The high thermal conductivity composite of PA 6/h-BN prepared by micron mixing in the solution

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Abstract

The polyamide 6 powder was prepared by the liquid phase method, and then mixed with hexagonal boron nitride (h-BN) in a high-pressure homogenizer for micron-level mixing, and finally the composite material is obtained by hot pressing. The thermal conductivity of composites was as high as 1.73 W/(m*K). The results showed that the dispersion of h-BN in the matrix was well and there was no obvious agglomeration in the composite from the scanning electron microscope. Differential scanning calorimetry and X-ray diffraction results showed that h-BN affects the crystalline of polyamide 6 and the thermal stability of the composites was improved. The composite is expected to be used in high thermal conductivity functional plastics.

Keywords: High pressure homogenization; Hexagonal boron nitride; Multilayer structure; Exfoliation; Composite.

1. Introduction:

The thermal conductivity of the material will greatly affect its life, reliability and safety. Therefore, the materials with high thermal conductivity are always the researcher’s pursuit. However, the thermal conductivity of traditional polymer materials is generally low. Hence, the high thermal conductivity composite have been paid great attention by scientists [1-3]. As a kind of good thermal conductive filler, h-BN had been concerned by many researchers [1-4]. As a relatively common engineering plastic, polyamide 6 (PA 6)
had good mechanical properties that make it popular. The preparation of PA 6 composites depends on the
dispersion of fillers, and good dispersion is beneficial to the performance of the composites. A lot of research
had been done on PA 6/h-BN composites mainly on flame retardant properties [1], thermal conductivity [4,5]
and crystallization properties [6,7]. The key to the preparation of PA 6 composites lies in the dispersibility
of the fillers. The well dispersibility is beneficial to the performance of the composites.

The problem of the dispersibility of the filler in the polymer will affect the thermal conductivity of the
composite. Therefore, how to prepare the composite with high thermal conductivity quickly and easily is
still a challenging problem. Recent studies had shown that chemical modification of thermally conductive
fillers such as h-BN could increase the thermal conductivity of composites. For example, exfoliated h-BN
with hydroxylation [8] or sulfonation [9], h-BN filler with three-dimensional network [10], h-BN treated
with silane coupling agent [11], and h-BN loaded with nano silver [12] can be used to improve the thermal
conductivity of the composite. In recent years, the polymer homogeneous solution had been directly modified
in the liquid phase to improve the thermal conductivity of the composites. Na [13] prepared the composite
having a thermal conductivity of up to 3.09 W/(m*K) by adding h-BN to a dissolved polycarbonate (PC)
solution. The well mixing of materials was the key point to solve the dispersibility of fillers. High pressure
homogenization (HPH) as a new type of micro-nano material preparation technology had received more
and more attention from researchers [14-17]. The HPH technology can be used to prepare the polymer
micropowder, and then the micro-level uniform mixing with the filler can be carried out on the basis of this
technology, thereby obtaining a composite material with good dispersion.

In this paper, PA 6 powder was prepared by reverse drop addition method. On the basis of this, PA 6/h-BN
composites were prepared by high pressure homogenization method. The results demonstrated that the
addition of h-BN affected the crystallization and melting properties of PA 6. SEM characterization showed
that the dispersion of h-BN in PA 6 was well, and its thermal conductivity is up to 1.73 W/(m*K).

2. Experimental section

The schematic diagram of the whole experiment was shown in Fig. 1.

2.1 Materials

PA 6 was purchased from Jisheng industrial Co., Ltd. and other chemical reagents such as formic acid and
ethanol were purchased from Tianjin Fuyu Technology Co., Ltd. All laboratory materials were used directly
without further purification.

2.2 The preparation of PA 6 micropowder

PA 6 micropowder was prepared according to following procedure. In a typical experiment, 200 mL of good
solvent formic acid was added to the three-necked flask with mechanical stirring under 80, and then 10 g of
PA 6 particles were added into the solution slowly. The above process was kept with constant temperature
and stirring rate until the nylon particles were completely dissolved. Then, the preliminary nylon powder
can be obtained by slowly adding 400 mL of bad solvent ethanol to the above mixture through constant
pressure drop funnel for precipitation. It should be noted that the control rate of the drop was 60 drops/min
in the whole process. The above mixture containing all solvents was suction filtered, and washed with a
large amount of water until the final solution was neutral. Finally, the fine nylon powder could be prepared
and easily dispersed in water.

2.3 Composite of PA 6/h-BN prepared by micron mixing in the solution by high-pressure
homogenization

The above water-dispersed PA 6 powder and h-BN powder were mixed in a high-pressure homogenizer with
certain pressure (100 MPa) for high-pressure homogenization with refining and exfoliating treatment. The
homogenization process was on the one hand peeling off h-BN to fewer layers. On the other hand, it was a
micron-level mixing of PA 6 and h-BN. The resulting mixture was filtered and dried. Then the dried mixed
powder material was placed in a mold and subjected to hot pressing treatment at 240°260°C to obtain
a circular sheet of the specification which was used for measurement of thermal conductivity and other characterizations.

