

## Low dielectric and high thermal conductivity epoxy nanocomposites filled with NH<sub>2</sub>-POSS/n-BN hybrid fillers

Yalan Wu,<sup>1</sup> Fang Li,<sup>1</sup> Juanni Huyan,<sup>1</sup> Xiaorong Zou,<sup>1</sup> Ying Li<sup>2</sup>

<sup>1</sup>PLA 323 Hospital, Xi'an Shaan Xi 710054, People's Republic of China

<sup>2</sup>Department of Material Science and Engineering, Xi'an University of Science and Technology, Xi'an Shaan Xi 710054, People's Republic of China

Correspondence to: X. R. Zou (E-mail: xiaorong\_zou@126.com)

**ABSTRACT:** Hybrid fillers of mono-amine polyhedral oligomeric silsesquioxane/nanosized boron nitride (NH<sub>2</sub>-POSS/n-BN) were performed to fabricate NH<sub>2</sub>-POSS/n-BN/epoxy nanocomposites. Results revealed that the dielectric constant and dielectric loss values were decreased with the increasing addition of NH<sub>2</sub>-POSS obviously, but increased with the increasing addition of BN fillers. For a given loading of NH<sub>2</sub>-POSS (5 wt %), the thermal conductivities of NH<sub>2</sub>-POSS/n-BN/epoxy nanocomposites were improved with the increasing addition of n-BN fillers, and the thermal conductivity of the nanocomposites was 1.28 W/mK with 20 wt % n-BN fillers. Meantime, the thermal stability of the NH<sub>2</sub>-POSS/n-BN/epoxy nanocomposites was also increased with the increasing addition of n-BN fillers. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41951.

**KEYWORDS:** composites; conducting polymers; dielectric properties; functionalization of polymers

Received 29 August 2014; accepted 4 January 2015

DOI: 10.1002/app.41951

### INTRODUCTION

Polymeric composites are widely applied in many areas because of its remarkable properties, such as low density, high specific strength, excellent corrosion resistance, easy fabrication and low cost, etc.<sup>1–3</sup> But the intrinsic low thermal conductivity of polymers limits their wider application, where requires low dielectric constant and dielectric loss values, high thermal conductivity, and easy processability.<sup>4,5</sup>

To effectively solve the thermal management issues above, the introduction of thermally conductive ceramic fillers into the polymeric matrix is a cost effective way. To our knowledge, lots of thermally conductive polymeric composites have been fabricated by filling different thermally conductive ceramic particles (aluminum nitride,<sup>6–8</sup> boron nitride,<sup>9–11</sup> silicon carbide,<sup>12–14</sup> and aluminum nitride<sup>15,16</sup> Polyhedral oligomeric silsesquioxanes (POSS) can be easily introduced into polymeric system, resulting in a local low dielectric constant in the polymeric composites.<sup>17–19</sup>

To fabricate the epoxy nanocomposites with a combination of optimal dielectric properties, high thermal conductivity and excellent thermal stability, the hybrid fillers of mono-amine POSS/nanosized boron nitride (NH<sub>2</sub>-POSS/n-BN) were introduced, herein, n-BN fillers were mainly helpful to increase the thermal conductivity of the epoxy resin, and NH<sub>2</sub>-POSS was performed to improve the dielectric property. Meantime, the

mass fraction of NH<sub>2</sub>-POSS/n-BN hybrid fillers affecting on the dielectric properties, thermal conductivity, and thermal stability of the epoxy nanocomposites was also investigated in detail.

