CHEMISTRY OF
MATERIALS
Article

Chem. Mater. **2010,** *22,* 3773–3778 3773
DOI:10.1021/cm1009306

Simple Approach for Preparation of Epoxy Hybrid Nanocomposites Based on Carbon Nanotubes and a Model Clay

Dazhi Sun, Chien-Chia Chu, and Hung-Jue Sue*

Polymer Technology Center, Department of Mechanical Engineering, Texas A&M University,
College Station, Texas 77843-3123

Received April 2, 2010. Revised Manuscript Received May 13, 2010

We report a simple, yet effective solution method for dispersion of carbon nanotubes and inorganic nanoplatelets into a thermosetting epoxy matrix. With an aid of exfoliated inorganic nanoplatelets, carbon nanotubes can be easily deroped in aqueous solution. Subsequently, the aqueous dispersion of carbon nanotubes and nanoplatelet hybrid can be easily transferred to organic solvents by a drying-redispersion process, and then to the epoxy matrix. Transmission and scanning electron microscopy images show that carbon nanotubes have been individually dispersed and nanoplatelets have been fully exfoliated in the epoxy matrix. X-ray diffraction is also used to investigate the dispersion mechanism. The resulting epoxy nanocomposites, containing both individually dispersed carbon nanotubes and exfoliated nanoplatelets, exhibit greatly improved modulus (up to 41%) and strength (up to 55%) at low nanotube loadings (up to 0.4 wt.%) without compromising the strain at failure. This approach is promising for large-scale preparation of highly reinforced polymer/carbon nanotube nanocomposites at low cost.

Introduction

Functional polymer nanocomposites containing a low level of carbon nanotubes (CNTs) have attracted substantial attention in the past decade due to their demonstrated remarkable enhancements in mechanical properties,[1−3] thermal conductivity,[4] flame retardancy,[5,6] electrical property,[7,8] and light weight. Among all the benefits that CNTs offer, mechanical reinforcement has been the main focus of many endeavors.[9−14] CNTs are small in diameter and have an extremely high aspect ratio (>1000), but are known to be stiff. Therefore, CNT-containing polymer nanocomposites are expected to have much higher modulus and are possibly stronger than the neat polymer matrices. Significant improvements in mechanical properties have indeed been shown in several polymer matrices. For example, water-soluble polyvinyl alcohol reinforced by surfactant-stabilized and polymer-wrapped single-walled CNTs (SWNTs) at 5 wt % loading shows an around 100% increase in both tensile strength and modulus.[15] Polyacrylonitrile/SWNT nanocomposites (up to 10 wt % loading) prepared through solution spinning exhibit 100% higher tensile modulus than the neat matrix.[16] In-situ polymerization of nylon with surface-functionalized SWNTs also results in over 100% increase in both tensile strength and modulus.[17]

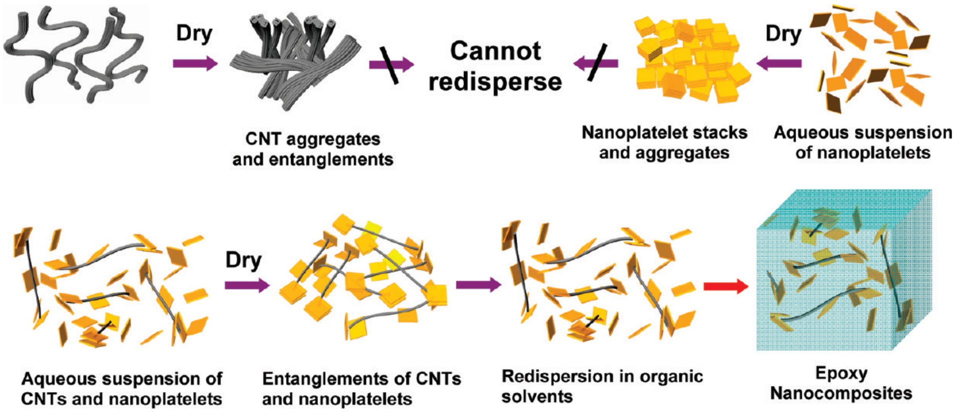
However, such superior mechanical properties have only been observed in thermoplastic polymers. In the case of brittle thermosetting polymers, such as epoxy, the improvement in mechanical properties using CNTs has been shown to be limited. For example, in a study by Moniruzzaman et al. epoxy/SWNT nanocomposites at 0.5 wt % loading prepared through solution mixing only shows less than 20% and 10% increase in flexural modulus and strength, respectively.[18] Incorporation of fluorinated SWNTs (1 wt %) into an epoxy matrix exhibits only a 30% increase in Young's modulus and 18% increase in

---

*Corresponding author e-mail: hjsue@tamu.edu.

