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Thermal and Mechanical Properties of Polypropylene/ Boron Nitride Composites

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Abstract

The purpose of this study is to improve thermal conductivity and properties of polypropylene (PP) by adding functionality fillers. Boron nitride (BN) was used for improving the thermal conductivity of polymers. Two types of BN with different particle sizes were used. In addition, two types of PP with different viscosities were used as the polymer matrix. The thermal conductivity, storage modulus and loss modulus increased with the content of BN. The thermal conductivity of PP can be effectively enhanced by adding BN with large particles. Moreover, the melting temperature and crystallization temperature of PP/BN composites were larger than those of neat PP. The degree of crystallization of PP increased with BN. The effect of BN with small particles on the crystallization of PP was slightly stronger than that of BN with large particles. From the SEM observation, the agglomeration of BN with small particles was locally observed. In contrast, BN with large particles dispersed well in the PP matrix. This study found that BN with large particles effectively enhanced the thermal and properties of PP/BN composites. In addition, the above properties were independent of the matrix viscosity.

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1. Introduction

The electrical industries are rapidly growing, and the need for electrical insulators, which are used to support electrical conductors and electrical devices, is increasing at the same time. Certain materials, such as glass, paper, air, polymers, rubber, and wood, are very good electrical insulators. The commonly used

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polymers, such as polyamide (PA), polyethylene (PE), polypropylene (PP), polyvinylidene fluoride (PVDF), polystyrene (PS), and epoxy, provide significant economic benefits in comparison with other materials as a result of their light weight and low costs [1]. However, these polymers have low thermal conductivities. Therefore, some researchers have worked to improve the thermal conductivity and electrical insulation of polymers by adding ceramic fillers, such as boron nitride (BN), alumina (Al_2O_3) [2], aluminum nitride (AlN) [3,4], mica, glass fiber, and zinc oxide (Zn_2O_3) [5].

Boron nitride (BN) has been widely used in the thermal management industry for years. BN is a good lubricant and abrasive, and it has a high thermal conductivity, high electrical resistance, and high temperature resistance. The common structures of BN are the hexagonal (hBN) and cubic (cBN) crystal structures. The structure of hBN is more stable than that of cBN [6]. The in-plane thermal conductivity is greater than $300 \text{ W}/(\text{m} \cdot \text{K})$, whereas the through-plane thermal conductivity is approximately $3 \text{ W}/(\text{m} \cdot \text{K})$. Polyphenylene sulfide (PPS) has been used to demonstrate the improvement in the thermal conductivity and mechanical properties by adding BN filler. The result supported that it is possible to increase up to 60wt% boron nitride with particle size of less than $45 \mu\text{m}$ which effectively enhanced thermal conductivity, impacting tensile strength or impact strength whereas strain at break is dropped [7]. As high-density polyethylene (HDPE) was added boron nitride at various contents. The result illustrated that the network structure of BN was formed at a high BN content in an HDPE matrix, and the dispersion state of BN changed with the BN particle size [8]. The effect of content of micro or nano size BN particle was studied on thermal and mechanical properties, and morphology of silicone rubber. BN was dispersed well in silicon rubber matrix while agglomerate was shown in some areas. Commonly, to add BN particles in silicone matrix reduces tensile strength and strain at break, whereas it increases modulus, hardness, and thermal conductivity. Nano size filler significantly contributes to the improvement of tensile strength of composites as compared with micro size filler at same content. However, the nano size filler does not promote thermal conductivity. The apparent aspect ratio of filler enhances high thermal conductivity [9].

Polypropylene (PP) is a balanced polymer from the point of the view of the physical and mechanical properties, very good electrical insulator, and also simple fabrication with a low thermal conductivity. The thermal and mechanical properties of polypropylene could be developed by melt compounding with particle and fibrous filler [10]. In both industry and research, it is interesting to consider experimental results dealing with developing properties of composites.

The purpose of this study is to improve thermal conductivity of PP by adding functionality filler. BN filler was selected as the functionality filler. PP/BN composites were prepared by melt compounding which is a useful mixing method in the industry. In addition, we discuss the effect of dispersion state of BN on thermal and other properties of PP/BN composites.