### EXPERIMENTAL

#### Main Materials

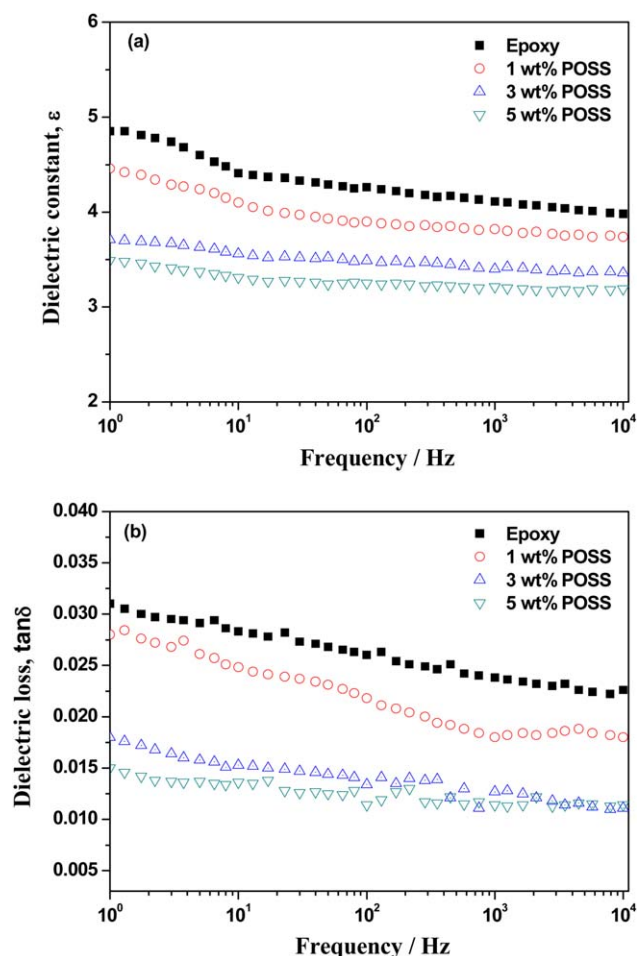
Epoxy resin (E-51), bisphenol-A, was received from Wuxi Resin Factory of Blue Star New Chemical Materials (Jiangsu, China); Methyl tetrahydrophthalic anhydride (MeTHPA), was purchased from Zhejiang Alpharm Chemical Technology (Zhejiang, China); NH<sub>2</sub>-POSS was purchased from Hybrid Plastics (Hattiesburg, USA); Nanosized boron nitride (n-BN), hexagonal crystal, with purity over 99.9%, mean grain diameter of 50 nm and specific surface area of 43.6 m<sup>2</sup>/g, was received from Shanghai Chaowei Nanometer Technology (Shanghai, China).

#### Preparation of Epoxy Nanocomposites

E-51, MeTHPA, NH<sub>2</sub>-POSS and n-BN were mixed, kept in a vacuum vessel to remove bubbles, and then to be poured into the preheated die. And the mixtures were cured in a vacuum oven for following technology: 100°C/1 h + 120°C/2 h + 160°C/4 h, followed by post-curing in vacuum oven at 200°C for 4 h.

#### Analysis and Characterization

The dielectric constant and dielectric loss of the samples were measured using high frequency Q instrument (QBG-3D) and



**Figure 1.** The dielectric constant and dielectric loss values of NH<sub>2</sub>-POSS/epoxy composites at entire frequency range of 1 Hz to 10<sup>4</sup> Hz. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

dielectric constant detector (S914) from Aiyi Electronic Equipment. (Shanghai, China); The thermal conductivity of the samples was measured using a Hot Disk instrument (AB Co., Sweden) according to standard ISO 22007-2: 2008, and the corresponding dimension of samples was 20 mm × 20 mm × 4 mm; Scanning electric microscope (SEM) morphologies of the samples were analyzed by VEGA3-LMH (TESCAN Corporation, Czech Republic); Dynamic mechanical analysis (DMA) was performed using DMA/SDTA861e (Mettler-Toledo Co., Switzerland) in the bending mode, at a heating rate of 5°C/min at 1 Hz; The thermo-gravimetric analyses (TGA) of the samples were performed using a thermoanalyzer (STA 449F3, Netzsch Group, Germany) in the temperature range of 40–900°C with a heating rate of 10°C/min under N<sub>2</sub> atmosphere.

