Study of Dielectric and Thermal Conductivity Characteristics of Polyimide Composite

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Abstract

The graphene is used to enhance the thermal conductivity, but it is difficult to obtain uniform dispersion and low dielectric property. We fabricate the polyimide composite with high thermal conductivity and low dielectric property. It changes the filler contents, and examines curing time and dispersion. The dispersion characteristics were quantified by absorbance measurement. The graphene 0.1 wt% and BN 0.5 wt% polyimide composites show a thermal conductivity of 6.6 W/m·K by LFA (Laser Flash Analysis) and a dielectric constant of 4.6@10 GHz by SPDR (Split Post Dielectric Resonators).

Keywords

Dielectric Property, Thermal Conductivity, Polyimide Composite, Flexible PCB

1. Introduction

Polyimide has high heat resistance characteristics. Polyimide is the main material for flexible printed circuit board. It has a high operating temperature system. If the ambient temperature rises, both transfer rate and durability deteriorate rapidly [1]. So, the use of thermal conductive materials is important.

Currently, the electric devices require a high transfer rate at high frequency. The faster transfer rate can be achieved by lowering permittivity. Therefore, polyimide requires low dielectric properties.

Generally, graphene was used to enhance the thermal conductivity, but it is difficult to obtain uniform dispersion and low dielectric property [2].

We fabricated the polyimide composite with high thermal conductivity and low dielectric property. It changed the filler various contents, and curing time and dispersion condition.

2. Methods

We used polyimide varnish (SKCKOLONPI Co.), graphene (XG science Co.) and BN (3 M cooling filler). Graphene and BN in solvent were dispersed using ultrasonic at 300 W for 3 min. And then mixed with polyimide varnish using plantary mixer (THINKY Co.) at 2000 rpm during 4 min (involved degasing time). Thin film was prepared by the knife coating using micro gauge device with adjustable applicator.

We observed dispersion stability of fillers in Dimethylformamide (DMF). The solutions were left for maximum 4 days. When the solution was not separated, the condition was determined. When it was applied 300 W ultrasonicwave for 3 min, the dispersion stability was good. The composite film was prepared by mixing PI varnish and graphene solution using the planetary mixer at 2000 rpm for 2 min. The solvent was removed at 100°C for 5 min in a convection oven. And then, it was cured for 20 minutes at 200°C. The curing time was long, because the catalyst was not used. The filler contents in composite are graphene 0.1 wt%, graphene(G) 0.1-BN(B) 0.1 wt%, G 0.1-B 0.3 wt%, G 0.1-B 0.5 wt%, G 0.1-B 0.7 wt%, G 0.1-B 0.9 wt%. Figure 1 shows diagram of the materials mixing, film making and curing process.

The curing behavior was predicted using LT-451 Dielectric Cure Monitor. The dispersion measured by UV-vis, and thermal conductivity using laser flash & hot disc. And then, the dielectric property measured using SPDR network analyzer at 1 - 10 GHz.
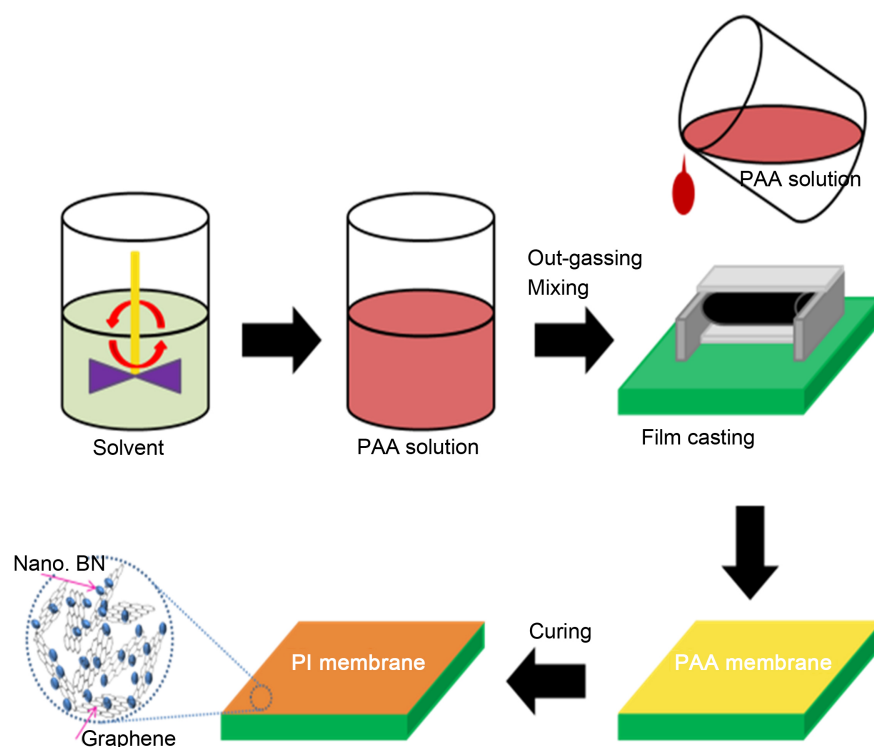
Figure 1. Manufacturing process of PI composite film.

