

Enhanced Thermal Conductivity in Polyimide/Silver Particle Composite Films Based on Spontaneous Formation of Thermal Conductive Paths

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A series of polyimide (PI)/silver composite films incorporating μm -sized metallic silver particles (Ag-MPs) were prepared using matrices of sulfur- (SD), fluorine- (TF), and silicon-containing (SIM) PIs as well as an immiscible blend of SD- and TF-PIs (*b*-SF). The thermal conductivity ($\lambda_{\perp}$) of the composited films accords well with the calculated value (λ_{cal}) based on the Bruggeman model below the particle contents (ϕ) of 30 vol%, whereas the composite films of SD/Ag and *b*-SF/Ag exhibited extraordinarily larger $\lambda_{\perp}$ values than λ_{cal} in the range of $\phi > 30$ vol%. Moreover, the $\lambda_{\perp}$ s of SD/Ag films with uniform dispersion of Ag-MPs are almost equivalent to those of *b*-SF/Ag films in which Ag-MPs are selectively dispersed in the SD phase. In contrast, the $\lambda_{\perp}$ s of SIM/Ag films with homogeneous dispersion accord well with the λ_{cal} and much smaller than those of SD/Ag and *b*-SF/Ag. These facts indicate that effective thermal conductive paths were spontaneously generated in SD/Ag films as well as in *b*-SF/Ag films.

Keywords: Polyimide / thin film / Ag / thermal conductivity / polymer-metal composite

1. Introduction

With recent miniaturization of electric devices, microelectronic components generate much of heat in tiny spaces. In case that heat is not efficiently dissipated, serious problems occur from individual devices and electronic modules to total system. Therefore, thermal conductivity of thermal interface materials (TIM) which make solid contact between the components and heat-dissipating fins or substrates has to be enhanced. Polymer composite materials incorporating metal or inorganic particles have been widely used as TIM [1]. However, as the particle loading increases, the viscosity of slurry or solution exponentially increases, and the adhesive strength decreases. Therefore, it is desirable to develop new composite materials exhibiting high thermal conductivity with a small amount of fillers. In addition, thermo-plasticity and good adhesion to metals and ceramics are required for the use of TIM.

White et al [2] reported that percolation behavior

of electrically conductive composites depends on both shape of filler particles and spatial distribution within the polymer matrix. Further, the percolation morphology could be achieved at low loading of fillers by using two-phase immiscible polymer blend, in which at least one phase is continuous and conducting fillers are selectively and preferentially localized only in the continuous phase. We have recently reported that immiscible PI blend films containing selectively dispersed particles of metallic silver (~ 20 nm) [3], zinc oxide (ZnO, ~ 0.5 μm) [4] and magnesium oxide (MgO, ~ 3 μm) [5] show much higher thermal conductivities (λ) than the PI composites containing homogeneously dispersed fillers. In the films, microphase-separated structures with “vertical double percolation” morphology [3,4] were spontaneously formed, in which two phases were separately aligned along the out-of-plane direction, and particles were preferentially precipitated in one phase.

2. Experimental

2.1 Materials

PIs exhibiting high decomposition temperatures (T_d) with moderate glass transition temperatures (T_g) were prepared to fabricate novel PI/Ag composites exhibiting high thermal conductivity, improved thermo-plasticity, and good adhesion to metal and ceramics. 3,3',4,4'-Biphenyltetra carboxylic dianhydride (BPDA) supplied by Ube industries, Ltd. was dried under reduced pressure at 180°C for 8 h prior to use. 2,2'-Bis[4-(3,4-dicarboxyphenoxy) phenyl]propane dianhydride (BPADA) supplied by Manac Inc, and 2,2'-bis(trifluoromethyl)-4-4'-diaminobiphenyl (TFDB) supplied by Central Glass Co., Ltd., were used as received. 4,4'-Thiodianiline (SDA) purchased from Wako Pure Chemical Industries Ltd., was purified by sublimation under reduced pressure. μ m-sized silver particles (Ag-MPs) were purchased from DOWA Electr. Mater. Co., Ltd (Ag-3-8W, D_{50} =2.4 μ m). *N*-methyl-2-pyrrolidone (NMP, anhydrous) from Sigma-Aldrich and toluene from Kanto Chemical Co., Ltd were used as received. Silicon-containing PI (SIM-PI) was manufactured and supplied by Sumitomo Bakelite Co., Ltd.