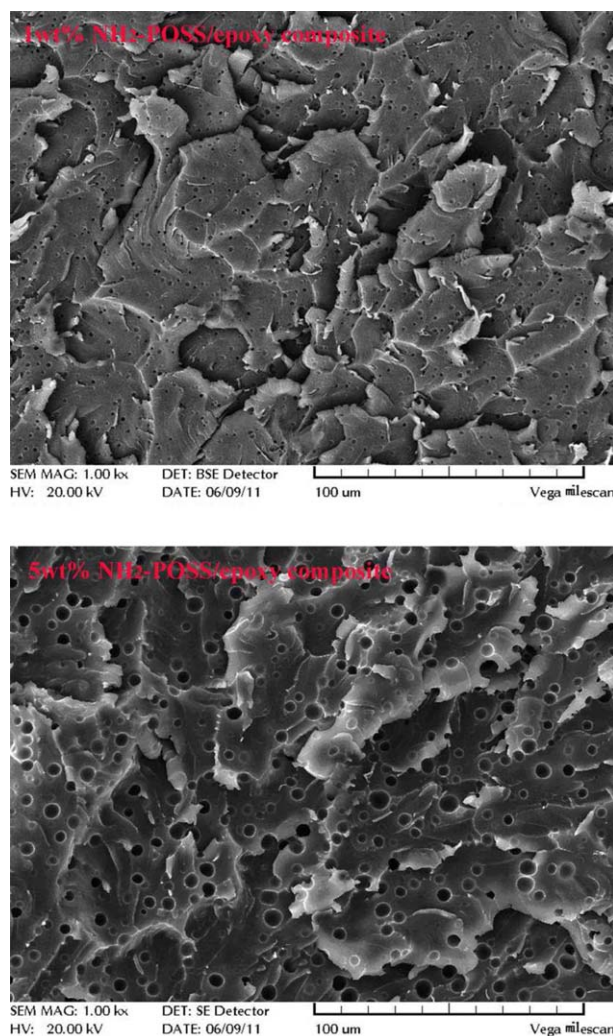
## RESULTS AND DISCUSSION

### Dielectric Properties of Epoxy Composites

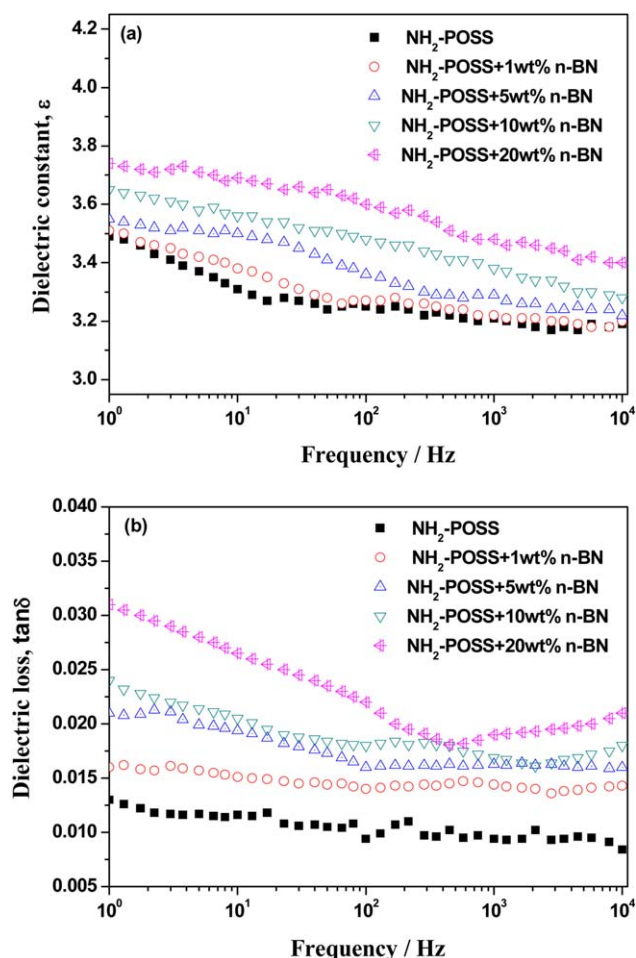
The dielectric constant and dielectric loss values of NH<sub>2</sub>-POSS/epoxy composites at entire frequency range (1 Hz to 10<sup>4</sup> Hz) were presented in Figure 1.

