Preparation and Properties of Composite Polyimide Films for the Application of Flexible Copper Clad Laminate

Long Jiao (矫龙), Guangliang Song, Chunhai Chen, Xiaogang Zhao, Guodong Dang* (党国栋)
Alan G MacDiarmid Institute, Jilin University, Changchun, China (吉林大学麦克德尔米德实验室)

AbstractThepolyamide acid contained ether ketone were synthesized by 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) and 1,3 - bis (3 - aminophenoxy -4 - benzoyl) benzene (BABB) ,the polyamide acid contained benzoxazole were synthesized by 5,4 '-diamino-2 - phenyl-benzoxazole(DAPBO)and 4,4 - oxydiphthalic anhydride(OPDA) .The novel PI composite films were got by the method of secondary coating with above two polyamide acids. The thermal properties 、mechanical properties and dielectric constant were characterized ，and the results indicate that the novel composite films combined the advantages of the two polyimdes , the storage modulus were more than 4.5GPa ,5% weight loss were more than 525℃ and 545℃， respectively in air and nitrogen ， dielectric consent were less than 3.42， moisture absorption rate were less than 1%.

Keywords: Polyimide, Bilayer flexible copper clad laminate, Composite film, Synthesis

Introduction

Polyimide (PI) resin is an ideal material for preparing flexible printed circuit board substrate due to its outstanding heat-resistance, high frequency dielectric property, mechanical property, electrical property, and dimensional stability.[1-6] In this paper, PI composite film with a bilayer structure was prepared, employing synthesized thermoplastic PIand PI containing benzoxazole unit as the substrate and the second layer, respectively. PI containing benzoxazole unitis the principal part of the composite film. Therefore, its mechanical property, heat-resistance, and dimensional stability are guaranteed. The excellent chain flexibility of thermoplastic PI assures the composite film's adhesive property. The composite film can be applied to the production of high performance flexible printed circuit board.[7-11]

The preparation of composite film is actually a self-adhesive process of two different polyimides, which is determined by two polyimides' degree of cure as well as molecular structure and state of aggregation at the interface after imidization. The first polyamide acid (PAA) was imidizedat a certain temperature, so that it could be partly dissolved in the upper solution but without penetration. To ensure a certain adhesive force between two layers but unlikely to penetrate, pre-imidization temperature was selected at 180°C, 210°C, and 240°C.

1 Experimental

1.1 Materials and Instruments

3,3',4,4'-benzophenenetetracarboxylic dianhydride (BTDA), 1,3 bis-(3-aminophenoxy-4-benzoyl) benzene (BABB), 4,4-oxydiphthalic anhydride (ODPA), and 5,4'-diamino-2-phenyl-benzoxazole unit (OAPBO) were purchased from Changzhou Sunlight Pharmaceutical Co. Ltd. N,N'-dimethylacetamide (DMAC) was obtained from Shanghai JinshanJingwei Chemicals.

Thermal gravimetric analysis was performed on a TA TGA2050, scanning from 100°C to 800°C with a heating rate of 5°C/min under both air and nitrogen atmosphere. Dynamic thermal mechanical analysis was implemented on a TA DMA Q800, scanning from 25°C to 400°C with a heating rate of 5°C/min at 1 Hz frequency under nitrogen atmosphere. Tensile test was carried out on a SHIMADUZ AG-1 universal testing machine with a tensile rate of 8mm/min. A UV-2501 UV-vis spectrometer was used to test composite film's transmittance and UV shielding performance under air atmosphere.

Dielectric properties were acquired from a Quad Tech Model 1920 impendence analyzer.

