Preparation and Properties of Composite Films Composed of Polyimide, Epoxy Resin and Silver Filler

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ポリイミド／エポキシ樹脂／銀フィラーコンポジットフィルムの調製と特性

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概要 デカメチレンビストリメリテート二無水物(DBTA)を酸成分として合成したポリイミド, エポキシ樹脂, および銀フィラーからなるコンポジットフィルムを調製し, それらの種々特性を検討した。硬化前においては, T_g を超える温度領域でメルトダウンし, 熱可塑性フィルムに特有の挙動を示したが, 硬化後においては, 含有するエポキシ樹脂成分の橋かけ化の効果により, 上記の温度領域での流動が抑制された。これらのフィルムを介して, 異なる熱ひずみを有する材料同士を貼り合わせたときの接着強度は, 主としてフィルムの弾性率と応力緩和特性の影響を受けることがわかった。本報では, ポリイミドの構造とフィルム特性との関係について詳細に論じた。

Abstract

Composite films composed of various polyimides derived from decamethylene bis(trimellitate)anhydride (DBTA), an epoxy resin and a silver filler were prepared and their properties were studied. The films showed thermoplastic behavior before curing with molten performance at high temperatures above their T_g s, and thermosetting behavior after curing with restricted flow behavior even above their T_g s. The limited flow behavior results from the network structure formation in the film. The adhesion strength of the film when used as an adhesive film between two adherents having different thermal strains was affected by two main factors: the modulus and stress relaxation property of the film. In this paper, the relationship between the chemical structure of the polyimides and the various properties of the composite films is discussed.

Key Words: Polyimide, Composite Film, Dynamic Mechanical Properties, Stress Relaxation, Adhesion Behavior

1. Introduction

Traditionally, polyimides have been used as materials for application in future aircraft and spacecraft because of their superior thermal, mechanical and electrical properties¹⁾. Recently, they have been applied in microelectronic devices as film or varnish for the purpose of miniaturization and improvement in performance and reliability²⁾.

However, most polyimides must be processed in the stage of their soluble poly(amic acid) precursors, which are subsequently imidized by heating at high temperatures over 350°C. Because they are insolubility and infusibility in their imidization form, polyimides are difficult to process. Furthermore, they must be processed or prepared at high temperatures over 300°C due to their

high T_g or high softening temperature, resulting in the thermal damage of the peripheral materials. Their application fields have been limited for this reason³⁾.

In order to obtain soluble polyimides and/or to prepare polyimides at lower temperatures, extensive study has been carried out on the synthesis of polyimides having lower T_g or lower softening temperatures by introducing flexible structures such as alkylene, ether, and siloxane connecting groups into the polymer backbone^{4)~6)}.

However, these polyimides will only melt down above their T_g or softening temperatures because of their inherent thermoplasticity. Therefore, it was difficult to develop polyimide-based materials which can be prepared at low temperatures and have high mechanical strength at high temperatures.

To solve above problem, material design as blending or mixing different polymers and fillers has been studied to develop new materials having various superior properties which cannot be achieved by one component materials^{7)~11)}. According to such material design, we tried to develop new composite materials, as high performance die attach adhesives for microelectronics applications, having lower fluidity and higher mechanical strength at high temperatures above T_g , by blending an epoxy resin as a crosslinking agent and a filler as a reinforcement. Extensive study of the mechanical strength of the composite materials will prove that this attempt was a successful approach.

A number of workers have reported the studies on polyimide-epoxy resin composites^{9)~11)}. However, the main purpose of these studies was the improvement of the inherent brittleness of the epoxy matrices. Few studies have been reported on the restriction of the flow of polyimide-based composite materials at high temperatures above T_g by blending epoxy resins and fillers.

