J Mater Sci (2008) 43:2653–2658
DOI 10.1007/s10853-008-2489-1

Effect of acid and TETA modification on mechanical properties of MWCNTs/epoxy composites

ShuQin Li · Fang Wang · Ye Wang · JingWen Wang · Jun Ma · Jun Xiao

Received: 24 August 2007 / Accepted: 18 January 2008 / Published online: 19 February 2008

Abstract Acid treatment and triethylene-tetramine (TETA) modification of multi-walled carbon nanotubes (MWCNTs) purposing to attain better dispersibility and stronger interfacial bonding between MWCNTs and epoxy matrix have been carried out in this paper. The epoxy and MWCNTs/epoxy composites were produced by cast molding method. Stress–strain curves show that TETA-MWCNTs/epoxy hold the greatest toughness of all samples with 0.5 wt.% nanoparticles. The Young's modulus of TETA-MWCNTs/epoxy has a significant increase about 38% compared to the neat epoxy, while the Young's modulus of unmodified MWCNTs/epoxy or acid-modified MWCNTs/epoxy has a bit of decrease. Tensile and impact strength tests reflect that TETA-MWCNTs reinforced epoxy composites have an obvious improvement of tensile strength about 30% and an enhancement of impact strength over 34% compared to the pure epoxy composites with only 0.5 wt.% loading of TETA-MWCNTs. Scanning electron microscopy images of fractured surface of MWCNTs/epoxy indicate homogeneous dispersibility of TETA-MWCNTs and strong interfacial adhesion between the TETA-MWCNTs and the epoxy in the MWCNTs/epoxy composite.

Introduction

Multi-walled carbon nanotubes (MWCNTs) have attracted great attention for their unique physical, mechanical, electrical, thermal, and optical properties as well as relatively low price. Polymer matrix nanocomposites using MWCNTs as reinforcing fillers have been explored for science and engineering applications [1–5]. Epoxy matrix composites are very important materials for aircraft, space shuttle, electronics products, and many other industrial applications. Hence, MWCNTs-reinforced epoxy systems hold the promise of delivering superior composite materials with high strength, lightweight, and multifunctional features [6, 7]. However, poor dispersibility and weak interfacial bonding between the MWCNTs and the epoxy matrix have limited the real application of MWCNTs/epoxy composites. The slipping in the bundles of nanotubes and weak interfacial interaction result in inefficient load transfer and this significantly decreases the mechanical properties of MWCNTs-reinforced epoxy composites [8, 9]. Thereby, the two main difficulties of weak interfacial bonding and poor dispersibility have to be overcome to effectively improve the material properties of polymers by adding carbon nanotubes as filler. The functionalization process is the most promising strategy for overcoming these difficulties [10, 11]. It has been reported that an enhancement of the interfacial adhesion between the carbon nanotubes and the polymers can be achieved by a chemical functionalization of the nanotubes surface [12–14]. Various chemical treatment and modification of MWCNTs have been investigated, such as oxidation in acid solution, amino functionalized, polymer graft, and UV/Ozone treatments [15–17]. In the present paper, MWCNTs were treated by acid and modified by triethylene-tetramine (TETA). Epoxy-based nanocomposites filled by unmodified and modified MWCNTs were prepared by cast

---

S. Q. Li (✉) · F. Wang · Y. Wang · J. W. Wang · J. Xiao
College of Material Science and Technology, Nanjing University of Aeronautics & Astronautics, 29, Yudao Street,
Nanjing 210016, China
e-mail: shuqli@nuaa.edu.cn

J. Ma
School of Aerospace, Mechanical & Mechatronic Engineering,
The University of Sydney, Sydney, NSW, Australia

molding method. The tensile and impact strength of MWCNTs/epoxy composites were measured and discussed, and morphologies of fractured surface of the composites were analyzed.

