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Heat dissipation properties of polyimide nanocomposite films

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Abstract–In development of modern electric fields, the growth of kinds of electronic devices has made the supply and research on heat dissipating films become important. To synthesize heat dissipation films with high thermal resistance for possible use in electronics applications, carbon black is doped into polyimide to increase the dissipating rate of films, at loadings of 50, 100, and 150 wt%. The resulting films display excellent thermal properties; the thermal conductivity of the film with 150 wt% carbon black is 5.59 $W\cdot m^{-1}K^{-1}$, a value that is 35 times higher than that of pure polyimide (0.16 $W\cdot m^{-1}K^{-1}$). To theoretically confirm the increased dissipating ability of composite films, the Nielsen equation is used for verification. The experimental results show an excellent fit with the theoretical values calculated by the Nielsen equation. The great thermal stability of polyimide composite film with carbon black is verified by using TGA and DSC, the temperature for 1% thermal decomposition of the 150 wt% film is 541°C, and the glass transition temperature is 315 °C. The heat conduction results also show high heat dissipation data, which make the carbon black composite polyimide films an excellent candidate for use in electric devices to deplete the heat generated.

Keywords: Polyimide, Composite, Carbon Black, Heat Dissipation, Conductivity, Nielsen Equation

INTRODUCTION

Developments in modern electronics have necessitated continual advances in miniaturization, high density integration, and performance. Because of these changes, however, significant amounts of heat are produced inside of the equipment [1-4]. This increase in temperature has the potential to damage the device. Many heat dissipation technologies are currently under development to solve this problem [5-8], and the most effective approach to date utilizes polymeric heat dissipation films [9]. In fact, the polymeric heat dissipation film itself can actually function as a heat insulating material, but the thinness of these films effectively conducts the generated heat to outside rather than insulate them [9]. To negate the insulating abilities for using as dissipating polymers, the polymers are generally prepared by incorporating inorganic materials with excellent thermal conductivity into a composite. In this study, carbon black (CB), which is known for its high thermal conductivity, was selected as inorganic filler. CB is easily obtainable in large quantities and is much less expensive than the carbon nanotubes or graphene used in prior work [9]. The chief reasons for selecting CB are its thermal and mechanical stabilities, which are higher than those of the epoxy, nylon-6, or urethane polymer backbones employed elsewhere [1,2,10-18]. Adding inorganic fillers allows the polymer composite to retain many of its excellent properties. It is reported that some of the basic properties of the polymer could be affected by addition of fillers, but in this study, the carbon black composite film only showed reduction in mechanical properties and its high thermal stabilities are remained [10,11,18]. The conductivity of CB has been reported to be in the range 6-174 $W\cdot m^{-1}K^{-1}$. Carbon nanotube (CNT) and graphene have a much higher conductivity: 3,000 $W\cdot m^{-1}K^{-1}$. However, according to our calculations, the high thermal conductivity of inorganic filler meagerly influences the thermal conductivity of the resultant polymer composite. We were able to utilize carbon black particles to synthesize polyimide; our material has similar thermal properties to polyimide synthesized with CNTs or graphene. Since carbon black is much less expensive than CNT or graphene, the PI-CB composite film is much more economical than the CNT composite film. This shows that the thermal conductivity of the filler is a slight influential factor on film conductivity. However, the morphology of the filler is a main factor that influences conductivity the most. Films with CNTs and graphene fillers do increase device performance, with a maximum thermal conductivity of about 6-8 $W\cdot m^{-1}K^{-1}$ [19-22]. These films are also easy to synthesize. However, the aggregation structure of carbon black can be manipulated to help polyimide films with CB achieve similar thermal conductivities. The shape and aggregation of the filler significantly impact the conductivity of the polymer composite. This suggests that a PI composite synthesized with CB can show the same properties as a material containing carbon nanotubes or graphene [23].

