

보론 나이트라이드와 탄소나노튜브로 충전된 실리콘 고무의 열전도도 향상

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Improvement of Thermal Conductivity of Poly(dimethyl siloxane) Composites Filled with Boron Nitride and Carbon Nanotubes

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초록: Poly(dimethyl siloxane)(PDMS, 실리콘 고무)의 열전도도 향상을 위하여 보론 나이트라이드와 탄소나노튜브를 열전도성 충전제로 사용하였다. 보론 나이트라이드의 함량은 0에서 100 phr로 증가시켰으며, 탄소나노튜브의 함량은 보론 나이트라이드의 함량을 100 phr로 고정시킨 상태에서 0에서 4 phr로 증가시켰다. 실리콘 고무 복합재료의 열전도도는 보론 나이트라이드 함량의 증가에 따라 증가하였으나, 탄소나노튜브를 추가로 첨가하더라도 열전도도 향상에 대한 효과는 미미하였다. 100 phr 함량의 보론 나이트라이드 함량에 탄소나노튜브를 충전 시 복합재료의 열분해가 가속화되는 예상치 못한 결과를 얻었다. 이를 해석하기 위하여 Horowitz-Metzger 방법을 이용하여 열분해 활성화 에너지를 계산하였다. 또한 보론 나이트라이드/탄소나노튜브가 충전된 실리콘 고무 복합재료의 경화거동, 전기저항 및 기계적 물성을 연구하였다.

Abstract: In order to enhance the thermal conductivity of poly(dimethyl siloxane) (PDMS), boron nitride (BN) and carbon nanotubes (CNTs) were incorporated as the thermally conductive fillers. The amount of BN was increased from 0 to 100 phr (parts per hundred rubber) and the amount of CNTs was increased from 0 to 4 phr at a fixed amount of the boron nitride (100 phr). The thermal conductivity of the composites increased with an increasing concentration of BN, but the incorporation of CNTs had only a slight effect on the enhancement of thermal conductivity. Unexpectedly, the thermal degradation of the composites was accelerated by the addition of CNTs in 100 phr BN filled PDMS. Activation energy for thermal decomposition of the composites was calculated using the Horowitz-Metzger method. The curing behavior, electrical resistivity, and mechanical properties of PDMS filled with BN and CNTs were investigated.

Keywords: poly(dimethyl siloxane), thermal conductivity, boron nitride, carbon nanotubes, thermal degradation.

Introduction

Currently, electronic devices have more functions and require higher performance in ever smaller sizes, and this causes heat accumulation in the devices because semiconductors such as central processing units (CPUs) with a fast clock rate are inevitably used. As reported by Intel Cooperation, a small difference in the operating temperature in the order of 10-15 °C can result in a two-fold reduction in the life-

time of electronic devices.¹ This explains why the heat dissipation of electronic devices is so important.

Metal oxides, metal, and ceramic powders are frequently used as thermally conducting fillers in polymer matrices. The most widely used thermally conductive fillers such as aluminum, diamond, copper, multi-walled carbon nanotubes (MWCNTs), and graphite have thermal conductivity of about 247, 2000, 398, 3000, and 25-470 W/m·K, respectively.²⁻⁶ Many researchers have demonstrated the enhancement in the thermal conductivity of polymer composites filled with various thermally conductive fillers. Some representative examples are as follows. Kim *et al.* reported a linear increase in the thermal

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conductivity of water and ethylene glycol containing boron nitride (BN), zinc oxide (ZnO), and titanium dioxide.⁷ Kou *et al.* explored the effect of the particle size of BN on the thermal conductivity of silicone rubber. The thermal conductivity of the prepared composites was improved with BN particles with a smaller diameter at the same volume fraction.⁸ Goh *et al.* prepared Al₂O₃ and ZnO filled silicone rubber in which approximately 70% of the thermal conductivity enhancement was achieved at 10 vol% of the filler loading.⁹ The improvement of the thermal conductivity has been explored for various systems including BN in polyethylene, ZnO in silicone rubber, metal oxides in ethylene vinyl acetate (EVA), modified ZnO in EVA, and ZnO in ethylene glycol.^{10,11}