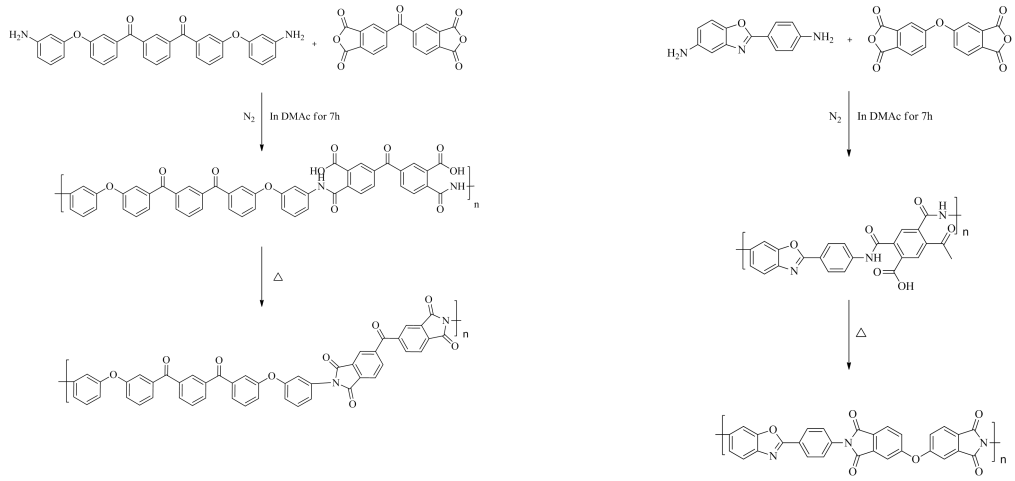
1.2 Experiments

First, BABB (7.0076g, 0,014mol) was dissolved into 100mL DMAc, then BTDA (4.5112g, 0.014mol)was slowly added into the solution. PAA solution was obtained after 7 hours reaction at ambient temperature under nitrogen atmosphere.

Second, DAPBO (5.9099g, 0.026mol) was dissolved into 100 mL DMAc, then ODPA (8.1391g, 0.026mol) was slowly added into the solution. PAA solution was obtained after 7 hours reaction at ambient temperature under nitrogen atmosphere.

Third, the second PAA solution was poured onto a glass plate and scraped evenly with a scraping knife. The solvent was removed by heating in an oven. Then it was pre-imidized for 1 hour in a vacuum oven. After cooling to the ambient temperature, the first PAA solution was poured onto the pre-imidized film and scraped evenly with a scraping knife. The solvent was removed by heating in an oven. Then it was imidized in a vacuum oven. The composite film was removed from the glass plate after cooling to the ambient temperature.

The polymerization reaction equation is indicated as Scheme 1:



Scheme 1 Preparation of polyimide molding powders

The total thickness of PI composite film was 70±5μm. The thicknesses of thermoplastic PI as the role of adhesive and PI containing benzoxazole unit as the role of dimension stabilizer were 20±2μm and 50±3μm, respectively.

2 Results and Discussions

2.1 Thermal Properties

The composite film's thermal property was investigated by TGA and DMA. Figure 1 illustrates loss factor tan δ curves. Figure 2 and 3 exhibit the TGA curves under air and nitrogen atmosphere, respectively. Since the change of tan δ valueisrelated to polymer chain's movement, the glass transition temperature T_g can be identified as the extreme value of tan δ. As can be seen, PI demonstrates a relatively high T_g, which fulfills the production requirements of copper clad laminate (CCL). Hence, PI can be employed as a flexible CCL material. The two peaks suggest its two different polymer compositions. The 5% weight loss under nitrogen and air atmosphere of three composite films are as high as over 545°C and 525°C. Meanwhile, the residual carbon contents under nitrogen atmosphere are more than 62%. All the data shows the extraordinary thermal decomposition stability of them. Overall, there are no obvious difference among them, which shows that the three

pre-imidization temperatures have no influence on composite film's thermal property.

