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Preparation of Exfoliated Epoxy/α-Zirconium Phosphate Nanocomposites Containing High Aspect Ratio Nanoplatelets

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High-crystallinity α-zirconium phosphate (α-ZrP) crystals which contain stacks of high aspect ratio nanoplatelets were synthesized and exfoliated with tetra-*n*-butylammonium hydroxide in aqueous dispersion. The exfoliated α-ZrP nanoplatelets were then transferred into water-miscible organic solvents, such as acetone, by centrifugation and re-dispersion. The resulting exfoliated α-ZrP nanoplatelets in organic solvents can be easily utilized to prepare polymer nanocomposites. Through such an approach, epoxy/α-ZrP nanocomposites containing high aspect ratio α-ZrP nanoplatelets have been prepared. The presence of the well-exfoliated nanocomposite structure is confirmed by powder X-ray diffraction and transmission electron microscopy.

1. Introduction

Layered silicate-based polymer nanocomposites have been studied extensively as a new generation of advanced composites[1−4] that exhibit significantly improved stiffness and strength,[1,5] enhanced gas barrier properties,[6−8] and superior flame retardancy.[9] Among a wide spectrum of layered materials that have been utilized for reinforcing the properties of polymer matrices, montmorillonite (MMT) clay has been the focus of numerous research efforts because of its relatively low cost and its ability to form well-dispersed and exfoliated morphology in polymer matrices.[2,10] The effectiveness of nanofillers on improving physical and mechanical properties of polymer nanocomposites strongly depends on a number of factors including size, shape, aspect ratio, strength, loading level, degree of exfoliation, and their interfacial adhesion to the polymer matrix. While achieving a high degree of exfoliation of nanoplatelets in polymer matrices has been the main focus of research in recent years, emphasis on how the aspect ratio of the nanoplatelets affects dispersion and exfoliation in polymer matrices, and therefore, their corresponding physical and mechanical properties, is still lacking.

It is intuitively evident and has also been validated by modeling that aspect ratio of nanoplatelets has a significant impact on the physical and mechanical properties of the polymer nanocomposite, especially on barrier properties[11−13] and modulus and strength.[14−18] Although a number of modeling studies have been reported, little experimental data are available to provide solid support for the modeling claims. In some cases, the discussions regarding the influence of aspect ratio on physical and mechanical properties were made based on the deduction of observations by comparing dissimilar nanoplatelets.[19,20] In some other cases, the exfoliated nanoplatelets were treated as if they had a higher aspect ratio than the intercalated ones.[12,21] Unfortunately, not only is the aspect ratio of the nanoplatelets changed in the above cases, but other important material parameters, such as degree of intercalation, dispersion, and interfacial characteristics, are also altered. Consequently, little fundamental knowledge can be unambiguously established.

To date, the only known designed experiment to alter the aspect ratio of the nanoplatelets in a polymer nanocomposite in the literature was through the breaking of the nanoplatelets by shear.[16] However, the changes in aspect ratio based on