Due to the excellent thermal conduction behavior of CNTs, they are also used to enhance the thermal conductivity of polymeric composites not only for improving thermal conductivity but also electric conductivity and mechanical properties.^{12,13} CNTs have a unique one-dimensional structure that enables the composites filled with CNTs to have low percolation threshold concentrations.^{14,15} Due to these characteristics, composites filled with CNTs show the enhancement of thermal conductivity even at low concentrations.^{16,17} Fan *et al.* reported a significant effect of the alignment of CNTs on thermal conductivity. When CNTs were aligned in a single direction, the composite material exhibited much increased thermal conductivity.¹⁸ The length effect of CNTs has also been explored. If the CNTs were too long, the CNTs coiled within the polymer matrix and the CNTs could not efficiently transfer the heat in the matrix. Furthermore, when the length of the CNTs was too short, the CNTs could not efficiently transfer the heat. The thermal conductivity of polymer composites incorporated with CNTs was the highest for CNTs with 1 μm in length.¹⁹ It has also been found that the thermal conductivity of pristine CNTs-loaded composites was higher than that of acid-purified CNTs-filled composites.²⁰ The effects of the purification and dispersion of CNTs have been investigated by several researchers.^{21,22}

However, the thermal conduction behavior of polymer composites using dual-fillers comprising ceramic fillers and CNTs has been rarely reported. In this work, BN and CNTs were incorporated in poly(dimethyl siloxane) (PDMS; silicone rubber), and electrical conductivity, thermal conductivity, curing behavior, mechanical properties were investigated.

Experimental

Materials. PDMS ($M_w = 674000$ g/mol, 2.48 wt% vinyl

group) was supplied by KCC Co. (Korea). CNTs (multi-walled CNTs, Hanwha Nanotech Co. Ltd. (Korea)) synthesized via a chemical vapor deposition (CVD) method had more than 95% purity. The diameter of the CNTs was 10-50 nm and the length was 10-50 μm . The aspect ratio was approximately 1000. 2,5-Bis(*tert*-butylperoxy)-2,5-dimethylhexane (DHBP; Akzo Nobel (Netherlands)) was used as a curing agent for curing PDMS. Hexagonal boron nitride (h-BN) powder purchased from Momentive Performance Materials (10 μm , USA) with a thermal conductivity of 121 W/m·K was used without any pre-treatment.

Compounding. The compounding of PDMS composites was accomplished using a planetary mixer (PTD-001, DNTEK Co. Ltd., S. Korea) and a two-roll mill. First, 100 g of PDMS was put into the chamber of the planetary mixer. Before loading the fillers, the appropriate amount of the pristine CNTs was mixed with BN for the distributive mixing. Then one third of the filler was added to the chamber three times at every 30 min at 30 rpm. After the incorporation of all the fillers, the rotation speed of the impeller was increased from 30 to 100 rpm, and then kept for 3 h at room temperature. After the additional mixing at 30 rpm for 1 h, the compound was discharged and roll-milled for 10 min prior to vulcanization. The compounded PDMS was additionally roll-milled with 1 phr DHBP. After incorporating the curing agent, the uncured compound was placed in the mold and cured at 170 °C for 15 min using a hot press. The pressure of the press was held at 9.8 MPa. The experimental formulation of the PDMS/BN/CNTs nanocomposites is presented in Table 1.

Characterization. A scanning electron microscopy (SEM) (S-4300, Hitachi) was used to observe the morphology of the prepared composites. To investigate the dispersibility and wettability of the CNTs and BN in the matrix, the prepared PDMS

Table 1. Formulation of Boron Nitride (BN) and CNTs Incorporated PDMS Composites

Code	PDMS	CNTs	BN	Curing agent
B5	100	0	5	1
B10	100	0	10	1
B20	100	0	20	1
B50	100	0	50	1
B100	100	0	100	1
BC 100-1	100	1	100	1
BC 100-2	100	2	100	1
BC 100-4	100	4	100	1