Experimental

Materials

Multi-walled carbon nanotubes were prepared by a chemical vapor deposition method with a purity of carbon content more than 95 vol% (supplied by Shenzhen Nanotechnologies Port Co.). The diameter of the MWCNTs was 40–60 nm and the length was 5–15 μm, the specific surface area was 40–300 m^2/g and the content of amorphous carbon was 2% according the producer. The low-viscosity epoxy resin 51, diglycidyl ether of biphenol A, was supplied by Wuxi resin factory. TETA was obtained from the Sinopharm Chemical Reagent Co, thionyl chloride ($SOCl_2$) was purchased from the Shanghai Jinshan Chemical Reagent Co. Tetrahydrofuran (THF) and other reagents and solvents were obtained from Shanghai Reagent Co.

Acid treatment and TETA modification of MWCNTs

The acid treatment procedure is as follows [18]: The unmodified MWCNTs (U-MWCNTs) were treated with a mixture of H_2SO_4 and HNO_3 with a volume ratio of H_2SO_4 to HNO_3 of 3:1 by ultrasonication for 4 h to obtain acid-modified MWCNTs (A-MWCNTs). After acid treatment, the MWCNTs were diluted using deionized water, filtered, and washed to neutral, then dried in vacuum at 70 °C till stable weight. And the A-MWCNTs were obtained.

The amino modification is as follows [19]: A-MWCNTs were stirred in a mixture of thionyl chloride and DMF (*N*,*N*-dimethyl formamide), at 70 °C with refluxing for 24 h. After reaction, the products were filtered, washed with anhydrous THF, and dried under vacuum at 70 °C till stable weight. Thus the acyl-chlorinated MWCNTs (AC-MWCNTs) were obtained. Then the AC-MWCNTs were reacted with TETA at 120 °C for 96 h. The excess TETA was washed by anhydrous ethanol. The products were then filtered and dried in vacuum. Then the TETA-modified MWCNTs (TETA-MWCNTs) were obtained. The reaction scheme of the functionalization of MWCNTs is shown in Fig. 1.

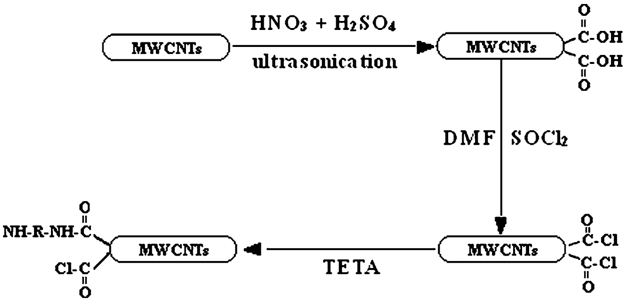

Fig. 1 The reaction scheme of the functionalization of MWCNTs

Preparation of MWCNTs/epoxy composites

The procedure using cast molding method for preparing MWCNTs/epoxy composites was as follows. First, a proper amount of U-MWCNTs, A-MWCNTs, and TETA-MWCNTs was dispersed in acetone by 40 min sonication separately, then epoxy resin was added and the mixture was sonicated at 50 °C for about 30 min and then weighed to constant weight until the acetone was removed entirely. Thereafter the curing agent TETA (10%) was added and further stirring was performed manually. The blend was degrassed to remove bubbles for 0.5 h in a vacuum oven. After degasification, the mixture was quickly poured into a stainless steel mold coated with the mold release agent. The curing cycle took 2 h at 50 °C followed by 2 h at 100 °C in an oven. The epoxy resin was mixed with weight percentages of 0.25, 0.5, 0.75 of unmodified or modified MWCNTs. Thus the unmodified carbon nanotubes, acid-treated carbon nanotubes, and TETA functionalized carbon nanotubes filling epoxy composites as U-MWCNTs/epoxy, A-MWCNTs/epoxy, and TETA-MWCNTs/epoxy are fabricated.

Characterization

Fourier-transform infrared (FTIR) spectra were recorded with a Bruker Vector-22 FTIR spectrometer to characterize the functionalized MWCNTs. Tensile strength of MWCNTs/epoxy composites was tested using a SANS CSS-2202 computer-controlled electronic universal tensile tester at room temperature. The test procedure followed GB/T2567-1995 standard. The loading speed was 0.5 mm/min. Impact strength of MWCNTs/epoxy composites was measured using XJ-300A impact tester according to GB/T2571-1995 standard. A minimum of five specimens of each composite was tested. The microstructures of fractured surface of the MWCNTs/epoxy composites coated with conductive gold paint by vacuum sputtering were observed by LEO 1550 scanning electron microscopy (SEM).