3. Results and Discussion

3.1. Curing Behavior

If the physical viscosity of curable polymer increases, the ionic viscosity increases. Increasing ionic viscosity is indicated by ionic current.

Figure 2 shows the PI and PI-graphene composite curing behavior with temperature. Depending on the curing temperature and holding time, the volatility of the solvent and the degree of curing of PAA, which can influence the film performance, are different.

During the volatilization of the solvent, bubbles may be generated on the surface or inside in the film to degrade performance. Therefore, the temperature and hold time must be optimized in the step-by-step curing program.

At a curing temperature of 100˚C, the viscosity of PI began to increase after 80min and PI-graphene composite after 15 min. The viscosity of PI-graphene composites is constant after about 12 min. At 200˚C of curing temperature, PI showed a large viscosity change after 5 min and becoming constant after around 15 min. In the case of PI-graphene composites, the curing started after 3 min and viscosity value is becoming constant within 10 min. Compared curing time
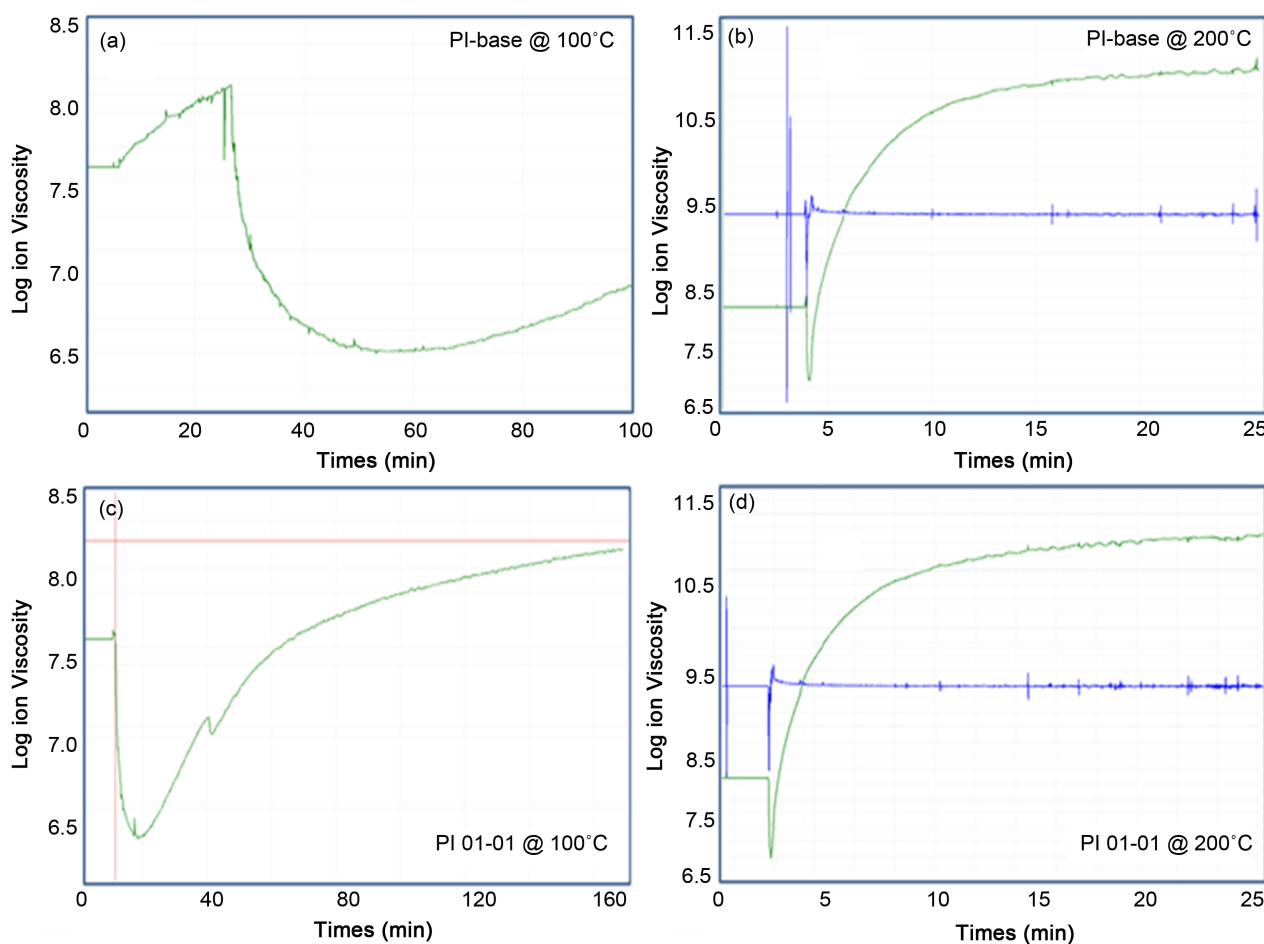
Figure 2. Measuring of Viscosity by dielectric curing monitoring. (a) PI @100˚C; (b) PI @200˚C; (c) PI composite @100˚C; (d) PI composite @200˚C.

