Thermal Conductivity of Poly Vinylidene Fluoride Composites Filled With Expanded Graphite and Carbon Nanotubes

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ABSTRACT: The composites composed of Poly (vinylidene fluoride), expanded graphite (EG), and carbon nanotubes (CNTs) have been prepared by solution mixing, followed by compression. The structure of the composites was examined with scanning electron microscope and their electrical and thermal properties were investigated. About 1.2 wt % content of CNTs could present a percolated network in the polymer matrix, characterized by the electrical conductivity. The incorporation of EG and CNTs in the polymer caused an enhancement in thermal conductivity for the composites. However, a hybrid of EG and CNTs as filler of the polymer yielded a further improvement in thermal conductivity as compared to single component filler. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Poly (vinylidene fluoride) (PVDF) is a semicrystalline thermoplastic engineering polymer widely used in various applications such as chemical, biomedical, and electronic industries due to its excellent thermal stability, chemical resistance, and high dielectric permittivity.[1] On the other hand, the conductive polymer composites have also gained great interest to the materials community due to their uses in a variety of technological applications.[2] Thus, PVDF can be used to prepare conductive composites for self-regulated heaters, over-current protectors, conducting electrodes for lithium batteries, and for other electrical applications.[3]

The most common used fillers for conductive polymer composites include carbon black, carbon nanotubes (CNTs), and graphite nanoplatelets. Carbon black can effectively improve the conductivity of polymer composites. However, it usually needs a rather high content due to its micrometer size and roughly spherical morphology. One-dimensional CNTs have excellent electrical and thermal conductivity as well as extraordinary high mechanical strength and are also attractive nanofillers for polymer composites.[2] Thus, CNTs filled PVDF composites have been the focus of the recent investigations.[4–18] However, the

high cost and large tendency for agglomeration are chief deficiencies of using CNTs as conducting fillers and limit wider applications. Additionally, there is now interest in graphite platelet as fillers, which can combine high performance with low prices. The electrical and thermal conductivities of graphite in-plane are close to those of CNTs.[19] Therefore, expanded graphite (EG), a product of exfoliation of graphite intercalation compounds, is deemed as a good and economical filler material for polymer composites and has gained increasing interest in research for composites applications.[20–24] However, the reports on EG filled PVDF composites are still limited.[20,21]

Most reports on carbonaceous fillers in PVDF matrix are concerned with electrical conductivity,[5,7,11,12,18] polymer crystalline structure,[4,6,15,17] as well as dielectric permittivity.[8,9] Only several describe improvement in the thermal conductivity.[25] Maleki et al.[25] presented thermal conductivity data for negative electrode materials of Li-ion batteries made of synthetic graphite, PVDF binder, and C-black at varying levels of compression pressure on the aspect of battery safety. Thermal conductivity is an important requirement for many applications in electronic components, and high thermal conductive PVDF composites have great potential applications in the microelectronics industry. As the reliability and speed of electronic and optoelectronic

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devices strongly depend on temperature, materials with high heat dissipation capability are required to spread the accumulated heat generated locally in the devices.[26] To the best of our knowledge, the investigation of the thermal conductivity of PVDF/EG is seldom addressed in studies.

The aim of this work is to evaluate the structure of CNTs and EG in PVDF matrices and investigate the thermal conductivity of the composites to estimate how to achieve a high thermal conductivity with ideal composition. The designed thermally conductive polymeric composites are prepared by a simple method from both economical and processing viewpoints.

EXPERIMENTAL

The PVDF used in this work was provided by Zhejiang Research Institute of Chemical Industry, Hangzhou, China, in powder form. Details on the synthesis of multiwalled CNTs were introduced elsewhere.[27] EG was purchased from Qingdao Yanxin, China. Natural graphite was soaked in sulfuric acid and heated to high temperatures thereby expanding to very fine flakes. The CNTs and EG were oxidized by refluxing in strong nitric acid for 4 h at 140°C to introduce oxygen-containing groups on their surfaces.[28–30] The product was filtered and washed with adequate distilled water until neutral, and then dried.