(1) Ajayan, P. M.; Schadler, L. S.; Giannaris, C.; Rubio, A. *Adv. Mater.* **2000**, *12*(10), 750.
(2) Thostenson, E. T.; Ren, Z. F.; Chou, T. W. *Compos. Sci. Technol.* **2001**, *61*(13), 1899.
(3) Coleman, J. N.; Khan, U.; Gun'ko, Y. K. *Adv. Mater.* **2006**, *18*(6), 689.
(4) Biercuk, M. J.; Llaguno, M. C.; Radosavljevic, M.; Hyun, J. K.; Johnson, A. T.; Fischer, J. E. *Appl. Phys. Lett.* **2002**, *80*(15), 2767.
(5) Kashiwagi, T.; Grulke, E.; Hilding, J.; Groth, K.; Harris, R.; Butler, K.; Shields, J.; Kharchenko, S.; Douglas, J. *Polymer* **2004**, *45*(12), 4227.
(6) Peeterbroeck, S.; Laoutid, F.; Swoboda, B.; Lopez-Cuesta, J. M.; Moreau, N.; Nagy, J. B.; Alexandre, M.; Dubois, P. *Macromol. Rapid Commun.* **2007**, *28*(3), 260.
(7) Sandler, J.; Shaffer, M. S. P.; Prasse, T.; Bauhofer, W.; Schulte, K.; Windle, A. H. *Polymer* **1999**, *40*(21), 5967.
(8) Allaoui, A.; Bai, S.; Cheng, H. M.; Bai, J. B. *Compos. Sci. Technol.* **2002**, *62*(15), 1993.
(9) Thostenson, E. T.; Ren, Z. F.; Chou, T. W. *Compos. Sci. Technol.* **2001**, *61*(13), 1899.
(10) Coleman, J. N.; Cadek, M.; Blake, R.; Nicolosi, V.; Ryan, K. P.; Belton, C.; Fonseca, A.; Nagy, J. B.; Gun'ko, Y. K.; Blau, W. J. *Adv. Funct. Mater.* **2004**, *14*(8), 791.
(11) Cadek, M.; Coleman, J. N.; Ryan, K. P.; Nicolosi, V.; Bister, G.; Fonseca, A.; Nagy, J. B.; Szostak, K.; Beguin, F.; Blau, W. J. *Nano Lett.* **2004**, *4*(2), 353.
(12) Moniruzzaman, M.; Winey, K. I. *Macromolecules* **2006**, *39*(16), 5194.
(13) Coleman, J. N.; Khan, U.; Blau, W. J.; Gun'ko, Y. K. *Carbon* **2006**, *44*(9), 1624.
(14) Ajayan, P. M.; Tour, J. M. *Nature* **2007**, *447*(7148), 1066.
(15) Zhang, X. F.; Liu, T.; Sreekumar, T. V.; Kumar, S.; Moore, V. C.; Hauge, R. H.; Smalley, R. E. *Nano Lett.* **2003**, *3*(9), 1285.
(16) Sreekumar, T. V.; Liu, T.; Min, B. G.; Guo, H.; Kumar, S.; Hauge, R. H.; Smalley, R. E. *Adv. Mater.* **2004**, *16*(1), 58.
(17) Moniruzzaman, M.; Chattopadhyay, J.; Billups, W. E.; Winey, K. I. *Nano Lett.* **2007**, *7*(5), 1178.
(18) Moniruzzaman, M.; Du, F. M.; Romero, N.; Winey, K. I. *Polymer* **2006**, *47*(1), 293.

Scheme 1. Scheme for the Preparation of Epoxy Nanocomposites Containing Individually Dispersed CNTs and Exfoliated Nanoplatelets



tensile strength.[19] One major reason may be due to the lack of a simple and effective method to disperse CNTs in the brittle epoxy matrices well, especially down to an individual tube level.

It has been demonstrated that CNTs can be well dispersed in water through ultrasonication-assisted surfactant stabilization or polymer wrapping.[20,21] This process facilitates the incorporation of CNTs into water-soluble thermoplastics. On the other hand, surface-functionalization of CNTs with organophilic groups has been shown to be an effective method to achieve good dispersion of CNTs in hydrophobic polymers.[22,23] However, the above two approaches are not suitable for preparing good-quality epoxy/CNT nanocomposites. First, most epoxies are hydrophobic. Second, surface-functionalization of CNTs normally involves complicated steps and can be expensive. Therefore, it has not been practical to prepare epoxy/CNT nanocomposites for structural applications. Moreover, literature results show that, to achieve a meaningful reinforcing effect on the polymer matrices with simple processing, relatively high CNT concentrations (>1 wt.%) are generally needed. Considering the cost of CNTs, it is highly desirable to improve the CNT dispersion in polymer matrices so that high-performance polymer/CNT nanocomposites can be obtained at low CNT loadings, thus lowering their cost. Here, we propose a simple and effective approach that utilizes inorganic nanoplatelets (synthetic alpha-zirconium phosphate, ZrP) to exfoliate CNTs in an aqueous solution, which can be further transferred into organic solvents, and then into epoxy matrices. Epoxy nanocomposites containing low concentrations of both CNTs (0.4 wt %) and nanoplatelets (2 wt %) show exceptionally high mechanical strength and modulus without reduction in elongation at break. It is anticipated that this approach can facilitate large-scale preparation of high-performance epoxy/CNT nanocomposites for engineering applications at low cost.