with PI and PI-graphene composites, it was more than 10 min at 200˚C and more than 30 min at 100˚C. The curing time difference is due to graphene has higher thermal conductivity effect than the polymer material. It is guessed that the volatile of the solvent on the graphene interface and the improved thermal conductivity of the material. I could have expected that the better the thermal conductivity of the composite material, the lower curing temperature and the shorter time.

3.2. Dispersion

The absorbance of the film was measured by UV-vis. High absorbance, the better the filler dispersion in the film. We used Horn type ultrasonic homogenizer as output 300 W in 20% of maximum power. The solution with graphene was dispersed in various ultrasonic time 1, 3, 5, 10, 15 min. After the 3 min or longer, the dispersion remained more than 48 hrs and that minimum time selected. Figure 3 shows the ultrasonic dispersion solution with time variation.

The dispersion degree measurement using the UV-vis was mainly performed as mainly used measuring the dispersion degree of CNT. The graphene is slightly different from the structure of CNT (CarbonNanoTube) but it is possible to measure the dispersion using UV-vis. It is difficult to quantify the degree of dispersion of highly concentrated solutions using UV-vis. A solution with a high degree of dispersion and low concentration are easy to measure the UV-vis spectrum. However, when the dispersion is poor, the UV-vis spectrum has high noise and low reliability due to particle agglomeration.

From Beer-Lambert's law, Equation (1) can be expressed for components [3] [4].

$$A = \epsilon \cdot t \cdot c = \epsilon_R \cdot t \cdot c_R^* + \epsilon_f \cdot t \cdot c_f^* \tag{1}$$

where:

A: absorbance,

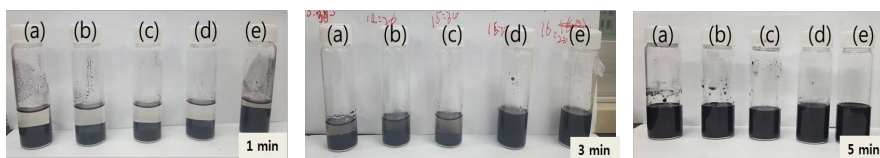ϵ_R: molar abs. coefficient of resin,

t: thickness,

c_R^*: concentration of resin,

ϵ_f: molar abs. coefficient of filler,

c_f^*: concentration of filler.

The products of the molar extinction coefficient and the concentration of components are a and b.

$$a = \epsilon_R \cdot c_R^*, \quad b = \epsilon_f \cdot c_f^*, \tag{2}$$

Figure 3. Ultrasonic dispersion solution with time variation. (a) PI 01-01; (b) PI 01-03; (c) PI 01-05; (d) PI 01-07; (e) PI 01-09.

