Research Article

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Enhanced thermal conductivity of flexible h-BN/polyimide composites films with ethyl cellulose

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Abstract: The present work focuses on fabricating a flexible and thermally conductive PI composite film. The PI composite film was obtained by blending hexagonal boron nitride (h-BN) combined with ethyl cellulose and 2,2'-Bis(trifluoromethyl) benzidine (TFMB) functionalized GO (TFMB-GO) in polyimide (PI). The ethyl cellulose successfully formed the thermal conduction network by promoting the dispersion of h-BN in PI matrix. Thus, the thermal conductivity of the PI composite film with ethyl cellulose could be twice than PI film without ethyl cellulose. Besides, the PI composite film containing 30 wt% of h-BN could still exhibit excellent flexibility. Moreover, the combination of TFMB-GO could increase the tensile strength of the PI composite film by up to 80%. Overall, we provided a novel idea for the preparation of flexible substrate materials with efficient heat dissipation which was convenient and possible to apply widely in the industrial production.

Keywords: polyimide; ethyl cellulose; hexagonal boron nitride; thermal conductivity; mechanical properties

1 Introduction

Polymer-based composites have been applied diversely in communication, aerospace and electronics industries (1-3). Its economic efficiency, light weight, recyclability, good process ability, and enhanced physical properties compared to polymer showed much benefit in industry (2-8). Nowadays, with the growing requirements of high density and speed circuits in electronic equipment, the

capability of heat dissipation of electrically insulating polymer-based materials has drawn public attention (9-15). In order to optimal the thermal conductivity (TC) of polymer composites, great efforts had been dedicated in this research.

As a matrix, PI has been widely applied in industry due to its high thermal stability, outstanding mechanical properties and low dielectric constant (16-21). However, PI, of which the TC is 0.1 W/mk, cannot meet the requirement of such fast heat conduction for the advanced electronic devices (22,23). The addition of high thermally conductive fillers in the PI matrix is helpful to overcome this drawback. Adding carbon materials, metal or ceramic materials to the polymer matrix would efficiently enhance the TC of PI matrix (24-32).

With the combination of diverse property, such as high thermal conductivity, high electrical resistivity, low thermal expansion coefficient, h-BN has been considered as a suitable material for ceramic filler (31,33). But the percolation theory indicates that the performance of thermal conductivity cannot be improved by adding thermally conductive inorganic materials to an inorganic/resin composite sheet, only if the filler content sur-passes the percolation threshold of 30 vol% (34). Researchers have attributed this phenomenon to the contact resistance at the interface of the inorganic materials and resin (35). Unfortunately, adding high filler content into the material is relatively costly and may decrease its flexibility (36,37). Owing to the fact that inorganic filler can agglomerate and become non-uniform, the final mixed material shows diverse weakness (38).

Recent research reveals that cellulose based composites (cellulose/BN) were prepared, because of the interaction between cellulose and h-BN (39). Based on this research, cellulose may be potential for optimizing the dispersion of h-BN in material.

In this study, we prepared a novel kind of PI composite film with excellent flexibility and thermal conductivity. The h-BN showed the good dispersion in the PI matrix by combination with ethyl cellulose, which was confirmed by SEM. Thus, the thermal conductivity of

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the PI composite film was promoted due to the formation of thermal conductive network. Moreover, the addition of TFMB-GO contributed to the further improvement of the tensile strength of PI composite film, which could be applied in the heat dissipation of electronic packaging and substrates.

2 Materials and methods

2.1 Materials

The h-BN powder (99%) was purchased from CWNANO Co., Ltd, China. The 4,4'-diaminodiphenyl ether (ODA, 98.5%), pyromellitic dianhydride (PMDA, 99%), 2,2'-Bis(trifluoromethyl) benzidine (TFMB, 98.0%), N-Methyl pyrrolidone (NMP, $\geq 99.9\%$) and N,N-Dimethylformamide (DMF, 99%) was provided by SINOREAGENT Co., Ltd, China. Graphene oxide powder ($>99\%$) was obtained from XFNANO Co., Ltd, China. Ethyl cellulose (EC, CP, 1.14 g/mL at 25°C) was from MACKLIN Co., Ltd, China.