(unit: phr)

composite was cryogenically fractured. The thermal conductivity of the prepared silicone sheets was measured using a QTM-500 (Kyoto Electronics, Japan). The electrical sheet resistivity was measured using a Loresta-GP MCP-T610 equipped with an ASP probe (Mitsubishi Chemical Corp., Japan). Curing tests were performed on a rubber process analyzer (RPA 2000, Alpha Technologies, USA) by following ASTM D6204-99. To remove the adsorbed water in the compounds, the uncured compounds without the curative were dried at 60 °C for 24 h in a vacuum oven prior to the cure test. It is noted that the adsorbed moisture was vaporized during the measurement in the hot biconical die, which resulted in misleading data. A thermogravimetric analysis was performed at a heating rate of 20 °C/min in a nitrogen atmosphere on a Q-50 (TA instrument, USA). The activation energy of the composites was calculated using the following equation:

$$\ln \ln \frac{W_o - W_t^f}{W - W_t^f} = \frac{E_{ac} \theta}{RT_s^2} \quad (1)$$

Eq. (1) for calculating the activation energy will be discussed in the next section. The mechanical properties of the composites were measured on an Instron 5569 system by following ASTM D412. Five Type 1 dumbbell-shaped specimens

were tested for each composite at the grip separation speed of 500 mm/min.

Results and Discussion

Figure 1 shows the cryogenically fractured cross section of the prepared 100 phr BN/PDMS and 100 phr BN/4 phr CNTs/PDMS composites at different magnifications. Hexagonal BN particles have an irregular shape and broad size distribution. The average diameter of the BN particles was approximately 10 μm. The shape and size distribution of the thermally conductive filler are very important factors in predicting the thermal conductivity of the polymer composites.^{2,3} They affect not only the filler-filler contact area which provides the pathway to transfer heat but also the critical concentrations for the site percolation.^{2,3} The critical concentration for the percolation of cubical particles in polymer matrices is known to be around 30 vol%. The 100 phr BN incorporated PDMS composite had a filler concentration higher than 30 vol%, so that dense packing of the BN fillers in PDMS was achieved. In Figure 1(a), BN particles are horizontally aligned against the applied pressure during the curing process. The horizontally aligned BN facilitated the heat transfer, and therefore the in-plane thermal con-

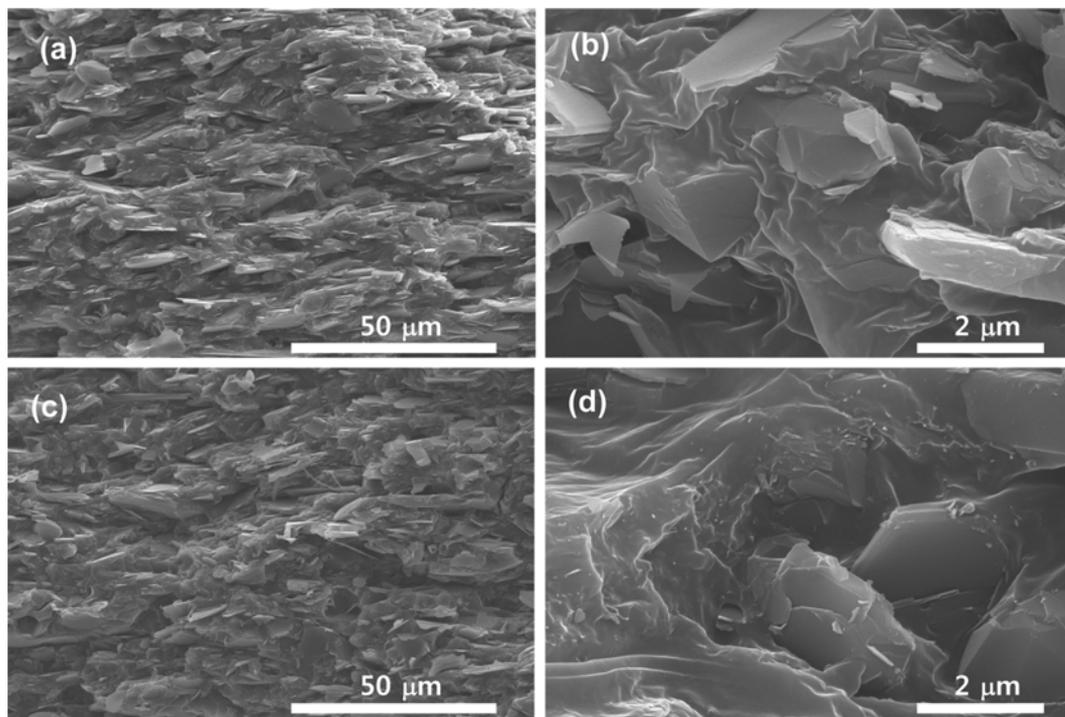


Figure 1. SEM microphotographs of cross-section of 100 phr BN incorporated PDMS at (a) low; (b) high magnification, and cross-section of the composites with 100 phr BN and 4 phr CNTs at (c) low; (d) high magnification.