PVDF was dissolved in an ethanol solvent at room temperature under ultrasonic irradiation. A right amount of CNTs or EG was suspended in the solution. Then, it was sonicated for 2 h to form a stable suspension and break the agglomerates. The mixture was kept at 60°C to evaporate the solvent to obtain a composite powder. The composite powder was compression molded at room temperature for 15 min under a pressure of about 10 MPa. Finally, the molded specimens were heated at 160°C for 30 min.

A concept of hybrid filler composed of CNTs and EG was also conducted in an effort to further improve the thermal conductivity of composites. For the hybrid filler, the weight contents of CNTs and EG were equal in all cases.

The surface area of EG sample was measured via N_2 adsorption at $-196°C$ on a Micromeritics ASAP 2020 analyzer and the functional groups on the EG were recorded by Fourier transform infrared (FTIR) spectra with wavenumber range of 400–4000 cm^{-1}. The morphology characterization of the composites was carried out with a scanning electron microscope (SEM, Hitachi S-4800). The freshly fractured surface of the composite was gold sputtered before SEM observation. The electrical conductivity of the PVDF/CNTs composites was determined using four-probe methods at room temperature. The thermal conductivity of the composites was measured using a thermal conductive analyzer (DRPL-I, Xiangtan Instrument & meter, China). In the procedure, the specimen was first polished using abrasive paper and then closely sandwiched between two copper plates. One plate was heated at about 50°C and the other was kept at room temperature. A thermal grease of high conductivity was applied on the contact surfaces between the specimen and copper plates to ensure good thermal exchange. The value of the thermal conductivity was determined by a plate heat flow meter with the surface area and thickness of the specimen, as well as
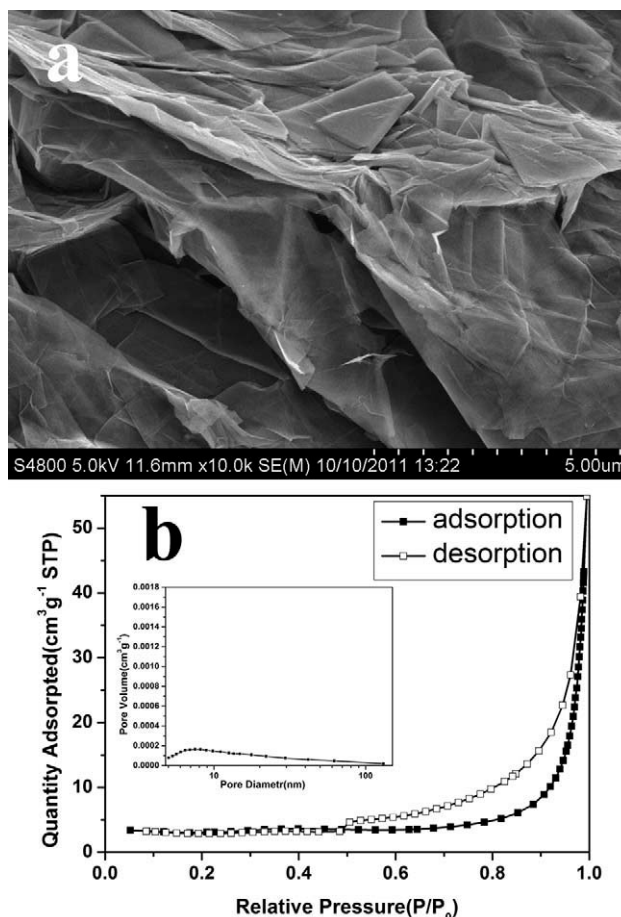

Figure 1. (a) SEM image of EG and (b) N_2 adsorption–desorpion isotherms and pore size distribution of EG.

the thermal equilibrium temperatures of the two copper plates. At least three samples were tested under the same conditions and the average values were used for analysis.

