

Dispersion of Graphite Nanosheets in Polymer Resins via Masterbatch Technique

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ABSTRACT: The dispersion of graphite nanosheets (GNs) in polymer matrices via the masterbatch technique was investigated. Modifying resin was added to GNs to prepare blend which is designated as the masterbatch. Such masterbatches, containing 70–80 wt % of GN filler, were blended with target polymers via melt extrusion process to prepare polymer/GN nanocomposites. The extruded nanocomposites showed characteristic conducting percolation behaviors with the percolation thresholds mainly dependent on the miscibility of the modifying resin with polymer matrix. The percolation thresholds of AS (Acrylonitrile-Styrene copolymer)/GN and high-

density polyethylene (HDPE)/GN nanocomposites prepared by this technique were about 9 and 14 wt % of GN, respectively. Scanning electron microscopy and other characterizations showed that the GNs were well dispersed in AS and HDPE resins. The extrusion process and compatibility of the modifying resin with target polymer proved to be important factors for the homogeneity of the nanodispersion. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 3470–3475, 2007

Key words: graphite nanosheets; masterbatch; nanocomposites; conductive composites; extrusion

INTRODUCTION

Conductive composites, made by a mixture of electrical conductive fillers and insulating matrices, have received much attention in the last decades.^{1,2} Various conductive fillers have been incorporated as a second phase into insulative polymer matrices to prepare electrical conducting composites, such as metallic powders,^{3,4} graphite powder,^{5,6} carbon black,^{7,8} and so forth. It is noted that for those conventional fillers rather high loadings are required to achieve satisfying electrical properties, resulting in materials redundancy and detrimental mechanical properties. Efforts have been made to lower the loading of the conductive fillers without reducing the conductivity of the filled composites. Recently, expanded graphite^{9–15} has been used as the conducting fillers for conducting polymer composites, which greatly reduced the filler content as compared to conventional fillers. More recently, exfoliated graphite nanosheets^{16–19} with diameter of 5 to 20 μm and thickness of 30 to 80 nm have been successfully incorporated into PMMA, PS, and nylon 6, and with only about 0.3, 0.32, and 0.75 vol %, respectively, required to satisfy the critical percolative transition.

This reveals that graphite nanosheets (GNs), which are inexpensive and convenient for mass preparation, should prove to be one of new conductive fillers with promising applications in polymer conductive composites.

Graphite nanosheets, whose thickness is in nanoscale, tend to accumulate when they are blended with polymer resins directly, and thus it is difficult to achieve good distribution in polymer matrices. However, they could be more readily dispersed in some liquid medium, such as some monomers or solvents, with the help of sonication.¹⁷ Therefore, solution blending or *in situ* polymerization could be an effective approach for the preparation of their composites.^{18,20} It is obvious, however, that the above methods could not meet the needs of blending the GN with polyethylene and other commercial resins.

The extrusion process is one of most effective processing techniques for polymer blending in the plastics industry. It has been adopted for almost all thermoplastic polymers to blend with ceramic fillers such as CaCO_3 and SiO_2 , or carbonaceous materials such as carbon black, graphite powder, and so on. Recent reports^{21,22} indicate that the extrusion technique is also effective in compounding polymer with expanded graphite. This article's aim is to modify the graphite nanosheets in order to prepare masterbatches so that the graphite nanosheets can be dispersed into commercial resins such as polyethylene, AS (Acrylonitrile-Styrene copolymer) resin, and so forth via the practical extrusion blending process. The as-prepared GNs were first coated with AS resin in order to

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prepare modified GNs, called the GN masterbatch, which contained 70–80 wt % of GNs. The masterbatch was then blended with target matrices via the extrusion process, resulting in good dispersion of GNs throughout polymer matrices.

EXPERIMENTAL

Preparation of graphite nanosheets

GNs were prepared according to the literature.²³ Briefly, 1 g of the expanded graphite was immersed into 400 ml of 70% of aqueous alcoholic solution, and subjected to powdering in an ultrasonic bath (KQ-100, Kunshan, China; power: 100 W) for 12 h. The resultant dispersion was filtered and dried to obtain the GN sample.