EXPERIMENTAL

1. Materials

3,3′,4,4′-Benzophenone tetracarboxylic dianhydride (BTDA) and

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Table 1. Heat dissipation data for PI and PI-CB composites

Sample	PI	PI-CB-50	PI-CB-100	PI-CB-150
Thermal diffusivity (mm^2s^{-1})	0.092	0.182	0.669	3.512
Thermal conductivity ($W{\cdot}m^{-1}K^{-1}$)	0.16	0.42	1.11	5.59

4,4-oxydianiline (ODA) were purchased from Sigma Aldrich. Carbon black N326 (CB) was purchased from the Evonik Carbon Black Korea Co., Ltd. Anhydrous 1-methyl-2-pyrrolidinone (NMP) was purchased from Aldrich and used as received. All reagents were used without further purification.

2. Synthesis of Polyimide Doped with Carbon Black, PI-CB

PI-CB was synthesized via a polymerization reaction between BTDA, ODA, and CB. The BTDA-ODA poly (amic)acid solution was prepared under N_2 by slowly adding BTDA (1.0906 g, 1 mmol) to ODA (1.012 g, 1 mmol) in NMP (15 mL). Varying amounts of CB (0, 50, 100, or 150 wt%) were added to the solution at room temperature and the mixture was stirred for 1 h for thorough dispersion. The resulting solutions were then magnetically stirred for 24 h at 20 °C to ensure uniform mixing [24]. Samples were designated PI-CB-50, PI-CB-100, or PI-CB-150 according to their CB content (PI-CB 50 represents CB 50 wt%).

All the PI-CB precursor solutions were spin-coated onto glass plates and soft-baked at 100 °C for 30 min on a hot plate. Here, the thickness of the coating was controlled by the speed of the spin coater. The soft-baked samples were placed in a curing oven and cured by the following imidization protocol: 150 °C/30 min, 200 °C/ 30 min, 250 °C/30 min, and 350 °C/120 min. The ramp rate was 2.0 °C/min, and the cooling rate was 2.0 °C/min.

3. Characterization

The samples were initially characterized by thermogravimetric analysis (TGA) using a Q50 thermogravimetric analyzer (TA Instruments, New Castle, DE, USA). The cured samples were placed in a platinum sample pan and characterized by scanning from 30 to 600 °C at a rate of 10 °C/min under N_2.

Next, the samples were evaluated by differential scanning calorimetric (DSC) analysis. The glass transition temperature (T_g) was measured by using a LABSYS evo DSC analyzer (SETARAM Instrumentation, Caliure, France) between 40 and 800 °C at a rate of 10 °C/ min under N_2.

Heat transfer coefficients were measured by using a laser flash method with thermal diffusivity measurements (NETZSCH, LFA 447 NanoFlash, InSb Sensor), according to ASTM E1461 (the standard test method for thermal diffusivity by the flash method) [25,26]. These data were used to calculate the thermal conductivities of the PI composites.

Mechanical properties, including modulus and elongation, were investigated using a Multitest 5-I (Mecmesin, UK) analyzer according to ASTM D882-91 (the standard test method for tensile properties of thin plastic sheeting). This is a standard test method for measuring the tensile properties of thin films.

The samples for transmission electron microscopy (TEM) analysis (200 kV, Cryo Tecnai® G2 F20; FEI, Hillsboro, OR, USA) were prepared with a Leica Ultracut UCT microtome (Leica Microsystems, Buffalo Grove, IL, USA), which afforded 80-90-nm-thick PI-CB slices. Subsequently, a layer of carbon about 3 nm thick was deposited onto these slices.

The surface morphology of the prepared films was characterized by scanning electron microscopy (SEM), JSM-840A (JEOL, Japan), operating at 10 kV. All samples were sputtered with a conductive layer of gold.