Experimental Section

Synthesis and Exfoliation of ZrP Nanoplatelets. ZrP nanoplatelets were synthesized through a refluxing method. Briefly, 15.0 g of $ZrOCl_2 \cdot 8H_2O$ (Fluka) was refluxed in 150.0 mL of 3.0 M H_3PO_4 (EM Science) in a Pyrex glass flask with stirring at 100 °C for 24 h. After reaction, the products were washed three times through centrifugation and resuspension, dried at 85 °C in an oven for 24 h, and then gently ground with a mortar and pestle into a fine powder. ZrP powders were exfoliated with tetra-*n*-butylammonium hydroxide (TBA^+OH^-, Aldrich, 1 mol/L in methanol) at a molar ratio of ZrP/TBA = 1:0.8 in water.

Pretreatment of CNTs. SWNTs were obtained from Carbon Nanotechnologies, Inc. (Houston, TX) and MWNTs were purchased from Aldrich. CNTs were first oxidized in a mixture of concentrated sulfuric acid and concentrated nitric acid with a volume ratio of 3:1 by ultrasonication in a sonication bath (Branson 2510) for 2 h. Then, deionized water was added to dilute the acids and the mixture was sonicated for another three hours. After the above processes, the oxidized CNTs were isolated by using a polyvinylidene difluoride (PVDF) filter membrane (Millipore, 0.45 μm pore size) under vacuum. The CNTs were washed several times with deionized water during filtration to remove the acid residue. The CNTs collected were then resuspended in water.

CNT Dispersion in Water and Organic Solvents. Two aqueous solutions containing oxidized CNTs and fully exfoliated ZrP nanoplatelets were directly mixed with various weight ratios of CNTs to ZrP nanoplatelets. The mixtures were sonicated in a sonication bath (Branson 2510) maintained at room temperature for 30 min. At the weight ratio between ZrP nanoplatelets and CNTs of 5, the aqueous dispersion can remain stable for over 1 year in concentrations up to 5 mg/mL. After dispersion, the aqueous mixtures were dried on a hot plate at 100 °C for several hours with stirring until all water was removed. The residues were then redispersed in acetone or THF by ultrasonication for 5−10 min with concentrations up to 5 mg/mL.

Preparation of Epoxy Nanocomposites. The acetone suspensions with ZrP-to-CNT weight ratio of 5 were mixed with the epoxy monomer, diglycidyl ether of bisphenol A (D.E.R. 332 epoxy resin, The Dow Chemical Company) to achieve a finial CNT concentration of 0.2 and 0.4 wt % in epoxy nanocomposites.

---

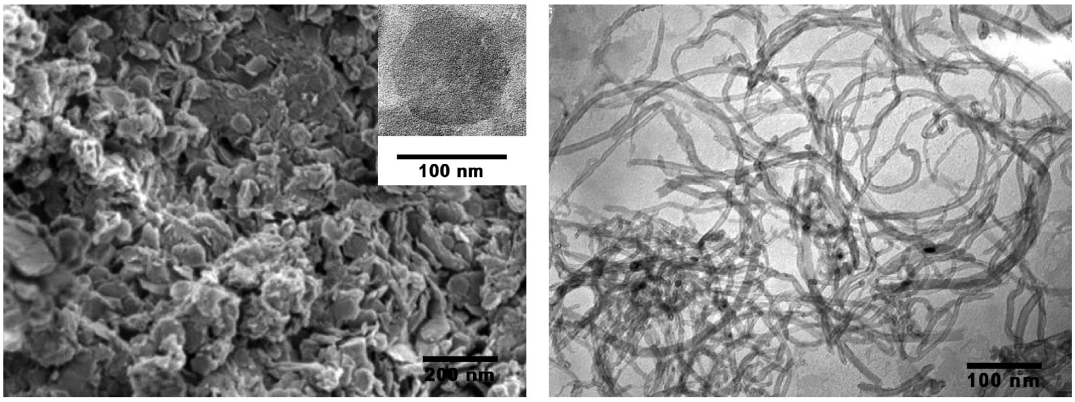
(19) Zhu, J.; Kim, J. D.; Peng, H. Q.; Margrave, J. L.; Khabashesku, V. N.; Barrera, E. V. *Nano Lett.* **2003**, *3*(8), 1107.