From this, effective concentration factor is $=\dfrac{A/(t-a)}{b \cdot c_f}$. In this case, β represents *a* value of 0 to 1. When β is 1, it is completely dispersion [3].

The absorbance of the composite material, which is not affected by each component, can be judged to start at about 440 nm. Therefore, the β value at 440 nm was calculated and shown in **Table 1**. As shown in **Table 1**, β value is low. β showed a low value of 1 or less, according to the calculation results. The higher the degree of dispersion, β is closer to 1, but in this study, the value is 0.1 or less.

The non-polar graphene in the DMF, polar protic solvent, is easier to aggregate. Therefore, it is considered that it is necessary to use a dispersing additive or to increase the external energy so that the substitution reaction can be facilitated. The coefficients calculated from **Figure 4** are shown in **Table 1**.

3.3. Thermal Conductivity & Dielectric Properties

Graphene increases not only the thermal conductivity of composites, but also the dielectric constant. Boron nitride was additionally used to lower the dielectric constant while maintaining the high thermal conductivity. The thermal conductivity of 3 wt% graphene polyimide composite is about 6 W/m·K and dielectric constant (D_k) is about 2.2. In general, the permittivity of polyimide is 3.4.

Table 1. The value of constituent materials dispersion coefficient of polyimide composite film.

|	PI 01-00	PI 01-01	PI 01-03	PI 01-05	PI 01-07	PI 01-09
ϵ_R	0.092	0.109	0.045	0.029	0.015	0.022
ϵ_f	0.065	0.096	0.039	0.025	0.012	0.019
β	0.111	0.058	0.034	0.026	0.022	0.020
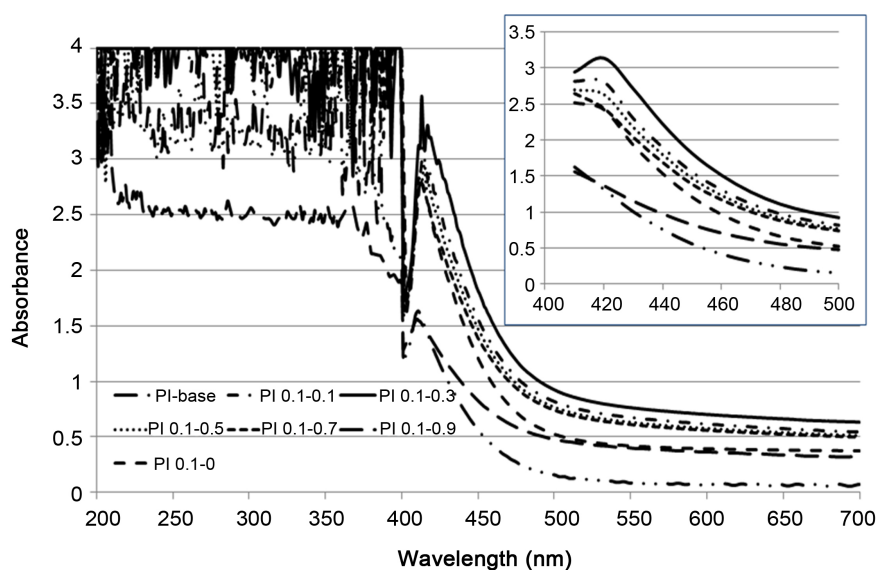
Figure 4. UV-vis spectrum of polyimide composite material.

However, the low the permittivity, the higher the transmission speed of the mobile device. Therefore, the dielectric constant of flexible printed circuit board is required to be 5 or less. Graphene composites have excellent in-plane thermal conductivity, but thru-plane thermal conductivity is low. The graphene and BN were combined to complement the thermal conductivity and permittivity. We predicted that graphene could make connections between BN particles. The PI composite was compounded with multi-filler to fill the gap between graphenes. The network of thermal path was formed by the difference in shape and size of graphene and BN. Figure 5 is a SEM image of fillers in PI composite.

As shown in Table 2, we could obtain a thermal conductivity of about 6 W/m·K and a dielectric constant of about 4 in composite materials. However, if the dispersive is better, the thermal conductivity improvement and the dielectric constant reduction effect will be further increased.