ductivity of the composites was greatly increased. Dense packing of the thermally conductive filler in the matrix is very important because it provides an effective pathway for phonon movement in an insulator. Figure 1(b) shows the morphology of the wettability between BN particles and PDMS. Since BN and PDMS do not exhibit strong interactions, protruding BN particles are clearly seen within the fractured PDMS cross-section. Figure 1(c) and (d) show the morphology of the cryogenically fractured composite with 4 phr CNTs/100 phr BN at different magnifications, respectively. In Figure 1(c), BN was horizontally aligned and the dispersed CNTs can be found in Figure 1(d). Even though the CNTs were incorporated without a proper surface treatment, the CNTs in the composite achieved excellent dispersion in the PDMS matrix. The high shear effect and the ball-milling effect caused by the BN particles complementarily promoted the dispersion of CNTs.

For measuring the curing properties of the composite, a rubber process analyzer (RPA 2000) with a biconical die was used. Figure 2 revealed that the maximum torque of the composites was proportional to the concentration of BN. Due to the reinforcing effect of BN particles in various polymer nanocomposites,²⁴ the maximum torque of the composites was naturally increased. In Figure 2, reversion, that is, the reduction in torque with time, was not observed for a prolonged time span because the BN-filled PDMS had excellent thermal stability at a high temperature. In this experiment, the T'10 (the time to reach 10% cure of the maximum torque) decreased with an increasing amount of the BN to 100 phr. That means that the curing took place faster with a high BN content since the heat

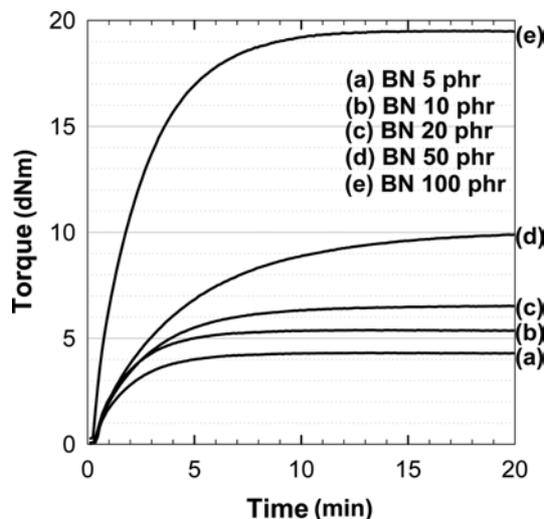


Figure 2. Cure curves of 5, 10, 20, 50, and 100 phr BN incorporated PDMS composites at 170 °C.

supplied from the surface of the composites easily penetrated into the center of the composites due to the enhanced thermal conductivity of the BN-filled PDMS composites. Eventually, the crosslinking reaction became faster, resulting in the reduction in T'10.

Figure 3 illustrates a hot-wire method for measuring the thermal conductivity of the materials. A QTM-500 measured the thermal conductivity of thick and thin samples quickly by using a hot wire. When the electric power was applied to the heating wire, the temperature of wire rose with time. Then the thermal conductivity is given by:

$$\lambda = \frac{q \cdot \ln(t_2/t_1)}{4\pi(T_2 - T_1)} \quad (2)$$

where λ refers to the thermal conductivity of the sample and q is the generated heat per unit length. T and t are the temperature and time, respectively.

Figure 4 displays the thermal conductivity of the composites filled with various amounts of BN and CNTs. BN was used as the main thermally conductive filler for enhancing the thermal conduction behavior of the BN/CNTs/PDMS nanocomposites. Figure 3(a) shows the thermal conductivity of PDMS composites with an increasing concentration of BN. As the thermally conductive filler, BN increased the in-plane thermal conductivity of the composites without the addition of CNTs. The thermal conductivity measured by the hot wire method using a QTM-500 was more significantly affected by in-plane thermal conductivity ($//k$) than the through-plane ($\perp k$). Horizontally aligned and densely packed BN particles in PDMS composites provided a thermal conduction path within the

