimide powder by cyclodehydration^[2].

A method of synthesizing polyimide directly from a tetracarboxylic acid or a dianhydride and a diamine at a high temperature with phenols as a solvent^[3].

Water also has been used as a medium to prepare polyimides, but this method need to be performed under pressure, and the molecular weight of the resulting polyimide is lower^[4-6].

However, when the polyimide powder is prepared using the first three methods, complicated post-treatments such as multiple washing etc. are needed to obtain a polyimide powder. When the resulting polyimide is soluble in a solvent, it is necessary to carry out solvent removal, grinding and other steps to obtain the polyimide powder, which is not only cumbersome and costly, but also toxic because of the solvent involved, which is not favorable for the polyimide production.

Recently, we have developed a technology to prepare polyimides powder in non-polar solvents, such as aromatic hydrocarbon, aliphatic hydrocarbon, halogenated aromatic hydrocarbon and halogenated aliphatic hydrocarbon with boiling point above 140°C^[8]. The monomers used for this method are dianhydrides, tetracarboxylic acids and monoanhydrides such as, phthalic anhydride, 4-phenylalkynyl phthalic anhydride, norbornene dicarboxylic anhydride and maleic anhydride and diamines. The solid content in the system is about 10-30%. The polymerization is carried out usually at the boiling point of the solvent, until the water generated during the reaction is totally removed. After reaction, the mixture is filtrated and simply washed with solvent used in polymerization, finally dried at 280-300°C to obtain polyimide powder. The inherent viscosity of polyimides derived from hydroquinone diether dianhydrides and 4, 4'-oxydianiline using xylene as the solvent spanned a range of 0.40-1.70 dL/g, which was comparable to those of polyimides synthesized via conventional one-step or two-step methods. The properties of polyimides from 3,4,3',4'-hydrophenone diether dianhydride and 4,4'-oxydianiline with and without using phthalic anhydride as

end-capping reagent can be seen in Table 1.

Table 1. Properties of polyimide with and without endcap

Items	3% phthalic anhydride	Without control
Tg/°C	232	232
Melting index/(g/10min)	2-6	-
Tensile strength/MPa	≥100	≥100
Elongation at break/%	≥15	24
Flexural strength/MPa	140	140
Flexural modulus/GPa	3.0	2.8
Charpy impact strength, Unnotched/(kJ/m ²)	≥80	150
Friction coefficient	0.20-0.25	0.20-0.25
Volume resistivity/Ω.cm	1.0×10 ¹⁵	1.0×10 ¹⁵
Shore D hardness/HD	85	85
Water absorption/%	0.3	0.3

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