2. Experimental

2.1. Material

Polypropylene (PP) was supplied by Sumitomo Chemical Co., Ltd., Japan. Two types of PP, low-viscosity PP (PP-L, Melt flow rate (MFR) = 26-29 g/10 min) and high-viscosity PP (PP-H, MFR = 7-8 g/10 min), were used in this study. Two types of BN with different particle sizes, such as small particle (BN-s, the average particle sizes 1-2 μm) and large particle (BN-l, the average particle sizes 7- 10 μm were added to PP matrices), were added to PP. They were produced by Showa Denko K. K., Japan. Figure 1 shows the SEM photographs of both BNs. The both BNs form the scale-like particles.

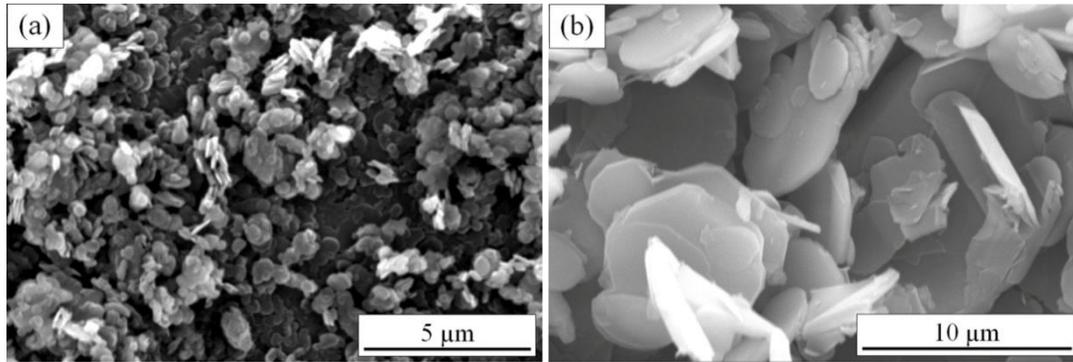


Fig. 1. SEM photograph of filler particles: (a) small particles (BN-s, particle size 1-2 μm)
(b) large particles (BN-l, particle size 7-10 μm)

2.2. Preparation of PP composites

PP/BN composites were mixed by using a batch kneader at a barrel temperature of 250 °C. The mixing time was 15 min. All blend ratios described related to percentage by volume. The loadings of BN were 15 vol%, 21 vol% and 29 vol%. Materials were dried under vacuum at 80 °C for at least 24 h before mixing. The mixing sample was the sheet molded by compression molding at 200 °C, and compression pressure 19.6 MPa for characterizing the properties of PP composites.

2.3. Testing

Differential scanning calorimetry (DSC) was carried out using an apparatus (DSC model 6220 produced by Seiko Instruments) for the characterization of the composites. Samples were sealed in an aluminum pans. The samples were heated from 25 to 200 °C at the heating rate of 10 °C/min. After that, they were cooled to – 40 °C at the cooling rate of 10 °C/min. During this period of time, matrix crystallization was completed and the samples were further heated from – 40 to 200 °C at the heat rate of 10 °C/min in order to obtain the melting endotherms.

The thermal conductivity was measured with the hotwire method using the QTM-500 by Kyoto Electronics Manufacturing Co., Ltd., Japan. The sample for measurement of thermal conductivity was the sheet molded by press molding. The sample size was 170x120x0.5 mm. In addition, we used reference plates and software for measuring thermal conductivity of sheet type samples. In this study, the orientation of BN can be assumed as randomness because the samples were molded by press molding.

The dynamic mechanical analysis (DMA) was measured using the E400-TYPE-DVE (UBM Co., Ltd., Japan). The temperature range was – 40 to 165 °C. The sampling frequency was 1 Hz (6.28 rad/s) and heating rate 2 °C/min in tension mode. In this study, storage modulus and loss modulus of PP composites were studied at 25 °C.

Scanning electrical microscopy (SEM) was carried out by using the instrument S-2600H. The instrument was produced by Hitachi, Co., Ltd., Japan, in order to investigate the dispersion behavior of BN in the composites.