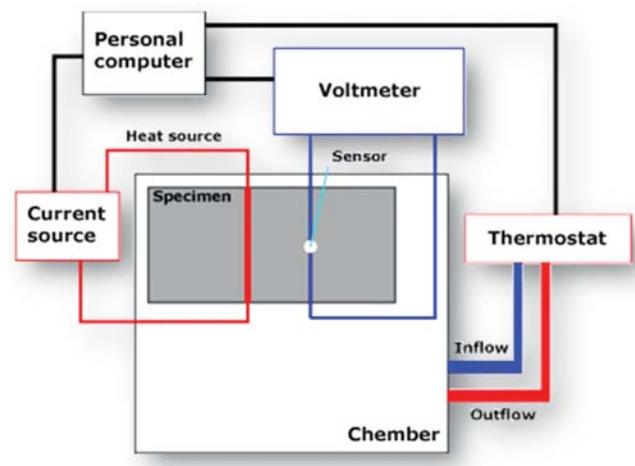


Figure 3. Hot-wire method for measuring the thermal conductivity of materials.

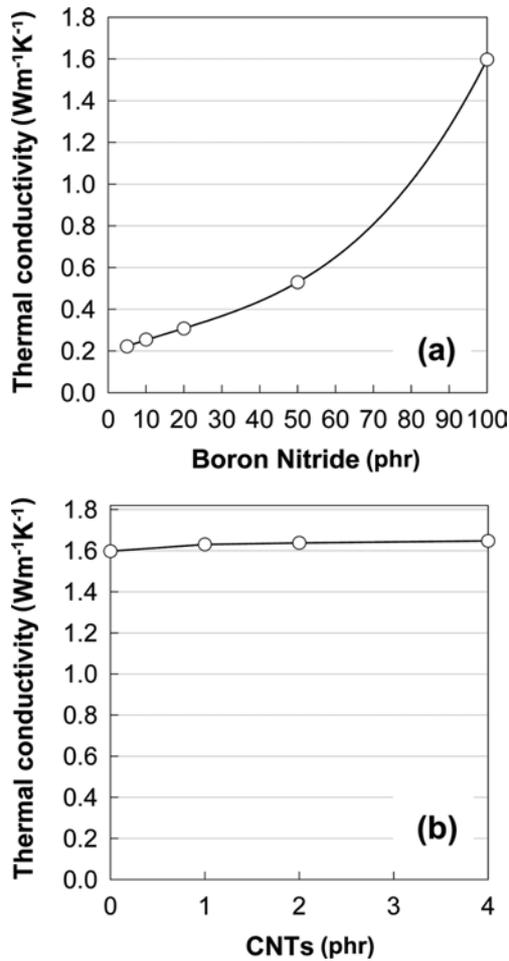


Figure 4. (a) Thermal conductivity of PDMS nanocomposites vs. BN concentration; (b) thermal conductivity of PDMS nanocomposites containing 100 phr BN vs. CNTs concentration.

insulating polymeric matrix. The thermal conductivity of BN incorporated PDMS composites increased from 0.2219 to 1.5971 $\text{W/m}\cdot\text{K}$. The addition of only 100 phr BN led to approximately 700 % thermal conductivity enhancement of the composites. In our previous work, 200 and 300 phr alumina incorporated PDMS composites had 0.590 and 0.855 $\text{W/m}\cdot\text{K}$, respectively. Not only the concentration of thermally conductive fillers affects the overall thermal conduction of composites, but also the thermal conductivity of the filled composites is affected by the geometrical formation of fillers.

The effect on the thermal conductivity of CNTs in 100 phr BN loaded PDMS is shown in Figure 3(b). Several researchers explored the thermal conductivity of CNTs incorporated polymer composites and found the thermal conductivity enhancement even at low CNTs concentration,^{25,26} but in Figure 3(b), CNTs incorporated PDMS composites containing 100 phr BN

