Thermo-mechanical property and adhesive property of Poly(imide-siloxane) and its composite material with benzoxazine

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Abstract

For the purpose to develop the adhesive films which can be laminated at lower temperature and have the excellent reliability such us high heat resistant and humidity resistant, the relationship between the structure of Poly(imide-siloxane)(SPI) and adhesive property was investigated Their adhesive properties was influenced by siloxane content in the polymer backbone. SPI with small amount of siloxane unit showed the better lap shear strength compared with the corresponding all- aromatic polyimide at initial and after the treatment under highly humid condition. However further siloxane modification lowered their adhesive strength and durability.

Further the composite films which consist of SPI and the benzoxazines were prepared and its thermal mechanical property and adhesive property were investigated. The composite films showed higher Tg compared to SPI solo films. And the lap shear strength of its composite films enhanced extremely by the addition of benzoxazine.

1.Introduction

Polyimide-siloxane(SPI) is heat-resistant blocked polyimide which consist of aromatic polyimide unit as hard segment and dimethyl polysiloxane unit as a soft segment, and is well-known as one of polymers with superior characteristics such us good electric properties, resistant to humidity, mechanic-cal properties, and the adhesion properties.[1)-13)] Recently the resin materials used for the component of the electric devices such us the printed circuit board is coming to be required to have excellent reliability at high temperature and humid condition from the background that their devices need the higher performance.

In this work, for the purpose to develop the adhesive films which have the excellent reliability, the adhesive properties of SPI films and the composite films consisting of SPI and the benzoxazines (BXZ) which are noted as the thermosetting resin which has superior properties such as high heat-resistance, high glass transition temperature and small volumetric shrinkage are investigated. Further their practical characteristic as the adhesive films for the multi-layered printed circuit board are also discussed.

2. Experiment

2-1. Preparation of polyimide and adhesive film

SPI were prepared from tetracarboxilic dianhydrides (DSDA,BTDA), aromatic diamines (BAPP,BAPS-M) and bis(γ-aminopropyl)-polydimethylsiloxane in NMP and Xylen according to the method shown in Scheme 1. All reagents were commercially obtained and used without further purification. Two series of polyimides with inherent viscosity, 0.5-0.6g/dL in NMP were given in this method. The polyimide films were obtained by drying polyimide solution at 100 ℃ for 1 hour, and then by heating at 200 ℃ for 1 hour. The thickness of films was 25 ± 1 μm.

2-2. Preparation of benzoxazine and the composite film of SPI and benzoxazine

BXZs were prepared from bis-phenol A, pholmaldehyde and aniline according to the method shown in Scheme 2. All reagents were commercially obtained and used without further purification.

The preparation of the composite film of SPI and benzoxazine derived from bisphenol-A was carried out by the same method as the case of polyimide film described in 2-2.

2-3. Measurement

Thermal and mechanical properties were performed with SSC5670, SSC5200(Seiko Electric Co.,Ltd.) REOBIVRON DDV-Ⅱ EP (Reology Co., Ltd.).

Adhesive property were defined by Single lap shear strength (SLSS) measured by Autogragh AG-500A (Shimazu CO.) according to JIS K 6850. The adhesive film was cured at Tg + 50 ℃under pressure of 19.6Mpa. The steel was used as a adherent according to JIS G 3141.

3. Result and discussion

3-1 Thermo-mechanical and adhesive property of SPI.

The relationship between Tg, tensile modulus and the siloxane content of DSDA/BAPP type was shown in Figure.1. The Tg and tensile modulus were decreasing with increasing siloxane content in the polymer backbone. It was suggested that incorporation of siloxane was enable to give the plasticity to the rigid polymer such us aromatic polyimide at voluntary.

The SLSS of two types of SPI film at initial stage and after the treatment under high humid condition was summarized in Table 1. Both types of polyimide with 10wt% of siloxane possessed better adhesive strength than the corresponding all aromatic polyimides, probably because the lower tensile modulus enhanced stress relaxation and the lower glass transition temperature increased fluidity as shown in Figure 1. On the other hand, further siloxane modification lowered the adhesive strength of SPI. It was suggested that the further siloxane incorporation leads to forming the weak boundary layer, which is composed of siloxane phase based on the surface analysis and fracture mode analysis.