(20) Moore, V. C.; Strano, M. S.; Haroz, E. H.; Hauge, R. H.; Smalley, R. E.; Schmidt, J.; Talmon, Y. *Nano Lett.* **2003**, *3*(10), 1379.

(21) O'Connell, M. J.; Boul, P.; Ericson, L. M.; Huffman, C.; Wang, Y. H.; Haroz, E.; Kuper, C.; Tour, J.; Ausman, K. D.; Smalley, R. E. *Chem. Phys. Lett.* **2001**, *342*(3−4), 265.

(22) Yang, B. X.; Pramoda, K. P.; Xu, G. Q.; Goh, S. H. *Adv. Funct. Mater.* **2007**, *17*(13), 2062.

(23) Zhu, J.; Peng, H. Q.; Rodriguez-Macias, F.; Margrave, J. L.; Khabashesku, V. N.; Imam, A. M.; Lozano, K.; Barrera, E. V. *Adv. Funct. Mater.* **2004**, *14*(7), 643.



A B

Figure 1. (A) SEM image of pristine ZrP nanoplatelets; inset in (A) is a TEM image of a monolayer ZrP nanoplatelet exfoliated by TBA; and (B) TEM image of MWNTs.

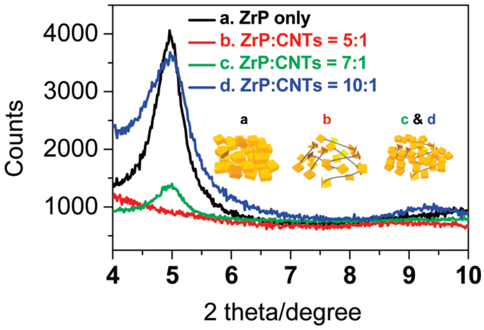


Figure 2. XRD patterns of the hybrid solids containing ZrP nanoplatelets and CNTs with different weight ratios prepared by drying aqueous suspensions. The inset cartoons show the morphologies of each hybrid solid.

The ZrP concentrations were 1.0 and 2.0 wt.%, respectively. The solvents were then removed via rotary evaporation in a water bath at 80 °C and curing agent, 4,4′-diamino-diphenyl sulfone (DDS, Aldrich), was added at stoichiometric ratio. This mixture was heated rapidly to 130 °C until the DDS was dissolved and then poured into a preheated glass mold with mold release agent on the glass mold surfaces. The epoxies were cured in an oven at 180 °C for 2 h, followed by 2 h of postcure at 220 °C. For comparison purposes, neat epoxy samples were also prepared using the same curing procedure.

Characterization. Transmission electron microscopy (TEM) was performed using a JEOL 2010 high-resolution transmission electron microscope, operated at 200 kV. The solution samples were coated onto carbon grids and then dried at room temperature. A Reichert-Jung Ultracut-E microtome was utilized to prepare thin sections of epoxy nanocomposites with thickness of 70−100 nm for TEM imaging. Scanning electron microscopy (SEM) was acquired using a Zeiss Leo 1530 VP Field Emission-SEM (FE-SEM). X-ray diffraction (XRD) patterns were recorded using a Bruker D8 Advanced powder X-ray diffractometer with Cu−Kα incident radiation (λ = 1.5418 Å).

Mechanical Testing. Tensile properties of the epoxy samples were obtained using the ASTM D638-98 standard. The tensile tests were performed using an MTS servo-hydraulic test machine at a crosshead speed of 5.08 mm/min at ambient temperature. Young's modulus, tensile strength, and elongation at break of each sample were obtained based on at least five specimens and the average values and standard deviations were reported.

Results and Discussion

A critical element of our approach is to utilize exfoliated inorganic nanoplatelets to facilitate the dispersion of CNTs in water. After drying the aqueous solution, the hybrid solid containing CNTs and nanoplatelets can be fully redispersed into organic solvents. Our previous study shows that through strong electrostatic tethering of highly charged nanoplatelets, slightly oxidized CNTs can be effectively dispersed in aqueous solution down to individual level.[24] Herein, we have dried the aqueous solution containing debundled CNTs and exfoliated nanoplatelets and found that after water evaporation, CNTs do not reaggregate and nanoplatelets do not restack with each other. This interesting result is probably due to the long-range electrostatic attractions between CNTs and exfoliated nanoplatelets which can disrupt the strong short-range van de Waals attractions between nanotubes and between nanoplatelets.[24] In any case, the dried hybrid solid containing CNTs and nanoplatelets can be easily redispersed with a mild sonication into various organic solvents, such as acetone or tetrahydrofuran (THF). Therefore, the preparation of well-dispersed epoxy/CNT/nanoplatelet hybrid nanocomposites can be realized in a straightforward matter. Scheme 1 systematically summarizes our approach.