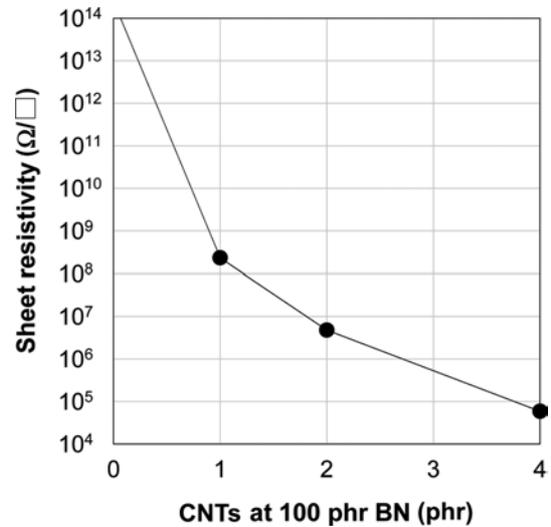


Figure 5. Effect of the amount of CNTs on the electrical resistivity of 100 phr BN filled PDMS nanocomposites.

particles show no noticeable increment in the thermal conductivity. The in-plane alignment of BN in the PDMS matrix might be geometrically hindered by the CNTs and the in-plane thermal conductivity of the PDMS/BN/CNTs composites was almost constant. 4 phr CNTs and 100 phr BN incorporated PDMS composite showed 1.6472 $\text{W/m}\cdot\text{K}$. This result confirms that the thermal conductivity of composites is greatly affected by not only the thermal conductivity of the filler but also geometrical alignment of a filler.

The electrical sheet resistivity of the BN/CNTs/PDMS composites is shown in Figure 5. The measurable resistivity range in our experimental apparatus was limited to values below $10^{14} \Omega/\square$. With high resistivity ($10^{14} \Omega/\square$) and good thermal conductivity, BN is widely used as a thermally conducting filler with an electrical insulator.¹¹ BN incorporated PDMS composites show excellent electrical insulating properties over $10^{14} \Omega/\square$. Because of a high aspect ratio, a percolation threshold of CNTs in a polymer such as polyamide is approximately 2-4 wt%.²⁷ Due to the high electrical conductivity of CNTs (10^3 S/m),²⁸ the electrical resistivity of the BN/CNTs/PDMS composites dramatically decreased from over $10^{14} \Omega/\square$ to about $10^5 \Omega/\square$ with an increasing concentration of CNTs.

The thermogravimetric thermograms of the composites are represented in Figure 6. With an increasing amount of BN (Figure 6(a)), the thermal degradation onset temperature of the composites became greater because the extraordinary thermal resistance endowed the composites with a much enhanced thermal stability because BN is durable up to 2973 °C. PDMS is completely decomposed above 650 °C in a nitrogen atmo-

sphere. After loading of the CNTs, the composites had an almost identical degradation onset temperature, but the rate of degradation significantly accelerated (Figure 6(b)). Initially, it was expected that CNTs would strengthen the resistance against thermal decomposition due to their high thermally stable properties. However, the result was opposite to our expectation and the reason is postulated as follows. The applied heat from the instrument can easily penetrate inside the samples through CNTs with a linear geometry. With an increased thermal penetration velocity, the temperature difference between the inside and outside of the sample becomes close, which indicates that the heat can quickly reach inside the sample, expediting a faster thermal decomposition of polymer chains. CNTs may also act as a heating element in thermally con-

ductive composites.

Using the data in Figure 6, the activation energy for thermal degradation was calculated using the Horowitz-Metzger method as shown in eq. (1).²⁹ The procedure is seen in Figure 7 as a plot of $\ln \ln [W_o - W_t^f / W - W_t^f]$ vs. θ and the results are summarized in Table 2. W_o , W , W_t^f , E_{ac} , R , and T_s are the initial weight of the sample, present weight, final total weight after pyrolysis, activation energy, gas constant, and reference temperature, respectively. According to the Horowitz-Metzger method, θ is defined from $T = T_s + \theta$, and T_s is defined where the $[W - W_t^f / W_o - W_t^f] = 1/e \approx 0.368$ because a derivation of the equation for activation energy is simplified to eq. (1) at this temperature. The activation energy of the composites was calculated from eq. (1) using the slope determined by plotting