In this study, new composite films composed of a polyimide, an epoxy resin and a silver flake as a filler, which has been filled in silver pastes widely used as current die attach materials, were examined to develop new die attach adhesives which can be attached at lower temperatures and have both good stress relaxation property and high mechanical strength at high temperatures above T_g . In the previous work^{12),13)}, the effect of con-

tents of the epoxy resin and the silver flake on adhesion properties, morphology and rheological properties of the composite films has been demonstrated in detail. In this paper, the composite films using various polyimides were examined and the relationships between the chemical structures of the polyimides and the various properties of the composite films were investigated.

2. Experimental

2.1 Materials

The structures of the monomers used in this study are shown in Fig. 1. 1,10-(Decamethylene)bis(trimellitate)anhydride (DBTA) and 1,12-(dodecamethylene) bis(trimellitate)anhydride (DDBTA) were used as the dianhydrides¹⁴⁾. 2,2'-Bis[4-(4-aminophenoxy)phenyl]propane (BAPP), 4,7,10-trioxatridecane-1,13-diamine (TODE), 4,9-dioxadecane-1,12-diamine (DODE), 1,3-bis(3-aminopropyl)tetramethyl disiloxane (TSX), and bis(γ -aminopropyl)polydimethyl siloxane (PSX, molecular weight: 914) were used as the diamines. Diglycidyl ether of bisphenol F (DGEBF) and diglycidyl ether of bisphenol AD (DGEBAD) were used as the epoxy compounds (epoxy equivalent weight: 160 and 175, respectively). Phenol novolak resin (PN) was employed as the hardener (OH equivalent weight: 106) and tetraphenylphosphonium tetraphenylborate (TPPK) was used as the curing accelerator. N-Methyl-2-pyrrolidinone (NMP) and xylene were adopted as the solvents for polyimide syn-

Fig. 1 Chemical structures of the monomers

Table 1. Preparation and characterization of the polyimides

Polyimide	Monomers [mol%]		Molecular weight distribution			T_g [°C]
	Dianhydride	Diamine	Mn	Mw	Mw/Mn	
PI-1	DBTA (100)	BAPP (100)	32500	121000	3.73	120
PI-2	DDBTA (100)	BAPP (100)	33200	102600	3.09	107
PI-3	DBTA (100)	BAPP (50)/TODE (50)	36700	115500	3.14	64
PI-4	DBTA (100)	BAPP (50)/DODE (50)	28900	88600	3.07	57
PI-5	DBTA (100)	BAPP (50)/TSX (50)	26900	80800	3.01	64
PI-6	DBTA (100)	BAPP (50)/PSX (50)	23800	68600	2.89	30

thesis, *N,N*-dimethylacetamide (DMAc) and cyclohexanone (CHN) were used as the solvents for film preparation. They were highly pure as received and were used without purification except for DBTA and DDBTA, which were used via recrystallization. Silver flake TCG-1 as the filler was obtained from Tokuriki Kagaku Co. (mean size: 2 μm).

2.2 Synthesis of the Polyimides

The monomer compositions of the polyimides in this study are summarized in Table 1. These polyimides were synthesized by a two-step method as shown in Fig. 2. The polyimide solution was then poured into water. The precipitate polymer powders were collected by filtration, washed with methanol for 6 h, and dried under vacuum at 60°C for 12 h, whereby original polyimide powders were obtained. For all the synthesized polyimides (PI-1 to 6), the characteristic absorption bands in the FT-IR spectra (KBr) were observed near 1780 (asym. C=O str.), 1720 (sym. C=O str.), 1370 (C–N str.), and 720 cm^{-1} (C=O bend), indicating an imide structure. Meanwhile those near 1650 cm^{-1} due to a poly(amic acid) has disappeared.

