

Co-condensed Polyimides For Glass-cloth Laminated Board

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Abstract

This paper presents soluble and meltable thermoplastic polyimide resins co-condensed by two di-anhydrides and two di-amines, and discusses the laminating process and the product properties of the glass-cloth composites, in which the presented resins were applied.

Keywords: polyimide, co-condensation, laminated board

1. Introduction

The laminated boards of thermoplastic polyimide resins and glass cloth have found their wide application in high technologies such as aerospace, electric and electronic engineering, because of their excellent heat-resistance, radio-resistance and perfect physical and electric properties under high temperature.

In synthesis of polyimide resin, Some high boiling-point solvents, such as DMF, DMAC and NMP have to be employed. Impossibility of removing the solvents involved thoroughly makes high rate of pinholes in the laminates thus. Produced, and results in unstabilities for the performance. Meanwhile, viscosity will be larger with a longer molecular chain during the imidization of polyamide acids. To obtain substantial composites in post-processes, Corresponding pressures are needed at various temperature points, Since the key process of thermoplastic polyimide laminates is to eliminate effectively the "bubbles" left-over within the system before the maximum pressure is applied on. Therefore, the method of co-condensation is chosen to synthesize polyamide acid so that the solvent "bubbles" can be effectively removed during coating and imidization.

2. Experimentation

2.1 Synthesis of Polyamide acid

Polyimide are produced by imidization of polyamide acid. polyamide acid are produced by condensation of aromatic dianhydrides (eg: 3,3', 4,4' - benzophenone tetracarboxylic dianhydride, diphenyl ether-3,3', 4,4'-tetracarboxylic acid dianhydride, ect.) and diamines (eg: 4,4'

diaminodiphenyl oxide, 4,4'-diaminodiphenyl methane ect.) in polarity solvents (eg: dimethylacetamide DMAC, dimethylformamide DMF, N-methyl-pyrrolidone NMP). To obtain the larger molecular weight polyimide acid, dianhydrides and diamines should be dried before synthesized. In order to ensure molecular weight of polyimide acid steady increasing, using solvents should be dehydrated too.

Synthesizing process of polyamide acid resins are as follows:

Firstly, Under room temperature feed in measured polarity solvent DMAC into the reaction vessel with cooling system, churn-dasher and thermometer. Secondly, feed in dried 4,4'-diaminodiphenyl oxide/4,4'-diaminodiphenyl methane, then churn up till it is dissolved downright, and the solution is limpidity. thirdly, feed in equal equivalent mixed dianhydrides group by group. Under normal temperature, Co-condensed reactions last out 4~5hr, and then we get brown and limpidity polyimide acid resins. Lastly, adjust solid content between 11~12.5% and viscosity is adjusted in 30 ± 5 S (25 ± 1 °C, coating cup 4[#]), standbys.

2.2 Preparation of grey cloth

Using basis material is 0.1mm thickness glass-cloth. It is high strength and non-basicy ey glass-cloth which treated with Olan. Dipping coating method and vertical coating machine are choosed, namely, let glass-cloth in uniform motion pass the dipping slat with filled of polyimide acid resins and extrusion rollers, following, impregnated fabric is entered in dryingpath of vertical coating machine to dry. The drying temperatures are setted for 80°C, 120°C, 140°C respectively. After (repetitions) many times coating and drying, resin content within grey cloth is controled to 45% about, and volatile of grey cloth is controled to 1% about. lastly, the grey cloth is separated into roll. which weight is 2kg about, then they are imidized at 250°C for 3hr.

2.3 Producing of Laminated sheet

Cut out imidized polyimide grey cloth for definite size and fold to needing thickness. Put the folded sample in the moulding board, and then place the moulding board between two heat plates. give pressure, go up the temperature at 3°C/min. At same time, corresponding pressures are needed at various temperature. When temperature is up to 380°C about, top up pressure and keep the temperature and pressure half hour. Soon afterwards, lower the temperature under 160°C, come out the pressed sample from moulding board. This is the laminated sheets of thermoplastic polyimide resins and glass cloth.

3. Results and Discussion

3.1 Co-condensed polyimides influenced to producing of laminated sheet.

As everyone knows, the viscosity of meltable polyimide is quite largish at high temperature,

Its fluidity is not quite sufficiency. So producing laminated sheet becomes difficulty and compact laminated sheet is difficulty to obtain. thus, mechanic property and electric insulated property of laminated sheet are influenced. The performances of laminated sheet are difficulty to pledge. In order to obtain to lower porosity and high quality laminated products during laminated, the monomer which has rigidity struction (eg: 3,3', 4,4'-benzophenome tetracarboxylic dianhydride or/and 4,4'-diaminodiphenyl methane. ect.) is added when the soluble and meltable polyimide resins are synthesized. So that air permeability increase and "bubbles" can be favorably removed during coating and imidization.