Preparation of AS-modified GN

The dried GN or graphite powder (7500 mesh) was dispersed in AS/2-butanone solution under ultrasonication. Precipitate was obtained by adding precipitant, 50% of aqueous alcoholic solution, into the mixture. The precipitate was filtered and dried, and designated as the masterbatch. It contained 70–80 wt % of graphite. In order to prepare the masterbatch, graphite particles were coated with enough modifying resin. In this work, 20 wt % of AS resin as the modifying resin was found to be appropriate for the modification. Figure 1 shows the process of the preparation of the masterbatch. AS resin was dissolved in 2-butanone at room temperature [Fig. 1(a)]. After the addition of the GNs, the mixture was sonicated, thus forming a homogeneous dispersion of graphite particles in AS solution [Fig. 1(b)]. The precipitation of graphite particles coated with AS resin occurred after adding the precipitant, aqueous alcoholic solution, to the mixture. Graphite particles, being isolated, were embedded in AS resin during the precipitation [Fig. 1(c)].

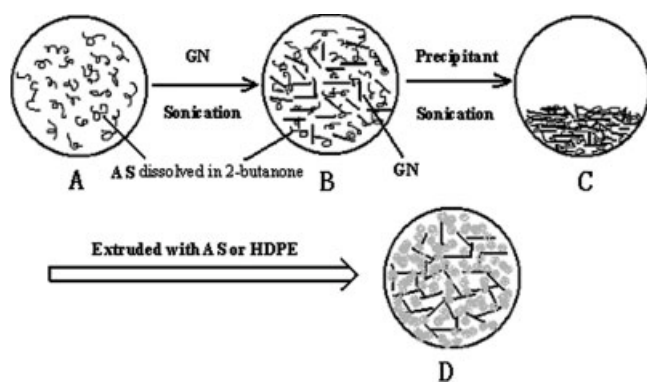


Figure 1 Schematic illustration of preparation of masterbatch and the target composites: (a) AS solution; (b) dispersion of GN in AS solution; (c) precipitate of the AS/GN mixture; (d) dispersion of GN in AS or HDPE resin.

Dispersion of masterbatch in polymer matrices

The masterbatches and polymer resins (AS or HDPE) were mixed thoroughly and were fed into a single-screw extruder ($L/D = 11$) to prepare the blends. The extruded temperature was 170°C and 190°C for AS and HDPE, respectively. After sampling, the extra extruded samples were chopped into pellets and put aside for the next extrusion. Commercially available natural graphite powders (7500 mesh, Shangdong, Heili Graphite Co., Qingdao, China) were also used as conducting filler for comparison.

For electrical measurements, short pieces of about 20–25 mm in length were cut from the extruded samples at different places. The volume resistivities of the nanocomposites were measured at room temperature using a DT 9205A (Hong Chang, China) or ZC-36 high-resistance tester (Shanghai, No. 6, Electrometer Factory, China). Scanning electron microscopies were obtained on a LEO-1530 SEM (Germany).

RESULTS AND DISCUSSION

Structure of graphite nanosheets

It is known that expanded graphite (EG) consists of graphite sheets with thickness of less than 100 nm. After fragmentation via sonication, EG was torn to fully exfoliated GNs with thickness in the range of 30–80 nm nanometers (Fig. 1), as described in our previous report.²² The diameter of the GNs was mostly in the range of 5–20 μm . Thus, they exhibited an aspect ratio (diameter to thickness) as high as around 100 to 500. In the SEM images, shown in Figure 2(a,b), the structure of the isolated GNs is very different from that of the EG before sonication [Fig. 1(c)].

Structure and properties of the GN masterbatch

Scanning electron microscopy (SEM) characterization accompanied by X-ray energy-dispersive spectroscopy (EDS) analysis showed that the GNs in the masterbatch were well coated by AS resin. Figure 3(a,b) shows the SEM micrographs of the masterbatch, with the AS resin fibre coating on the graphite nanosheets detected by EDS clearly marked. The resin wrapping around the GNs effectively prevented the graphite nanosheets from accumulation during the process of blending with polymer matrices. The conductivity of the prepared masterbatch was as high as 104 s/m at room temperature.

