

Rapid Communication

CONDUCTIVE POLYMER NANOCOMPOSITES CONTAINING *IN SITU* ULTRA-FINE METAL PARTICLES

Yi-lei Zhu^{a, b}, Xiao-hong Zhang^b, Mei-fang Guo^b, Wen-qing Huang^b, Jin Yang^b,
Zhong-wei Liang^b and Jin-liang Qiao^{a, b*}

^a College of Materials Science and Engineering, Beijing University of Chemical Technology,
Beijing 100029, China

^b Sinopec Beijing Research Institute of Chemical Industry, Beijing 100013, China

Abstract A conductive polymeric composite containing *in situ* ultra-fine metal particles is prepared by melt blending. Incorporation of elastomeric nano-particles and carbon nanotubes hinders the coalescing of metal particles and causes a shift to the breakup direction in the breakup/coalescence equilibrium of metal particles. The prime metal particles (about 26 μm) are *in situ* converted into the ultra-fine metal particles (UFMP, about 932 nm). The network of carbon nanotubes has been improved due to *in situ* ultra-fine metal particles and the percolation threshold of the composite with 1.96 vol% UFMP is only 0.25 vol% carbon nanotubes.

Keywords: Polymeric composites; Ultra-fine metal particle; Carbon nanotubes; Conductive.

INTRODUCTION

The Nobel Prize in Chemistry 2000 was awarded jointly to Alan J. Heeger, Alan G. MacDiarmid, and Hideki Shirakawa “for the discovery and development of conductive polymers”^[1–3]. In fact, conductive polymers have been the focus of considerable research interest over the past two decades because of its potential for broad applications, including those in electronics such as stretchable electronic devices, biosensors and electromagnetic interference (EMI) shielding^[4–6]. Among the conductive polymer materials, conductive polymer composite (CPC) was found to be the most promising due to its tractability and low cost^[7–10]. However, the electrical properties of CPC are heavily dependent on the types of fillers^[11, 12]. Nanoscale conductive filler is one of the best candidates for high performance CPC. The high aspect area ratio of the nanoscale conductive fillers, however, easily causes aggregation or/and oxidization (especially for the nano-metal fillers); therefore, polymer/nano-filler composites usually require high amount of fillers^[13], which decreases the mechanical properties of conductive polymer composites. It has been found extremely difficult to avoid the aggregation and/or oxidization of conductive fillers^[14].

Low-melting point metal (LMPM) is a possible conductive filler without aggregation and oxidization because its particles are *in situ* formed during blending with polymers^[15]. However, it is difficult to make a conductive material with only polymer and LMPM. Because the amount of LMPM allowed to disperse in polymer matrix is too little and the particle size of LMPM is too large to form a conductive network. The conductivity of material containing LMPM particles can be achieved only if LMPM particles of ultra-fine size disperse in polymer matrix.

* Corresponding author: Jin-liang Qiao (乔金樑), E-mail: qiaojl.bjhy@sinopec.com

Received March 25, 2013; Revised May 9, 2013; Accepted May 10, 2013

doi: 10.1007/s10118-013-1316-6

In current study, the elastomeric nano-particles (ENP)^[16] and multi-walled carbon nanotubes (CNT) are employed to assist the dispersion of LMPM in maleic anhydride grafted polypropylene (PPMA) matrix by traditional blending process. Thanks to the tractability of LMPM, the *in situ* conversion of LMPM particles not only results in ultra-fine metal particles but also avoids the oxidation and agglomeration of the metal particles. Furthermore, the ultra-fine LMPM particles with CNT bridges can form excellent conductive network, therefore, the composites of PPMA/ENP/LMPM/CNT with ultra-low percolation threshold is prepared. It is interesting to understand why ENPs and CNTs can reduce the particle size of LMPM during blending.