RESULTS AND DISCUSSION

1. Thermal Conductivity of Composites Containing CB

As the main purpose of this study is increasing heat dissipating ability of polyimide composite film, the various loading of carbon black fillers in polymer matrix was tested for checking thermal conductivity. CB shows great influence on polymer matrix and it increased the thermal conductivity of polymer composite in a large range. The PI-CB-50, PI-CB-100, PI-CB-150 were synthesized and their conductivities were measured. The most increased conductivity is shown in PI-CB-150; the measurement of thermal conductivity yielded a value of 5.59 $W{\cdot}m^{-1}K^{-1}$, which is a 35-fold increase compared to the pure PI (Table 1). For PI-CB-50 and PI-CB-100, the thermal conductivity was 0.42 and 1.11 $W{\cdot}m^{-1}K^{-1}$, respectively. Although in the cases of PI-CB-50 and PI-CB-100 showed slightly increased value of thermal conductivity, compared with the conductivity of original pure PI film (0.16 $W{\cdot}m^{-1}K^{-1}$). However, these results show that the thermal conductivity increases exponentially as the CB concentration increases, which is in accordance with earlier reports [27,28]. Thus, the relationship between the CB loading and the thermal conductivity was exponential and not linear. To prove this point, the Nielsen equation was used to see the important factors which greatly influence the conductivity of composite film. According to the Nielsen equation, the shape and aggregation of the inorganic filler are the most influential factors on changes in thermal conductivity [28]. In addition, as the content of the inorganic filler increases, the contact surface of the inorganic filler also increases. This causes a significant rise in the thermal conductivity of the films [29,30]. In short, the increase in CB content results in an exponential increase of the carbon contact [31].

The agreement between the experimental results and theory was checked using the Nielsen equation, which is widely accepted as the most suitable model for polymer composites [32].

The Nielsen equation, which is used to evaluate the thermal conductivity, is based on the Kerner equation or the Halpin-Tsai equation as modified by Lewis and Nielsen. The modified equation (Eq. (1)) was used to evaluate the thermal conductivity as a function of volume fraction as follows: [30,32]

$$\frac{K}{K_1}=\frac{1+AB\Phi_2}{1-B\Psi\Phi_2}$$

Where,

$$A=k_E-1 \tag{1}$$

Table 2. Values of A for various two-phase systems

Type of dispersed phase	Direction of heat flow	A
Spheres	Any	1.50
Aggregates of spheres	Any	3.160[a]
Randomly oriented rods Aspect ratio=2	Any	1.58
Randomly oriented rods Aspect ratio=4	Any	2.08
Randomly oriented rods Aspect ratio=6	Any	2.8
Randomly oriented rods Aspect ratio=10	Any	4.93
Randomly oriented rods Aspect ratio=15	Any	8.38
Uniaxially oriented fibers	Parallel to fibers	2L/D
Uniaxially oriented fibers	Random loose	0.5

[a] $3.160=(2.50/\Phi_m)-1$, Φ_m is maximum packing fraction. And aspect ratio=length, L/diameter, D

Table 3. Maximum packing fractions Φ_m

Shape of particle	Type of packing	Φ_m
Spheres	Hexagonal close	0.7405
Spheres	Face-centered cubic	0.7405
Spheres	Body-centered cubic	0.60
Spheres	Simple cubic	0.524
Spheres	Random close	0.637
Spheres	Random loose	0.601

$$B=\frac{\frac{K_2}{K_1}-1}{\frac{K_2}{K_1}+A}$$

$$\Psi=1+\left(\frac{1-\Phi_m}{\Phi_m^2}\right)\Phi_2$$

K: Thermal conductivity of the composite.

K_1 and K_2: Thermal conductivities of the polymer and filler, respectively.

A: Constant related to the generalized Einstein coefficient kE.

B: Constant related to the relative conductivity of the components.

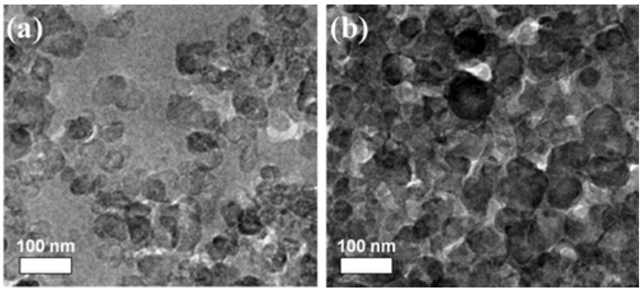


Fig. 1. Morphological dispersion of carbon black particles in films observed by TEM image of (a) PI-CB-50, (b) PI-CB-150.