Structure and electrical properties of polymer/GN composites

Figures 4 and 5 show the logarithmic volume resistivities of composites as a function of the weight fraction of the GNs presenting in the AS and HDPE matrices, respec-

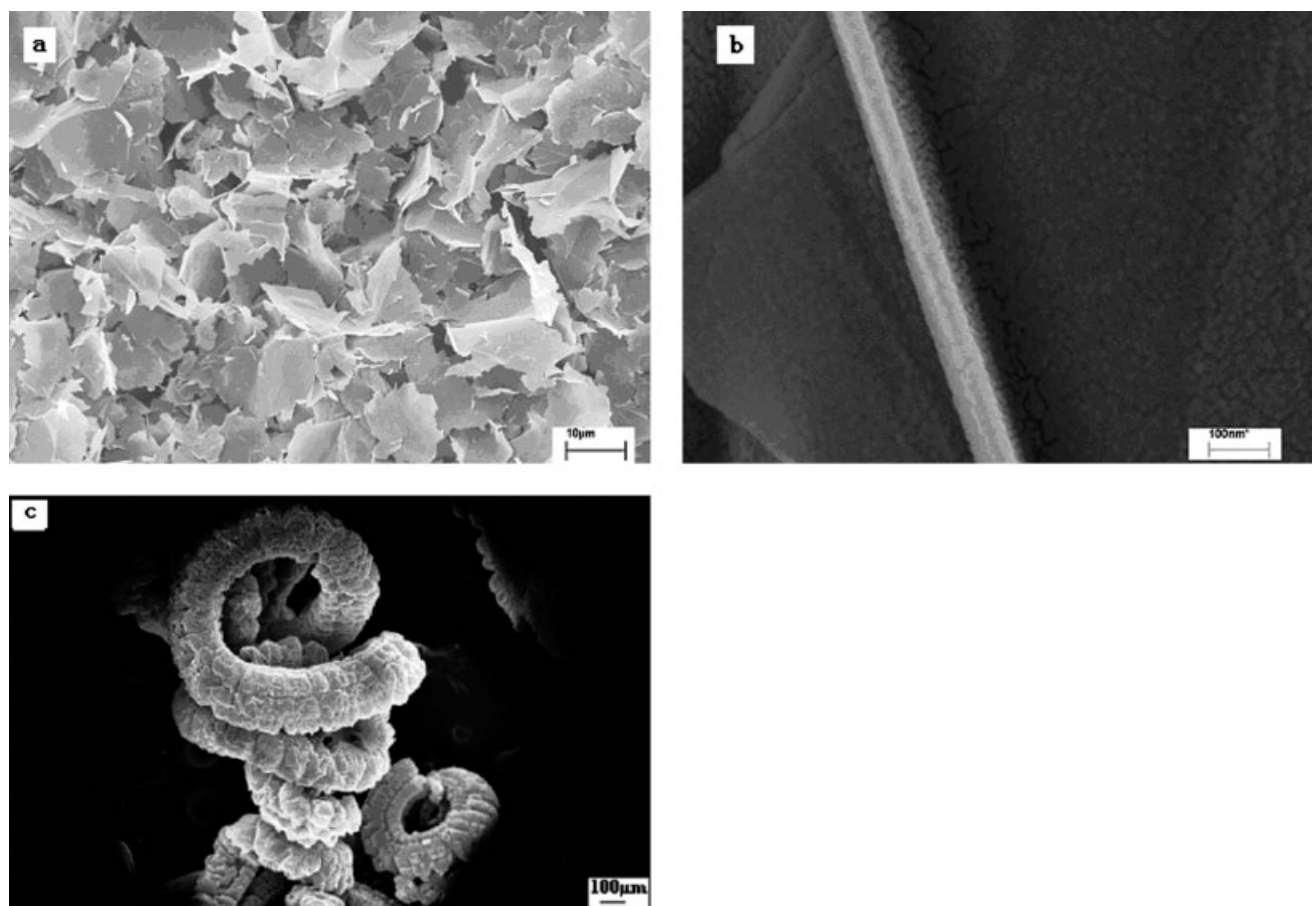


Figure 2 SEM micrographs of GNs and expanded graphite: (a) lower magnification; (b) high magnification; (c) expanded graphite before sonication.