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(1) Giannelis, E. P. *Adv. Mater.* **1996**, *8*, 29−35.
(2) Alexandre, M.; Dubois, P. *Mater. Sci. Eng. R* **2000**, *28*, 1−63.
(3) Ray, S. S.; Okamoto, M. *Prog. Polym. Sci.* **2003**, *28*, 1539−1641.
(4) Ahmadi, S. J.; Huang, Y. D.; Li, W. *J. Mater. Sci.* **2004**, *39*, 1919−1925.
(5) Lan, T.; Kaviratna, P. D.; Pinnavaia, T. J. *Chem. Mater.* **1995**, *7*, 2144−2150.
(6) Yano, K.; Usuki, A.; Okada, A.; Kurauchi, T.; Kamigaito, *O. J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 2493−2498.
(7) Shi, H.; Lan, T.; Pinnavaia, T. J. *Chem. Mater.* **1996**, *8*, 1584−1587.
(8) Tsai, T.-Y.; Li, C.-H.; Chang, C.-H.; Cheng, W.-H.; Hwang, C.-L.; Wu, R. J. *Adv. Mater.* **2005**, *17*, 1769−1773.
(9) Zhu, J.; Start, P.; Mauritz, K. A.; Wilkie, C. A. *Polym. Degrad. Stab.* **2002**, *77*, 253−258.
(10) Drummy, L. F.; Koerner, H.; Farmer, K.; Tan, A.; Farmer, B. L.; Vaia, R. A. *J. Phys. Chem. B* **2005**, *109*, 17868−17878.
(11) Lu, C.; Mai, Y.-W. *Phys. Rev. Lett.* **2005**, *95*, 088303/1−088303/4.
(12) Osman, M. A.; Mittal, V.; Lusti, H. R. *Macromol. Rapid Commun.* **2004**, *25*, 1145−1149.
(13) Osman, M. A.; Mittal, V.; Morbidelli, M.; Suter, U. W. *Macromolecules* **2004**, *37*, 7250−7257.
(14) Sheng, N.; Boyce, M. C.; Parks, D. M.; Rutledge, G. C.; Abes, J. I.; Cohen, R. E. *Polymer* **2004**, *45*, 487−506.
(15) Luo, J. J.; Daniel, I. M. *Comp. Sci. Technol.* **2003**, *63*, 1607−1616.
(16) Weon, J. I.; Sue, H. J. *Polymer* **2005**, *46*, 6325−6334.
(17) Vlasveld, D. P. N.; de Jong, M.; Bersee, H. E. N.; Gotsis, A. D.; Picken, S. J. *Polymer* **2005**, *46*, 10279−10289.
(18) Kuelpmann, A.; Osman, M. A.; Kocher, L.; Suter, U. W. *Polymer* **2005**, *46*, 523−530.
(19) Wang, Y.; Zhang, H.; Wu, Y.; Yang, J.; Zhang, L. *J. Appl. Polym. Sci.* **2005**, *96*, 324−328.
(20) Maiti, P.; Yamada, K.; Okamoto, M.; Ueda, K.; Okamoto, K. *Chem. Mater.* **2002**, *14*, 4654−4661.
(21) Loyens, W.; Maurer, F. H. J.; Jannasch, P. *Polymer* **2005**, *46*, 7334−7345.

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the above approach are limited and cannot be easily controlled. The lack of literature information on how the variation in aspect ratio affects material properties is mainly due to the experimental difficulty in controlling aspect ratios based on MMT clay or other natural layered compounds. For the MMT clay system, the aspect ratio of individually exfoliated clay nanoplatelets is about 80−200, which is limited by the nature of the clay particles.

To obtain high aspect ratio nanoplatelets, synthetic α-zirconium phosphate (α-ZrP), $Zr(HPO_4)_2 \cdot H_2O$, has been selected to prepare polymer nanocomposites. Through controlling the reaction conditions, α-ZrP with different crystal sizes can be synthesized[22,23] to prepare nanoplatelets with different aspect ratios. In addition to the ease of dimensional control, α-ZrP has a number of additional advantages over natural clay, including a much higher ion exchange capacity, ease of intercalation/exfoliation, and controllable surface functionality. Fully exfoliated polymer nanocomposites based on α-ZrP have been successfully prepared in the past few years.[24−27]

In this study, epoxy nanocomposites containing exfoliated α-ZrP nanoplatelets with aspect ratio >1000 are reported. Meanwhile, a new approach for preparing pre-exfoliated α-ZrP nanoplatelets in organic solvents for polymer nanocomposites applications is reported.

2. Experimental Section

The α-ZrP crystals used in this study were synthesized from a slightly modified HF approach, which was originally developed by Alberti and Torracca,[28] by refluxing zirconyl chloride ($ZrOCl_2 \cdot 8H_2O$, Aldrich), phosphoric acid (EM Science), and hydrofluoric acid (EMD Chemicals) in a Teflon flask coupled with a Teflon condenser. The α-ZrP prepared was exfoliated by tetra-*n*-butylammonium hydroxide (TBA^+OH^-, Aldrich) in an aqueous dispersion maintained at 0 °C in an ice bath to minimize hydrolysis.[29−31] The concentration of α-ZrP aqueous dispersion was controlled at a low value (ca. 5.0×10^{-3} mol/L) to make sure that the dispersed α-ZrP particles were completely reacted with TBA^+OH^-. The intercalated/exfoliated α-ZrP was characterized by X-ray diffraction (XRD) under both dry (cast on a silicon wafer and dried overnight at room temperature) and wet (in aqueous dispersion) states. The wet samples were characterized directly by forming a thin layer of liquid film on a silicon wafer and covered by a Mylar film (Complex Industries, Inc., Palm City, FL) to maintain a flat liquid surface and minimize evaporation during XRD experiments. The epoxy monomer used in this study was a diglycidyl ether of bisphenol A (DGEBA) epoxy resin (D.E.R. 332 epoxy resin, The Dow Chemical Company), which has a narrow monomer molecular weight distribution (171−175 g/mol). The curing agent was 4,4′-diaminodiphenyl sulfone (DDS, Aldrich). All the regents were used as received except for epoxy resin, which was dried in a vacuum oven for 24 h prior to sample preparation.