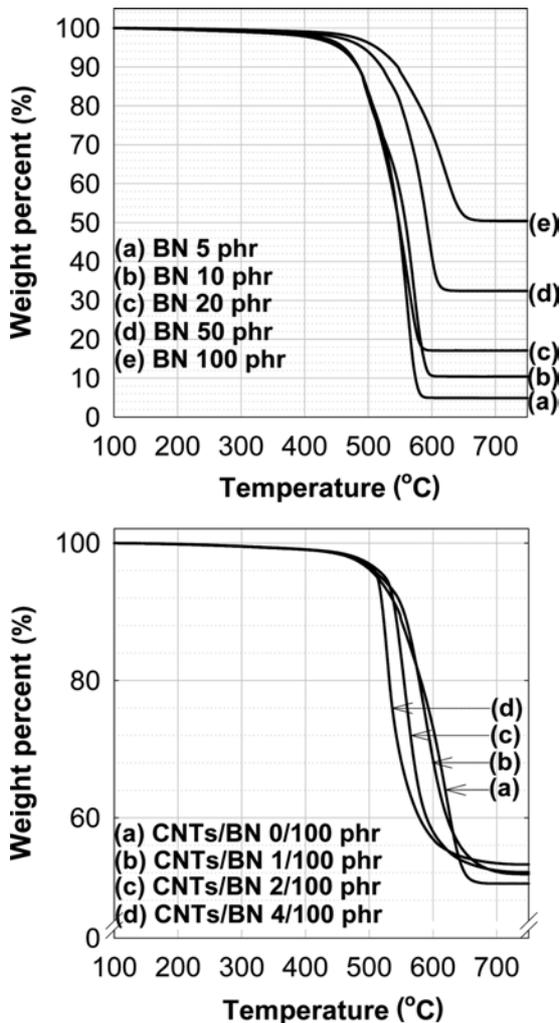


Figure 6. Thermogravimetric analysis of BN and CNTs incorporated PDMS with increasing amount of (top) BN and (bottom) CNTs with 100 phr BN.

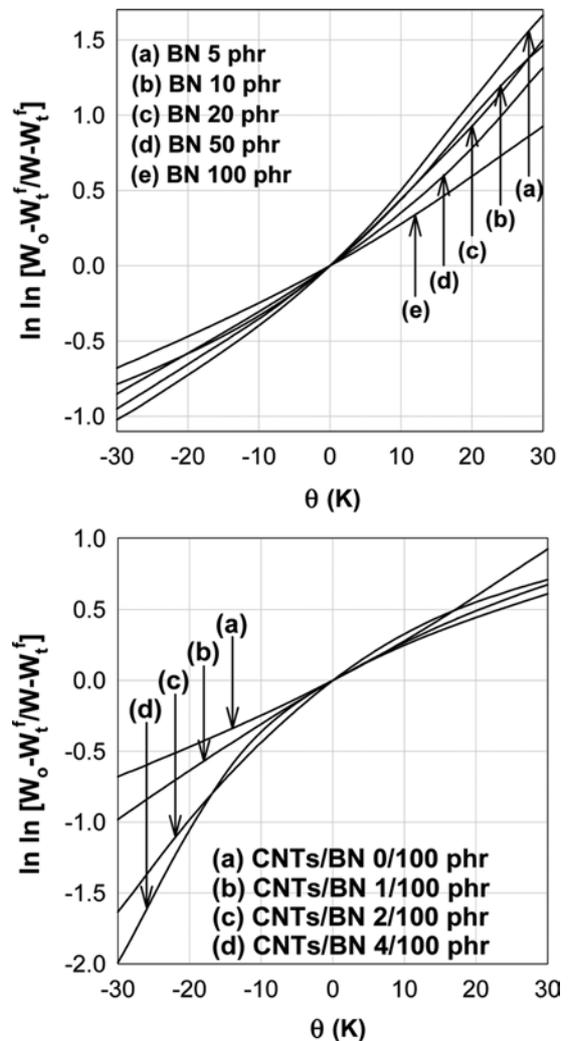


Figure 7. Plot of $\ln \ln [W_o - W_t^f / W - W_t^f]$ vs. θ for calculating the activation energy of BN and CNTs incorporated PDMS with increasing amount of (top) BN and (bottom) CNTs with 100 phr BN.