Both the dielectric constant and dielectric loss values of the NH<sub>2</sub>-POSS/epoxy composites were much lower than those of original epoxy resin over entire frequency range. Moreover, the dielectric constant and dielectric loss values were also decreased with the increasing addition of NH<sub>2</sub>-POSS. When the mass fraction of NH<sub>2</sub>-POSS was 5 wt %, compared with original epoxy resin (4.26 of dielectric constant and 0.026 of dielectric loss at 100 Hz), the corresponding dielectric constant and dielectric loss of the NH<sub>2</sub>-POSS/epoxy composites was decreased by 23.7% and 56.2%, respectively. The reason was that the intrinsic dielectric constant and dielectric loss values of NH<sub>2</sub>-POSS were far below those of original epoxy resin.

Fracture morphologies of NH<sub>2</sub>-POSS/epoxy composites by SEM observation were shown in Figure 2. With the addition of NH<sub>2</sub>-POSS, lots of cavities were appeared on the fracture surface of NH<sub>2</sub>-POSS/epoxy composites. It was attributed that, during the curing reaction of epoxy resin, NH<sub>2</sub>-POSS could be introduced into the cross-linked network *via* chemical covalent bonds, to present the heterogeneous phase distribution, finally



**Figure 2.** Fracture morphologies of NH<sub>2</sub>-POSS/epoxy composites by SEM observation. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 3.** The dielectric constant and dielectric loss values of  $\text{NH}_2\text{-POSS}/\text{n-BN}/\text{epoxy}$  nanocomposites with the increasing addition of n-BN at entire frequency range of 1 Hz to  $10^4$  Hz. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

to form the micron-sized cavities. Moreover, the compatibility between  $\text{NH}_2\text{-POSS}$  and epoxy resin is possibly bad, which can also result in the formation of voids. Also, the formed cavities were also beneficial to further decrease the dielectric constant and dielectric loss values of the  $\text{NH}_2\text{-POSS}/\text{epoxy}$  composites.

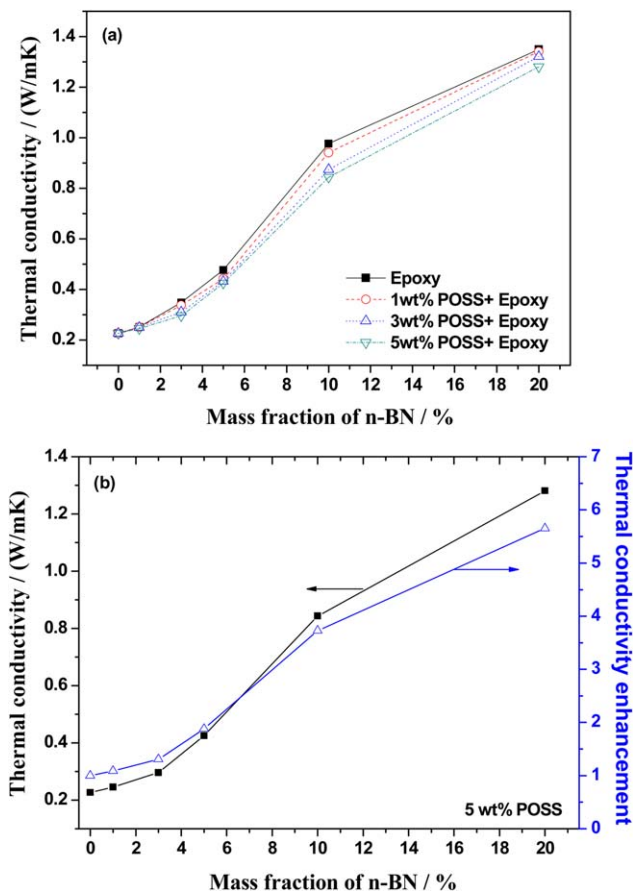
The dielectric constant and dielectric loss values of  $\text{NH}_2\text{-POSS}/\text{n-BN}/\text{epoxy}$  nanocomposites with the increasing addition of n-BN at entire frequency range (1 Hz to  $10^4$  Hz) were also presented in Figure 3.