X-ray diffraction (XRD) was measured by using the SWXD-FK manufactured by Ringaku Corporation, Japan. The wide-angle X-ray spectrum of the specimen was inspected using Cu-K α radiation. The XRD parameters were 40 kV, 40 mA for the X-ray source under vacuum in the 2θ scan range of 10° to 50° and a scan rate of 0.2°/s at room temperature.

3. Results and discussions

3.1. Thermal conductivity

Firstly we will discuss the thermal conductivity of PP/BN composites. Figure 2 shows the thermal conductivity of the composites as a function of the BN contents. Obviously, the thermal conductivity increased with BN contents. And the thermal conductivity of PP/BN composite is almost independent of the melt viscosity of PP at various BN content. The thermal conductivity of PP/BN-l composite was larger than that of PP/BN-s one at the same BN content. This result is a preserved one. In addition, the increasing rate of thermal conductivity as a function of BN content in case using large size of BN (BN-l) became large in high BN contents

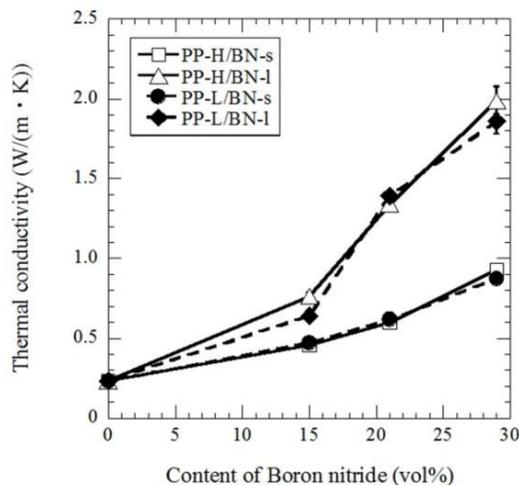


Fig. 2. Thermal conductivity as a function of BN content for each PP/BN composite.

3.2. Morphological investigation

The thermal conductivity of PP/BN composites would depend on the dispersion state of BN in the composites. Then, we will discuss the dispersion state of BN in the composites by using SEM photographs.

Figure 3 shows the SEM photographs on the cutting surface of the composites after cooled by liquid nitrogen. The dark part and the white one represent the PP and BN, respectively. From Fig. 3. (a), for PP-H/BN-s composite at BN content of 15 vol%, it is observed clearly that the small particles agglomerated and non-uniformly dispersed in the PP matrix. In contrast, in Fig. 3. (c), for the PP-H/BN-l composites at BN content of 15 vol%, the large particles were uniformly dispersed and were well connected with other particles. The difference of the connection of BN particles between BN-l using case and BN-s using case would contribute the thermal conductivity of the composite. At the high content of BN (the content of 29 vol%) shown in Figs. 3. (b) (for PP-H/BN-s) and (d) (for PP-H/BN-l), the BN filler displayed closely packed particles in the PP matrix. It should be noted that at a high BN content, the denseness of packing particles contributed to improve connections between the large particles. As a result, the increased BN network structure caused a dramatic increase in the thermal conductivity of the composites. In addition,

the cracked particles of the BN in the PP matrix is shown in Fig. 3. (d) (for PP-H/BN-I at content of 29 vol%). This would be occurred by filler friction in the melt compounding process.