2.2 Methods

2.2.1 Preparation of TFMB-GO

Firstly, 0.1 g graphene oxide powder (GO) was added to 100 mL NMP solvent. To fully disperse GO into solvent NMP, the solution was ultrasonicated for 10 h using an ultrasonic cleaner. Next, 100 mL GO suspension (1.0 mg/mL) was poured into a threenecked flask, then 0.3 g TFMB was added. Under nitrogen atmosphere, the flask was magnetically stirred for 24 h at a temperature of 80°C. After 24 h, it was washed several times with solvent (NMP) and dried to obtain TFMB-GO. The reaction process is shown in Figure 1.

Figure 1: Synthesis process of TFMB-GO.

2.2.2 Preparation of PI composite film

At the first step, ODA (0.2002 g, 1 mmol) and DMF (6 mL) were added to a 250 mL round flask equipped with a mechanical stirrer at ambient temperature. The solution was stirred until ODA was totally dissolved. After the ODA was completely dissolved, certain amount of h-BN was added into the container with ultrasonic for 30 min. When the h-BN was fully dispersed in the solvent, the ethyl cellulose was added (the weight ratio of ethyl cellulose/BN was 0.1) and ultra sonicated for 1 h. Then the 1 wt% TFMB-GO was added with ultrasonic for 30 min to fully disperse the TFMB-GO in the solvent. After that, PMDA (0.2225 g, 1.02 mmol) was added into the solution. A viscous poly(amic acid) solution was obtained after magnetic stirring for 24 h subsequently. Then, the solution was placed in 80°C vacuum oven for 2 h to obtain the h-BN_EC+TFMB-GO/ PAA composite film. In the next step, the film was placed in a muffle furnace. Switch on the muffle furnace and let the internal temperature raise from room temperature to 100°C in 3 min. After 5 min of heat preservation, the internal temperature was increased to 300°C in 10 min at the rate of 20°C/min. Keep 300°C for 15 min, then the h-BN_EC+TFMB-GO/PI composite film was finally obtained after being naturally cooled down to room temperature. The preparation process was shown in Figure 2.

In addition, some control samples without ethyl cellulose or TFMB-GO were prepared with the similar methods mentioned above.

2.2.3 Characterization

Fourier transform infrared (FTIR) spectra were taken by using a Bruker (Germany) EQUINOXSS Fourier transform infrared spectrometer with a wavenumber range of 4000 cm^{-1} and 600 cm^{-1} . The morphology and microstructure of TFMB-GO and PI composites films were

Figure 2: Procedure of preparation of PI composite film.

observed by transmission electron microscopy (TEM, JEOL JEM-2100, Japan) and scanning electron microscopy (SEM, Quanta FEG250, USA), respectively. X-ray diffraction (XRD) patterns of the composites and the raw materials were obtained using Rigaku X-ray machine operating at 40 kV and 150 mA. Thermal conductivities of the composites were characterized with laser flash apparatus (LFA, NETZSCH 447, Germany) at room temperature. The DXLL-5000 universal testing machine (Shanghai Dengjie Machinery Co., Ltd.) was used to test the films strip of 1 cm $\times$ 3 cm at a tensile speed of 10 mm/min.

3 Results and discussion

3.1 Characterization of TFMB-GO

Figures 3a and 3b were electron transmission electron micrographs of GO and TFMB-GO, respectively. Figure 3a indicated that GO was distributed in a sheet structure and had good light transmittance. It could be observed

Figure 3: Electron transmission electron micrographs of GO and TFMB-GO: (a) TEM images of GO (b) TEM images of TFMB-GO.

from Figure 3b that TFMB-GO exhibited a lamellar sheet structure while the edge of the sheet was curled. Since a new functional group was introduced into the functionalized structure, which destroyed the structure of GO, resulted in the curl of the sheet. It indicated that the TFMB-GO was prepared.