For a given loading of  $\text{NH}_2\text{-POSS}$  (5 wt %), both dielectric constant and dielectric loss values of the  $\text{NH}_2\text{-POSS}/\text{n-BN}/\text{epoxy}$  nanocomposites were all increased with the increasing addition of n-BN fillers. The reason was that n-BN had a much higher dielectric constant value than that of origin epoxy resin. Furthermore, the more two-phase interfaces could increase the polarization performance of the nanocomposites, resulting in the improvement of the dielectric constant. Meanwhile, the interface defects of the  $\text{NH}_2\text{-POSS}/\text{n-BN}/\text{epoxy}$  nanocomposites were also increased with the increasing addition of n-BN, finally

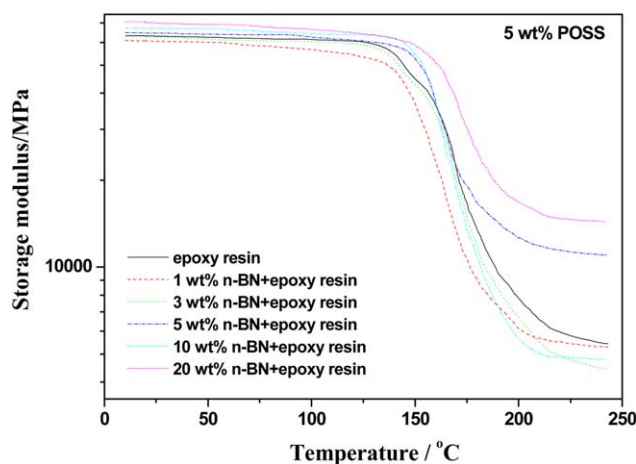
to increase the dielectric loss of the  $\text{NH}_2\text{-POSS}/\text{n-BN}/\text{epoxy}$  nanocomposites.

### Thermal Conductivities of $\text{NH}_2\text{-POSS}/\text{n-BN}/\text{Epoxy}$ Nanocomposites

The mass fraction of  $\text{NH}_2\text{-POSS}$  and n-BN fillers affecting on the thermal conductivities of  $\text{NH}_2\text{-POSS}/\text{n-BN}/\text{epoxy}$  nanocomposites were shown in Figure 4. From Figure 4, at the same loading of n-BN, the corresponding thermal conductivities of the  $\text{NH}_2\text{-POSS}/\text{n-BN}/\text{epoxy}$  nanocomposites were decreased with the increasing addition of  $\text{NH}_2\text{-POSS}$ . For a given loading of  $\text{NH}_2\text{-POSS}$  (5 wt %), the thermal conductivities of the  $\text{NH}_2\text{-POSS}/\text{n-BN}/\text{epoxy}$  nanocomposites were improved with the increasing addition of n-BN fillers obviously, and the thermally conductive coefficient of the  $\text{NH}_2\text{-POSS}/\text{n-BN}/\text{epoxy}$  nanocomposites was 1.28 W/mK with 20 wt % n-BN fillers, six times higher than that of original epoxy resin. The reason was that, with the increasing addition of n-BN fillers, the contacts between n-BN and n-BN fillers were enhanced, and the more thermally conductive pathways and networks were formed easily, thus to increase the ultimate thermal conductivities of the  $\text{NH}_2\text{-POSS}/\text{n-BN}/\text{epoxy}$  nanocomposites.