2.4. Characterizations

Thermal conductivity is a common test method, testing its density, specific heat and thermal diffusivity through a laser flash technique (LFA 467 NanoFlash, Netzsch), and with the sample size of 12.7 mm small wafer. The scanning electron microscope (SEM) images of PA 6/h-BN composites were taken by using a field-emission SEM (X) with 10 kV accelerating voltage. Fourier transform infrared (FTIR) spectra were carried out on a Frontier MIR Perkin Elmer spectrometer. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) results were recorded on a TG instruments analyzer under N2 atmosphere and with a heating rate of 10 °C/min. The XRD patterns were performed by X-ray power diffraction (X) with Cu Kα radiation (λ = 1.5418 Å).

Fig. 1 Schematic illustration of composite of PA 6/h-BN prepared by micron mixing in the solution

3. Results and discussion

The whole schematic illustration was shown in Fig 1. As shown in Fig. 2(a), the thermal conductivity of PA 6/h-BN composites increased linearly with the increase of h-BN content. When the content of h-BN was 40%, the thermal conductivity of composites was as high as 1.73 W/(m*K). The composite exhibited a high thermal conductivity mainly due to the micron-scale mixing process of PA 6 and filler h-BN.

![Thermal conductivity of PA 6/h-BN composites with different h-BN loadings](image)

Fig. 2 (a) Thermal conductivity of PA 6/h-BN composites with different h-BN loadings, (b) TG curves a of prepared samples

The Thermogravimetric (TG) analysis curve showed that the composite had good thermal properties. In the Fig 2(b), the composite curves were shifted to the right relative to the raw PA 6. The characteristic decomposition temperature of the composite material was significantly improved by T5%, T10% and T50%.
In particular, the semi-decomposition temperature was increased from 474.3°C for pure materials to 492.8°C (40% for h-BN content), with an increase of nearly 19°C. The maximum weight loss temperature increased from 467°C to 480°C. It can be seen from the residual carbon content that this was consistent with the content of the filler in the composite. Therefore, the addition of h-BN can significantly improve the thermal properties of the composite.

The addition of h-BN could affect the crystallization, melting and other properties of the composite. As shown in the Fig 3(a), it was the differential scanning calorimetry (DSC) cooling curve of the composite materials with different contents of h-BN. The crystallization temperature (Tc) of pure PA 6 is 189.2 °C, and the Tc of the composite materials was improved, mostly concentrated between 195 and 197°C. Among them, when the content of h-BN was 40%, the Tc raised to 197.0°C.

Fig. 3 Characterization of fabricated raw materials and composites: (a) DSC curves indicating melting temperature, (b) DSC curves indicating crystallization temperature, (c) XRD patterns and (d) FTIR spectrums of prepared materials

Fig. 3(b) showed the melting temperature (T_m) of pure PA 6 was 221.8 °C, and the T_m of the composite was reduced to a small extent, both decreasing by 2-3°C. This indicated that the addition of h-BN caused the composite to enter the molten state relatively quickly. In Fig. 3(c), the X-ray diffraction (XRD) figure demonstrated that the main peak of the X-ray diffraction peak of the pure h-BN raw material was located at 26.7°, and the other weaker diffraction peaks are 41.6, 43.9, 50.2 and 55.2°. The main diffraction peaks of PA 6 pure material were located at 20.1 and 23.3° which attribute to the alpha crystal form. The diffraction peaks of the h-BN and PA 6 raw materials appeared in the composite material, and the crystal structure did not change much. FTIR characterization (Fig. 3 (d)) also showed that the composites exhibited characteristic absorption peaks of PA 6 and h-BN. The main absorption peak of h-BN was located at 810 cm⁻¹ which attributed to the out-of-plane bending vibration absorption peak of B-N-B, and the peak of 1383 cm⁻¹ that belongs to the in-plane stretching vibration absorption peak of B-N which partially overlaps with the PA 6 raw material and its composite materials, but the absorption peak near 810 cm⁻¹ appeared in the composite material, indicating that h-BN exists in the composite material. In addition, as the h-BN content increased, the absorption peak here would be enhanced. It can be seen from the scanning electron microscope (SEM)
Fig. 4 that there was no obvious phase separation of the composite material subjected to high pressure homogeneous mixing. Even when the amount added reaches 40%, it can be uniformly dispersed in the PA 6 matrix. The black circle in the picture indicated the dispersion of h-BN in the matrix.

![Image](image1.png)

In summary, PA 6 fine powder can be precipitated by adding a poor solvent in homogeneous solution of formic acid. After the preliminary mixing of the PA 6 micropowder and the conductive filler h-BN, they were placed in a high pressure homogenizer and carried out under a homogenizing pressure of 100 MPa. On the one hand, the homogenization process will reduce the number of layers of h-BN to a certain extent; this can increase the volume fraction of h-BN in the composite, making h-BN more widely distributed in the composite. On the other hand, PA 6 and h-BN can be uniformly mixed on the micron level. Therefore, the preparation method can make the dispersibility of the filler h-BN in the composite material well, and the thermal conductivity of the composite material was well improved to 1.73 W/(m*K).

4. Conclusion

In this work, we describe a preparation method for preparing high thermal conductivity PA 6/h-BN composites. The process uses high pressure homogenization to exfoliate h-BN, and the PA 6 fine powder and h-BN are well mixed at the micron level. The resulting composites have a thermal conductivity up to 1.73 W/(m*K). Various characterizations indicated that the addition of h-BN affects the crystallization and melting properties of the composite. The filler h-BN has good dispersibility in the composite and the composite exhibits good thermal stability.

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Reference