2.2 Preparation of Polyimide (PI) Solution

Precursor solutions of PIs, poly(amic acid)s (PAAs), were prepared by addition polymerization of equimolar amounts of dianhydride (BPADA) and diamine (TFDB or SDA). A powdery BPADA was added to an NMP / toluene solution of a diamine in a nitrogen-purged glove box and stirred at room temperature for 24 h. During the subsequent refluxing at 170°C for 2.5 h, water evolved from imidization was distilled away using a Dean-Stark apparatus. Finally, the solution was heated to 200°C to remove residual toluene, and then an NMP solution of soluble PI was obtained.

2.3 Preparation of PI films

For preparing PI/Ag composite films with a single BPADA-SDA (SD-PI) matrix, Ag-MPs were blended with an NMP solution of SD-PI. After mixing and defoaming by using a rotation / revolution mixer (Thinky, ARE-310), the solution was bar-coated on a glass substrate, followed by drying at 200°C for 1h on a hotplate and at 200 °C for 1h in a vacuum oven. The completion of imidization of PIs was confirmed by FT-IR spectra. On the other hand, for preparing composite films composed of dual PI matrices of (*b*-SF blend), a mixture solution of SD and Ag-MPs was blended with an equimolar amount of BPADA-TFDB (TF-

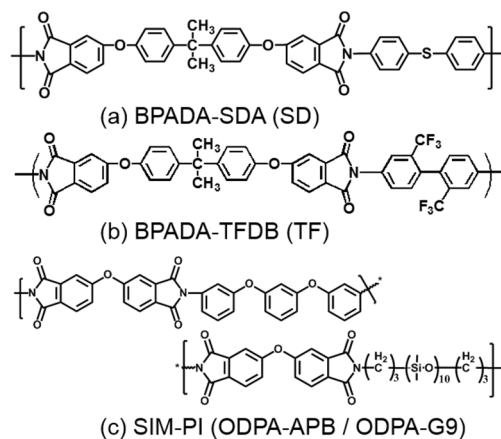


Fig. 1 Molecular structures of matrix PIs

Table 1. Glass transition temp, 5 wt% thermal degradation temp, and thermal diffusivities of PIs.

Matrix PI	T_g [°C]	T_d^5 [°C]	$D_{\perp}$ [$\times 10^{-8}$ m ² /s]
BPADA-SDA (SD)	242	480	14.4
BPADA-TFDB (TF)	238	488	11.3
SIM-PI	190	482	10.4
BPADA-TFDB	350	567	15.3

PI) solution followed by stirring for 4 h. The same procedure was adopted for the preparation of *b*-SF/Ag composite films.

2.4 Measurements

Out-of-plane thermal diffusivity ($D_{\perp}$) of pristine and composite films was measured using a temperature wave analyzer (ai-phase mobile 1u) at room temperature [6,7]. The applied voltage was 1.8 V, and the film thicknesses were 25–100 μ m. Out-of-plane thermal conductivity ($\lambda_{\perp}$) of the films was evaluated based on the following relation:

$$\lambda_{\perp} = \rho \cdot C_p \cdot D_{\perp},$$

where ρ is the density, and C_p is the specific heat at a constant pressure. Values of ρ and C_p for the composited films were estimated by the rule of mixture (ROM) [8]. Cross-sectional scanning electron microscope (SEM) images of the films were observed using a table-top electron microscope (Hitachi, TM-3000). Out-of-plane electrical conductivity of the films was measured by the four-terminal method. Thermal mechanical analysis (TMA) was conducted with a Shimadzu TM-60 analyzer, in which the tensile load was 5 g, and the heating rate was 10 °C/min. Thermo-gravimetric analysis (TGA) was conducted with a Shimadzu TGA-50 at a heating rate of 5 °C/min under N₂.

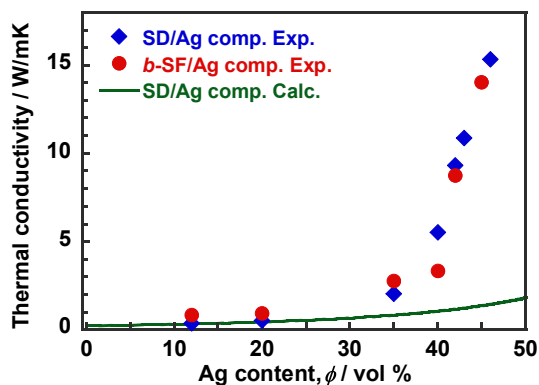


Fig.2 Comparison of experimental (symbols) and calculated (line) $\lambda_{\perp}$ values of PI/Ag composite films.