Ψ: A function related to the maximum packing fraction.

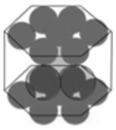
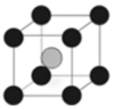
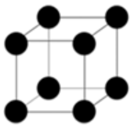
Φ_m: Maximum packing fraction of the filler.

Φ_2: The volume fraction of the filler.

Here, we are interested in K, which provides information about the thermal and/or electrical conductivity of two-phase material. Subscripts 1 and 2 indicate the matrix and the filler, respectively. Component A depends on the shape of the dispersed particles and is related to the generalized Einstein coefficient k_E. Factor B is the constant relative conductivity of the two components. Ψ is a function related to the maximum packing fraction (Φ_m) of the filler, and Φ_2 is the volume fraction of the filler. In Table 2, values of A are listed as a function of the different types of the dispersed phases.

TEM and SEM data are very important for Nielsen equation calculations, because they help to determine not only the value of component *A* in the equation but also the value of Ψ function. The maximum packing fraction was also determined by the order and morphology of TEM image and was related to the shape of the particles (Table 3). According to the SEM data, the shape of the CB was aggregates of spheres. Also, the morphology of the CB appeared to be either random loose packing or random close packing depending on the volume fraction of the filler. To figure out whether the film was shaped in random loose or close packing, the volume fraction was calculated. In result, when the filler volume fraction increased above 0.64, the morphology adopted a random close packing structure. According to the calculation of PI-CB's weight percentage to volume fraction, PI-CB 50 is 0.5437 and PI-CB-150 is 0.7814; therefore, PI-CB-50 is random loose and PI-CB-150 is random close packed. TEM image in Fig. 1(a) shows the random loose (PI-CB-50) and Fig. 1(b) shows close (PI-CB-150) composition structure of CB. Using the information in Table

Table 4. Packing shapes of particles

Shape of particle	Sphere	Sphere	Sphere	Sphere	Sphere
Type of packing	Hexagonal close	Face-centered cubic	Body-centered cubic	Simple cubic	Random close / loose
Φ_m	0.7405	0.7405	0.60	0.524	0.637/0.601
Shape					

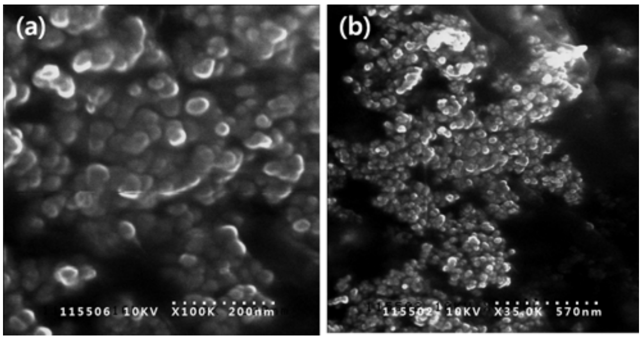


Fig. 2. Crossing surface of PI-CB is pictured by SEM to determine the packing type of PI-CB.

3, Φ_m was determined to be 0.601 (as shown in Table 4), which suggests the presence of random loose particles. A can be calculated using Table 2 and was determined to be 3.160. Also, looking at TEM (Fig. 1) and SEM (Fig. 2) images, we can see that the dispersed phase was comprised of aggregated spheres.