2.3 Preparation of the Composite Films

The composite films composed of the polyimides (100 parts), the epoxy resin (10 parts, consisting of either DGEBF or DGEBAD, PN, and TPPK), and the silver filler (40 wt% of the total compositions) were prepared as follows: First, polyimide powders, 50/50 wt% DGEBF/DGEBAD mixture, PN (stoichiometric equivalent of epoxy groups of the epoxy resin and hydroxyl groups of the hardener) and 1 wt% of TPPK per 100% of the epoxy compounds were weighed and completely dissolved in 50/50 wt% DMAc/CHN solvent. Next, the silver filler was added with mechanical stirring. This varnish was casted onto a carrier OPP (biaxially stretched polypropylene) film, followed by heating in an 80°C oven for 30 min and a 120°C oven for 75 min to remove the residual solvents. The resulting composite film

Fig. 2 Synthesis of the polyimide by two-step method

was peeled from the OPP film. Thus, the composite film with 25 μm thickness was obtained. Furthermore, to cure the composite film completely, the film was held on an iron frame and heated in a 180°C oven for 1 h. The curing condition of the film was determined from the exothermic behavior of the epoxy resin (T init: 118, T onset: 158, T exo: 171, and T end: 199°C, T_g : 97°C) measured with DSC.

2.4 Measurements

2.4.1 Characterizations of the Polyimides

Molecular weights (number-averaged M_n and weight-averaged M_w) and their distributions (polydispersity index: M_w/M_n) of the polyimides were obtained by GPC with a Shimadzu HPLC C-R4A (standard: polystyrene). The T_g of the polyimides was obtained by DSC with a Perkin-Elmer DSC-7 at a heating rate of 5°C/min in air. The solubility of the polyimides was evaluated in various solvents (10 wt% polyimide powders in solvent). The water absorptivities of the polyimides were calculated from the following equation:

$$\text{Water absorptivity (wt\%)} = \frac{W_2 - W_1}{W_1} \times 100 \quad (1)$$

where W_1 is the weight of the polyimide film after cured in a 180°C oven for 1 h and dried in a 120°C vacuum

dryer for 3 h, W_2 is the weight of the same film after immersed in distilled water for 48 h at room temperature.

2.4.2 Properties of the Composite Films

TGA was carried out in air at a heating rate of $5^\circ\text{C}/\text{min}$ using a Shinku Riko TGD-7000. Dynamic mechanical analysis was performed on a solid analyzer RSA-2 from Rheometrics. The dynamic viscoelasticity of the film was measured at a heating rate of $5^\circ\text{C}/\text{min}$ and a frequency of 1 Hz. Stress relaxation properties were evaluated as follows: The composite film (size: $5\text{ mm} \times 13\text{ mm}$) was inserted between a silicon chip ($5\text{ mm} \times 13\text{ mm} \times 400\text{ }\mu\text{m}$ thick) and a copper substrate ($16\text{ mm} \times 20\text{ mm} \times 250\text{ }\mu\text{m}$ thick) or a silicon chip ($15\text{ mm square} \times 400\text{ }\mu\text{m}$ thick). The samples were compression-bonded under 0.15 MPa at 250°C for 5 s, followed by heating in a 180°C oven for 1 h to cure the composite film completely. Silicon chip warpage, which is the index of the stress relaxation property of the composite film, was measured using a surface roughness meter (scan distance: 11 mm) as shown in Fig. 3A. The adhesion strength of the composite film was measured as follows: The composite film (size: 5 mm square) was inserted between a silicon chip ($5\text{ mm square} \times 400\text{ }\mu\text{m}$ thick) and a silicon chip of a larger size or a copper substrate. The samples were compression-bonded under 0.08 MPa at 250°C for 5 s and cured under the same condition as above. The adhesion strength was measured with a push-pull gauge by peeling the silicon chip at a pulling rate of 0.5 mm/s as shown in Fig. 3B. The measurement was carried out at 250°C for all specimens (the pulling started 20 s after the specimen was set on the 250°C heater plate).

3. Results and Discussion

3.1 Effect of Monomer Structure on the Characteristics of the Polyimides

3.1.1 Molecular Weight Distribution and T_g

All of the polyimides as-synthesized had M_n of 23000–36000 and M_w of 68000–121000, and only polyimide PI-6 with polysiloxane diamine PSX had slightly lower M_n and M_w values (Table 1). PSX having longer siloxane units, which will lower the miscibility with NMP during polyimide synthesis due to lowering the polarization of the monomer, may result in the decrease in polymerizability in the solvent.