tively. AS and HDPE are traditional insulative polymers at room temperature. The addition of GNs significantly lowered the resistivities of the composites. The S-shape curves indicate that the nanocomposites exhibited typical percolative transition from an insulator to semiconductor. The percolation threshold values of the AS/GN and HDPE/GN nanocomposites were 9 and 14 wt % of

the GNs, respectively. The percolation threshold value of the HDPE/7500 mesh graphite was 34 wt % (Fig. 6), which is markedly higher than that of the HDPE/GN composite. The conductivity of the composites was determined by the structure of the conducting network formed by the conductive fillers. GNs with elongated geometry have great advantage in forming conducting

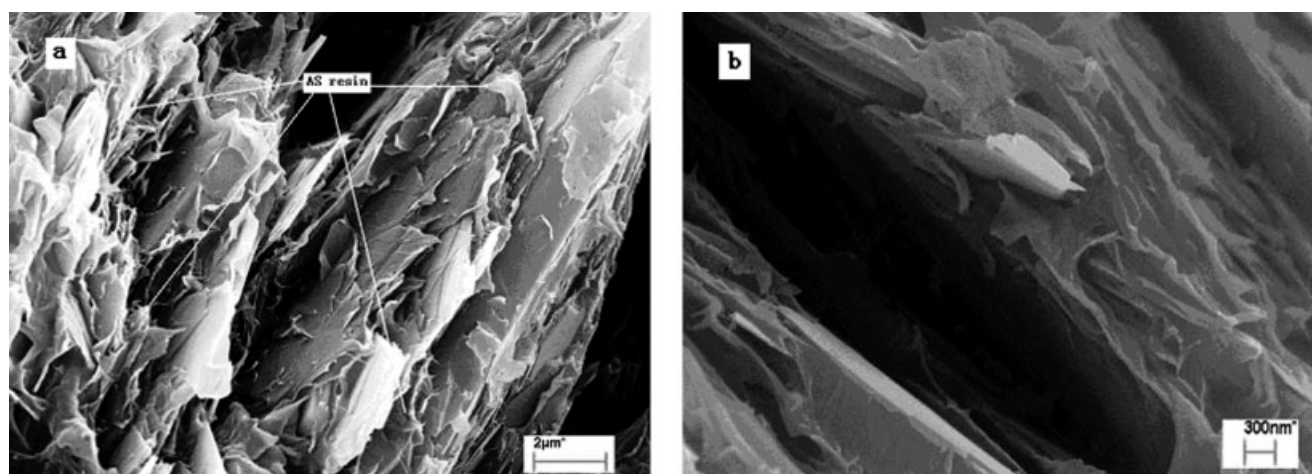


Figure 3 SEM micrographs of the as-prepared masterbatch: (a) lower magnification; (b) higher magnification.

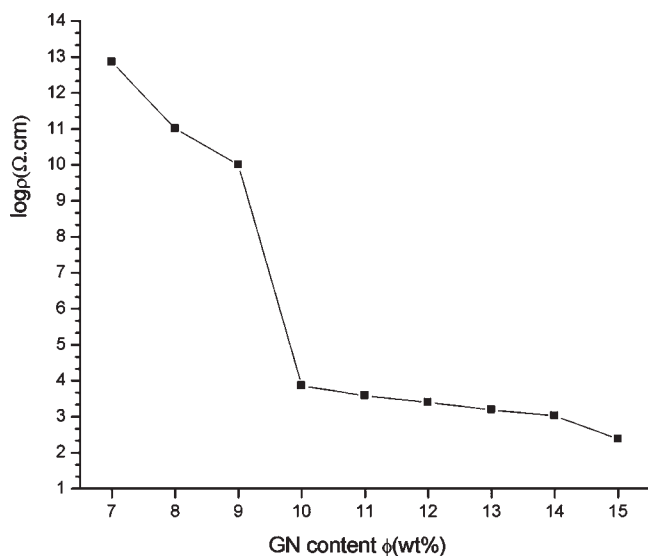


Figure 4 Resistivity versus concentration of GNs for AS/GN nanocomposites.

networks in a polymer matrix, thus leading to the lower percolation threshold of the conducting composite.