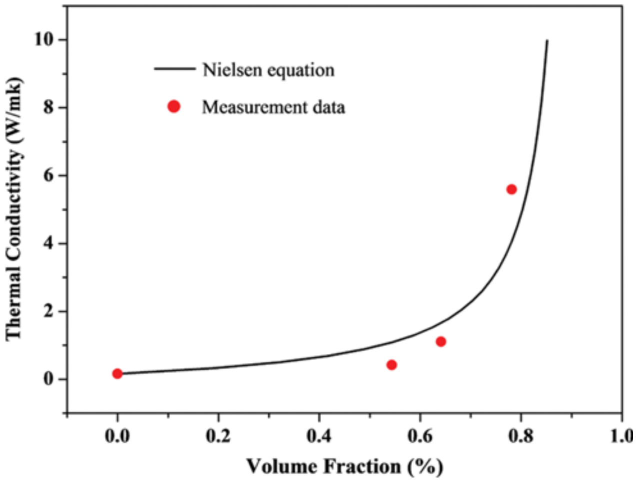


Fig. 3. Heat conduction rate data for the PI-CB composites compared with theoretical data of Nielsen equation.

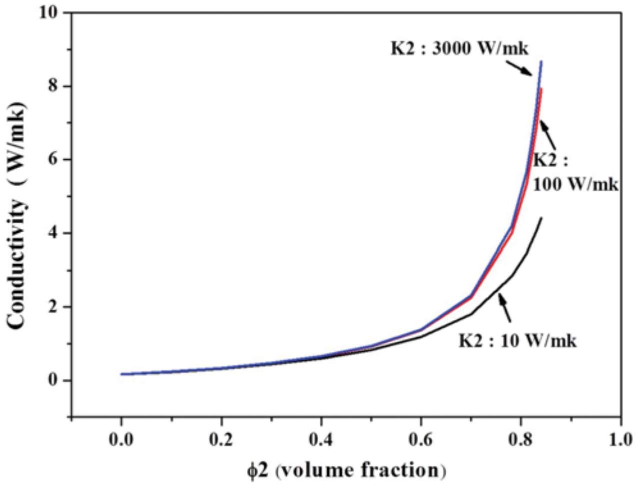


Fig. 4. Heat dissipation data of polyimide film with different fillers, K2=10 W/mk, K2=100 W/mk, K2=3,000 W/mk, respectively.

Using the Nielsen equation, we can graph the theoretical conductivity as a function of the volume fraction of the filler (Φ_2). By inspection, the theoretical data shows exponential behavior. A rapid increase in conductivity occurred at volume fractions of 60-70% (Fig. 3). To test which factors influence the conductivity most, the values of filler conductivity were given three values, 10, 100, 3,000 $W \cdot m^{-1}K^{-1}$, respectively; all total film conductivity showed similar exponentially increasing tendency, but the film conductivity was not significantly affected by the conductivity of the filler (Fig. 4) which can be proved by two increasing lines showed by the value of K2 of 100 $W \cdot m^{-1}K^{-1}$ and 3,000 $W \cdot m^{-1}K^{-1}$. Since the filler conductivity is not a significant influencing factor, it turns out that the materials with low conductivity can also be a great candidate for improving thermal conductivity of total film. In the Nielsen equation calculations, the most influential factor on the total conductivity is component A, which is determined by the particle type. The calculated thermal conductivity of PI-CB 50 was 0.42 $W \cdot m^{-1}K^{-1}$. This trend is similar to what occurs in the experimental data (Table 1). The difference between the two values is likely due to the dispersion of the carbon particles.

The calculated and measured outcomes were in good agreement with one another, indicating that the CB is comprised of aggregated spheres. This is important in that it shows that for heat dissipation film synthesis, the inexpensive inorganic filler CB can theoretically impart the same conductivity as carbon nanotubes or graphene, which are more expensive than CB [18].