RESULTS AND DISCUSSION

Characterization of EG

SEM morphology of the EG platelets is shown in Figure 1(a). It is observed that many adhesive and overlapped graphite platelets are presented and the lateral size of them is in the range of micrometer. The nitrogen adsorption/desorption isotherms and the pore size distribution plots of EG sample are shown in Figure 1(b). Its Brunauer-Emmett-Teller (BET) specific surface area is determined to be 9.8 m^2 g^{-1}. The X-ray diffraction (XRD) profiles for EG showed a strong peak at about $2\theta = 26.4°$ and a weak peak at around $2\theta = 54°$, attributing to the (002) and (004) planes of graphite, respectively. The FTIR technique was used for the group characterization on the EG platelets surfaces. The absorbance peaks of —OH stretching mode, —C—OH vibration mode and —C—O vibration were detected in the spectrum, indicating that polar groups were introduced on the surface of the EG platelets after acid treatment.

Electrical Conductivity of PVDF/CNTs Composites

Figure 2 shows the relationship between the electrical conductivity and the weight content of CNTs in the PVDF composites.
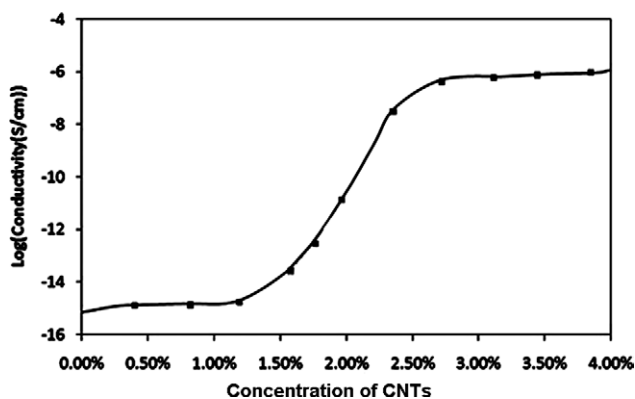
Figure 2. Electrical conductivity as a function of CNTs content for PVDF/CNTs composites.

At a very low concentration of CNTs (<1.2 wt %), the conductivity slowly increases with increasing CNTs content. However, when the CNTs concentration is above 1.2 wt %, the conductivity of the composites abruptly increases by about 9 orders of magnitude to approximately 10^{-6} Scm^{-1}. When CNTs loading is above 2.5 wt %, further increase in the content of CNTs does not increase conductivity substantially. This change in electrical conductivity is clear proof of the formation of an interconnected network in the polymer matrix, showing an electrical percolation threshold. That is, about 1.2 wt % CNTs loading, a critical filler concentration, permits electrons to flow through the composite in the applied electric field.

Two representative SEM micrographs of 0.4 and 1.8 wt % CNTs loadings are shown in Figure 3. In Figure 3(a), the dispersed short bright lines are the ends of the broken CNTs with 0.4 wt % loading, implying that the interconnected network has not formed. Nevertheless, many CNTs can be clearly detected in Figure 3(b) with a higher loaded content of CNTs. The low value of threshold proves the feasibility of our method in the well dispersion of fillers in PVDF matrix using ethanol as the solvent.

Thermal Conductivity of PVDF/EG and PVDF/CNTs Composites

Figure 4 shows the SEM images of the prepared PVDF/EG composite with 3.1 wt % EG loading, in which Figure 4(a) is the composite before final heat treatment at 160°C and Figure 4(b) presents the fracture morphology of the composite after heat treatment. In the PVDF/EG composite before heat treatment, it can be seen that the PVDF particles has an average diameter of ~200 nm and a narrow size distribution. The aggregation of the PVDF particles is caused by the compression in the preparation process and the EG is also observed in the micrograph. However, few PVDF particles can be seen in the composite due to their merging under high temperature [Figure 4(b)]. EG platelets with sizes of several micrometers can be clearly seen immersed and incorporated into polymer matrix, marked with white arrows in the image, because PVDF chains can effectively coat on graphite platelets and form a very thin polymer layer on their surfaces.[8]

