

Immiscible Polyimide/BN Blend Films with Enhanced Thermal Conductivity

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Abstract The immiscible polyimide blend films containing nano-/micro-sized BN with vertical double percolation structure were prepared, and optical images of corresponding polyimide blend films were obtained by experiment. The result indicated that the thermal conductivity of polyimide blend film with 25 wt.% of nano-sized BN reached 1.16 W/m·K, which was 236% increment as comparing with the homogenous film containing the same BN ratio. The significant enhancement in thermal conductivity was attribute to the good phase separation of polyimide matrix, which lead the inorganic fillers selectively localized in one continuous phase with high packing density, consequently, forming the effective thermal conductive pathway.

Keywords Polyimide; Boron nitride; Blend films; Thermal conductivity

1. INTRODUCTION

Polyimide (PI) films are generally with intrinsic low thermal conductivity in the range of 0.1-0.2 W/m·K, which can not effectively dissipate the heat generated from high packing and power-density devices^[1]. In order to solve the problem of heat dissipation, the thermal conductive and electronically insulating ceramic fillers, such as alumina (Al₂O₃), aluminum nitride (AlN), boron nitride (BN), and silicon nitride (Si₃N₄), have been introduced to the polyimide matrix to form the composite films^[2,3]. Many efforts have been made to develop the homogeneous polyimide composite films by incorporation the ceramic fillers in polymeric matrix. It is found that a high loading of inorganic fillers in the polymer matrix (in general over 30 wt.%) is necessary for achieving high thermal conductivity, which is associated with the formation of continuous heat dissipation networks throughout the polymeric matrix. Unfortunately, the polyimide composite films with high fraction of fillers inevitably lead to poor processability and poor mechanical properties due to aggregation of inorganic fillers, as well as high cost.

Many other researches have been done on improving the thermal conductivity of polyimide films with less filler loading by introducing hybrid fillers or controlling filler distribution to construct effective thermal conductive networks^[4,5]. In recent years, immiscible polymer blend films have attracted more attention because they exhibited higher thermal diffusivity along the out-of-plane direction than the monophasic PI blend films^[6-8].

In this research, the mesoscopic simulation technique was applied to describe the morphology of polyimide blends and used for design the immiscible polyimide/BN blend films with better vertical double percolation structure. According to the simulation and experimental results on the phase separation behavior of polyamic acid (PAA) blend systems, the immiscible polyimide blend films containing different ratio of nano-/micro-sized BN were prepared. The morphology of the PI/BN blend films was investigated. Their thermal conductivity was discussed and compared with the homogenous ones.

2. EXPERIMENTAL

Model Description

The morphology of polyimide blend is mainly depended on the property of its precursor-PAA due to the high viscosity. The macromolecular structures of PAAs with different molecular volume used in the simulations are shown in Fig.1. Single repeat unit of PMDA/ODA was chosen as the basic coarse-grained (CG) particle to construct polymer system^[9]. All the simulations were performed using Mesocite module in the Material Studio suite of programs. The structures of particles were optimized before set into Mesostucture Template. The dimensions of the simulation lattice were 300×300×300 Å³, time step was 250 fs and the number of time steps was 8000.

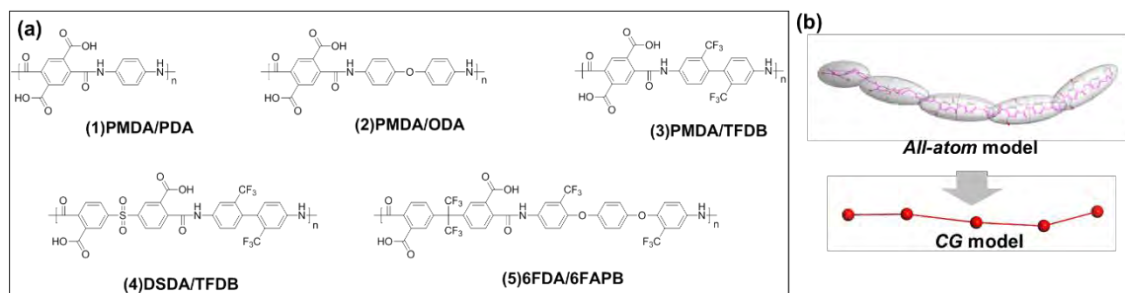


Fig. 1. (a) Macromolecular structures of PAAs in all-atom model; (b) Coarse-grained structure of PMDA/ODA.

Materials

The dianhydrides and diamines were respectively dried in a vacuum oven prior to use. Hexagonal boron nitride powders with platelet morphology and the particle size of 70 nm (nBN) and 2.7 μm (mBN), respectively, were used.

Polymer Synthesis and Film Preparation

The immiscible polyimide blend film containing BN filler were prepared from the mixture of PAA2/BN and PAA5 solutions in the similar pure PAA solution procedure. The obtained PAA2/BN solution was mixed with pure PAA5 solution and stirred for 1 h. The immiscible polyimide blend film (PI2/PI5/BN) with different mBN or nBN content was obtained after casting the BN blended solution on a glass substrate followed by thermally imidization. The films were 30-40 μm in thickness. Homogenous BN blended polyimide films were prepared from PAA2/BN solution for comparing.