Furthermore, the polyimide from BTDA/BAPS-M with 10wt%of siloxane have excellent adhesive durability under the high humid condition (at 25℃, 90%RH,72hours) compared with the corresponding all aromatic polyimides. However the 20wt% and 30wt% of siloxane incorporation lowered the adhesive durability of SPIs. This results is thought to be due to lower moisture sorption and lower moisture permeability of the polyimides with small amount of siloxane component.

3-2. The thermo and adhesive property of the composite film of SPI and BXZ

The Tg of the composite film of SPI and BXZ synthesized from bis-phenol A was shown in Figure 2. In case of the curing at 200 ℃, the Tg rose according to increasing the content of BXZ. This means that cross-linking structure was formed by open-ring reaction of BXZ with heating. However the Tg of the composite film containing more than 30wt% of BXZ was lower compared to that of non-containing BXZ. On the other hand, the Tg of the film cured at 150 ℃ was decreased according to the increase of the content of BXZ. This is thought that the curing at 150 ℃ was insufficient for the formation of cross-linking structure, and BXZ remaining in the film not undergoing open-ring reaction behaved as a plasticizer as well as the composite film containing more than 30wt% of BXZ cured at 200 ℃.

The relationship between the SLSS and the content of BXZ was indicated in Figure 3. SLSS of the films containing BXZ were higher compared to that of non-containing BXZ. This seems to attribute to the enhancement of the fluidity by addition of BXZ and lower curing shrinkage derived from its open-ring reaction after curing.

3-3. Practical characteristic of adhesive film derived from SPI

These materials are excellent candidates for adhesive in printed circuit industries because of their excellent adhesive durability. Based on these results, a new type of adhesive film for multi-layer printed circuit construction was developed. The developed adhesive film was composed of SPI as a major component and small amount of additives for an improvement in peel strength. The developed adhesive film possessed excellent adhesive strength even at high temperature as shown in Figure 4. Furthermore, the reliability under hot/wet condition (at 121℃, 2atem, 85%RH) of the developed adhesive film was indicated in Figure 5. Measurement of electric leakage currents on interdigitated-comb circuit are used for estimating fracture rates as inter-layer dielectrics of multi-layer printed circuit boards. The measured values of leakage currents were extremely lower compared to those of conventional adhesive films.

Conclusion

Incorporation of siloxane into polyimide backbones showed the excellent adhesive property at initial and under humid condition due to good processability at low temperature and lower moisture sorption. Furthermore, the composite material of SPI and BXZ showed the good adhesive property derived from the properties of BXZ such us plasticity before curing and lower volumetric shrinkage after its open-ring reaction. The adhesive film prepared from SPI is useful for multi-layer printed circuit boards due to its superior reliability.

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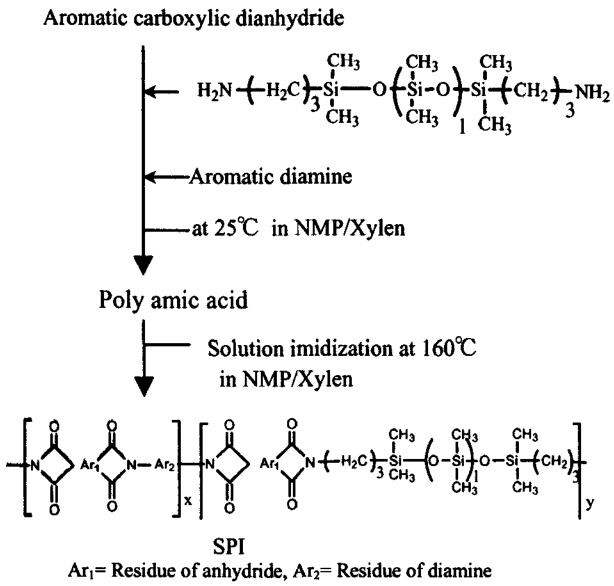
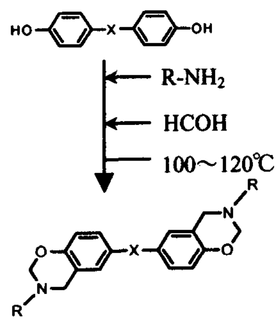