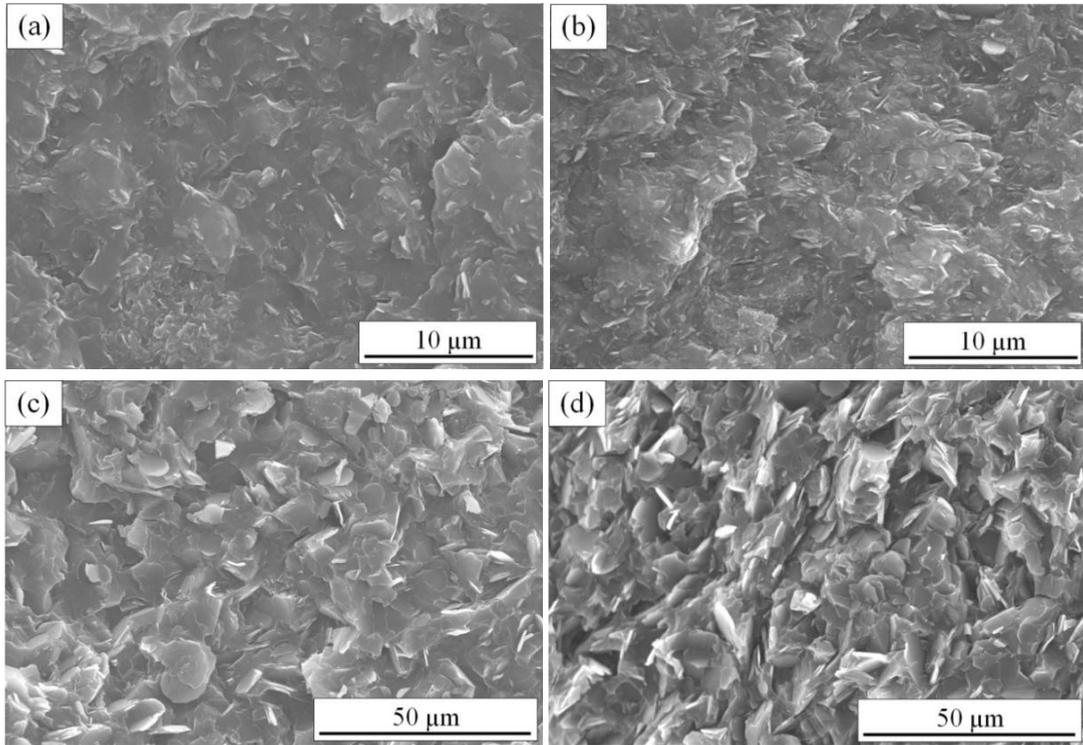


Fig. 3. SEM photographs of PP/BN composites on the cutting surface of the composites after cooled by liquid nitrogen.

(a) PP-H/BN-s at 15 vol%, (b) PP-H/BN-s at 29 vol%, (c) PP-H/BN-I at 15 vol%, and (d) PP-H/BN-I at 29 vol%.

3.3. Dynamic mechanical analysis

Next, we will discuss dynamic mechanical analysis results. From these results, we focused the results at a solid state. Figure 4 shows the dynamic mechanical analysis data of the composites with different contents of BN at 25 °C. The storage modulus and loss modulus increased with the BN content for each composite. The correlativity between the modulus and melt viscosity of PP could not be clear. On the contrary, the storage and loss moduli of PP/BN-I composite were totally larger than those of PP/BN-s one, especially at high BN content. In addition, large particles significantly become increasing the storage modulus and loss modulus of composites. This tendency would agree with thermal conductivity at high BN content. This implies that the network structure of BN in PP/BN composite would have an influence on the solid mechanical properties.

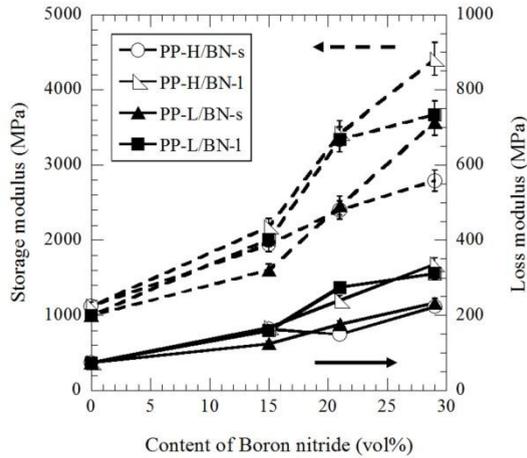


Fig. 4. Storage modulus and loss modulus as a function of BN content for various PP/BN composites at temperature of 25 °C.

3.4. Thermal analysis

The heat characteristics of polymer composites are also important for developing a new material. Then, we will discuss the thermal analysis results measured by DSC. Figure 5 shows DSC curves of neat PP and PP/BN composites at cooling in the neighborhood of the crystallization temperature. The crystallization temperature (T_c) shown by the peak increases and the crystallization enthalpy (ΔH_c) shown by the area of the peak decreases with an increase of BN content in case using both PP and BN. The existence of BN in the composites would block the crystallization of the matrix PP. In addition, the BN particle size has a little influence on the crystallization temperature. The crystallization temperature of PP/BN-s is larger than that of PP/BN-l except for the case of PP-H matrix at BN content of 29 vol%. The crystallization temperature that started at a high temperature resulting in the small particle may rapidly release energy in the form of heat.