Table 2. Activation Energy and Mechanical Properties of BN and CNTs Incorporated PDMS Composites

BN-CNTs (phr-phr)	T_s (K)	Slop	E_{ac} (kJ/mol)	Tensile strength at break (MPa)	Elongation at break (%)
5-0	827.8	0.0453	258.10	0.418	19.0
10-0	837.5	0.0379	221.01	0.596	24.3
20-0	823.7	0.0348	196.31	0.836	29.0
50-0	858.1	0.0306	187.33	1.742	37.3
100-0	883.1	0.0266	172.51	2.827	30.0
100-1	871.1	0.0280	176.63	3.724	24.4
100-2	841.2	0.0386	227.07	4.080	23.8
100-4	828.6	0.0398	227.19	4.684	23.4

In $\ln [W_o - W_t^f / W - W_t^f]$ vs. θ . The activation energy of PDMS composites decreased with an increasing amount of BN. With an increased amount of CNTs, PDMS chains can have more chance to meet the filler interface and the activation energy of

composites increases with an increased filler-polymer chain connection. The addition of CNTs in polymer matrices often results in an increase in the thermal stability of composites. Therefore, the activation energy of CNTs loaded composites proportionally increases with the amount of CNTs. The activation energy is influenced by the dispersion state of fillers; the more uniform dispersion of fillers, the greater the activation energy.³⁰

Figure 8 presents the tensile properties of BN and CNTs with 100 phr BN incorporated PDMS composites. Without a reinforcing filler, such as silica, the composites exhibit very weak mechanical properties. The tensile strength and elongation at break are summarized in Table 2. Although the interaction between the filler and PDMS was weak, the tensile stress at break linearly increased with an increasing concentration of fillers from 0.418 to 4.684 MPa since BN and CNTs act as semi-reinforcing fillers. The percent of elongation of BN incorporated PDMS composites increased up to 50 phr BN and decreased at 100 phr BN. With an increasing concentration of BN, the composites hardened and the elongation at break decreased at over 50 phr BN content. The geometrical character of CNTs led to a great increase in tensile strength at break from 2.827 to 4.684 MPa by small concentrations of CNTs.

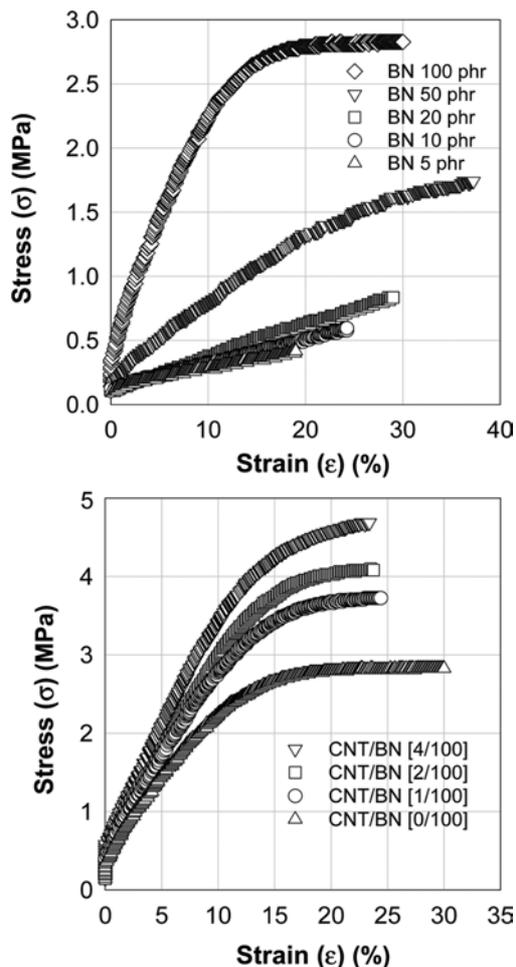


Figure 8. Stress-strain curves of (top) BN and (bottom) CNTs with 100 phr BN incorporated PDMS nanocomposites.

Conclusions

The thermal properties including thermal conductivity and thermal stability of BN/CNTs filled PDMS composites were investigated. The thermal stability of the BN incorporated composites was enhanced; however, unexpectedly, the addition of CNTs significantly decreased the thermal stability of the composites. CNTs may act as a heating wire in the thermally conductive polymeric matrix, leading to faster decomposition.

The activation energy of the composite calculated using the Horowitz-Metzger method decreased with an increasing amount of BN and increased with an increasing concentration of CNTs. Due to the electrical insulating properties of BN, BN loaded PDMS composites had high resistivity. However, the electrical resistivity of the composites significantly decreased by adding a small amount of CNTs. The tensile strength of the composite increased from 0.418 to 4.684 MPa by addition of various amount of BN and CNTs.

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