2. Thermal Properties

To verify whether or not PI-CB composites can work as stable heat dissipation films at high temperature, two factors are very important to be analyzed to assure thermal properties of PI-CB composites. Therefore, the 1% and 10% thermal degradation temperatures (T_d) and glass transition temperatures (T_g) were measured by TGA (Fig. 5) and DSC (Fig. 6). Numerical results are listed in Table 5. The measurements for PI-CB composite film showed

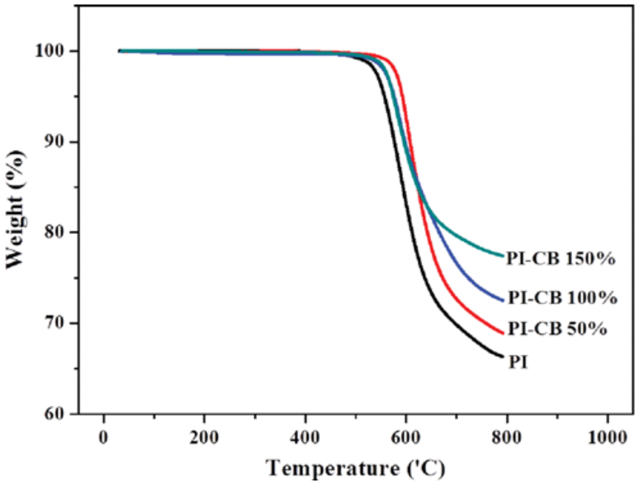


Fig. 5. Thermal decomposition data for the PI and PI-CB composites in various loading of carbon black of 150%, 100%, and 50%, respectively.

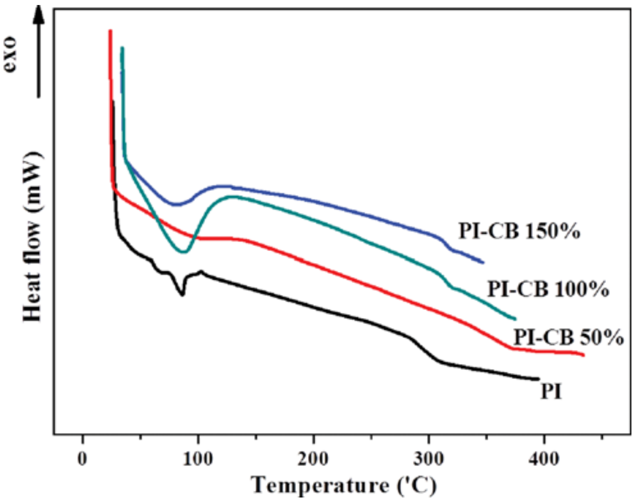


Fig. 6. DSC data for the PI and PI-CB composites in various loading of carbon black of 150%, 100%, and 50%, respectively.

Table 5. TGA and DSC results for the PI and PI-CB composites

Sample name	PI	PI-CB-50	PI-CB-100	PI-CB-150
$T_{d1\%}$	515	561	534	541
$T_{d10\%}$	577	608	597	595
T_g	289	365	314	315

Table 6. Modulus data for PI and PI-CB composites

Sample	Tensile strength (MPa)	Elong. at break (%)
PI	115.9	9.33
PI-CB-50	78.6	3.2
PI-CB-100	70.2	1.42
PI-CB-150	58.3	1.25

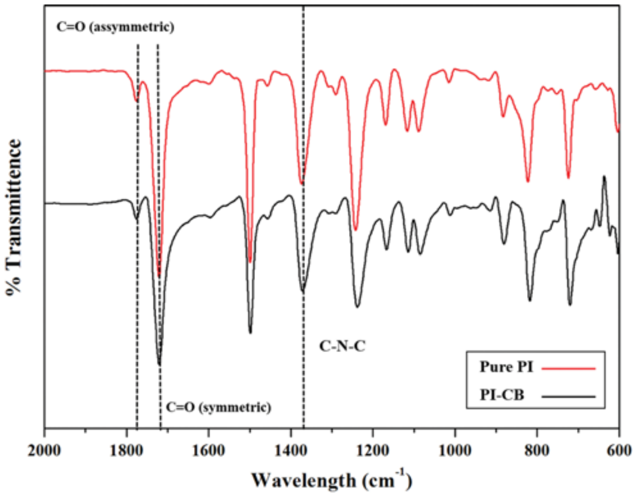


Fig. 7. FT-IR results for observing the fully polymidized PI-CB by comparint with the peaks of pure PI.