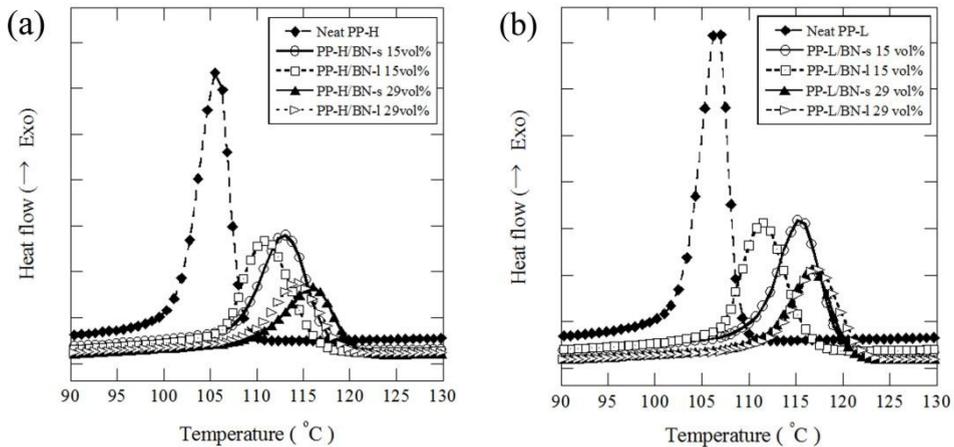


Fig. 5. DSC curves of neat PP and PP composites as various amounts of filler content at cooling in the neighborhood of the crystallization temperature (T_c). (a) PP-H matrices and (b) PP-L matrices.

Figure 6 shows the DSC curves of neat PP and PP/BN composites at second heating in the neighborhood of the melting temperature. The melting temperature (T_m) shown by the peak increases and the melting enthalpy (ΔH_m) shown by the area of the peak decreases with an increase of BN content in case using both PP and BN. The existence of BN in the composites would also block the melting of the matrix PP. In addition, the BN particle size has a little influence on the melting temperature. The melting temperature of PP/BN-s is larger than that of PP/BN-l. The SEM photographs shown in Fig. 3 indicates a non-uniform polymer matrix in which some areas illustrated do not contain filler (small particle regions), whereas the large particles were uniformly distributed in the polymer matrix. Then, PP surrounding the large particle was uniform. In addition, the temperature for melting the polymer matrix was lower than the case using small particles. It is probably to say that the filler dispersion is influenced by the melting temperature.

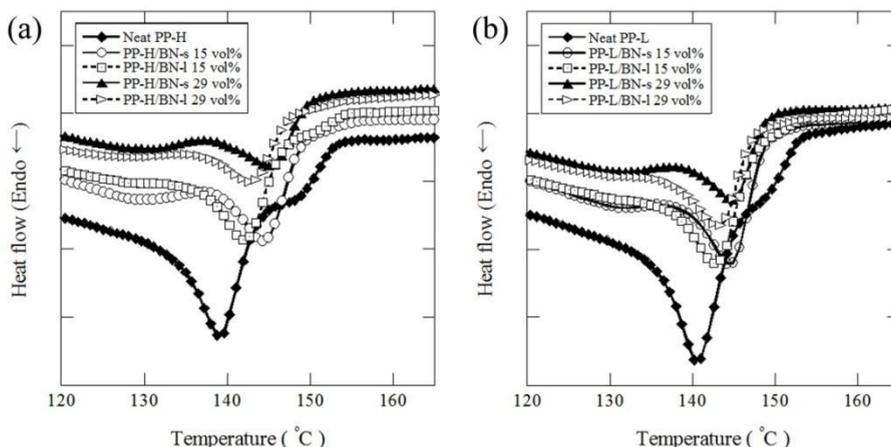


Fig. 6. DSC curves of neat PP and PP composites as various amounts of filler content at second heat in the neighborhood of the melting temperature (T_m). (a) PP-H matrices and (b) PP-L matrices.