Figure 4 illustrated the FTIR spectra of GO, TFMB, and TFMB-GO separately. As shown, the characteristic

Figure 4: The FTIR spectrum of GO, TFMB, and TFMB-GO.

absorption peaks of GO is 3315 cm^{-1} , 1715 cm^{-1} and 1615 cm^{-1} which assigned to the characteristic peaks of -OH , C=O and H_2O , respectively (40-41). And the peak at 3440 cm^{-1} was attributed to the characteristic peak of -NH_2 in TFMB while the peak at 1110 cm^{-1} was assigned to the characteristic peak of C-F bond. 1450 cm^{-1} , 1500 cm^{-1} and 1580 cm^{-1} are characteristic peaks of C=C in the aromatic ring. On the TFMB-GO spectrum, the stretching vibration absorption peak of the 1715 cm^{-1} carbonyl group had moved to 1639 cm^{-1} where the absorption peak corresponds to the carbonyl group in the amide bond (42). In the meantime, the bending vibration absorption peak of N-H in TFMB-GO at 1516 cm^{-1} could also prove the formation of an amide bond. It could be known from above results that the formation of an amide bond was caused by the amino group in the TFMB reacting with the carboxyl group of GO.

3.2 The stability of the dispersion

Figures 5 and 6 respectively show the dispersion of h-BN/PAA (h-BN content 10 wt%) and h-BN_EC /PAA (h-BN content 10 wt%) during 4 h of standing state. Obviously, the dispersion of h-BN_EC/PAA added with EC was much more stable than h-BN/PAA. Since the solution should be placed in 80°C vacuum oven for 2 h to obtain the composite films, the stability of the dispersion in the first 2 h was critical. For the h-BN_EC /PAA group, only a small amount of h-BN settled to the bottom in the first 2 h of standing state; while, for the h-BN/PAA group, a large amount of h-BN already settled to the bottom in the first 2 h. Accordingly, the addition of EC contributes to the stability of the dispersion of h-BN in PAA.

Figure 5: The digital photo of h-BN /PAA (h-BN content 10 wt%) dispersion

Figure 6: The digital photo of h-BN_EC /PAA (h-BN content 10 wt%) dispersion

3.3 XRD analysis of PI composites films

The XRD patterns of PI, h-BN/PI and h-BN_EC/PI were shown in Figure 7. The sharp peak of BN at 2θ value of 26.7° was due to crystalline peak of boron nitride. The crystal peak at 2θ value of 18° was assigned to crystal plane

Figure 7: The XRD curve of PI, h-BN/PI and h-BN_EC/PI.

Figure 8: Scanning electron microscope of (a) pure PI film, (b) h-BN /PI (h-BN content 10 wt%) composite film, (c) h-BN_EC/PI (h-BN content 10 wt%) composite film, (d) h-BN_EC+TFMB-GO/PI (h-BN content 10 wt%) composite film.

of PI. In the case of h-BN_EC/PI, the crystal peaks of PI in h-BN_EC/PI were with a slight offset. This was due to the interaction between the ethyl cellulose, boron nitride and PI. Besides, the peaks of boron nitride were less intense to the h-BN/PI of boron nitride. This may be due to interaction between matrix and filler, confirming the formation of the composite. The analysis of SEM (Figure 8) results is also in agreement with the formation of composites.

3.4 Morphological study of PI composite film

Figure 8 illustrated the tensile fracture surfaces of PI composite film. As shown in Figure 8a, the fracture surface of pure PI film was very flat, homogeneous and smooth, which was similar to the typical brittleness fracture feature (43). This phenomenon indicated that pure PI film was high brittleness, as a result of rigid chain structure of the benzene. Figure 8b showed cross-sectional SEM image of h-BN/PI (h-BN content 10 wt%) composite film without adding ethyl cellulose. The

cross section of the film was no uniform and most of BN fillers settled to the bottom of composite film. The poor compatibility of h-BN with PI resulted in phase separation. Figure 8c was the SEM of h-BN_EC/PI (h-BN content 10 wt%) composite film. With the addition of ethyl cellulose, the uniformity of h-BN distribution in PI was significantly improved. The surface was rugged, which was very similar to the typical material ductile fracture characteristics. In addition, Figure 8d was a cross-sectional electron micrograph of h-BN_EC+TFMB-GO/PI (h-BN content 10 wt%) composite film. Compared to h-BN_EC/PI composite film, the addition of TFMB-GO lets h-BN more uniform in PI. Moreover, the concave interface was more regular and had a certain depth while the cross-section orientation was biased to one side, which indicated that the filler had strong cohesiveness in polyimide. Lastly, the toughness was enhanced effectively, which could be shown in the mechanical properties analysis below.