Scheme 1 Synthesis of Poly imide-siloxane (SPI)



Scheme 2 Synthesis of Benzoxazine (BXZ)

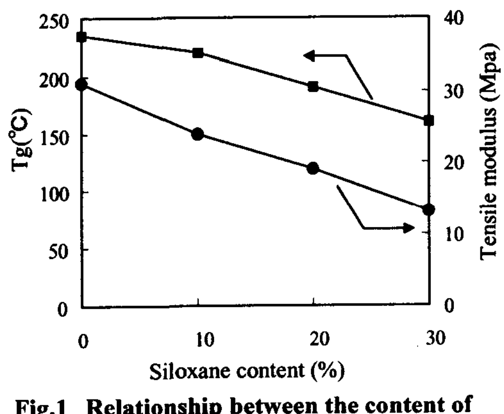


Fig.1 Relationship between the content of Siloxane diamine and Tg, Tensile modulus of SPI

Table 1 Single lap shear strength

Siloxane content (wt%)	DSDA/BAPP type	BTDA/BAPS-M type			
	SLSS(Mpa) Initial	SLSS(Mpa) Initial	(F.M)*1	SLSS(Mpa) After treatment*2	(F.M)
0	12.7	28.4	(co)	17.6	(co)
10	29.4	28.9	(co)	28.0	(co/ad)
20	9.8	18.1	(co/ad)	13.7	(co/ad)
30	4.9	14.2	(co/ad)	7.8	(ad)

*1 Fracture mode of SPI films (co:cohesive, ad:adhesive)

*2 After 72hr at 25℃, 90%RH(JIS K 6856)

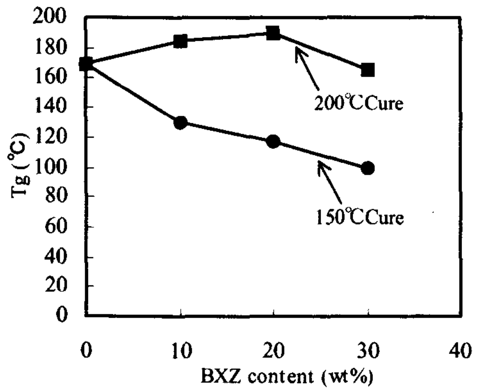


Figure 2. Glass transition temperature of SPI/BXZ films

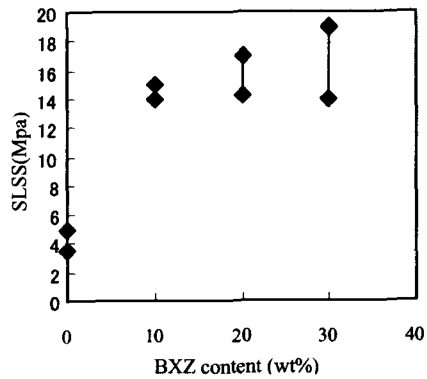


Figure 3. Single lap shear strength of SPI/BXZ films

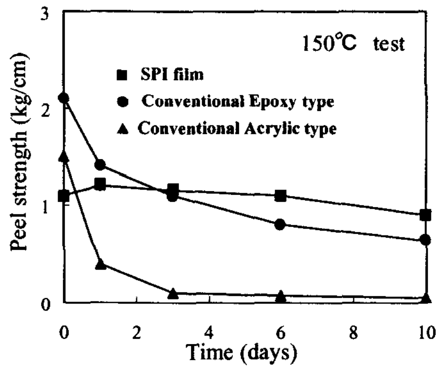


Figure 4. Peel strength (for Cupper plate) of three kinds of adhesive films thermally exposed in air at 150 for 10 days

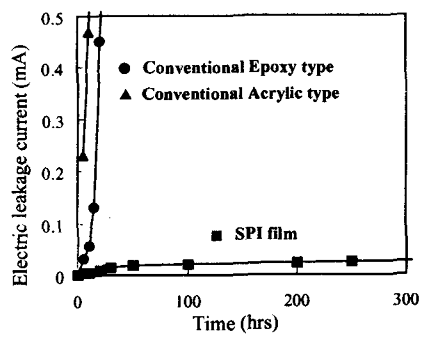


Figure 5. Electric leakage current of three kinds of adhesivefilms at high temperature and humidity