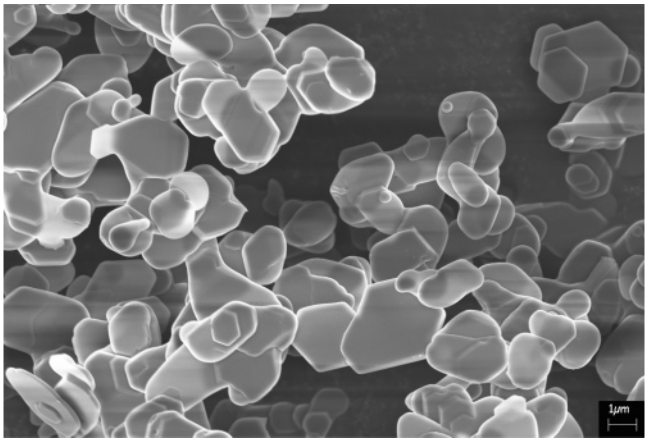

Figure 1. SEM image of crystalline α-ZrP.

XRD patterns were recorded using a Bruker D8 diffractometer with Bragg−Brentano $\theta-2\theta$ geometry (40 kV and 40 mA), using a graphite monochromator with Cu Kα radiation. Scanning electron microscope (SEM) images were acquired using a Zeiss Leo 1530 VP Field Emission-SEM (FE-SEM). The samples were sputter-coated with a thin layer (ca. 3 nm) of Pt/Pd (80/20) prior to SEM imaging. Transmission electron microscopy (TEM) was performed using a JEOL 1200EX, operated at 100 kV. A Reichert-Jung Ultracut-E microtome was utilized to prepare thin sections with 70−100 nm in thickness for TEM imaging.

3. Results and Discussion

The high-crystallinity α-ZrP has a large average size of about 1.5 μm (Figure 1) and its structure is confirmed by X-ray diffraction (XRD) analysis. While the intercalation of relatively low crystallinity, low aspect ratio α-ZrP (ca. 80−300 nm in lateral dimensions) with long-chain amines and the subsequent exfoliation in epoxy monomers enables the preparation of fully exfoliated epoxy nanocomposites,[24] the same approach to intercalate and exfoliate high aspect ratio α-ZrP nanoplatelets becomes ineffective. It is difficult to achieve complete intercalation of high aspect ratio α-ZrP nanoplatelets with long-chain amines even after a long intercalation process. A small amount of α-ZrP crystals usually remain partially intercalated. The possible reasons for the difficulty in achieving complete intercalation are the relatively higher van der Waals forces between the layers and the diffusion-limiting process of intercalating agents to migrate toward the center of the gallery.[32] The intercalation process presumably starts from the edge and migrates toward the interior of the layers. When the crystal sizes are large, it will require a long residence time for the intercalating agents to insert deep into the gallery, especially when the size of the intercalating molecule is also large. To overcome this problem, smaller bulky tetra-*n*-butylammonium hydroxide