The T_g of PI-1 measured by DSC was 120°C , while those of general polyimides such as ULTEMTM are over 200°C ¹⁵⁾. The lower T_g is due to the introduction of the decamethylene connecting group, a long and flexible

Fig. 3 Measurements of silicon chip warpage (A) and adhesion strength (B)

molecular chain, into the polyimide backbone. Furthermore, the introduction of a dodecamethylene connecting group (PI-2) or several aliphatic ether connecting groups (PI-3 and 4) or siloxane linkages (PI-5 and 6) lowered the T_g less than 120°C . In particular, the introduction of the polysiloxane linkage lowered the T_g to 30°C (PI-6).

3.1.2 Solubility and Water Absorptivity

Each polyimide was found to be soluble in polar solvents like NMP, DMAc, CHN, and THF at room temperature (Table 2). However, the solubility for MIBK was different among the polyimides, and each polyimide was sparingly soluble in DMF and insoluble in DMSO. These differences in solubility can be explained by comparing the solubility parameters (SPs) of the solvents with those of the polyimides. According to the solubility theory, a polymer and a solvent having near SP values are miscible with each other¹⁶⁾. The SP of the solvents and polyimides were calculated from their chemical structures according to the Okitsu method¹⁷⁾. As shown in Table 2, the SP value (11.3) of PI-3 was the highest, and that of PI-6 (9.9) was the lowest among the polyimides. The reason for the former is due to that PI-3 contains many ether linkages with relative high polarization, and that for the latter is assigned to that because PI-6 contains polysiloxane linkage with lower cohesive force in the polyimide structure. On the other hand, the SP value of DMF (12.1) was the highest, and that of MIBK (8.4) was the lowest among the solvents. From the relationship between the SP and the solubility of the polyimides, it is found that PI-6 is very easy to soluble in MIBK because the SP values of PI-6 (9.9) and MIBK (8.4) are very near each other.

Table 2. Solubility^{a)} and water absorptivity of the polyimides

Polyimide	Solvent ^{b)} /SP ^{c)} [(MPa) ^{1/2}]							SP ^{c)} [(MPa) ^{1/2}]	Water absorptivity [wt%]
	MIBK /8.4	THF /9.1	CHN /9.9	DMAc /10.8	NMP /11.3	DMSO /12.0	DMF /12.1		
PI-1	±	++	++	++	++	±	+	10.8	0.12
PI-2	±	++	++	++	++	±	+	10.6	0.10
PI-3	±	++	++	++	++	±	+	11.3	0.33
PI-4	±	++	++	++	++	±	+	11.2	0.28
PI-5	±	++	++	++	++	±	+	10.9	0.10
PI-6	++	++	++	++	++	±	+	9.9	0.01

a) ++: soluble at room temperature, +: soluble on heating at 60°C, ±: only swelling on heating

b) MIBK: methyl isobutyl ketone, THF: tetrahydrofuran, CHN: cyclohexanone, DMAc: *N,N*-dimethylacetamide, NMP: *N*-methyl-2-pyrrolidinone, DMSO: dimethyl sulfoxide, DMF: *N,N*-dimethylformamide

c) solubility parameter

The polyimides having the SP ranging from 9.9 to 11.3 are soluble in the solvents having the SP ranging from 9.1 to 11.3, and are sparingly soluble or insoluble in the solvents with the SP of 12.0 and over. It is not clear why these polyimides show different solubility between DMSO and DMF, which have almost the same SP values. Polyimides may be more soluble in amide type solvents than sulfoxide type solvents.

The water absorptivities of the polyimides were dependent on their chemical structures (Table 2). Among the polyimides examined, PI-3 containing many hydrophilic ether linkages had the highest water absorptivity, and PI-6 containing hydrophobic polysiloxane linkage had the lowest one. As a result, a close correlation between the SP and the water absorptivities of the polyimides was found. That is, the increased SP of a polyimide towards the SP of water (23.4), results in the increased water absorptivity of the polyimide.