EXPERIMENTAL

Maleic anhydride grafted polypropylene (PPMA, melting point = 150 °C, $\rho = 0.91 \text{ g/cm}^3$) was purchased from Nengzhiguang Co., Ltd. (GPM200A, $\rho = 0.91 \text{ g/cm}^3$). The elastomeric nano-particles were carboxylic acrylonitrile butadiene ultra-fine full-vulcanized powdered rubber (ENP, NarpowTM, $\rho = 0.91 \text{ g/cm}^3$). Carbons nanotubes (CNT) were obtained from CNano Technology (FloTubesTM 9000, $\rho = 1.75 \text{ g/cm}^3$ ^[17]). The low-melting point metal (LMPM) was an alloy of lead and tin (melting point = 183 °C, $\rho = 8.78 \text{ g/cm}^3$) with lead to tin weight ratio of 63:37. PPMA/ENP/CNTs/LMPM composites were prepared by blending PPMA, ENP, CNT and LMPM simultaneously in an internal mixer (HAAKE PolyLab) at 210 °C with 70 r/min for 10 min. Before melt blending, all components were premixed. For comparison, the PPMA/CNT and the PPMA/CNT/LMPM and the PPMA/ENP/CNTs composites were also prepared according to the above process. The volume fraction of CNT varied from 0 vol% to 3.5 vol%. The volume fraction of ENP and LMPM was 68.6 vol% and 1.96 vol% to obtain the best electrical conductivity.

Plates with diameter of 100 mm and thickness of 2 mm were prepared by melt-compression at 200 °C for 7 min with 10 kN and were subsequently cool-compressed at 25 °C for 3 min with 5 kN. For the measurement of resistivity above $10^7 \Omega\cdot\text{cm}$, the plates were measured by using a PC68 Digital Teraohmmeter (Shanghai Precision & Scientific Instrument Co., Ltd) according to the ASTM D257-2007. For the measurement of resistivity below $10^7 \Omega\cdot\text{cm}$, the strips cut from the plate were measured by four-point test fixture combined with a Resistivity Tester (Gibitre Instruments) according to the ASTM D991. The morphologies of the samples were observed by using a scanning electron microscope (SEM, FEI XL-30) at 15 keV on the ultra-smooth surface of samples, which were cut using a glass knife at -60 °C with a cut angle of 45°.

RESULTS AND DISCUSSION

When LMPM and PPMA are blended, the particle size distribution of LMPM particles with prime diameter of about 26 μm (see Fig. 1a and Fig. 2a) becomes much wider. There are much larger LMPM particles with diameter of 60 μm and much smaller LMPM particles with diameter of 5 μm in the blend (see Fig. 1b), which indicates the existence of breakup and coalescence processes among LMPM particles during blending. The size of LMPM particles depends on not only the shear rate of blending, but also the breakup rate and coalescence rate. The particle size distribution is a result of equilibrium between the breakup and the coalescence of LMPM particles when the breakup rate equals to the coalescence rate during the blending of LMPM with PPMA (see Fig. 3).

It is well known that the particle size of LMPM will reduce if the breakup/coalescence equilibrium shifts to the breakup direction. Fortunately, the CNT or/and ENP form the railings around LMPM particles which hinder the coalescing and cause the shift to breakup direction in the breakup/coalescence equilibrium of LMPM particles in PPMA matrix. In the PPMA/LMPM/CNT composite, the average diameter of LMPM particles decreases to about 25 μm and the distribution of LMPM particles becomes narrower when compared with the PPMA/LMPM composite (see Fig. 1c).