Figure 5 presents the relationship between thermal conductivity and filler content. The thermal conductivity of neat PVDF was measured to be 2.19 Wm^{-1} K^{-1}. The thermal conductivity of EG platelet is much higher than that of PVDF. As their content increases, they begin to touch one other in the composite, providing a route for phonon transfer. Therefore, the incorporation of EG would improve the conductivity of the PVDF/EG composites. The composite with 3.1 wt % EG content possesses a high conductivity of 2.52 Wm^{-1} K^{-1}. However, when the content was further increased, there was a small decline in thermal conductivity. Similarly, when the content of CNTs in the composite increased, a gradual increase in their thermal conductivity was also observed. A high value of 2.66 Wm^{-1} K^{-1} was achieved with 6.1 wt % CNTs loading. Subsequently, there was also a slight decrease in thermal conductivity with further increase of CNTs content. Both kinds of PVDF composites have similar trend. The clear reason for this phenomenon is the deterioration in the dispersion of fillers in composites. As plenty of fillers are incorporated into the polymer matrix, they will significantly aggregate with a poor dispersion state and suppress the thermal conductivity. We even observed aggregated CNTs and small pores in the composite matrix under high filler loading. This implies that there may be an optimum content for different fillers.
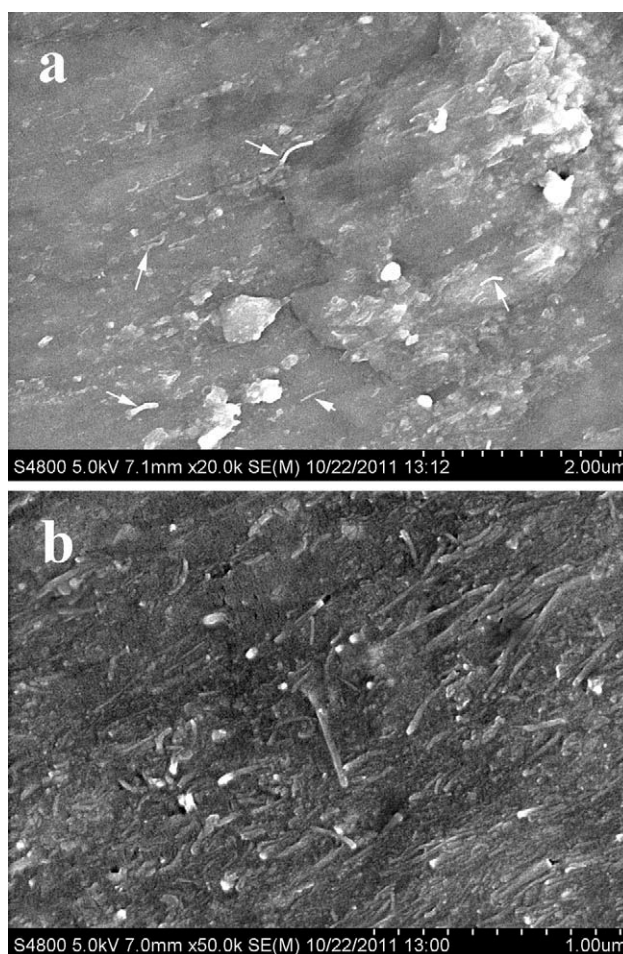