3.2 Preparation and Properties of the Composite Film Based on PI-1

3.2.1 Thermal Property

The weight loss behavior of PI-1 film and PI-1/epoxy resin blend film (both cured at 180°C for 1 h) was evaluated by TGA in air and is shown in Fig. 4A. The former film was 20°C higher than the latter film at 5% weight loss temperature (378 and 358°C). However, its weight loss at over 400°C was higher than the latter. The oxidative degradation of PI-1 will occur at over 400°C. The blend of the epoxy resin into the polyimide results in reducing the weight loss of the film at these temperatures. This result suggests that the compatible behavior of the polyimide/epoxy resin blend is a chemical blend such as semi-interpenetrating polymer network (semi-IPN)¹⁸⁾ with some chemical reactions each other.

The weight loss behavior of the composite film of PI-

Fig. 4 TG thermograms of PI-1 and PI-1/epoxy blend films (A) and the composite film of PI-1/epoxy resin/silver filler (B)

1/epoxy resin/silver filler is shown in Fig. 4B. The uncured film showed 5% weight loss at about 120°C. This weight loss is due to the volatilization of the residual solvents in the film. On the other hand, that of the cured film was 358°C. This temperature agreed with that of the base resin (PI-1/epoxy resin blend) shown in Fig. 4A. The result indicates that the thermal degradation behavior of the composite film depends on the property of the base resin, and the silver filler does not affect the degradation of the composite film.

3.2.2 Dynamic Mechanical Properties

The effect of curing on the dynamic mechanical properties of the composite film is shown in Fig. 5. A clear difference in the storage modulus (E') was observed be-

Fig. 5 Effect of curing on the dynamic mechanical properties of the composite film using PI-1

tween the uncured and cured films in the rubbery state region, while no difference was observed in the glassy state region (Fig. 5A). Because it is thermoplastic and has no network structure, the uncured film melted down over its T_g . Moreover, because it has the network structure by the crosslinking of the epoxy resin component, the cured film was restrained from flowing even over its T_g .

The main peak temperatures of the loss modulus (E'') and $\tan \delta$ of the uncured film were 87 and 103°C, and those of the cured film were 121 and 126°C (Figs. 5B and 5C). These temperature rises are due to the effect of crosslinking of the epoxy resin component. On the other hand, the E'' peak of the cured film was slightly separated into two peaks, i.e., 115 and 121°C (Fig. 5B). Here,

the T_g values of PI-1 and the fully cured epoxy resin were determined to be 120 and 97°C by DSC. Therefore, the separated E'' peak will be resulted from the phase separation of the base resin consisting of the polyimide and epoxy resin phases. The morphological structure of the base resin, which is the polyimide rich composition, would be the micro-phase separation structure consisting of the continuous phase of the polyimide component and the fine dispersed phase of the epoxy resin component. However, the separation of the $\tan \delta$ peak of the cured film was not observed (Fig. 5C). The compatible behavior of the cured base resin is probably not simple micro-phase separation but semi-IPN¹⁸⁾ between the linear polyimide and the epoxy resin network with some chemical reactions each other. The morphological behavior will affect to the reduced weight loss of the blend resin at over 400°C shown in Fig. 4A. In addition, it was observed that the $\tan \delta$ peak of the uncured film was broader than that of the cured film (Fig. 5C). The uncured film will cure gradually during measurement, resulting in the apparent T_g rise and broader $\tan \delta$ peak.