**Figure 4.** The mass fraction of  $\text{NH}_2\text{-POSS}$  and n-BN fillers affecting on the thermal conductivities of  $\text{NH}_2\text{-POSS}/\text{n-BN}/\text{epoxy}$  nanocomposites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



**Figure 5.** DMA curves of  $\text{NH}_2$ -POSS/n-BN/epoxy nanocomposites. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

### Thermal Properties of $\text{NH}_2$ -POSS/n-BN/Epoxy Nanocomposites

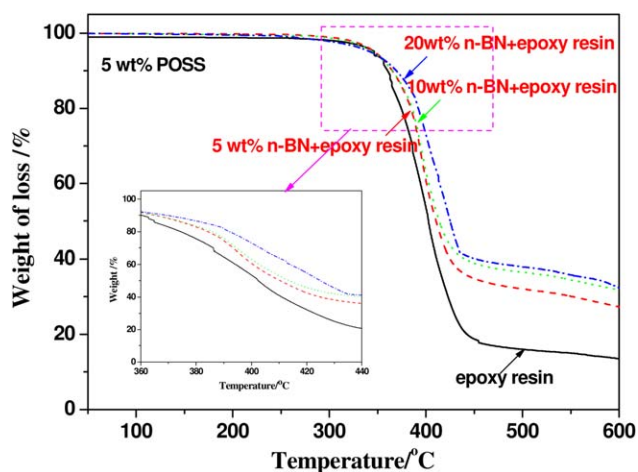
Figure 5 presented the DMA curves of the  $\text{NH}_2$ -POSS/n-BN/epoxy nanocomposites. And the corresponding glass transition temperature ( $T_g$ ) values of the  $\text{NH}_2$ -POSS/n-BN/epoxy nanocomposites were listed in Table I.

From Table I, the corresponding  $T_g$  value of the  $\text{NH}_2$ -POSS/n-BN/epoxy nanocomposites was increased with the increasing addition of n-BN fillers. The results were ascribed that the addition of n-BN fillers could restrain the molecular chain movement in the interface of epoxy resin, finally to increase the  $T_g$  of the  $\text{NH}_2$ -POSS/n-BN/epoxy nanocomposites.

Figure 6 presented the TGA curves of the  $\text{NH}_2$ -POSS/n-BN/epoxy nanocomposites. From Figure 6, with the increasing addition of n-BN fillers, the corresponding weight loss temperatures of the  $\text{NH}_2$ -POSS/n-BN/epoxy nanocomposites were all increased at the same stages. When the weight loss was 50 wt %, the weight loss temperature was 402°C ( $\text{NH}_2$ -POSS/epoxy resin), 409°C (5 wt % n-BN), 413°C (10 wt % n-BN) and 424°C (20 wt % n-BN), respectively. It suggested that the thermal stabilities of the  $\text{NH}_2$ -POSS/n-BN/epoxy nanocomposites were increased slightly. The reason was that, compared with original epoxy resin, n-BN fillers possessed relatively higher heat capacity and intrinsic thermal conductivity, resulting in epoxy resin degraded at higher temperatures.

**Table I.** The Corresponding Glass Transition Temperature ( $T_g$ ) Values of the  $\text{NH}_2$ -POSS/n-BN/Epoxy Nanocomposites

Samples	$T_g/^\circ\text{C}$
Epoxy resin	135.7
1 wt % BN+epoxy resin	137.1
3 wt % BN+epoxy resin	139.4
5 wt % BN+epoxy resin	142.3
10 wt % BN+epoxy resin	146.5
20 wt % BN+epoxy resin	151.2



**Figure 6.** TGA curves of the  $\text{NH}_2$ -POSS/n-BN/epoxy nanocomposites. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