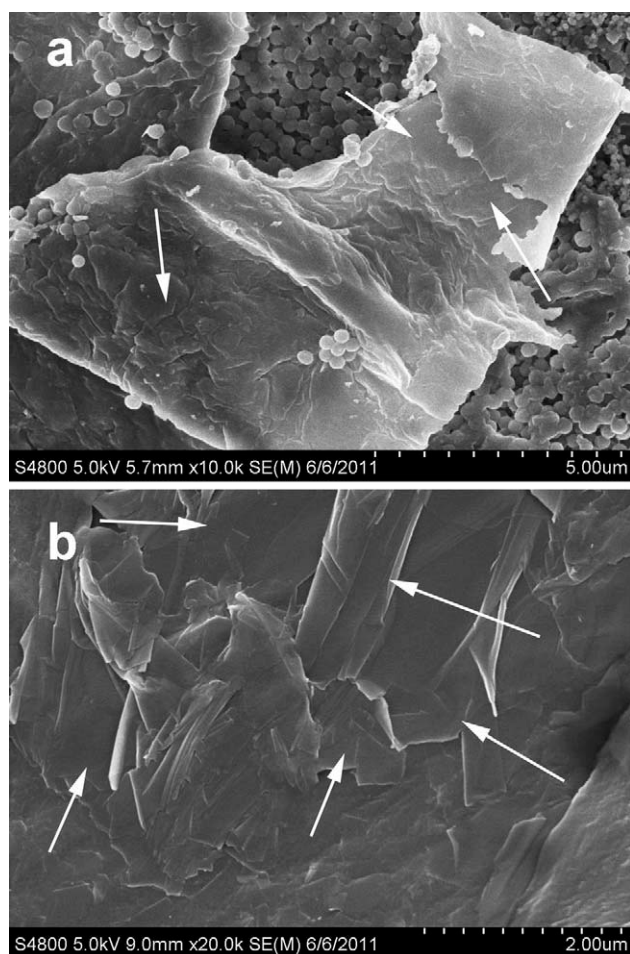**Figure 3.** Fracture surface mophologies of (a) PVDF/0.4 wt %CNTs and (b) PVDF/1.8 wt %CNTs.

Figure 4. Fracture surface morphologies of PVDF/3.1% EG (a) before and (b) after heat treatment.
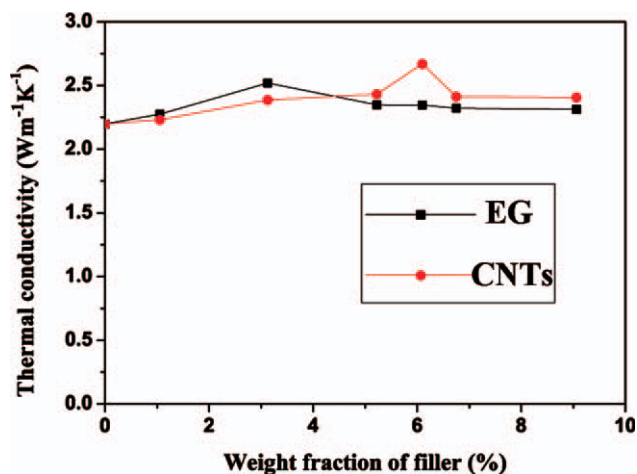

Figure 5. Thermal conductivity of PVDF/EG and PVDF/CNTs composites varied with fillers content. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

quently declines with increasing filler loading. We hypothesize that it is still caused by the aggregation of fillers under a plentiful content. In the case of hybrid fillers, thermal conductivity is
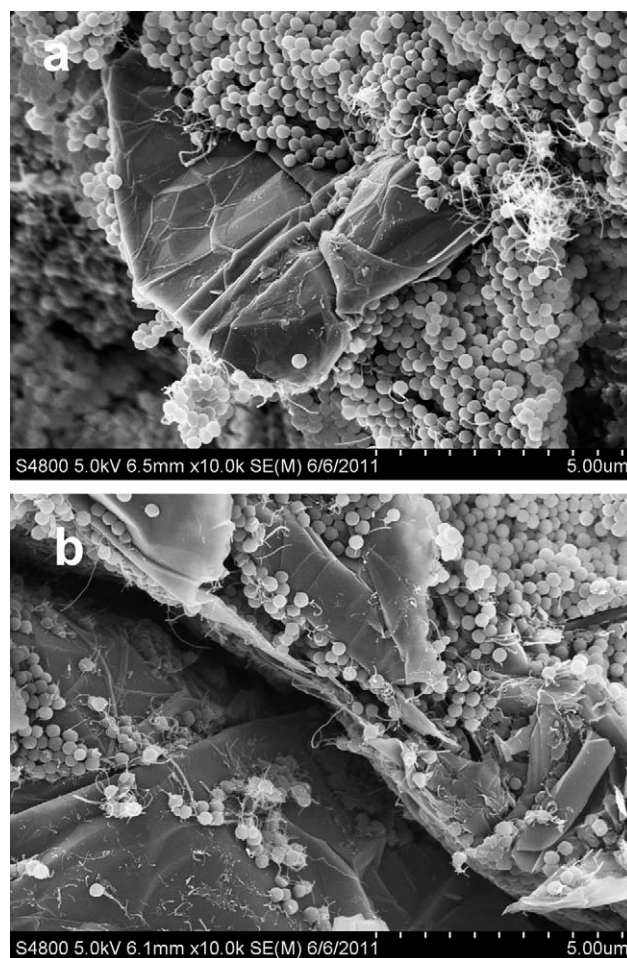