A large amount of crystallinity in composites was significant to increase modulus and stiffness of materials. In addition, we tried to estimate the degree of crystallization X_c of the PP composites from DSC data by using Eq. (1) [11]:

$$X_c (\%) = \frac{\Delta H_m / \phi_{PP}}{\Delta H_m^0} \times 100 \quad (1)$$

where ΔH_m^0 is melting enthalpy of PP crystal (208 J/g) [12] and ϕ_{PP} is PP content in the composite.

The degree of crystallization as a function of BN content is shown in Fig. 7. This results illustrated that the degree of crystallization of PP/BN composites seem to increase as compared with neat PP. Since BN fillers promoted the crystallization of PP by heterogeneous nucleation, the crystallization temperature was started at a high temperature and the amount of time for crystal formation increased. Therefore, it can be predicted that the modulus of PP composites increased with adding BN filler.

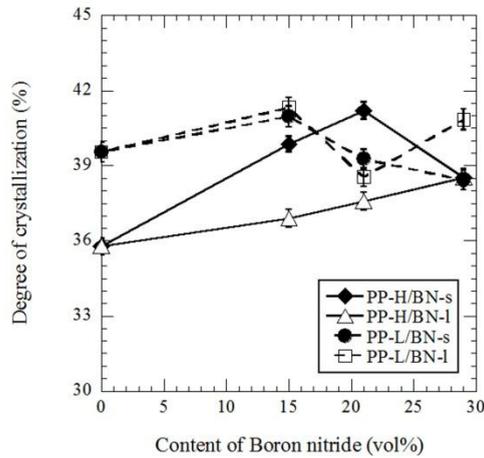


Fig. 7. Degree of crystallization (%) as a function of filler content for the PP-H and PP-L matrices.

3.5. X-ray diffraction

We will consider the mechanical properties of PP/BN composites. X-ray diffraction (XRD) measurement is necessary to study the internal structure of the composites because PP used as the matrix is the crystallinity polymer. Figure 8 shows XRD patterns of PP-H/BN-l composites and neat PP-H. A sharp peak at 27° represents hexagonal boron nitride in the composite. In addition, the peak location of PP neat is almost the same as that of PP/BN composite. The tendency of intensity peak of PP would coincide with the degree of crystallization by estimating from DSC data. It could be explained that BN filler tends to improve crystallinity of PP. In addition, this result implies that BN filler mainly contributes to mechanical properties of PP/BN composite in this study.

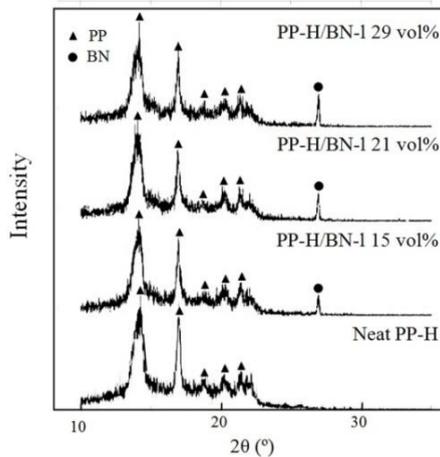


Fig. 8. XRD patterns of PP-H/BN-l composites.

4. Conclusion

In this study, we selected Boron nitride (BN) as a functionality filler for improving thermal conductivity of Polypropylene (PP). PP/BN composites were prepared by melt compounding. We discussed the properties and characteristics of PP/BN composites. Results obtained are follows.

1) The thermal conductivity of the composites increased with BN content. And the thermal conductivity of PP/BN composite using BN with large size is larger than that using BN with small size. The network structure of BN would be typically easy to be created by using BN with large size.

2) According to DMA results, the storage modulus and loss modulus increased with BN content for each composite. And, the storage modulus and loss modulus of PP/BN composite using BN with large size were totally larger than that of PP/BN composite using BN with small size, especially at high BN content.

3) According to DSC measurement results, the melting and crystalline temperature increased with BN content. The melting and crystallization enthalpies tended to decrease when the BN content was increased.

4) As mentioned above, this study found that large particles produced well-dispersed and densely networked structures. On the contrary, the thermal and mechanical properties were independent of the viscosity of the polymer.

Acknowledgements

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