### CONCLUSIONS

Both the dielectric constant and dielectric loss values of the  $\text{NH}_2$ -POSS/n-BN/epoxy nanocomposites were decreased obviously with the increasing addition of  $\text{NH}_2$ -POSS, but increased with the increasing addition of n-BN fillers. For a given loading of  $\text{NH}_2$ -POSS (5 wt %), the thermal conductivities of  $\text{NH}_2$ -POSS/n-BN/epoxy nanocomposites were improved with the increasing addition of n-BN fillers, and the thermally conductive coefficient of the nanocomposites was 1.28 W/mK with 20 wt % n-BN fillers, six times higher than that of original epoxy resin. DMA analyses revealed that the corresponding  $T_g$  of the  $\text{NH}_2$ -POSS/n-BN/epoxy nanocomposites was increased with the increasing addition of n-BN fillers. TGA analyses revealed that the thermal stabilities of the  $\text{NH}_2$ -POSS/n-BN/epoxy nanocomposites were increased slightly with the increasing addition of n-BN fillers.

### ACKNOWLEDGMENTS

The authors are grateful for the support and funding from National Natural Science Foundation of China (No.81400765, Y.L. Wu) and Shaanxi National Science Foundation of Shaanxi Province (No. 2012SF2-24, X.R. Zou). Xiaorong Zou contributed equally to this work and should be considered co-first authors.

### REFERENCES

- Shahil, K. M. F.; Balandin, A. A. *Nano Lett.* **2012**, *12*, 861.
- Pecht, M. G.; Nguyen, L. T.; Hakim, E. B. *Plastic Encapsulated Microelectronics*. New York: Wiley, **1995**.
- Gu, J. W.; Du, J. J.; Dang, J.; Geng, W. C.; Hu, S. H.; Zhang, Q. Y. *RSC Adv.* **2014**, *4*, 22101.
- Huang, X. Y.; Zhi, C. Y.; Jiang, P. K.; Golberg, D.; Bando, Y.; Tanaka, T. *Adv. Mater.* **2013**, *23*, 1824.
- Huang, X. Y.; Tanaka, T.; Jiang, P. K.; Ohki, Y. *J. Phys. Chem. C* **2012**, *116*, 13629.
- Gu, J. W.; Zhang, Q. Y.; Dang, J.; Zhang, J. P.; Yang, Z. Y. *Polym. Eng. Sci.* **2009**, *49*, 1030.

7. Choi, S.; Im, H.; Kim, J. *Compos. Part A* **2012**, *43*, 1860.
8. Agrawal, A.; Satapathy, A. *Procedia Eng.* **2013**, *51*, 573.
9. Gu, J. W.; Zhang, Q. Y.; Dang, J.; Xie, C. *Polym. Adv. Technol.* **2012**, *23*, 1025.
10. Kim, K.; Kim, M.; Hwang, Y.; Kim, J. *Ceram. Int.* **2014**, *40*, 2047.
11. Pak, S. Y.; Kim, H. M.; Kim, S. Y.; Youn, J. R. *Carbon* **2012**, *50*, 4830.
12. Gu, J. W.; Zhang, Q. Y.; Dang, J.; Zhang, J. P.; Chen, S. J. *Polym. Bull.* **2009**, *62*, 689.
13. Yang, K.; Gu, M. Y. *Compos. Part A* **2010**, *41*, 215.
14. Gu, J. W.; Zhang, Q. Y.; Dang, J.; Yin, C. J.; Chen, S. J. *J. Appl. Polym. Sci.* **2012**, *124*, 132.
15. Zhu, Y.; Chen, K. X.; Kang, F. Y. *Solid State Commun.* **2013**, *158*, 46.
16. He, H.; Fu, R. L.; Shen, Y.; Han, Y. C.; Song, X. F. *Compos. Sci. Technol.* **2007**, *67*, 2493.
17. Gu, J. W.; Bai, T.; Dang, J.; Feng, J. J.; Zhang, Q. Y. *Polym. Compos.* **2014**, *35*, 611.
18. Kuo, S.-W.; Chang, F.-C. *Prog. Polym. Sci.* **2011**, *36*, 1649.
19. Li, H. L.; Tang, Y. S.; Gu, J. W.; Dang, J.; Bai, T.; Feng, J. J. *Polym. Compos.* **2013**, *34*, 2026.