Figure 6. SEM images of fracture surfaces of PVDF/EG-CNTs with total loadings of (a) 3.13 wt % and (b) 5.22 wt % before heat treatment, showing the dispersion state of fillers.
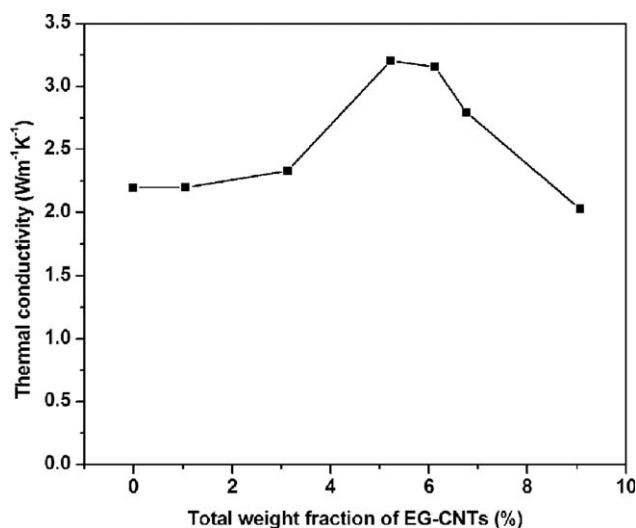
Thermal Conductivity of PVDF/EG-CNTs Composites

The high cost of producing CNTs is a major drawback, severely limiting its applications as polymer filler. In this work, two components of CNTs and EG were tried for filling into PVDF to improve the thermal conductivity, in which equal concentrations of CNTs and EG are filled in the composites. Figure 6 presents SEM images of PVDF/EG-CNTs composites with 3.13 and 5.22 wt % total loadings before heat treatment to observe the original arrangement of these fillers in the composites. The images clearly indicate that EG platelets and CNTs are homogenously dispersed in PVDF particle matrix, where the spherical particles are PVDF. It can be seen that a small fraction of CNTs is dispersed on EG platelets with a higher loading. We expect these CNTs can provide multiple pathways through a synergy between EG and CNTs to improve thermal conductivity.[31]

Figure 7 shows the thermal conductivity of PVDF composites reinforced by hybrid EG-CNTs under different amounts of filler content. The composite with 5.22 wt % hybrid fillers has the highest thermal conductivity of 3.2 Wm^{-1} K^{-1}. Interestingly, the trend of the thermal conductivity on filler loading is also similar to those of EG and CNTs filled PVDF as shown in Figure 5. The value of thermal conductivity increases and subse-

Figure 7. Thermal conductivity of PVDF/EG-CNTs composites varied with total filler content.

higher than that of the composites with single EG and CNTs filled under identical loading (Figure 5). This result suggests that there should exist a synergistic effect between two kinds of fillers and the use of hybrid fillers leads to improved thermal conductivity of the composite by forming more conductive pathways to reducing the interfacial phonon scattering between the matrix and fillers.[32] Thus, the hybrid filler system shows a positive effect on the thermal conductivity of composites.