The properties of the polymer matrix are another factor affecting the electrical properties of the composites. In this research, the masterbatch (in which GNs were coated by AS resin) possessed excellent miscibility with the AS matrix. The dispersion of the GNs was homogeneous throughout the AS matrix [Fig. 1(d)], and the percolation threshold was only about 9 wt %, which is much lower than that of traditional conducting fillers. This low percolation-threshold value also revealed the good dispersion of the GNs in the masterbatch, indicating effective modification via the coating treatment. The SEM micrograph in Figure 7(a) clearly shows that the isolated GNs were evenly embedded in the polymer matrix and the distribution of

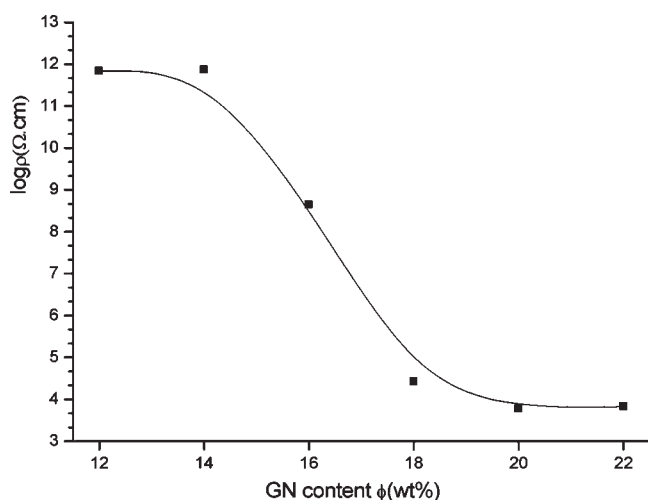


Figure 5 Resistivity versus concentration of GNs for HDPE/GN nanocomposites.

the GNs was relatively homogeneous. Closer inspection [see Fig. 7(b)] reveals that the interface between the GN and the AS resin was clear, and many of the GNs had even been pulled out of the nesting resin, indicating the poor interaction between the GN and the AS resin. Hence, chemical modification of graphite, for example, improving the polarity of the GNs, should be considered in future work.

HDPE is a high-crystalline nonpolar polymer. Its miscibility with AS resin is poor. Thus, although the GNs were well coated by AS resin, the dispersion of the GNs in HDPE was not as good as that in the AS matrix. Some accumulations of GNs could be found via SEM, as shown in Figure 7(c). Nevertheless, the percolation threshold value of 14 wt % (see Fig. 5) was still encouraging, as compared with the percolation threshold value of HDPE/7500 mesh graphite composite, which was 34 wt % (see Fig. 6).

Extrusion times also affected the electrical properties of the composites significantly. The extrusion process enhanced the GN dispersion within the polymer matrix, but the experiments showed that its inferences on the conductivities were varied with the GN contents.

Figures 8 and 9 show the composite resistivities as a function of extrusion times for the AS/GN and HDPE/GN composites, respectively. For the AS/GN composite (Fig. 8), the resistivity appeared to slightly increase with an increment of extrusion times from the first to the fourth extrusion, when the GN content was below the percolation threshold value of 9 wt %. It is obvious that when the GN content was in the percolative range, 9–11 wt % of GN content in the AS system and 14–18% of GN content in the HDPE composite, the composite resistivities fluctuated violently with the increasing extrusion times, as shown in Figures 8 and 9, respectively. It is understood that for the samples

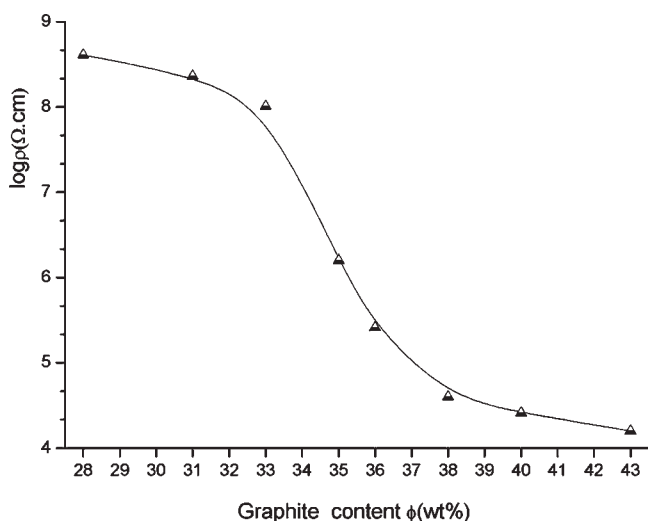


Figure 6 Resistivity versus concentration of graphite for HDPE/7500 mesh graphite composites.