3. RESULTS AND DISCUSSION

3.1 Phase Separation Behavior of Polyimide Blends

The PI blend films were prepared from the corresponding PAA blends after thermal imidization. The optical images of these PI blend films were detected and compared with the mesoscopic simulation results. It is found that only the PI blend films based on the PAA2/PAA5 and PAA1/PAA5 blends exhibited sharp phase-separated morphology.

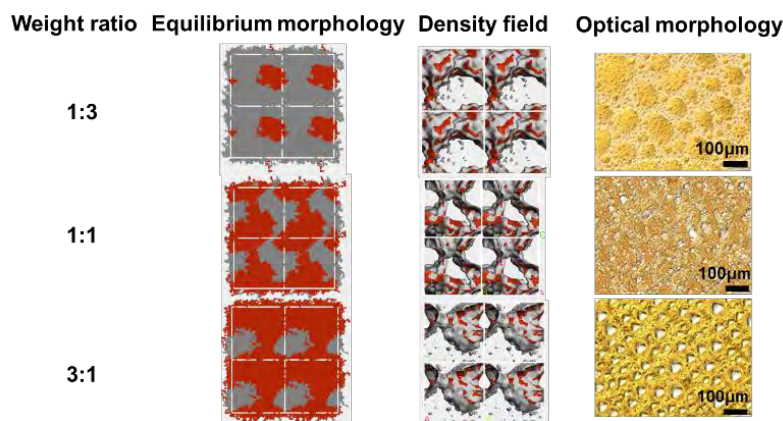


Fig.2. Simulation equilibrium morphologies and optical images of PAA2/PAA5 blends films.

The influence of weight ratio of PAA2/PAA5 blend on the phase separation behavior was investigated. As shown in Fig. 2, the experimental results are consistent with the mesoscopic simulation ones. The weight ratio of was varying from 1:3, 1:1 to 3:1. it is confirmed that the blend films prepared from the PAA blends with the equivalent weight ratio have continuous phase separation structure. It is favorable to obtain the immiscible polyimide films when the thermal conductive fillers are incorporated. With the help of this good phase separation structure (1:1), the fillers can be selective localized in one continuous phase with high density and consequently forming an effective thermal conductive pathway.

Tensile properties of polyimide blend films prepared from different PAA systems with the weight ratio of 1:1 were also evaluated. It is noticed that PI2/PI5 blend film exhibited preferable flexibility due to the presence of flexible ODA structure. In consideration of the good balance of separating ability and mechanical property, PI2/PI5 blend was selected as the matrix to prepare the immiscible polyimide

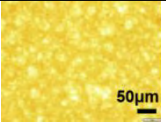
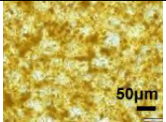

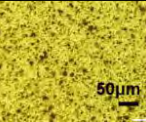
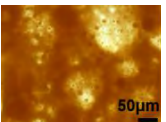
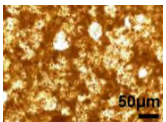

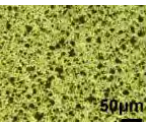
composite films containing BN filler.

3.2 Morphology of Polyimide/BN Blend Films

The morphologies of PI2/PI5/BN blend films and PI2/BN films with different content of nano-sized or micro-sized BN were detected by optical microscopy. As shown in Table 1, the PI2/PI5/BN blend films revealed a microphase separation structure, which consisted of a continuous BN-rich phase (PI2, dark region) and a BN-poor phase (PI5, bright region). It is suggested that the highly connected thermally conductive pathway was formed in the immiscible PI2/PI5/BN blend films. There is no large particle cluster or aggregate of nBN or mBN particles detected for the blended films even when the filler content increased to 25wt.%.

On the other hand, the PI2/BN films showed a homogenous morphology, in which the BN fillers (black spots) individually dispersed in the polyimide matrix. It is also found that the nano-sized BN particles were still uniformly dispersed in PI2 matrix with the BN content increasing, whereas, the micro-sized BN particles became larger because of the aggregation.

Table 1. Optical images of polyimide/BN blend films with different filler content.

BN content (wt.%)	PI2/PI5		PI2	
	nBN	mBN	nBN	mBN
15				
25				

The cross-section of PI2/PI5/nBN blend film containing 25wt% of nano-sized BN was investigated by SEM micrographs. As shown in Fig. 3, the brighter regions correspond to BN-rich phase and the dark region correspond to BN-poor phase were clearly observed. Moreover, the magnified SEM micrographs of the BN-rich phase and BN-poor phase exhibited a rough morphology for the former and a smooth morphology for the latter. As comparison, the PI2/mBN film with 25wt% of filler revealed a uniform structure.