higher T_d and T_g when compared to pure PI. The T_d increased to 561 °C and the T_g increased to 365 °C. These values represent increases of 9% and 26%, respectively, when compared to pure PI. This is very interesting because there is no other inorganic that improves the thermal properties of polyimide composite film while being physically blended into the matrix without any chemical reaction between matrix and fillers. This may lead to a new study about the effect of carbon black inside of the polyimide matrix. The final result data shows the PI-CB composite film has an advanced thermal stability compared with pure PI, and this improvement is likely showing that the carbon black fillers inside the composite film can reinforce the polymer matrix structure. This improvement may be based on the uniform dispersion of carbon black fillers. The increased thermal decomposition temperature and glass transition temperature can act as great factors utilized in electric devices tolerating high temperature without losing its morphology and effects while controlling the temperature condition inside the devices by dissipating extra heat produced.

3. Mechanical Characterization

In general, the incorporation of an inorganic filler into a polymer reduces its mechanical strength, assuming there is no reinforcement through some sort of chemical reaction. However, if the film is too rough or weak, it is hard to apply in electronic devices. In this study, PI-CB composite films were synthesized without any chemical reaction to improve their mechanical properties. To numerify the actual mechanical strength of PI-CB, the measurement is conducted. The result shows mechanical strength of the 150 wt% composite is 58.3 MPa. This represents a 50% decrease in strength compared to pure polyimide (115.9 MPa). This decrease is caused by the incorporation of inorganic fillers, because it is not chemically bonded with polymer matrix. By checking the tendency of PI-CB composite, the mechanical strength gradually decreases as the CB content increases (Table 6). In Table 6, the tensile strength of PI-CB-0, 50, 100, 150 is 115.9 MPa, 78.6 MPa, 70.2 MPa, 58.3 MPa, respectively, which well shows the influence of inorganic fillers on the polymer/inorganic composite. Therefore, further study for maintaining of reinforcing mechanical properties of PI-CB films is needed. However, reducing the mechanical properties of films was unavoidable, but still the numerical result of 58.3 MPa is strong enough for the application of film.

4. Structure Characterization

In researching polyimide, the full completion of imidization reaction is important. Therefore, Fourier transform infrared analysis was conducted for verifying the completion of polyimidization which is a widely used method for evaluating the imidization degree and chemical structure of polyimide material. In Fig. 7, the fully imidized peaks are observed. According to the result data of FT-IR, the symmetric and asymmetric absorptions of carbonyl group at ~1,722 and 1,782 cm^{-1} showed, respectively, which increases with the imidization of poly (amic) acids. Also, the degree of imidization can be determined by C-N-C stretching vibration of the imide ring observed at ~1,342 cm^{-1}. According to this result, we can prove the full completion of the imidization of PI-CB film.

CONCLUSIONS

The PI-CB composite films synthesized in this work showed greatly improved thermal properties, and a high heat conductivity that approached 5.59 $W\cdot m^{-1}K^{-1}$. These results compare favorably to heat conductivity films containing carbon nanotubes and graphene. Using the Nielsen equation, we determined that the thermal conductivity of our composite films was not significantly affected by the conductivity of the filler above a specific value, but that the shape and aggregation of the filler were the most important factors. For this reason, although the conductivity of CB is lower than that of carbon nanotubes or graphene, the conductivity of the composite films showed the same properties as composite films made with the other fillers. CB is easily obtainable and readily available in large quantities, which is in sharp contrast to other, more expensive inorganic dopants. This polymer composite can replace expensive heat dissipation films with satisfactory thermal and mechanical properties. Through this study, the shape and aggregation state of the inorganic filler was found to be very important. In future studies, various inorganic fillers with different shapes and aggregation states will be studied in an attempt to prepare heat dissipation films with significantly improved properties.

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