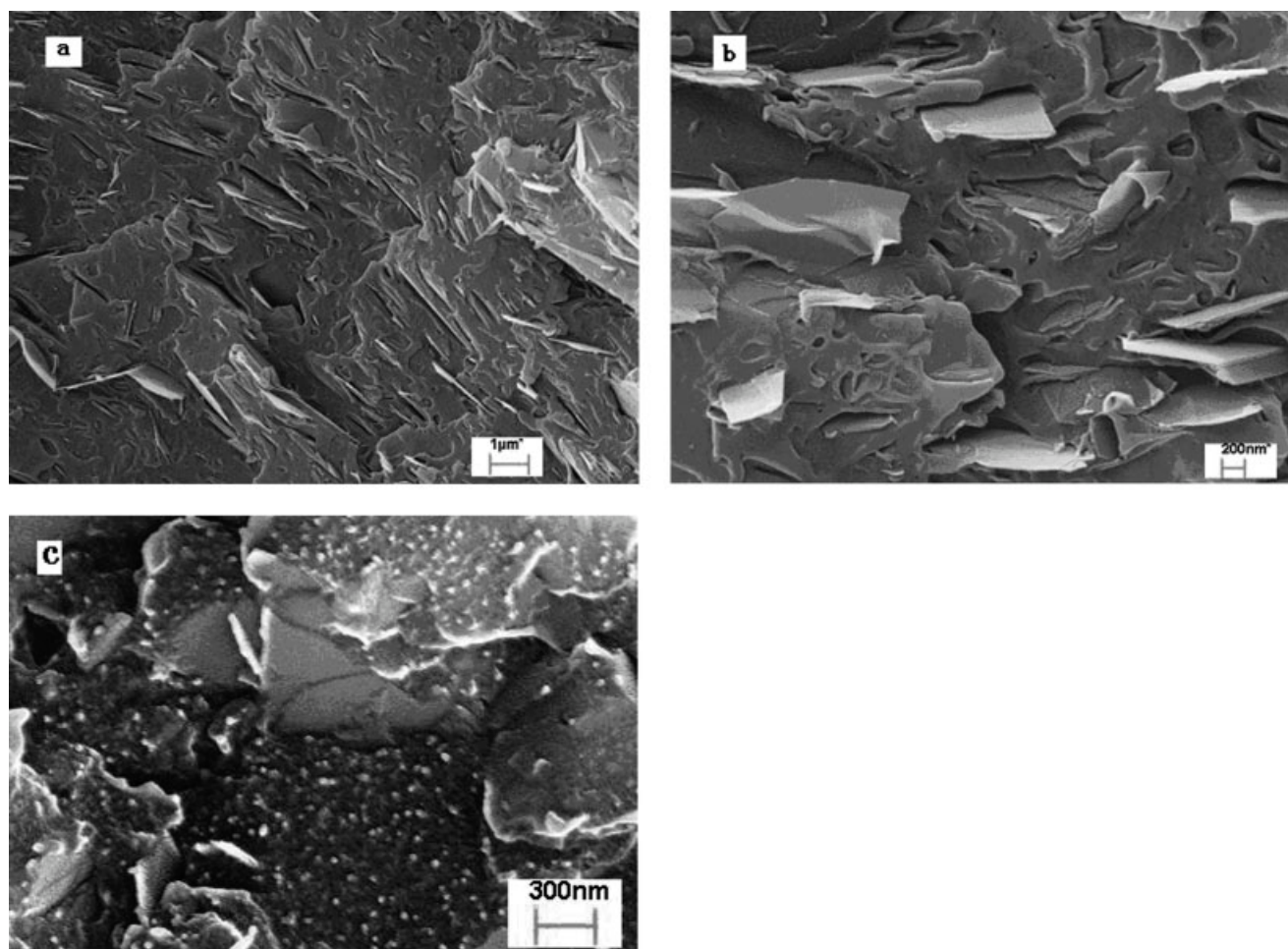


Figure 7 SEM micrographs of the section of polymer/GN composites: (a) lower magnification for the AS/GN composite; (b) high magnification for the AS/GN composite; (c) PE/GN composite section etched slightly with toluene.

with GN content within the percolative range, the conducting networks are at the critical point of consumption; linkage or destruction of conducting networks always accompanies the extrusion process and leads to fluctuation of the conductivities. Below the percolative range, the conducting network is far from consummation; hence, it is not sensitive to the extrusion process. For GN content far above the percolative range, such as 13% and 15% in the AS composites and 20% and 22% of GN in the HDPE composites, the conducting networks were well built; the fluctuations of the resistivities were mild due to these well-built conducting networks.