A few recent papers have shown that clay nanoplatelets may be effective for dispersing CNTs.[25−27] Nanoplatelet-nanotube synergistic effect on mechanical properties of polymer nanocomposites has also been suggested. However, none of these papers have demonstrated that CNTs or nanoplatelets have been made to be individually dispersed, especially in the case of hydrophobic polymer matrices. In our study, we utilized a highly pure crystalline synthetic layered compound—alpha-zirconium phosphate

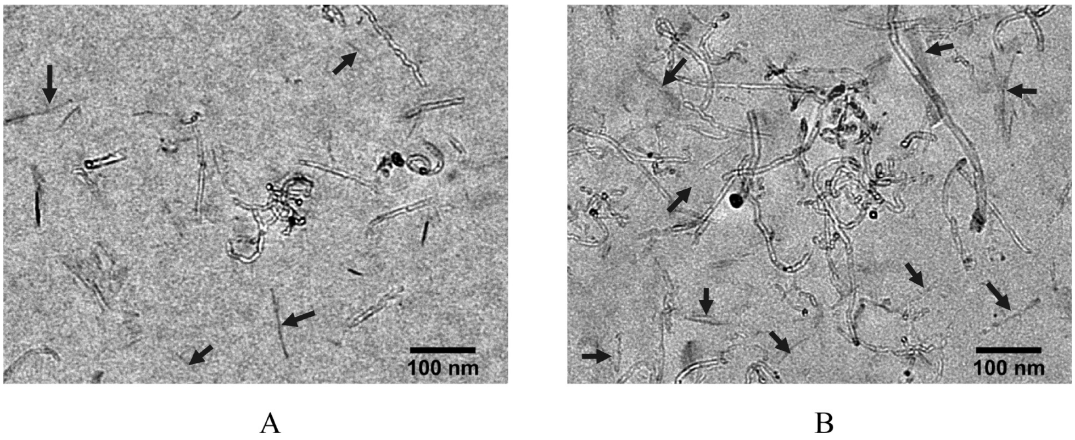
---

(24) Sun, D. Z.; Everett, W. N.; Chu, C.-C.; Sue, H.-J. *Small* **2009**, *5*(23), 2692.

(25) Lan, Y. F.; Lin, J. J. *J. Phys. Chem. A* **2009**, *113*(30), 8654.

(26) Tang, C. Y.; Xiang, L. X.; Su, J. X.; Wang, K.; Yang, C. Y.; Zhang, Q.; Fu, Q. *J. Phys. Chem. B* **2008**, *112*(13), 3876.

(27) Peeterbroeck, S.; Alexandre, M.; Nagy, J. B.; Pirlot, C.; Fonseca, A.; Moreau, N.; Philippin, G.; Delhalle, J.; Mekhalif, Z.; Sporken, R.; Beyer, G.; Dubois, P. *Compos. Sci. Technol.* **2004**, *64*(15), 2317.



A B

Figure 3. TEM images of epoxy nanocomposites containing (A) 0.2 wt % of MWNTs and 1.0 wt % of ZrP nanoplatelets and (B) 0.4 wt % of MWNTs and 2.0 wt % of ZrP nanoplatelets. The blue arrows indicate some exfoliated ZrP nanoplatelets.

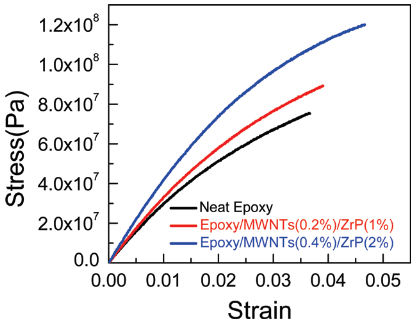


Figure 4. Stress−strain curves of the neat epoxy and epoxy nanocomposites containing exfoliated ZrP nanoplatelets and MWNTs.