3.3 Effect of Polyimide Structure on the Properties of the Composite Films

3.3.1 Dynamic Mechanical Properties

Dynamic mechanical behaviors of the cured composite films composed of the various polyimides (PI-1 to 6), the epoxy resin, and the silver filler were investigated (Fig. 6). The E' at 20°C of the film based on PI-1 was 4.0 GPa, and those of the films based on PI-2, 3, 4, 5, and 6 were 3.5, 2.8, 3.9, 2.8, and 0.8 GPa, respectively (Fig. 6A). This difference in E' depends on the chemical structure of the polyimide as used. In particular, the E' of the film based on PI-6 was the lowest among the films, resulting from the flexible polysiloxane linkage having a rubbery state even at 20°C. On the other hand, the E' at 250°C of the films based on PI-2 to 6 were similar (ranging from 2 to 3 MPa) irrespective of the polyimide as used. They were lower than that of the film based on PI-1 (6 MPa). The crosslinking of the epoxy resin component will restrict the flow of the films at the temperatures over their T_g s in spite of the decreased T_g of the polyimide as used.

The main peak temperatures of the E'' and $\tan \delta$ of the film lowered with decreasing T_g of the polyimide (Figs. 6B and 6C). The $\tan \delta$ peak temperature of the film closely depended on the T_g of the polyimide.

In the films based on PI-2 to 5 as well as PI-1, slightly separated peaks of E'' indicating the phase separation of the base resin were observed (Fig. 6B). In these shoulder-

Fig. 6 Dependence of the dynamic mechanical properties of the composite films on polyimide structure

like shape E'' peaks, the higher peak is related to the T_g of the polyimide phase; the lower peak due to the T_g (97°C) of the epoxy resin phase has shifted near to the T_g of the polyimide phase. These behaviors suggest that the epoxy resin phase is partially compatible with the polyimide phase.

On the other hand, the peak behaviors of E'' and $\tan \delta$ in the film based on PI-6 were different from those of the other films (Figs. 6B and 6C). The E'' peak related to the T_g of PI-6 (30°C) was not clearly observed. The $\tan \delta$ peak of the film was observed at about 55°C. However, the peak was broader and its intensity was lower than those of the other films. In addition, for the film based on PI-6, both the small peaks of the E'' and $\tan \delta$ were observed at about -110°C, which is the transition tempera-

ture related to the siloxane units in PI-6⁵⁾. This phenomenon suggests the existence of the phase separation between the polysiloxane unit and the other units in PI-6. The heterogeneity of this polyimide results in broadening the transition region to hide the E'' peak separation observed for the other films. Such peaks of the E'' and $\tan \delta$ were not observed for the film based on PI-5 in spite of siloxane units. This result suggests that the compatibility between the siloxane units and the other units in the polyimide will improve with shortening the length of the siloxane linkages. The length of the siloxane linkages will affect the cohesion behavior of the polymer chains in the polyimide, resulting in further affecting the dynamic mechanical behavior of the film.

3.3.2 Stress Relaxation Property

Two materials having different coefficient of thermal expansion (CTE) are attached with an adhesive material by heat-pressing to yield thermal stress at the interface. If the adhesive material cannot relax the thermal stress, an internal stress will remain at the interface to yield a residual strain. When using a silicon chip (Si) and a copper substrate (Cu) as the adherents having different CTE (3.5 and 17.0 ppm/°C, respectively), a warpage of the silicon chip is caused as the result of the residual stress or the resultant strain (Fig. 3A). Here, the maximum thermal stress $\sigma_{\max}$ at the die corners was determined by the following equation¹⁹⁾:

$$\sigma_{\max} = K \cdot \Delta\alpha \cdot \Delta T \cdot (E_a \cdot E_s \cdot L/d)^{1/2} \quad (2)$$

where K is the geometric constant, $\Delta\alpha$ the difference in the CTE, ΔT the difference between the T_g of the adhesive material and room temperature, E_a and E_s the elastic moduli of respective adhesive material and copper substrate at room temperature, L the side length of the silicon chip, and d the thickness of the adhesive material. T_g and E_a are the two main factors to affect the thermal stress for the adhesive material.