3. Results and Discussion

3.1 Thermal properties of matrix PIs

Table 1 lists the thermal properties of pristine PI films used as matrices. The PIs containing ether (–O–) linkages in the dianhydride moiety, BPADA-SDA (SD), BPADA-TFDB (TF), and SIM-PI exhibit sufficiently high T_d^5 s ($> 480^{\circ}\text{C}$) but lower T_g s ($< 250^{\circ}\text{C}$) than a quasi-linear PI of BPADA-TFDB [9]. SIM-PI shows a much lower T_g due to its long silicone (–Si(CH₃)₂O–) linkages with *meta*-linked phenylenes. These PIs with moderate T_g s are beneficial for good solubility to polar solvents, thermal elasticity for film forming, and good adhesive property to metals/ceramics. The thermal diffusivities ($D_{\perp}$) of TF- and SIM-PIs are slightly lower than the other PIs due to the loose polymer chain packing caused by two –CF₃ groups (TF) and the enhanced local molecular motion around the silicone linkages (SIM) [10]. Moreover, SD-, TF-, and SIM-PIs are soluble in polar organic solvents, such as *N,N*-dimethylformamide (DMF), *N,N*-dimethyl acetamide (DMAc), and NMP. In addition, TF- and SIM-PIs show high optical transparency in the visible region. The colorlessness of these matrices gives quasi-metallic colored silver-dispersed composite films.

3.2 Thermal conductivity of PI composite films

Fig. 2 shows the experimental ($\lambda_{\perp}$) and calculated (λ_{cal}) thermal conductivities of the PI composite films prepared in this study. The λ_{cal} values were estimated based on the Bruggeman theory [11] by assuming the homogeneous dispersion of Ag-MPs in the SD film. The $\lambda_{\perp}$ values of SD/Ag and *b*-SF/Ag films show good agreement with the λ_{cal} up to the Ag-MPs content (ϕ) of 30 vol%. In general, $\lambda_{\perp}$ of composite materials gradually increases with increasing the filler content (ϕ). However, it should

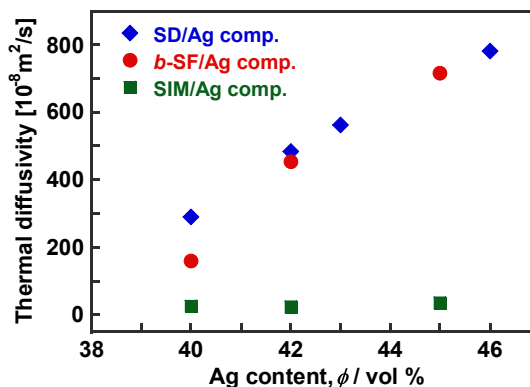


Fig.3 Experimental $D_{\perp}$ values for SD/Ag, *b*-SF/Ag, and SIM/Ag films in the range of $\phi=40$ –46 vol%.

be noted that the $\lambda_{\perp}$ of both SD/Ag and *b*-SF/Ag films exhibits abrupt increases above $\phi=30$ vol%. Two possible reasons can be hypothesized for the anomalous upward deviation of $\lambda_{\perp}$ from λ_{cal} as follows. (i) significant increase in heat transfer carried by conductive electrons of Ag-MPs, and (ii) formation of thermal conductive paths by percolation of agglomerated Ag-MPs. First, in case of a high content of conductive fillers like copper or silver, the electric conductivity could become a dominant factor for enhanced $\lambda_{\perp}$ of composites [12]. However, experimental volume resistivity of the SD/Ag film with $\phi=46$ vol% was measured as $6.19 \times 10^{-5} \Omega \cdot \text{cm}$. According to the Wiedemann-Franz law, the calculated contribution of conductive electrons to $\lambda_{\perp}$ is only 0.15 W/m·K which is two digits smaller than the total $\lambda_{\perp}$. Thus, the electric conductivity makes little contribution to the abrupt increase in $\lambda_{\perp}$. Second, we have reported that, in case of high concentrations of particles, number of physical contacts between particles increases, and the agglomerated particles spontaneously form thermal conductive paths in PI/Ag, PI/ZnO, and PI/MgO composites [3–5]. In this study, PI films having similar phase-separated structures were prepared by mixing of SD-PI containing Ag-MPs and TF-PI, and their $\lambda_{\perp}$ values are compared with those of uniformly dispersed composite films (see Fig. 2). Because the $\lambda_{\perp}$ values of SD/Ag is nearly equivalent to those of the PI films containing selectively dispersed Ag-MPs (*b*-SF/Ag) at higher particle contents ($\phi>30$ vol%), we can conclude that effective thermal conductive paths were spontaneously generated with similar densities in both of the composite films. Fig. 3 shows the ϕ -dependence of experimental $D_{\perp}$ values. The SIM/Ag films, in which Ag-MPs are homogeneously dispersed and mutually separated in