Results and discussion

FTIR spectroscopy

In order to characterize the MWCNTs modified chemically with acid and TETA, we measured the FTIR spectrum as

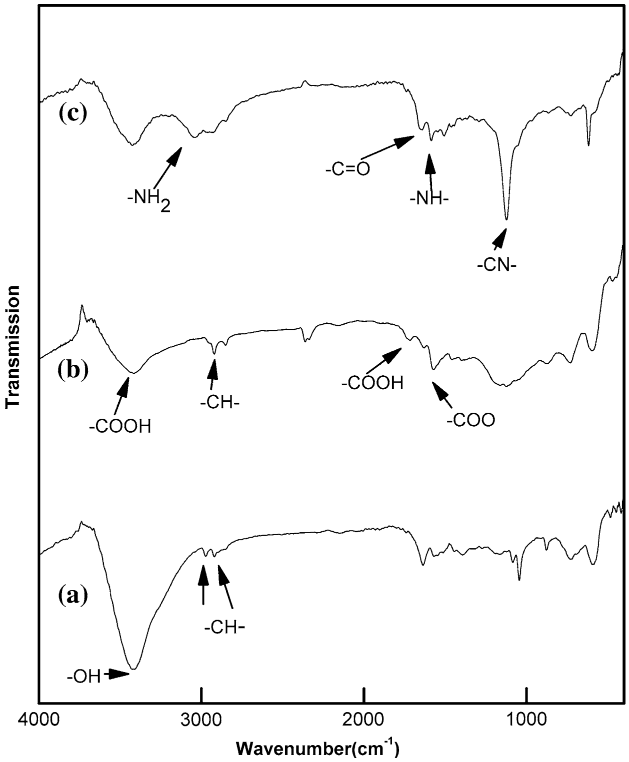

Fig. 2 FTIR spectra of (**a**) U-MWCNTs, (**b**) A-MWCNTs, (**c**) TETA-MWCNTs

shown in Fig. 2. In Spectrum a, which is for the U-MWCNTs, the feature at wavenumbers 3,000–2,800 cm^{-1} corresponds to –CH stretching and that at 3,402 cm^{-1} corresponds to –OH stretching. The FTIR result (–CH stretching) indicates that U-MWCNTs contain defects, which may be formed during their manufacture. Figure 2b presents the FTIR spectrum of A-MWCNTs: carboxylic groups stretching (COOH) appears at 1,724 cm^{-1}. Features at wavenumbers 1,610–1,550, 3,000–2,800, and 3,650–3,000 cm^{-1} are the absorption peaks of COO^{-} symmetric stretching, –CH stretching, and $–\text{COO}^{-}$ stretching, respectively [2]. Figure 2c shows the FTIR spectrum of TETA-MWCNTs: the feature at wavenumbers 1,600 cm^{-1} corresponds to the absorption of –NH bending and stretching [20]. The –NH stretching of the amide group was at 3,100 cm^{-1} and the –C=O stretching was at 1,650 cm^{-1} [17]. The strong peak at 1,126 cm^{-1} reveals –CN stretching in TETA. The FTIR spectra confirm that MWCNTs were successfully modified by acid and TETA.