Similar results can be found in the HDPE/GN composite shown in Figure 9, demonstrating that the violent fluctuation of the conductivities occurs in the range of 14–18 wt % of GN content, which was the percolative range of the HDPE/GN composite (see also Fig. 5).

From Figure 8, it can also be found that the resistivity of HDPE/GN composite decreased slowly and reached a steady-state region with the increasing

extrusion times when the GN content was far from the percolation range. This can be explained as follows. The first extrusion may not achieve good dispersion of GNs in the HDPE matrix, due to the poor

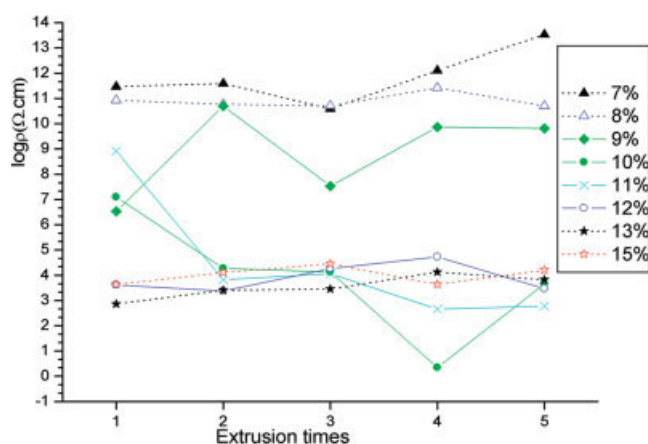


Figure 8 Log_p plot of AS/GN nanocomposites versus extrusion times. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

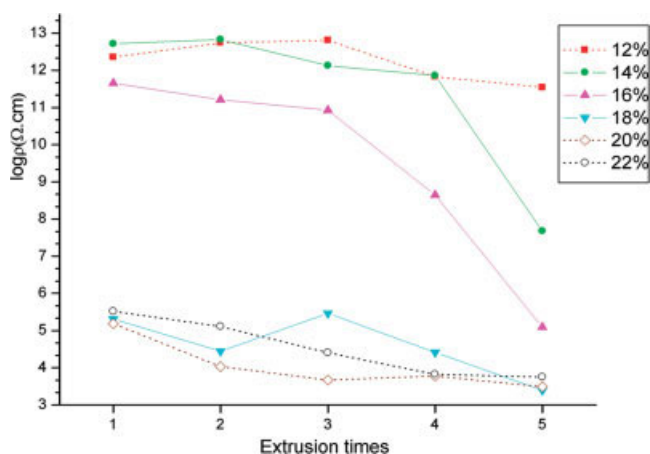


Figure 9 Logp plot of HDPE/GN nanocomposites versus extrusion times. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

miscibility of AS (modifying resin) with HDPE. The increasing extrusion process enhanced the dispersion of GNs, leading to better formation of conducting networks in the polymer matrix and lower resistivities of the resultant composites. On the contrary, good dispersion of GNs may be achieved at the first extrusion in the AS/GN composite; the resistivities, instead of showing a decrease as happened in the HDPE composite, tend to increase with increasing extrusion times, as shown in Figure 9. This increase of resistivities may be attributed to the fragmentation of the GNs during the extrusion process.

Figure 9 also shows that the resistivity of the HDPE/GN composite with the GN content over the percolation range (20 and 22 wt %) decreased gradually at the first two extrusions and reached a steady-state region after the third and fourth extrusions. This indicates that the first three or four extrusions have achieved maximum dispersion of GNs within HDPE and the dispersion could not be further improved with further extrusion process under the current extrusion condition. Whereas in the case of AS/GN in Figure 8, the first four extrusions resulted in similar of composite resistivities, indicating that GN coated AS masterbatch has much better compatibility with the target matrix (AS resin). The first extrusion may have achieved maximum dispersion of GNs within the AS matrix.