The hybrid filler combined single-walled CNTs and graphitic nanoplatelets could provide the highest efficiency in the thermal conductivity enhancement of epoxy composites reported by Yu et al.[33] Yang et al.[34] also found a synergetic effect between multigraphene platelets and CNTs in improving the mechanical properties and thermal conductivity of epoxy composites, because the stacking of graphene was inhibited by CNTs and CNTs could bridge adjacent grapheme platelets.[34] In our cases, we posit that the synergism between EG and CNTs facilitates phonon transfer and leads to improved conductivity.
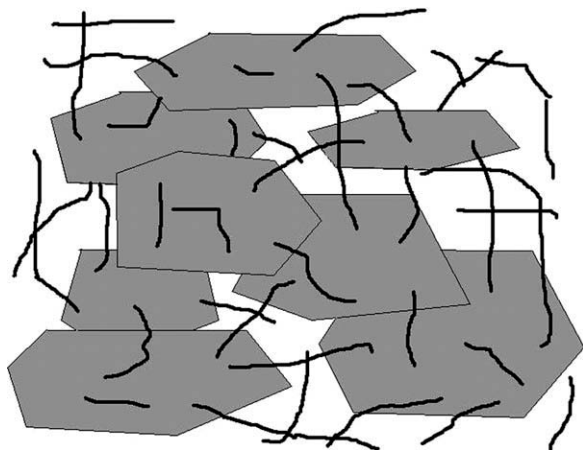

Figure 8. Schematic diagram of a net work in PVDF/CNTs-EG, black curves and gray polygon representing CNTs and EG, respectively.

A schematic diagram showing the formation of a conducting network in PVDF/EG-CNTs composites is depicted in Figure 8. The higher conductivity of EG-CNT filler composites attributes to the improved dispersion of fillers in the matrix, as well as the CNTs bridges that enhance the connecting conductance of EG platelets. The presence of CNTs can also prevent the agglomeration of EG platelet due to the π–π interaction between EG platelets. Consequently, the hybrid system may form three-dimensional architecture of the fillers and the thermal conductivity of the composites is considerably improved. EG is much easier to produce as compared to CNTs and costs less. Thus, the hybrid filler is more applicable in thermally conductive composites as it forms enhanced conducting networks that can provide synergetic effects and cost reduction simultaneously.[32]

CONCLUSIONS

This study used CNTs and EG as fillers to prepare PVDF composites. The solution mixing yielded good dispersion of CNTs filler in the polymer matrix and the electrical conductivity of the CNTs filled PVDF followed the classical percolation theory. The thermal conductivities of the composites generally increased with filler content. Experimental results showed that the thermal conductivities in the hybrid filler composites were higher than those of EG and CNTs filler composites due to the synergistic effects of the hybrid filler, and more than 45% increase was achieved with 5.22 wt % EG-CNTs loading. This preparation process was easily conducted with low cost and environmental friendliness.

REFERENCES

1. Yang, Y. S.; Shi, Z. Q.; Holdcroft, S. *Macromolecules* **2004,** *37*, 1678.

2. Liu, F.; Zhang, X. B.; Li, W. C.; Cheng, J. P.; Tao, X. Y.; Li, Y.; Shen, L. *Compos. Part A* **2009,** *40*, 1717.

3. Giannelis, P. E.; Ansari, S. J. *Polym. Sci. B* **2009,** *47*, 888.

4. He, L. H.; Sun, J.; Zheng, X. L.; Xu, Q.; Song R. J. *Appl. Polym. Sci.* **2011,** *119*, 1905.

5. Bao, S. P.; Liang, G. D.; Tjong, S. C. *Carbon* **2011,** *49*, 1758.

6. Ke, K.; Wen, R.; Wang, Y.; Yang, W.; Xie, B. H.; Yang, M. B. *J. Mater. Sci.* **2011,** *46*, 1542.

7. Martins, J. N.; Bassani, T. S.; Barra, G. M.; Oliveira, R. V. *Polym. Int.* **2011,** *60*, 430.

8. Yuan, J. K.; Yao, S. H.; Dang, Z. M.; Sylvestre, A.; Genestoux, M.; Bai, J. B. *J. Phys. Chem. C* **2011,** *115*, 5515.