Tensile and impact strength

The reinforcement potential of the MWCNTs can only be activated if an effective load transfers from the surrounding epoxy matrix into the carbon nanotubes [21]. So, a strong interfacial compatibility between MWCNTs and epoxy matrix would play an important role on mechanical properties of epoxy nanocomposites. Figure 3 shows the mechanical properties of the composites. The experimental data are the average values of five specimens from different batches of samples. Figure 3a displays the typical stress–strain curves of neat epoxy and the MWCNTs/epoxy composites containing 0.5 wt.% nanotubes filler. The stress–strain curves show non-linearity before reaching the maximum stress, but no obvious yield point can be found in the curves. The fracture work of composites, which reflect the fracture toughness, can be observed from the area under the stress–strain curves. We found that TETA-MWCNTs/epoxy hold the greatest toughness of all samples. The Young's modulus of samples (see Fig. 3b) can also be obtained from stress–strain curves. The Young's modulus of TETA-MWCNTs/epoxy has a significant increase about 38%, relative to the neat epoxy, while the Young's modulus of U-MWCNTs/epoxy or A-MWCNTs/epoxy has a bit of decrease. The increase in Young's modulus can be explained by the improved dispersibility of TETA-MWCNTs in the polar epoxy resin due to strong interaction with the polar amino-groups [3]. It can be seen in Fig. 3c that the tensile strength of MWCNTs/epoxy composites reduces slightly with the increase loading of U-MWCNTs. Intensive agglomeration of U-MWCNTs and weak interfacial adhesion between U-MWCNTs and epoxy matrix resulted in the poor ability of stress transfer to internal layers of U-MWCNTs, consequently decrease in tensile strength of nanocomposites. In contrast, the tensile strength of composites increases when the weight percentage of A-MWCNTs is from 0.25 to 0.75. The carboxylic groups of A-MWCNTs originated from acid treatment enable a direct bonding to the epoxy matrix, which would be advantageous for enhancement of mechanical properties of composites [22]. For TETA-MWCNTs, an enhancement of 30% of the tensile strength as compared to neat epoxy composites and a 53% increase as compared to the U-MWCNTs are exhibited, when the loading of MWCNTs filler is 0.5 wt.%. The functional amino groups of carbon nanotubes introduced by TETA modification make TETA-MWCNTs more compatible both with polymer hosts and solvents. The free amino functions of TETA-MWCNTs will react with the epoxy molecules forming equivalent bonds [22], which lead to an improved interfacial bonding between MWCNTs and epoxy matrix. This tends to dramatically improve mechanical properties of nanocomposites [23]. In addition, there is a light reduction of tensile strength of composites when the amount of TETA-MWCNTs reaches 0.75 wt.%. The decrease in strength with higher TETA-MWCNTs content may be ascribed to the following two factors: first factor is the relatively poor dispersion ability of TETA-MWCNTs in higher loading systems; the other is the void produced