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(22) Clearfield, A. *Ann. Rev. Mater. Sci.* **1984**, *14*, 205−229.
(23) Sun, L.; Boo, W. J.; Clearfield, A.; Sue, H.-J. *New J. Chem.* **2007**, *31*, 39−43.
(24) Sue, H.-J.; Gam, K. T.; Bestaoui, N.; Spurr, N.; Clearfield, A. *Chem. Mater.* **2004**, *16*, 242−249.
(25) Sue, H.-J.; Gam, K. T.; Bestaoui, N.; Clearfield, A.; Miyamoto, M.; Miyatake, N. *Acta Mater.* **2004**, *52*, 2239−2250.
(26) Boo, W. J.; Sun, L.; Liu, J.; Clearfield, A.; Sue, H.-J. *Comp. Sci. Technol.* **2007**, 262−269.
(27) Boo, W. J.; Sun, L.; Liu, J.; Moghbelli, E.; Clearfield, A.; Sue, H.-J. *J. Polym. Sci., Part B: Polym. Phys.* **2007**, in press.
(28) Alberti, G.; Torracca, E. *J. Inorg. Nucl. Chem.* **1968**, *30*, 317−318.
(29) Garcia, M. E.; Naffin, J. L.; Deng, N.; Mallouk, T. E. *Chem. Mater.* **1995**, *7*, 1968−1973.
(30) Kim, H.-N.; Keller, S. W.; Mallouk, T. E.; Schmitt, J.; Decher, G. *Chem. Mater.* **1997**, *9*, 1414−1421.
(31) Kaschak, D. M.; Johnson, S. A.; Hooks, D. E.; Kim, H.-N.; Ward, M. D.; Mallouk, T. E. *J. Am. Chem. Soc.* **1998**, *120*, 10887−10894.
(32) Sun, L.; Boo, W. J.; Browning, R. L.; Sue, H.-J.; Clearfield, A. *Chem. Mater.* **2005**, *17*, 5606−5609.

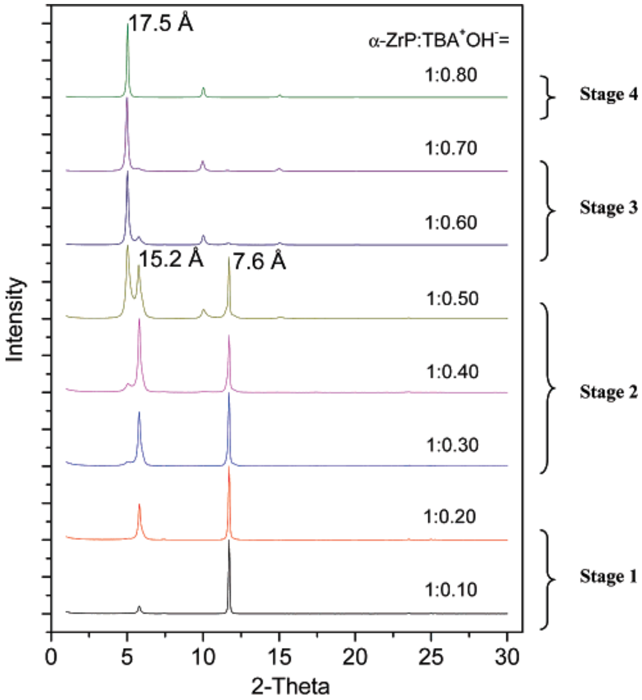

Figure 2. XRD patterns of α-ZrP intercalated by TBA^+OH^- at 0 °C in aqueous dispersion. Intercalated and exfoliated α-ZrP nanoplatelets are restacked and dried on a silicon wafer before testing.

(TBA^+OH^-) molecules were selected to achieve intercalation and exfoliation of high-crystallinity α-ZrP.

The intercalation and exfoliation of α-ZrP with TBA^+OH^- in aqueous solution is straightforward, especially at low temperatures.[30,31] The XRD patterns in Figure 2 are from the intercalated and exfoliated α-ZrP nanoplatelets that were restacked and dried on a silicon wafer. The patterns clearly show the progression of intercalation and exfoliation. At low intercalation molar ratios of α-ZrP:TBA^+OH^- = 1:0.10 and 1:0.20, the small peak at 5.8° (15.2 Å) is due to the intercalated α-ZrP with a single layer of TBA^+ ions in the gallery.[30] The strong peak at 11.7° (7.6 Å) indicates that a large amount of α-ZrP nanoplatelets remain intact.