3.2 Heat resistance of co-condensed polyimide resin

Heat resistance of co-condensed polyimide resin can be obtain by Thermogravimetry Analysis. Fig 1 is the TGA curve of it.

Testing conditions:

Powder specimen granularity: 100~150 mesh

Specimen weight: 5~10 mg

Warming rate: 5°C/min

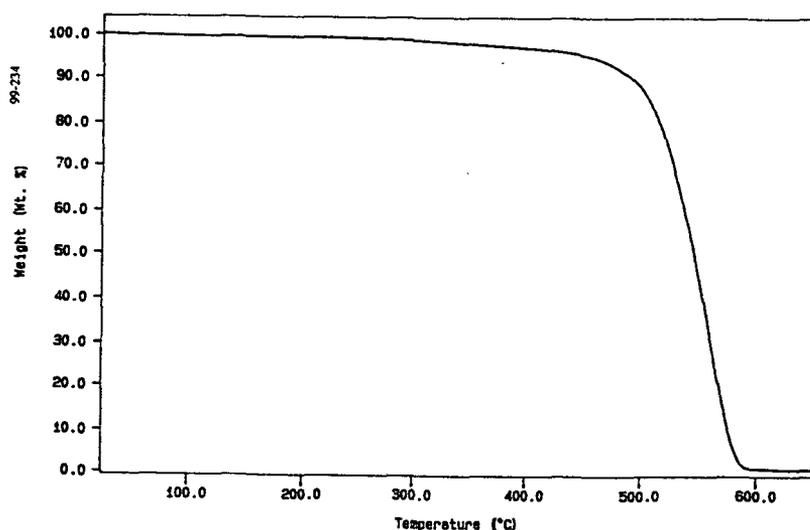


Fig 1. TGA curve

Fig 1 shows: the heat-resisting index of co-condensed meltable polyimide is 242. Its bending strength at 230°C is 230 Mpa, compare with 380 Mpa that is initial value, it has higher conservation rate. Dielectric strength and resistivity of it can retain goodish level. This indicates the thermoplastic polyimide laminated sheet can be used in high temperature with its credible heat resistance.

3.3 Moisture resistance of laminated sheet

Because polyimide laminated sheets are often used in moisture and heat circumstance which affects properties of laminated sheet. So we have done different solutions soak tests, 6 days later, we tested mechanical properties of laminated sheet which soaked in three kind of solutions respectively.

Table 1. mechanical properties of laminated sheet which soaked 6 days in different solutions

item \ solution property	initial value	100°C thermostated water	3% NaOH solution normal temp	3% NaCl solution normal temp.
bending strength Mpa	381.4	362.3	320	352.3
shock strength kJ/m ²	70	60	45.5	58

Table 1 shows the mechanical properties of laminated sheet which soaked in three kind of solutions have somewhat dropped, but retain fairly good level. The properties of laminated sheet which soaked in 3% NaOH solution dropped by a bigger margin, the reason may be chemical reaction easy occurring between polyimide and basic solution.

3.4 Properties of laminated sheet

Properties of laminated sheet by co-condensed for polyimides and glass cloth are as the follows.

Table 2. Properties of laminated sheet

Table 2. shows the co-condensed polyimide laminated sheet has excellent mechanical strength and electric insulating property and goodish heat-resistance.

Number	testing item	unit	actual value
1	bending strength, normal	Mpa	381
2	shock strength, normal	kJ/m ²	70
3	volume resistivity, normal 230°C soaked in 20°C ± 5°C water for 24hr	Ω · m	2.4 × 10 ¹³ 4.8 × 10 ¹² 1.3 × 10 ¹²
4	dielectric strength, normal, in oil 230°C soaked in 20°C ± 5°C water for 24hr	MV/m	52 47 33.1
5	dielectric dissipation factor (1MHz)		3.6 × 10 ⁻³
6	relative permittivity (1MHz)		3.8

4. Conduision

- 1) Co-condensed soluble and meltable polyimide resins can be dissolved in polarity solvent DMAC etc, and synthesizing process of it is steady. The glass-cloth by impregnated polyimide resin has goodish impregnability. The dipping coating method suit to large batch process, because of coating range width and adjustable, and good technological process, Moreover, the laminated sheet which is producted has stable property.
- 2) The laminated sheet has excellent electric insulating properties, mechanical properties and moisture-heat resistnce, moreover, it has goodish heat-oxygen resistarce. The laminated sheet not only can satisfy using needs of electrical equipment under the moisture environment, but also satisfy in advanced science and technology field, such as aerospace, electric and electronic engineering etc.