DMF and graphene are factors that increase the permittivity of polyimide composites. However, in the process of manufacturing the polyimide film, the solvent, DMF, is volatilized. In the curing process of the polyimide film, the temperature condition was optimized so as not to affect the dielectric constant by sufficiently volatilizing the DMF to leave no residue.

As shown in Table 2, the dielectric loss (D_f) is extremely low. Dielectric loss is caused by electric conduction and polarization due to the impurities contained
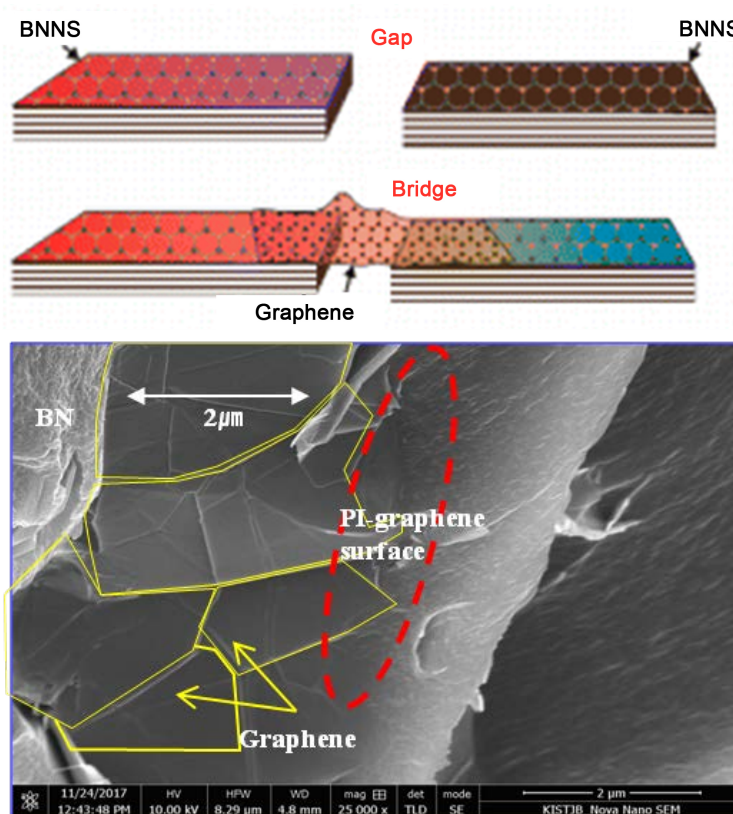
Figure 5. Diagram of filler structure and SEM morphology in polyimide composite.

Table 2. Properties of polyimide-graphene composites.

	Thick. (μm)	Thermal conductivity (Laser Flash Analysis)			Permittivity	
		TC[a]	TD[b]	HC[c]	D_k	D_f
PI 0.1-00	22.70	8.185	11.708	1.032		
PI 0.1-01	11.95	4.575	6.472	1.014	4.338	0.017
PI 0.1-03	13.58	3.344	4.704	1.035	4.773	0.018
PI 0.1-05	14.98	6.674	9.878	1.03	4.646	0.018
PI 0.1-07	13.97	-	-	-	4.914	0.022
PI 0.1-09	13.70	7.564	11.098	0.99	5.381	0.026

[a]TC: Thermal Conductivity (W/m·K), [b]TD: Thermal Diffusivity (mm^2/s), [c]HC: Heat Capacity (J/g/K).

in the material. Therefore, it can be predicted that the graphene acts as a functional filler that enhances thermal conductivity rather than acting as an impurity.

4. Conclusions

From this study, the followings were obtained. In order to improve the properties of the polyimide composite, graphene and BN filler were compounded. The dispersion characteristics were quantified as β value from absorbance measurement. The optimal conditions were determined as a function of ultrasonic time and filler concentration.

The graphene 0.1 wt% and BN 0.5 wt% polyimide composites showed a thermal conductivity of 6.6 W/m·K by LFA and a dielectric constant of 4.6 by SPDR @10 GHz. The heat transfer effect was enhanced by the network between fillers. However, it is necessary to continuously observe the tendency of dielectric constant and loss.

Acknowledgements

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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