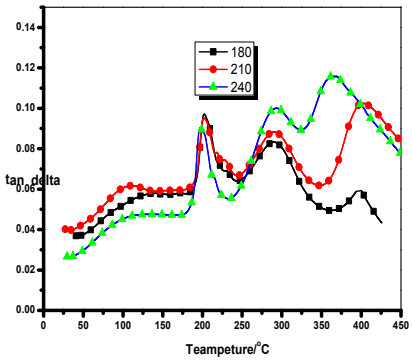


Figure 1 DMA curves of cured

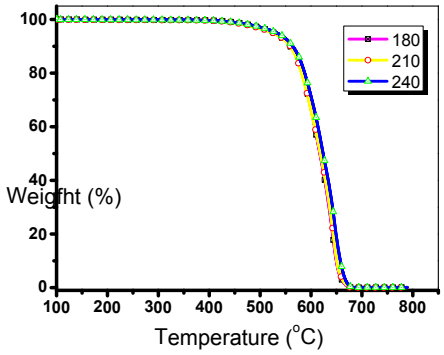


Figure 2 TGA curves of PI resin

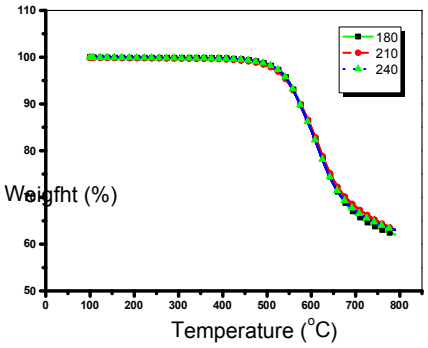


Figure 3 TGA curves of PI resin under N_2 atmosphere

2.2 Mechanical Properties and Water Absorption

Table 1 lists the mechanical properties and water absorption rates of composite films and PI containing benzoxazole unit. As indicated in Table 1, the composite films show an excellent mechanical property with modulus of 4.5- 4.6 GPaand strength of 151.7-166.2 MPa. The excellent service performance of composite film is attributed to the outstanding mechanical property of PI containing benzoxazole unit.

Additionally, the composite films possess an exceptional moisture resistant performance with moisture absorption rates of lower than 1%. Thus, the composite film provides CCL with an excellent moisture resistant performance and can be used under damp circumstance.

Table 1 Mechanical properties and water absorption

Composite films	Modulus(GPa)	Strength (MPa)	Elongation (%)	Water absorption(%)
180°C	4.5	151.7	7.7	0.85
210°C	4.5	160.6	7.6	0.89
240°C	4.6	166.2	7.3	0.80
DAPBO-ODPA	5.0	203.5	13.2	0.72

2.3Dielectric Properties

The results of dielectric constant and loss tests are listed in Table 2. Aimed at raising the signal propagation velocity, materials with low dielectric constant should be chosen. Meanwhile, CCL material's dielectric loss needs to be reduced to prevent materials from heating and aging.[12-14]The dielectric constantsand loss values of composite filmsare 3.25-3.45 and approximately 0.11, which fulfills the requirements of PI film for CCL, and is proper for producing high performance CCL

because of its good performance.

Table 2 Dielectric properties

Composite films	Dielectric constant (1 MHz)	Dielectric loss (%)
180°C	3.24	0.014
210°C	3.28	0.012
240°C	3.42	0.011

2.4 Optical Properties

Liquid photosensitive solder resist and simultaneous double sided UV exposure process are widely used in the production of flexible CCL. In order to avoid ghosting effect during the exposure process, film materials for CCL should have UV blocking property. As shown in Figure 6, the 100-400 nm UV transmittance of composite film is 0%, which means it can block the UV light effectively.

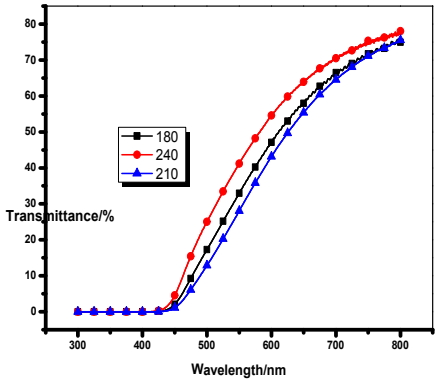


Figure 6 UV-vis light transmittance spectra of composite films

3.Conclusions

The novel PI composite film, which is prepared with thermoplastic PI and PI containing benzoxazole unit, exhibits the strengths of two different polyimides: its$T_g$are more than 200°C; itswater absorption rate is less than 1%; it is non-UV absorptive, and owns excellent mechanical, thermal, optical, and dielectric properties. The bilayer flexible CCL, which is made of this PI composite film, is worthy being utilized in the flexible circuit board field.

4. References

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