Table 1. Mechanical Properties of the Neat Epoxy and Epoxy Nanocomposites Containing Exfoliated ZrP Nanoplatelets and MWNTs

	neat epoxy	epoxy/ MWNTs(0.2%)/ ZrP(1.0%)	epoxy/ MWNTs(0.4%)/ ZrP(2.0%)
Young's modulus (GPa)	3.04 ± 0.04	3.40 ± 0.06	4.27 ± 0.07
tensile strength (MPa)	75.3 ± 4.2	83.1 ± 4.8	116 ± 5.5
elongation at break (%)	3.7 ± 0.1	3.9 ± 0.3	4.3 ± 0.4

(ZrP)—as a model platelet system due to its advantages over the nature clays in its: (i) well-defined chemical structure and purity,[28] (ii) well-controlled diameter and size distribution,[29] and (iii) ease of preparation into fully exfoliated monolayer platelets.[30,31] Figure 1A shows the SEM image of pristine ZrP nanoplatelets with a diameter of ∼100 nm prepared through a refluxing method. Tetra-*n*-butyl-ammonium hydroxide (TBA) was further utilized to achieve full exfoliation of ZrP into monolayer nanoplatelets in water (inset in Figure 1A). We have also found that ZrP nanoplatelets functionalized through TBA ions show high stability in an aqueous suspension and that the strong electrostatic tethering on the nanoplatelet surface with a positive charge is highly effective in dispersing and stabilizing CNTs with a negatively charged surface.[24]

Multiwalled CNTs (MWNTs) were pretreated by slight oxidation in the mixture of concentrated nitric acid and sulfuric acid (3:1) at room temperature; Figure 1B shows the TEM image of the pretreated MWNTs. It has been shown that careful treatment of CNTs by short-time exposure in oxidative acids under relatively low temperatures would not cut the tubes short, but merely open the defect sites on the tube surfaces (C−O−C) into carboxylic groups (−COOH).[32] Therefore, after the pretreatment, MWNTs would still retain their high aspect ratio and exhibit a negatively charged surface. However, the slightly charged MWNTs alone cannot maintain stability in aqueous solution. Entanglement and aggregation of MWNTs can still be observed without further treatment.

The pretreated MWNTs and exfoliated ZrP nanoplatelets were directly mixed in aqueous suspensions with various ZrP-to-MWNT (ZrP/MWNT) weight ratios and were exposed to ultrasonication for 30 min in a sonication bath at room temperature. The resulting hybrid aqueous suspensions with the ZrP/MWNT weight ratio higher than 5 can remain stable for more than a year. The aqueous mixtures were dried at elevated temperature (80−100 °C) until all the water was evaporated. Subsequently, acetone or THF was directly added to the remaining hybrid solids and they were sonicated for 5−10 min.

The redispersion mechanism and the optimal ZrP/MWNT weight ratio to achieve a full redispersion were obtained by performing XRD on the dried hybrid solids with various weight ratios between ZrP nanoplatelets and MWNTs which is depicted in Figure 2. It is anticipated that exfoliated nanoplatelets will irreversibly restack into a layered structure upon drying (curve **a** in Figure 2). However, with the presence of MWNTs, the nanoplatelet restacking process can be significantly disrupted, as shown by the XRD of the dried hybrid mixture of ZrP nanoplatelets and MWNTs with a weight ratio of 5:1

---

(28) Clearfield, A. *Annu. Rev. Mater. Sci.* **1984**, *14*, 205.
(29) Sun, L. Y.; Boo, W. J.; Sue, H. -J.; Clearfield, A. *New J. Chem.* **2007**, *31*(1), 39.
(30) Kim, H. N.; Keller, S. W.; Mallouk, T. E.; Schmitt, J.; Decher, G. *Chem. Mater.* **1997**, *9*(6), 1414.
(31) Sun, L. Y.; Boo, W. J.; Sun, D. H.; Clearfield, A.; Sue, H. -J. *Chem. Mater.* **2007**, *19*(7), 1749.
(32) Ziegler, K. J.; Gu, Z. N.; Peng, H. Q.; Flor, E. L.; Hauge, R. H.; Smalley, R. E. *J. Am. Chem. Soc.* **2005**, *127*(5), 1541.

(curve **b** in Figure 2). The disappearance of the diffraction peaks from the hybrid system is caused by full intermixing between the exfoliated ZrP nanoplatelets and the dispersed MWNTs through electrostatic attraction.[24] The hybrid solids with a weight ratio of ZrP/MWNT < 5 cannot lead to full redispersion of MWNTs as illustrated by the observation of the CNT aggregates after mixing with acetone or THF. When the weight ratio of ZrP/MWNT ≥ 5, the diffraction peaks from the layered structure of the restacked ZrP nanoplatelets reappear (curves **c** and **d** in Figure 2), which, judging from the peak position, is due to presence of the excessive exfoliated nanoplatelets that have restacked. Therefore, a full exfoliation of ZrP nanoplatelets in the redispersed organic suspension cannot be achieved from the hybrid solids with the weight ratio of ZrP/MWCNT higher than 5. The possible morphologies of the dried solids containing different weight ratios between MWNTs and ZrP nanoplatelets are depicted in the insets of Figure 2. The above results also demonstrate that a weight ratio of 5 between exfoliated ZrP nanoplatelets and MWNTs is an optimal ratio to achieve full dispersion of both.