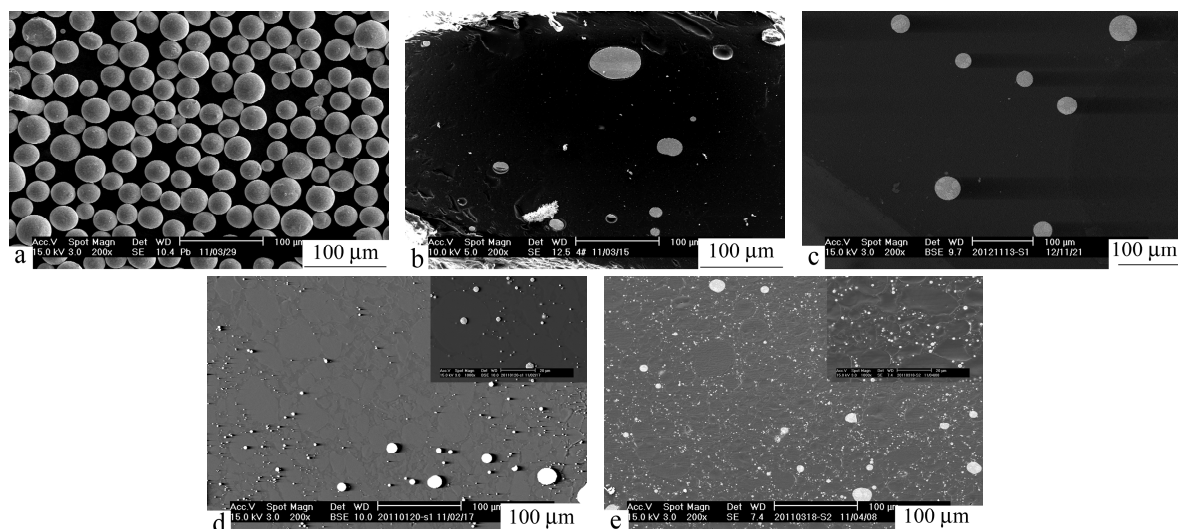


Fig. 1 SEM pictures of the micro-morphologies of LPM and PPMA composites: (a) prime LPM particles, (b) PPMA/LPM composite with 1.96 vol% LPM, (c) PPMA/CNTs/LPM composite with 1.96 vol% LPM and 0.21 vol% CNTs, (d) PPMA/ENP/LPM composite with 1.96 vol% LPM and 68.6 vol% ENP and (e) PPMA/ENP/CNTs/LPM composite with 1.96 vol% LPM, 0.21 vol% CNTs and 68.6 vol% ENP. The backscattering mode is used. The inset (d and e) shows a magnified morphology. The white circles represent the LPM particles in SEM images.

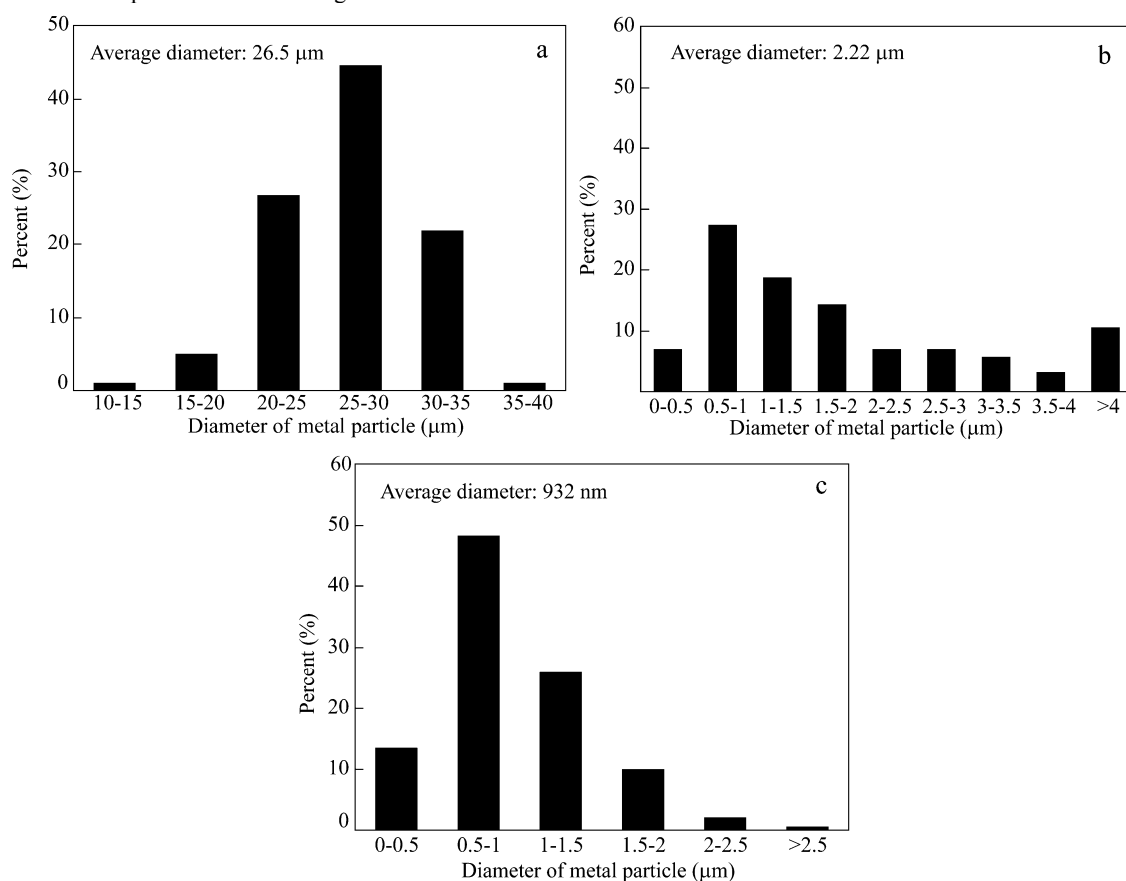


Fig. 2 The diameter distribution of the LPM particles for (a) prime LPM particle, (b) the PPMA/ENP/LPM composites with 1.96 vol% LPM and 68.6 vol% ENP and (c) the PPMA/ENP/CNT/LPM composites with 1.96 vol% LPM, 0.21 vol% CNTs and 68.6 vol% ENP