Thus, the better the compatibility of the filler carrier with target polymer, the less extrusion time is needed to achieve homogeneous dispersion. Hence, it is important to choose as the filler carrier a modifying resin which is compatible as possible with the target polymer matrices when preparing a masterbatch. In other words, with a more effective extruder and a more suitable modifying resin, one can anticipate the homogeneous dispersion of GNs in the preparation of polymer/graphite nanosheet composites.

CONCLUSION

A practical technique for the dispersion of graphite nanosheets (GNs) in polymer matrices has been proposed via blending a GN masterbatch with polymer matrices using the extrusion process. The conducting properties of the as-prepared composites depended mainly on the miscibility of the modifying resin in masterbatches with matrices. Compatibility between the modifying resin and target polymer matrices and the efficiency of the extruder are important factors affecting the dispersion of GNs within polymer matrices. With a suitable modifying resin and an effective extruder, one can anticipate homogeneous dispersion of GNs in the preparation of polymer/graphite nanosheet composites.

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References

- Saunders, D. S.; Galea, S. C.; Deirmendjian, G. K. *Composite* 1993, 24, 309.
- Ezquerro Y. A.; Kulesza M.; Alta-Calleja, F. J. *Synth Met* 1991, 41, 915.
- Pinto G.; Jimenez-Martin, A. *Polym Compos* 2001, 22, 65.
- Flandin, L.; Bidan, G.; Brechet, Y.; Cavaille, J. Y. *Polym Compos* 2000, 21, 165.
- Medalia, A. I. *Rubber Chem Tech* 1986, 59, 432.
- Carmona, F. *Physica A* 1989, 157, 461.
- Sichel, E. K. *Carbon Black-Polymer Composites*. Marcel Dekker: New York, 1982.
- Shigure, Y.; Iijima, S.; Ito, H.; Ota T.; Unuma, H.; Takahashi, M. *J Mater Sci* 1999, 34, 2979.
- Pan, Y. X.; Yu, Z. Z.; Ou, Y. C.; Hu, G. H. *J Polym Sci Part B: Polym Phys* 2000, 38, 1626.
- Chen, G. H.; Wu, D. J.; Weng, W. G.; Yan, W. L. *J Appl Polym Sci* 2001, 82, 2506.
- Zheng, W.; Wong, S.-C.; Sue, H. J. *Polymer* 2002, 43, 6767.
- Celzard, A.; McRae, E.; Mareche, J. F.; Furdin, G.; Dufort, M.; Deleuze, C. *J Phys Chem Solids* 1996, 57, 715.
- Xiao, P.; Xiao, M.; Gong, K. *Polymer*, 2002, 43, 2245.
- Shen, J. W.; Huang, W. Y.; Zuo, S. W. *J Appl Polym Sci* 2005, 97, 51.
- Uhl, F. M.; Yao, Q.; Nakajima, H. *Polym Degrad Stab* 2005, 89, 70.
- Chen, G. H.; Wu, D. J.; Weng, W. G.; Wu, C. L. *Carbon* 2003, 41, 619.
- Chen, G. H.; Wu, C. L.; Weng, W. G.; Wu, D. J.; Yan, W. L. *Polymer* 2003, 44, 1781.
- Weng, W. G.; Chen, G. H.; Wu, D. J.; Chen, X. F.; Lu, J. R.; Wang, P. P. *J Polym Sci Part B: Phys Ed* 2004, 42, 2844.
- Lu, J. R.; Weng, W. G.; Chen, X. F.; Wu, D. J.; Wu, C. L.; Chen, G. H. *Adv Funct Mater* 2005, 15, 1358.
- Chen, G. H.; Weng, W. G.; Wu, D. J.; Wu, C. L. *Euro Polym J* 2003, 39, 2329.
- Zheng, W.; Lu, X.; Wong, S.-C. *J Appl Polym Sci* 2004, 91, 1.
- Kalaitzidou, K.; Fukushima, H.; Drzal, L. T. *Proc Society of Plastics Engineers Annual Technical Conference* 2004, 62, 1533.
- Chen, G. H.; Weng, W. G.; Wu, D. J.; Wu, C. L.; Lu, J. R.; Wang, P. P.; Chen, X. F. *Carbon* 2004, 42, 753.