With reference to the above theoretical interpretation, the stress relaxation properties of the composite films used as the adhesive materials were investigated. Fig. 7 shows the silicon chip warpage as a function of the storage modulus E' at 20°C and the $\tan \delta$ peak temperature (regarded as the T_g) of the composite film. The warpage decreased (the stress relaxation property of the composite film improved) with decreasing E' and $\tan \delta$ peak temperature. In particular, the film based on PI-6 was the most effective in relaxing the stress among the films examined. The correlation coefficient value between the

Fig. 7 Relationship between the storage modulus (A), $\tan \delta$ peak temperature (B) of the composite film and the silicon chip warpage

chip warpage and the E' was 0.466 (Fig. 7A), whereas that between the warpage and the $\tan \delta$ peak temperature was 0.969 (Fig. 7B). Therefore, the influence of the T_g on the warpage is more remarkable than that of the E' . The difference in the thermal strain between the silicon chip and copper substrate during cool down after the die attachment is partly released by the movement of the film. This result indicates that lowering the T_g , rather than the E' of the adhesive film, is more effective in stress relaxation and in decreasing residual strain.

3.3.3 Adhesion Property

The adhesion strengths of the composite films at 250°C are summarized in Table 3. The failure modes were all cohesive failure of the film itself. The adhesion strength showed different behavior between the two groups of the specimens. Good correlation between the adhesion strength and the storage modulus E' at 250°C was observed for Si/Si specimens: the adhesion strength tended to increase with increasing E' . However, such correlation was not observed for the Si/Cu specimens. The difference in adhesion behavior could be explained by the difference in the warpage. That is, while the E' of the film

mainly affects the adhesion strength of the Si/Si specimens because there is little or no warpage caused by the thermal stress, the stress relaxation property of the film additionally affects the adhesion strength of the Si/Cu specimens because there will exist a thermal stress and the resultant warpage. For the films based on PI-1 and 2, the adhesion strength of the Si/Cu specimen was remarkably low compared with that of the Si/Si specimen, because the silicon chip warpage was far larger for the former than the latter. On the other hand, for the film based on PI-6, the adhesion strength of the Si/Cu specimen was almost similar to that of the Si/Si specimen, because the silicon chip warpage for both specimens was far smaller. Thus, the E' and the stress relaxation property of the adhesive film would be the two main factors to affect the adhesion strength in the case of specimens attaching two adherents having different CTE.

4. Conclusions

The polyimides synthesized from DBTA or DDBTA as a dianhydride and BAPP, TODE, DODE, TSX or PSX as a diamine had the Mn ranging from 23000 to 36000, the

Table 3. Adhesion property of the composite films^{a)}

Polyimide used in the film	Adhesion strength at 250°C [MPa]		E' at 250°C [MPa]	Silicon chip warpage [μm]	
	Si/Si ^{b)}	Si/Cu ^{c)}		Si/Si ^{b)}	Si/Cu ^{c)}
PI-1	0.84	0.53	6.1	1	40
PI-2	0.43	0.26	2.2	1	36
PI-3	0.51	0.47	3.0	0	15
PI-4	0.58	0.51	3.3	0	18
PI-5	0.59	0.46	3.3	0	21
PI-6	0.50	0.49	2.4	0	3

a) Die attaching temperature: 250°C

b) Between silicon chips

c) Between silicon chip and copper substrate

Mw from 68000 to 121000, the T_g from 30 to 120°C. They showed excellent solubility in NMP, DMAc, CHN, and THF, and low water absorptivity below 0.3 wt%. The composite films composed of the polyimides, an epoxy resin and a silver filler showed thermoplastic behavior before curing with molten performance above their T_g s, and thermosetting behavior after curing with restrict flow behavior above their T_g s. The limited flow behavior is resulted from the network structure formation in the film due to the crosslinking of the epoxy resin component. Furthermore, it was found that the adhesion strength of the specimen composed of two solid adherents having different CTE and interfacial adhesive film was affected by the modulus and the stress relaxation property of the film. The stress relaxation property of the film will improve with decreasing the T_g of the polyimide.

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