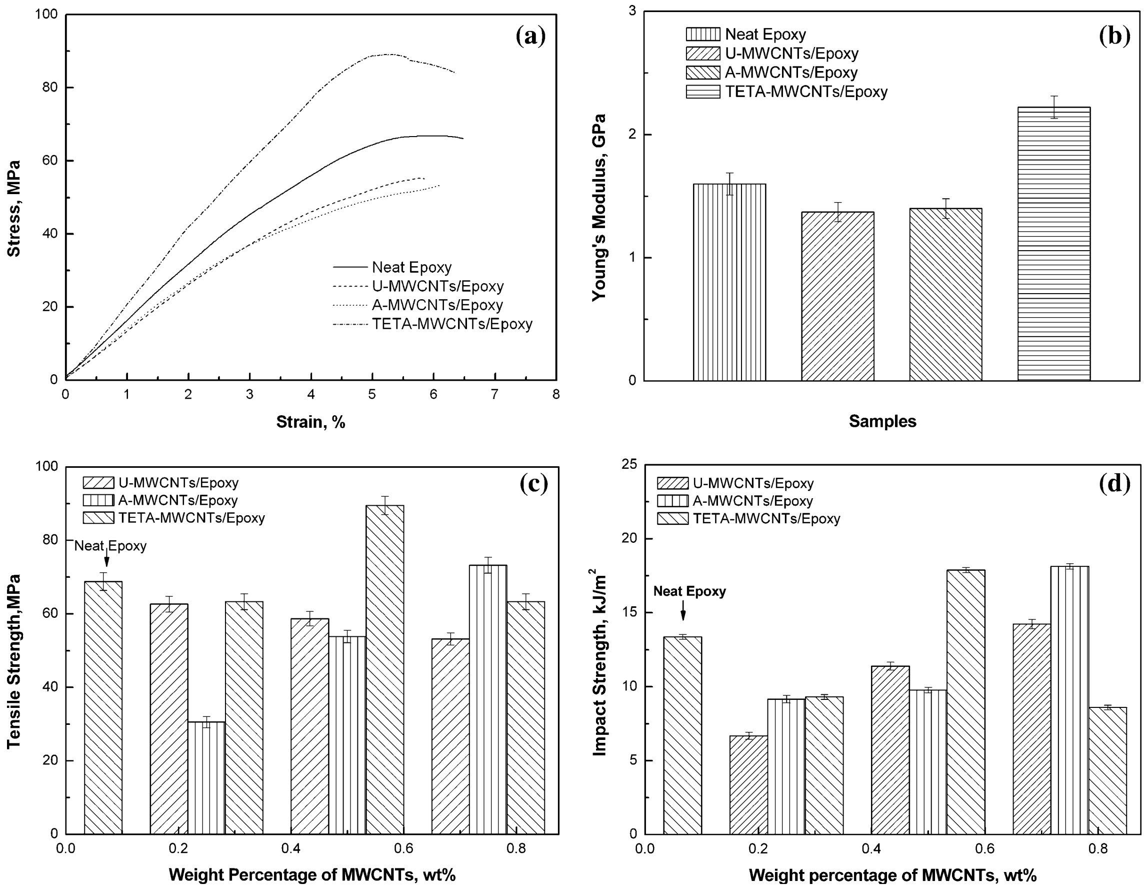

Fig. 3 (**a**) Stress–strain curves; (**b**) Young's modulus; (**c**) tensile strength; (**d**) impact strength of epoxy matrix composites

during the fabrication process [24]. That also hints an upper limit of the content of carbon nanotubes can be filled into the epoxy resin needing to be investigated, and similar conclusions have been made by Zhu et al. [6]. The impact strength (see Fig. 3d) has a same behavior as the tensile strength of composites. The impact strength of TETA-MWCNTs/epoxy presents a rise about 34% compared to the relatively brittle neat epoxy polymer, in contrast to the 14% decrease in the U-MWCNTs/epoxy composites, when the loading of MWCNTs filler is 0.5 wt.%. It indicates that the ductility increase effect is better when the MWCNTs are modified by acid and TETA. It is obvious that TETA-MWCNTs can disperse more homogeneously in epoxy resin and exert better toughening effects on the epoxy matrix. The increases in toughness, Young's modulus, tensile strength, and impact strength of TETA-MWCNTs/epoxy demonstrate the immediate effective load transfer of modified carbon nanotubes through strong interfacial bonding due to a number of amino groups covalently attached to the side chains on the carbon nanotubes. Full integration was obtained by direct chemical bonding to these groups to the epoxy matrix [8].

Scanning electron microscopy

The dispersion of MWCNTs in epoxy resin matrix plays a crucial role on the properties of MWCNTs/epoxy composites. Figure 4 shows the SEM microphotographs of the fractured surface of the epoxy matrix composites with 0.5 wt.% nanotubes filler. Figure 4a reveals that the U-MWCNTs were curled, entangled seriously, and easy to conglomerate in bundles in the epoxy matrix. It was noticed that there were many extraction carbon nanotubes appearing at the fractured surface, which testified poor dispersibility and weak interfacial bonding between U-MWCNTs and epoxy matrix. In order to reduce the agglomeration, a control of surface polarity and resulting interactive forces between nanotube particles and polymer matrix is needed [21]. This can be achieved by chemical functionalization of the MWCNTs, enabling the formation of covalent bonds or polar interactions between polymers and MWCNTs. Figure 4b demonstrates that the A-MWCNTs was shortened and entwist was seldom found due to acid treatment for MWCNTs. It also indicates that A-MWCNTs can disperse in epoxy matrix more uniformly