Epoxy nanocomposites containing full dispersion of both ZrP nanoplatelets and MWCNTs were prepared by solution mixing using the redispersed acetone suspensions at weight ratio of ZrP/MWCNT = 5. Figure 3 shows the TEM images of epoxy nanocomposites with 0.2 and 0.4 wt % of MWNTs. The concentrations of exfoliated nanoplatelets are 1.0 and 2.0 wt %, respectively. Well-dispersed MWNTs and full exfoliation of nanoplatelets can be observed. A few reports in the literature have shown the efficacy of using clay nanoplatelets to disperse CNTs into polymer matrices.[26,27] It was suggested that due to the interaction between CNTs and clay particles, large CNT aggregates would break into small segregates to become well dispersed in polymers. However, clay particles were still found to form stacked morphology and CNTs were also not completely disentangled. The TEM images shown here clearly suggest that through our aqueous dispersion−organic redispersion approach, both MWNTs and nanoplatelets can be fully dispersed down to individual level in epoxy matrices. These results suggest that the most important reason for being able to achieve such a good dispersion is the proper manipulation of the surface characteristics of both CNTs and nanoplatelets so that they have strong affinity to each other via the electrostatic attraction between opposite charges.

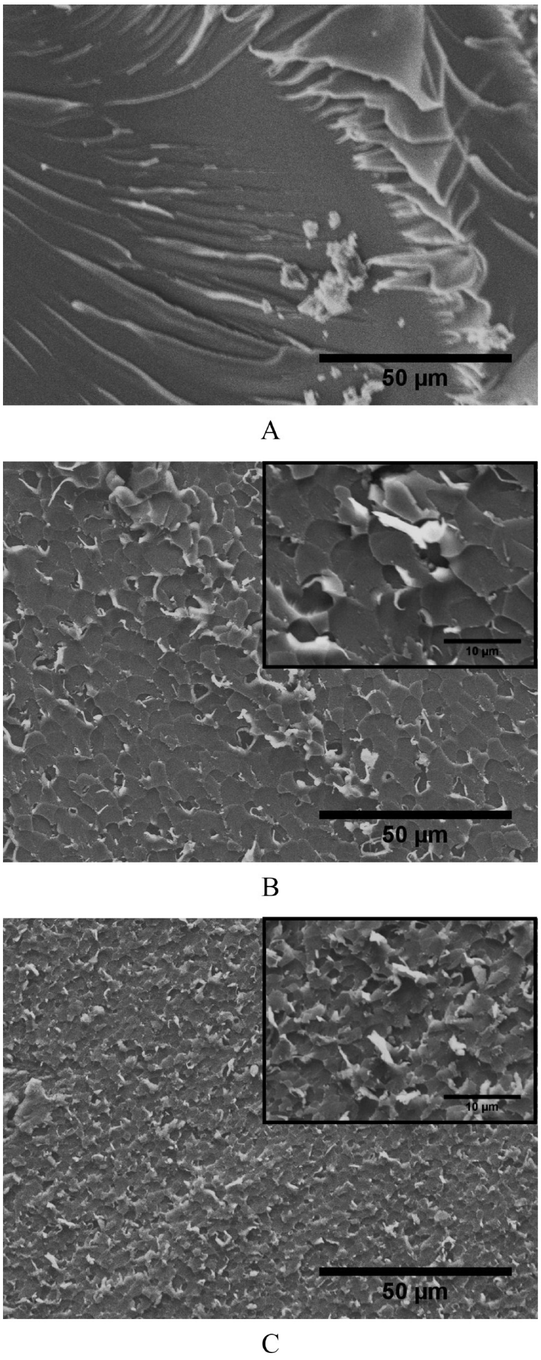


Figure 5. SEM of (A) neat epoxy and epoxy nanocomposites containing (B) 0.2 wt % of MWNTs and 1.0 wt % of ZrP nanoplatelets, and C) 0.4 wt % of MWNTs and 2.0 wt % of ZrP nanoplatelets. The insets in (B) and (C) are high-magnification images of epoxy nanocomposites.

Here, we also demonstrate the effectiveness of the above approach to exfoliate bundled SWNTs in epoxy as shown in Figure S1. The pretreated-SWNTs are still in a bundled state with significant bundle-to-bundle entanglements (Figure S1A). After mixing with exfoliated ZrP nanoplatelets using the above drying-redispersion method, SWNTs can be fully debundled and well dispersed in epoxy matrix (Figure S1B and S1C). The ZrP nanoplatelets have maintained their exfoliated morphology, as well. It should be noted that after debundling, SWNTs become straight in epoxy matrix, whereas that is not the case for the MWNTs. This may be because of the fact that SWNTs possess nearly perfect structure with high stiffness, allowing the tube to remain straight even after curing of epoxy.