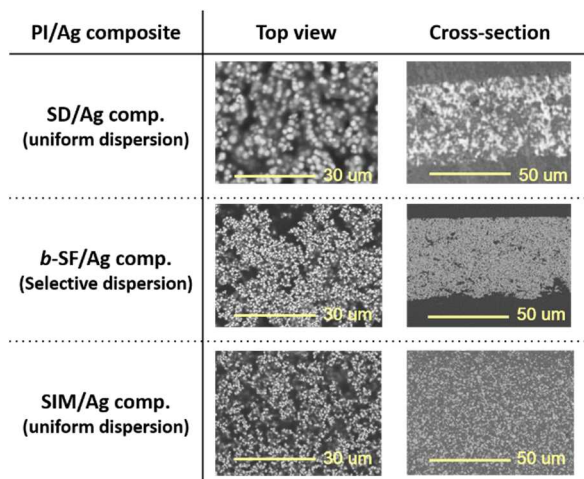


Fig.4 Top and cross sectional views of the three kinds of PI/Ag composite films ($\phi=42$ vol%).

the films, exhibit much lower $D_{\perp}$ values than those of SD/Ag and *b*-SF/Ag films. The $D_{\perp}$ values of SIM/Ag films accord well with the calculated values by assuming the same ρ and C_p as Kapton. Therefore, SIM/Ag films can be treated as an ideal example of uniformly dispersed composite films.

3.3 Dispersion states of Ag-MPs in composite films

Fig. 4 displays the top and cross sectional views of the three kinds of PI/Ag composite films ($\phi=42$ vol%). In contrast, the Ag-MPs dispersed in SD/Ag are obviously agglomerated compared with SIM/Ag, and high contrast densities can be observed in the cross-sectional SEM images. Yu et al. [12] recently reported that polymer composites with three-dimensional Cu thin film networks have isotropic and enhanced conductivity at low Cu contents. Since the $\lambda_{\perp}$ of metallic silver is much higher than those of PIs, these results indicate that the abrupt increase in $\lambda_{\perp}$ observed for SD/Ag and *b*-SF/Ag above $\phi=30$ vol% was induced by spontaneous formation of thermal conductive paths of Ag-MPs in the film. In other words, effective conductive paths were formed by mutually interacting Ag-MPs and SD-PI, which exhibited larger $\lambda_{\perp}$ values than the films containing uniformly dispersed and separated Ag-MPs (SIM/Ag). Although the reason why such effective conductive paths were preferentially formed in the composite films, not only *b*-SF/Ag but also SD/Ag films, is still unclear, the SD-PI matrix provides a specific basis for the percolation morphology of Ag-MPs.

4. Conclusion

The thermal conductivity ($\lambda_{\perp}$) of a series of PI/silver composite films prepared from SD-, TF-, and SIM-PI matrices as well as an immiscible blend

of SD- and TF-PI matrices (*b*-SF) were systematically evaluated. The SD/Ag films with Ag-MPs contents (ϕ) more than 30 vol% exhibited extraordinarily larger $\lambda_{\perp}$ values than the predicted values (λ_{cal}) based on the Bruggeman model. The values of $\lambda_{\perp}$ for SD/Ag are close to those of the PI composites forming the vertical double-percolation (VDP) structure. Cross sectional SEM images show that Ag-MPs incorporated in SIM/Ag are uniformly dispersed and mutually separated. In contrast, Ag-MPs dispersed in the SD/Ag and *b*-SF/Ag films are partially agglomerated, forming efficient thermal conductive paths in the films. These results indicate that the content of Ag-MPs can be simply reduced in the manufacturing of thermal conductive composites by using the SD-PI as matrix. These results are useful for the development of novel TIMs with high $\lambda_{\perp}$, good processability, good adhesion, improved flexibility, and low production costs.

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