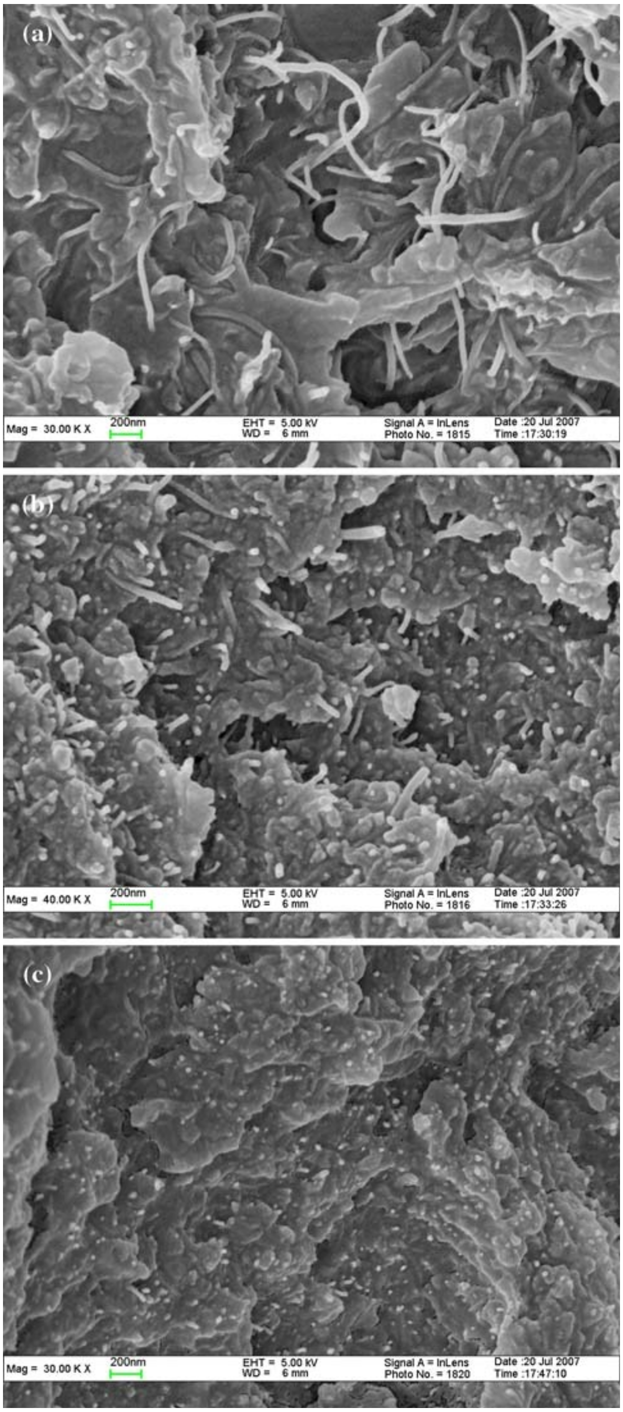

Fig. 4 SEM image of fracture surface of the composites: (**a**) U-MWCNTs/epoxy; (**b**) A-MWCNTs/epoxy; (**c**) TETA-MWCNTs/epoxy

as a result of the steric and electrostatic repulsion of the carboxylic acid groups on the surface of A-MWCNTs [18]. But some pull-outs of the A-MWCNTs from the surrounding epoxy matrix still can be observed, which proves that the stress transfer from the epoxy matrix to the A-MWCNTs is lower than that of the TETA-MWCNTs. Figure 4c displays the fractured surface of TETA-MWCNTs/epoxy composites. Many broken segments of nanotube ropes rather than just pull outs can be observed. And most nanotubes are embedded and tightly held to matrix. It indicates that the dispersibility of TETA-MWCNTs is homogeneous and the interfacial bonding between TETA-MWCNTs and epoxy resin is strong in the nanocomposites. This is favor of transferring the stress load and preventing the sliding of nanotube bundles during tension. And therefore generate the nanoreinforcement effect of the composites [25, 26]. These observations are in good agreement with the investigation reported by Zhu et al. [6]. So, the amino groups of TETA-MWCNTs lead to better compatibility of nanotubes and epoxy matrix, thus the mechanical properties of MWCNTs/epoxy nanocomposites can be improved.