Since MWNT has a much higher aspect ratio and much lower cost than SWNT, MWNTs are chosen to demonstrate the possible benefits of exfoliated CNT for strengthening epoxy matrices. The tensile stress−strain curves of the neat epoxy and epoxy nanocomposites containing individually dispersed MWNTs and ZrP nanoplatelets are shown in Figure 4. The Young's modulus, tensile strength, and elongation at break of the neat epoxy and the corresponding nanocomposites are listed in Table 1.

According to Table 1, it is evident that both of the epoxy nanocomposites exhibit noticeably higher Young's modulus, tensile strength, and elongation at break. In particular, the epoxy hybrid nanocomposite containing 0.4 wt % of MWNTs and 2.0 wt % of exfoliated ZrP nanoplatelets exhibits a significant improvement in mechanical properties, having 41% increase in Young's modulus, 55% increase in tensile strength, and 24% increase in elongation at break, respectively. The above findings are considered to be significant when compared against what has been shown in the literature.[18,19]

It should be noted that our previous study on using ZrP nanoplatelets alone to strengthen epoxy at 2 wt % level shows only a slight increase in modulus, while reduction in ductility and strength was found.[33] Additionally, some literature results on polymer/CNT nanocomposites show an improvement in modulus and strength, but with reduction of elongation to break, especially in epoxy.[18,19] The mechanical properties shown here clearly suggest that with the presence of exfoliated nanoplatelets, MWNTs are effective in strengthening epoxy matrices.

We also conducted SEM study of the tensile fracture surfaces for both neat epoxy and epoxy nanocomposites containing exfoliated nanoplatelets and MWNTs (Figure 5). For neat epoxy, the tensile fracture surface is rather smooth and shows little sign of plastic deformation. On the other hand, widespread micrometer-scale patches are found on the tensile fracture surfaces of the epoxy hybrid nanocomposites. These patches are around 5 and 2 μm in size for the 0.2 wt % MWNT and 0.4 wt % MWNT containing nanocomposites, respectively. Careful investigation indicates that no MWNT tubes inside the patches were pulled out from the fracture surfaces. Only short tube ends were exposed, suggesting excellent bonding between MWNTs and the epoxy matrix, and the MWNT tubes were likely broken off when fracture occurred. Furthermore, the length of the MWNTs exposed to the fracture surfaces appear to be quite similar throughout the tensile fracture surfaces, with their exposed lengths of about 2 and 1 μm for the 0.2 wt % MWNT and 0.4 wt % MWNT containing nanocomposites, respectively.

The underlying mechanism(s) leading to such impressive mechanical property improvements is still unknown. One possible reason the epoxy nanocomposites containing MWNTs and inorganic ZrP nanoplatelets can improve both strength and ductility is the synergistic effect from the 1-dimensional and 2-dimensional inorganic fillers that are both well dispersed in polymer matrices down to nanoscale. The presence of the ZrP nanoplatelets prevents the slippage or pull-out of the MWNT from the epoxy matrix. A systematic investigation on the toughening mechanisms in epoxy nanocomposites containing CNTs and inorganic nanoplatelets is underway and will be reported in the near future.

Conclusion

In conclusion, by utilizing exfoliated inorganic nanoplatelets, we have introduced a simple and effective method to fabricate epoxy nanocomposites containing CNTs. Through the strong electrostatic affinity between exfoliated inorganic nanoplatelets and CNTs, excellent dispersion of CNTs in aqueous suspensions can be easily transferred to organic solvents for the preparation of exfoliated epoxy nanocomposites. The epoxy nanocomposites containing well-dispersed MWNTs and exfoliated ZrP nanoplatelets show superior modulus, strength, and strain at failure at low tube loading. Such kind of low cost, high-performance epoxy nanocomposites are ideal for engineering structural applications.

Acknowledgment. We acknowledge financial support from the Dow Chemical Company, Boeing Company, and the Defense Logistic Agency (SP0103-02-D-0024). D.S. thanks Dr. Zhiping Luo at Microscopy Imaging Center (MIC) in Texas A&M University (TAMU) for his assistance in the TEM work.

Supporting Information Available: Figure S1 shows an example of dispersion of SWNTs in brittle epoxy using exfoliated nanoplatelets. This material is available free of charge via the Internet at http://pubs.acs.org.

---

(33) Boo, W. J.; Sun, L. Y.; Liu, J.; Clearfield, A.; Sue, H. -J.; Mullins, M. J.; Pham, H. *Compos. Sci. Technol.* **2007**, *67*(2), 262.