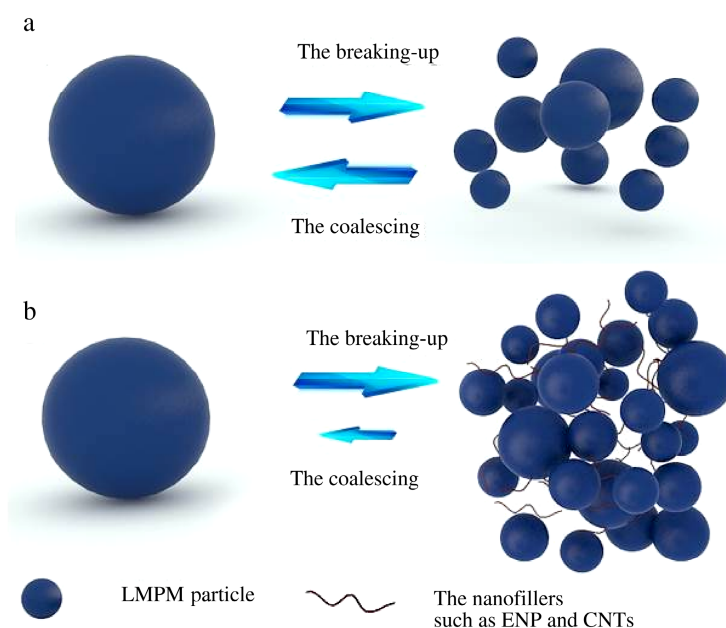


Fig. 3 Schematic illustration of the mechanism of ultra-fine metal particle formation: (a) the breakup/coalescence equilibrium of LMPM particles in polymer/LMPM blends; (b) shift of the breakup/coalescence equilibrium to the breakup direction due to the function of nano-filler preventing the coalescence of LMPM particles during blending

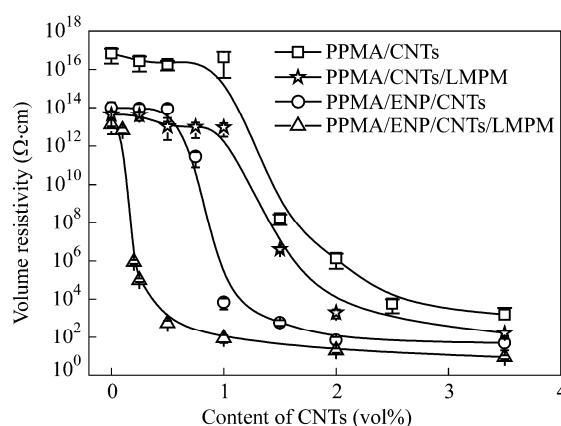


Fig. 4 The relationship of composite volume resistivity and CNT level

The LMPM content is 1.96 vol% in PPMA/CNTs/LMPM composite and PPMA/ENP/CNTs/LMPM composite. The ENP content is 68.6 vol% in PPMA/ENP/CNTs composite and PPMA/ENP/CNTs/LMPM composite. The percolation threshold of PPMA/CNT, PPMA/CNT/LMPM, PPMA/ENP/CNT and PPMA/ENP/CNT/LMPM composites are 2.53 vol%, 2.0 vol%, 1.03 vol% and 0.25 vol% CNTs respectively.

Amazingly, the particle size of LMPM is reduced to 2.2 μm in the PPMA/ENP/LMPM composites (see Fig. 1d and Fig. 2b). Unfortunately, the distance between LMPM particles is still too far to form a conductive network, thus the volume resistivity of PPMA/ENP/LMPM composite is still as high as $1.30 \times 10^{13} \Omega\cdot\text{cm}$ (see Fig. 4). When both ENP and CNT are incorporated into the PPMA/LMPM system, LMPM particle size decreases and its distribution is further narrowed. The average diameter of LMPM is only 932 nm (see Fig. 1e), and the particle size distribution becomes much narrower with 65% of the metal particles at diameters less than 1 micron (see Fig. 2c). The fresh surface of the ultra-fine LMPM particles bridged by CNTs results in the obvious improvement of the electrical properties of PPMA/ENP/LMPM/CNT composites^[17]. The percolation

threshold of composite with 1.96 vol% LMPM is only 0.25 vol% CNT and the resistivity of the composite is only 89 $\Omega\cdot\text{cm}$ when the CNT content reaches 1.0 vol% (see Fig. 4).