And the tensile fracture surfaces of PI composite films with different h-BN contents can be seen in Figure 9.

Figure 9: Scanning electron microscope of (a) h-BN_EC/PI (h-BN content 10 wt%) composite film, (b) h-BN_EC/PI (h-BN content 20 wt%) composite film, (c) h-BN_EC/PI (h-BN content 30 wt%) composite film.

3.5 Mechanical properties of PI composite films

The tensile strength of PI composite films was shown in Figure 10. It also could be observed from the Figure 10 that the tensile strength of the PI composite film decreased remarkably with the increase of h-BN content, which conformed to the characteristics of brittle fracture shown in SEM image. As for h-BN_EC/PI composite film, the introduction of ethyl cellulose increased the tensile strength of the PI composite film significantly. This was related to the unevenness of the fracture surface shown in the SEM image. Then, TFMB-GO contributed to the further improvement of the tensile strength of PI composite film. This was due to the filler has a strong adhesion to the PI matrix confirmed by the SEM result of h-BN_EC+TFMB-GO/PI composite film.

Figure 10: The tensile strength of h-BN /PI composite film, h-BN_EC/PI composite film, and h-BN_EC+TFMB-GO/PI composite film.

3.6 The thermal conductivity of PI composite films

Figure 11 shows the thermal conductivity of different PI films. Also, the h-BN/PI composite film in Figure 11 reveals that the thermal conductivity exhibited positively relationship with the h-BN content. However, when the filler h-BN was added to 30 wt%, the thermal conductivity that increased to 0.697 W/mK was only three times higher than that of the pure PI film. The result could be attributed to the high interfacial thermal resistance which resulted from the discontinuity of h-BN in PI matrix, and it was also reflected in the SEM image. The thermal conductivity of h-BN_EC/PI composite film with ethyl cellulose appeared a significant improvement under the same filler conditions, up to 1.308 W/mK, which was 6 times higher than pure PI film. It could be observed from SEM image that the dispersion of h-BN in PI matrix was more uniform by the addition of ethyl cellulose. As for the reason of excellent thermal conductivity, we assumed that the h-BN easily

Figure 11: The thermal conductivity of h-BN /PI composite film, h-BN_EC/PI composite film, and h-BN_EC+TFMB-GO/PI composite film.

settled to the bottom before PAA film forming. While, when both ethyl cellulose and h-BN existed in the PI matrix, the aggregation settlement of h-BN was prevented, because of the interaction between ethyl cellulose and h-BN. That means the ethyl cellulose acts as a support barrier between h-BN sheets, enabling h-BN fully dispersed in PI matrix. At the same time, the interaction between ethyl cellulose and h-BN contributes to the link-age between h-BN sheets, thus forming a heat conduction path. As for the h-BN_EC+TFMB-GO/PI composite film, the addition of TFMB-GO can lead to a slight decrease in thermal conductivity. Because compared to graphene, TFMB-GO introduced oxygen-containing functional groups and compounded organic matter, which reduced the heat conductivity of the composite films. On the other hand, the increase of h-BN contributes to gradually mitigating the effect of TFMB-GO on the overall thermal conductivity.

4 Conclusion

In summary, the flexible PI composite film with high thermal conductivity was prepared through the solution casting process of h-BN combined with ethyl cellulose, which is a relatively convenient method. With the help of ethyl cellulose, the dispersity of h-BN in PI was improved which contributed to the double increase of the thermal conductivity of the PI composite film. Moreover, the thermal conductivity increased up to 6 times than that of the pure PI film. At the same time, the combination of TFMB-GO can increase the tensile strength of the PI composite film by up to 80%. Therefore, this PI composite film is very promising for thermal management of electronic products.

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Authors' contribution: Lin Liu and Siyu Shen conceived and co-designed the study. Lin Liu, at the same time, supervised the project. Yiyao Wang assisted with the pre-synthesizing of PI. Siyu Shen oversaw the research work on the improvement of thermal conductivity and mechanical properties of PI composite film.

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