9. Yuan, J. K.; Li, W. L.; Yao, S. H.; Lin, Y. Q.; Sylvestre, A.; Bai, J. B. *Appl. Phys. Lett.* **2011,** *98*, 032901.

10. Wen, R.; Ke, K.; Yang, W.; Xie, B. H.; Yang, M. B. *J. Appl. Polym. Sci.* **2011,** *121*, 3041.

11. Bryan, G. O.; Yang, E. L; Zifer, T.; Wally, K.; Skinner, J. L.; Vance, A. L. J. *Appl. Polym. Sci.* **2011,***120*, 1379.

12. He, L. H.; Xu, Q.; Hua, C. W.; Song, R. *Polym. Compos.* **2010,** *921*.

13. Jin, Z. X.; Pramoda, K. P.; Goh, S. H.; Xu, G. Q. *Mater Res. Bull.* **2002,** *37*, 271.

14. Chen, D.; Wang, M.; Zhang, W. D.; Liu, T. X. *J. Appl. Polym. Sci.* **2009,** *113*, 644.

15. Chae, D. W.; Hong, S. M. *Macromol. Res.* **2011,** *19*, 326.

16. Su, C.; Xu, L. H.; Zhang, C.; Zhu, J. *Compos. Sci. Technol.* **2011,** *71*, 1016.

17. Kang, D. J.; Pal, K.; Bang, D. S.; Kim, J. K. *J. Appl. Polym. Sci.* **2011,***121*, 226.

18. Chen, G. X.; Li, Y. J.; Shimizu, H. *Carbon* **2007,** *45*, 2334.

19. Lee, C.; Wei, X.; Kysar, J. W.; Hone, J. *Science* **2008,** *321*, 385.

20. Potschke, P.; Abdel-Goad, M.; Pegel, S.; Jehnichen, D.; Mark, J. E.; Zhou, D.; Heinrich, G. J. *Macromol. Sci. A* **2010,** *47*, 12.

21. Li, Y. C.; Tjong, S. C.; Li, R. K. Y. *Synth. Met.* **2010,** *160*, 1912.

22. Li, Y. C.; Li, R. K. Y.; Tjong, S. C. *E-Polymers* **2009,** *019*.

23. Zheng, G. H.; Wu, J. S.; Wang, W. P.; Pan, C. Y. *Carbon* **2004,** *42*, 2839.

24. Zheng, W. G.; Wong, S. C. *Compos. Sci. Technol.* **2003,** *63*, 225.

25. Maleki, H.; Selman, J. R.; Dinwiddie, R. B.; Wang, H. *J. Power Sources* **2001,** *94*, 26.

26. Ravi, P. *Science* **2010,** *328*, 185.

27. Cheng, J. P.; Zhang, X. B.; Luo, Z. Q.; Liu, F.; Ye, Y.; Yin, W. Z.; Liu, W.; Han, Y. X. *Mater. Chem. Phys.* **2006,** *95*, 5.

28. Cheng, J. P.; Zhang, X. B.; Yi, G. F.; Ye, Y.; Xia, M. S. *J. Alloys Compd.* **2008,** *455*, 5.

29. Cheng, J. P.; Zhang, X. B.; Ye, Y. J. *Solid State Chem.* **2006,** *179*, 91.

30. Shi, D.; Cheng, J. P.; Liu, F.; Zhang, X. B. *J. Alloys Compd.* **2010,** *502*, 365.

31. Li, J.; Wong, P. S.; Kim, J. K. *Mat Sci Eng A-Struct* **2008,** *483–484*, 660.

32. Lee, G. W.; Park, M.; Kim, J. K.; Lee, J. I.; Yoon, H. G. *Compos. Part A* **2006,** *37*, 727.

33. Yu, A. P.; Ramesh P.; Sun X. B.; Bekyarova, E.; Itkis M. E.; Haddon, R. C. *Adv. Mater.* **2008,** *20*, 4740.

34. Yang, S. Y.; Lin, W. N.; Huang, Y. L.; Tien, H. W.; Wang, J. Y.; Ma, C. C.; Li, S. M.; Wang, Y. S. *Carbon* **2011,** *49*, 793.