It is clear that the nano-particles, ENP and/or CNT, can hinder the coalescing of LMPM particles during blending (see Fig. 3), therefore, it can cause a shift to the breakup direction in the breakup/coalescence equilibrium of LMPM particles. The network of carbon nanotubes was improved due to *in situ* ultra-fine metal particles^[18, 19].

CONCLUSIONS

To summarize, a new method has been developed to make conductive polymer nanocomposites with low volume fraction of conductive fillers, and consequently a new type of conductive polymer nanocomposites of polymer/CNT/ENP/ultra-fine metal particle with low resistivity has been produced by this method. In addition to volume exclusion effect, the nano-particles including ENPs and CNTs have been found to have the ability to reduce the particle size of the conductive filler, the LMPM particles by causing shift to the breakup direction in the breakup/coalescence equilibrium of LMPM particles during blending. Further, CNT can not only reduce the particle size of LMPM particles, but also form bridges among LMPM particles to make a perfect conductive network.

REFERENCES

- 1 MacDiarmid, A.G., *Angew. Chem. Int. Ed. Engl.*, 2001, 40(14): 2581
- 2 Shirakawa, H., *Angew. Chem. Int. Ed. Engl.*, 2001, 40(14): 2574
- 3 Sariciftci, N.S., Smilowitz, L., Heeger, A.J. and Wudl, F., *Science*, 1992, 258(5087): 1474
- 4 Ata, S., Kobashi, K., Yumura, M. and Hata, K., *Nano. Lett.*, 2012, 12(6): 2710
- 5 Sanghvi, A.B., Miller, K.P.H., Belcher, A.M. and Schmidt, C.E., *Nat. Mater.*, 2005, 4(6): 496
- 6 Xu, F. and Zhu, Y., *Adv. Mater.*, 2012, 24(37): 5117
- 7 Deng, H., Skipa, T., Bilotti, E., Zhang, R., Lellinger, D., Mezzo, L., Fu, Q., Alig, I. and Peijs, T., *Adv. Funct. Mater.*, 2010, 20(9): 1424
- 8 Sahoo, N.G., Rana, S., Cho, J.W., Li, L. and Chan, S.H., *Prog. Polym. Sci.*, 2010, 35(7): 837
- 9 Wang, H., Zhang, X., Zhu, Y., Song, Z. and Qiao, J., *Mater. Lett.*, 2011, 65(13): 2055
- 10 Lu, C., Liu, C., Li, Z., Jiang, T., Liu, J., Peng, S. and Zhang, Y., *Chinese J. Polym. Sci.*, 2010, 28(6): 869
- 11 Kirkpatrick, S., *Rev. Mod. Phys.*, 1973, 45(4): 574
- 12 Xue, Q., *Eur. Polym. J.*, 2004, 40(2): 323
- 13 Quan, H., Zhang, S., Qiao, J. and Zhang, L., *Polymer*, 2012, 53(20): 4547
- 14 Jiang, H., Moon, K.S., Li, Y. and Wong, C.P., *Chem. Mater.*, 2006, 18(13): 2969
- 15 Bormashenko, E., Sutovski, S., Pogreb, R., Sheshnev, A., Bormashenko, Y., Musina, A., Nir, A. and Luban, L., *J. Mater. Proce. Techn.*, 2005, 168(2): 367
- 16 Wang, X., Qi, G., Zhang, X., Gao, J., Li, B., Song, Z. and Qiao, J., *Sci. China Chem. (in Chinese)*, 2012, 55(5): 713
- 17 Al-Saleh, M.H. and Sundararaj, U., *Carbon*, 2009, 47(1): 2
- 18 Fang, Y., Zhao, J., Zha, J., Wang, D. and Dang, Z., *Polymer*, 2012, 53(21): 4871
- 19 Kyrlyuk, A.V., Hermant, M.C., Schilling, T., Klumperman, B., Koning, C.E. and van der Schoot, P., *Nat. Nano.*, 2011, 6(6): 364