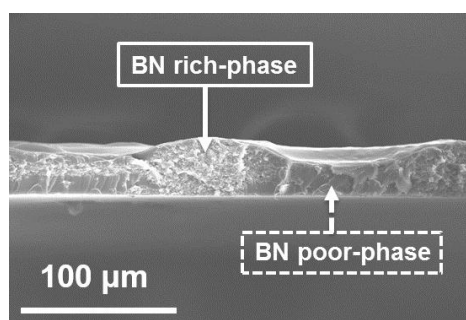


Fig. 3. SEM micrographs of PI2/PI5/nBN(25wt%) blend film cross section

A combination of these results clearly suggests the formation of co-continuous separated structures, in which two phase are separately aligned along the out-of-plane direction to the film plane^[9]. This type of phase separation has been designated as vertical double percolation structure, which is an effective thermal conductive pathway.

3.3 Thermal Conductivity of Polyimide/BN Blend Films

The thermal conductivity of immiscible and homogenous PI/BN blend films with different filler content and particle size were evaluated (Fig. 4). In the case of homogenous PI2/nBN and PI2/mBN films, they exhibited a gradually increase in thermal conductivity with the BN content raising. The PI2/nBN and PI2/mBN with 25 wt.% of BN gave the thermal conductivity values of 0.49 and 0.41 W/m·K, respectively.

In contrast, the immiscible PI/BN blend films displayed an abrupt increasing in thermal conductivity with the incorporation of BN fillers. The PI2/PI5/nBN blend film gave the thermal conductivity value of 1.16 W/m·K, which was 236% of the homogenous PI2/nBN film. The significant improvement in thermal conductivity of immiscible polyimide blend films containing BN fillers was attributed to the existence of vertical double percolation structure, which constructed the effective thermal conductive pathway. The

thermal conductivity of PI2/PI5/nBN are better than PI2/PI5/mBN because of the well dispersion of nano-sized BN.

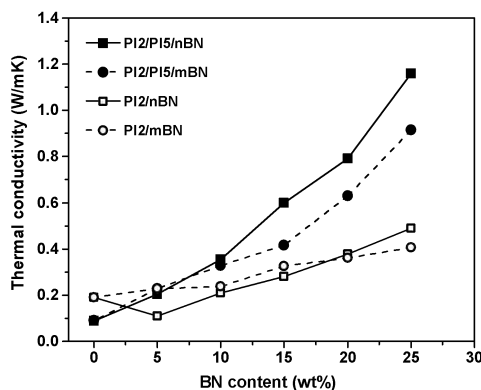


Fig. 4. Thermal conductivity of PI/BN blend films.

3.4 Mechanical Properties of Polyimide/BN Blend Films

The tensile properties of immiscible PI/BN blend films with different filler content and particle size were also investigated and illustrated in Fig. 5.

The blend films revealed a decline trends in tensile strength and elongation at break with the incorporation of BN. The drop in the tensile properties may be attributed to the relatively weak interface between the polymer matrix and BN particles. However, these PI/BN blend films still displayed reasonable tensile properties even for the film with BN content as high as 25 wt.%. The PI2/PI5/nBN and PI2/PI5/mBN films with 25 wt.% of BN content gave the tensile strengths of 49 and 47 MPa, respectively. The tensile modulus of these films still kept around 2-3 GPa no matter the changes of filler content and the particle size.

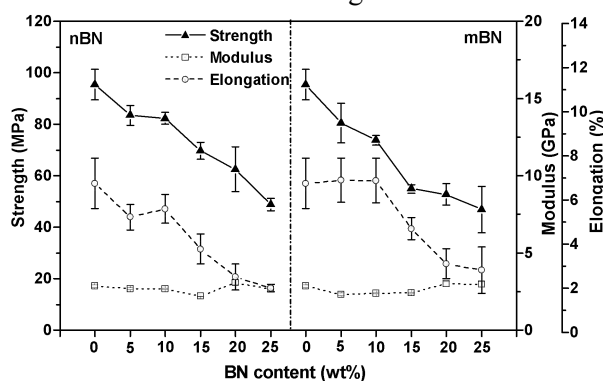


Fig. 5. Tensile properties of PI2/PI5/nBN and PI2/PI5/mBN blend films.

4. CONCLUSIONS

A series of polyamic acids were selected with the help of mesoscopic simulation. The polyimide blends containing PI2(PMDA/ODA) and PI5(6FDA/6FAPB) with equivalent weight ratio showed good balance between separating ability and mechanical property, which was selected for preparing the polyimide blend films containing BN fillers. The thermal conductivity for the immiscible PI/BN blend films with 25 wt.% of nano-sized BN reached as high as 1.16 W/m·K. The significant enhancement in thermal conductivity attributed to the good phase separation of polyimide matrix, which lead the inorganic fillers selectively localized in one continuous phase with high packing density. It is believed that this simple procedure might provide a facile method to design and fabricate high thermally conductive polyimide composite films with low filler mass fraction.

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