Conclusion

Preliminary tests of tensile and impact strength showed that the TETA-MWCNTs reinforced epoxy composites have a substantially improvement of toughness, Young's modulus, tensile strength, and impact strength compared to the pure epoxy composites with only 0.5 wt.% loading of MWCNTs filler. Homogeneous dispersibility of TETA-MWCNTs and strong interfacial bonding between the TETA modified nanotubes and the epoxy in the MWCNTs/epoxy composite can be observed. It is concluded that the TETA functionalization of MWCNTs are helpful to improve the interfacial interaction between nanotubes and epoxy, which can be able to transfer the stress load and preventing the sliding of nanotube bundles during tension. Therefore, the proposed TETA-MWCNTs can significantly reinforce the mechanical properties of epoxy composites by improving the dispersibility and interfacing bonding. In addition, a proper usage of MWCNTs adding to epoxy resin still needs to be investigated further in future experiments, since there is a light reduction of tensile or impact strength of composites when the amount of TETA-MWCNTs reaches 0.75 wt.%.

References

1. Yuen SM, Ma CM, Lin YY, Kuan HC (2007) Compos Sci Technol 67:2564
2. Kovacs JZ, Velagala BS, Schulte K, Bauhofer W (2007) Compos Sci Technol 67:922
3. Gojny FH, Wichmann MHG, Köpke U, Fiedler B, Schulte K (2004) Compos Sci Technol 64:2363
4. Zhou YX, Pervin F, Lewis L, Jeelani S (2008) Mater Sci Eng A 475:157
5. Paiva MC, Zhou B, Fernando KAS, Lin Y, Kennedy JM, Sun Y-P (2004) Carbon 42:2849

6. Zhu J, Peng H, Macias FR, Margrave JL, Khabashesku VN, Imam AM, Lozano K, Barrera EV (2004) Adv Funct Mater 14:643
7. Allaoui A, Bai S, Cheng HM, Bai JB (2002) Compos Sci Technol 62:1993
8. Wang SR, Liang ZY, Liu TN, Wang B, Zhang C (2006) Nanotechnology 17:1551
9. Yu MF, Lourie O, Dyer MJ, Moloni K, Kelly TF, Ruoff RS (2000) Science 287:637
10. Zhu J, Kim JD, Peng H, Margrave JL, Khabashesku VN, Barrera EV (2003) Nanoletters 3:1107
11. Gojny FH, Schulte K (2004) Compos Sci Technol 64:2303
12. Weglikowska UD, Benoit JM, Chiu PW, Graupner R, Lebedkin S, Roth S (2002) Curr Appl Phys 2:497
13. Wang YB, Iqbal Z, Malhotra SV (2005) Chem Phys Lett 402:96
14. Zheng YP, Zhang AB, Chen QH, Zhang JX, Ning RC (2006) Mater Sci Eng A 435–436:145
15. Saito T, Matsushige K, Tanaka K (2002) Physics B 323:280
16. Hong CY, You YZ, Pan CY (2006) Polymer 47:4300
17. Sham ML, Kim JK (2006) Carbon 44:768
18. Gojny FH, Nastalczyk J, Roslaniec Z, Schulte K (2003) Chem Phys Lett 370:820
19. Wang Y, Zafar I, Malhotra SV (2005) Chem Phys Lett 402:96
20. Shen JF, Huang WS, Wu LP (2007) Mater Sci Eng A 464:151
21. Gojny FH, Wichmann MHG, Fiedler B, Schulte K (2005) Compos Sci Technol 65:2300
22. Fiedler B, Gojny FH, Wichmann MHG, Nolte MCM, Schulte K (2006) Compos Sci Technol 66:3115
23. Coleman JN, Khan U, Gun'ko YK (2006) Adv Mater 18:689
24. Choi YK, Sugimoto K, Song SM, Gotoh Y, Ohkoshi Y, Endo M (2005) Carbon 43:2199
25. Jiang MJ, Dang ZM, Xu HP (2006) Appl Phys Lett 89:182902
26. Ren Y, Li F, Cheng HM, Liao K (2003) Carbon 41:2159