With an increase of the intercalation ratio to 1:0.30, more TBA^+ ions are intercalated into α-ZrP layers, which corresponds to a more intense peak at 5.8° (15.2 Å) and a less intense peak at 11.7°. Meanwhile, a second peak at 5.0° (17.5 Å) begins to appear. The peak at 5.0° is believed to result from the restacking of the exfoliated α-ZrP nanoplatelets. This is because, during intercalation, α-ZrP can theoretically accommodate two layers of TBA^+ ions in each interlayer space. However, this unstable double-layer arrangement, which introduces cation−cation contacts between layers, leads to exfoliation.[30] The restacked exfoliated α-ZrP layers have a slightly larger interlayer spacing than intercalated α-ZrP, suggesting a single-layer arrangement of TBA^+ ions plus some water molecules in the restacked layers. The incorporation of water between the interlayer space can be confirmed by the XRD pattern of annealed sample (110 °C overnight), which shows a slightly decreased interlayer distance.

Further increase of intercalation ratio up to 1:0.50 gives rise to more exfoliation, which results in a shift in the intensities between the two peaks at 5.0° (17.5 Å) and 5.8° (15.2 Å). However, the presence of the peak at 11.7° (7.6 Å) indicates that some amount of α-ZrP nanoplatelets still remain intact. This, again, suggests that the intercalation/exfoliation occurs gradually from the edge toward the center of the α-ZrP layers.

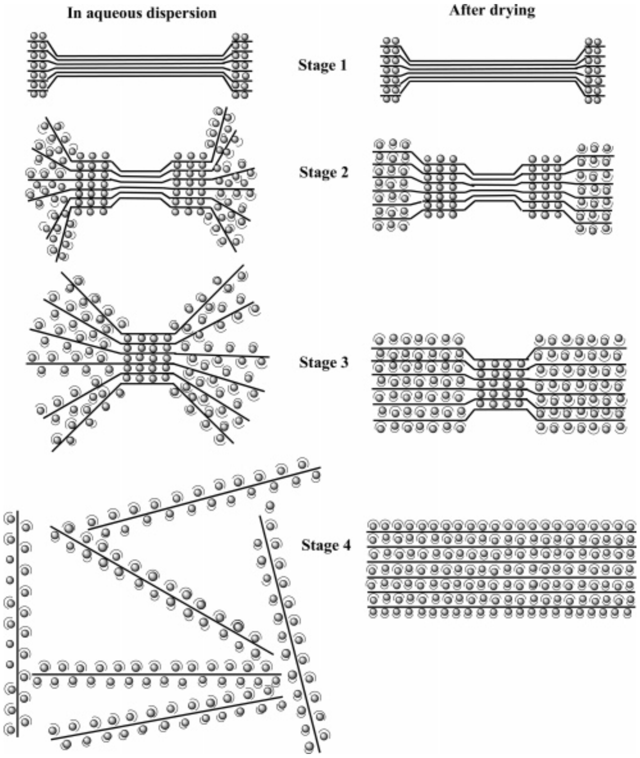

Figure 3. Schematic of α-ZrP intercalation/exfoliation mechanism when treated with TBA in aqueous dispersion. The dots represent TBA molecules and the curves adjacent to the dots represent water molecules. The straight lines represent α-ZrP layers.

Beyond the above TBA concentration level, when the intercalation ratio increases to 1:0.60 and 1:0.70, more and more α-ZrP nanoplatelets become exfoliated. But the presence of the peak at 5.8° (15.2 Å) indicates that a small amount of α-ZrP nanoplatelets is still intercalated.

At the 1:0.80 intercalation ratio, all the α-ZrP nanoplatelets are exfoliated, leaving no peaks at 5.8° and 11.7° for dried samples. The four stages of intercalation/exfoliation progresses described above are illustrated in Figure 3.

When α-ZrP was intercalated at an intercalation ratio of 1:0.80 or above, the α-ZrP/TBA dispersion becomes completely homogeneous. Although it is still not transparent, the dispersion is stable at room temperature over a 2-week period. After 2 weeks standing still, a small amount of gel can be observed at the bottom of the solution. However, no solid residue can be observed even after more than 3 months of storage.

To further confirm that the peak at 5.0° (17.5 Å) is from the restacked exfoliated α-ZrP nanoplatelets, the intercalated and exfoliated α-ZrP samples were characterized directly in the liquid state. In this state, if the α-ZrP is exfoliated, the peak at 5.0° should be absent, while the peaks corresponding to intercalated α-ZrP (5.8°) and intact α-ZrP (11.7°) should remain. Two selected XRD patterns at intercalation ratios of 1:0.30 and 1:0.80 are presented in Figure 4. Compared with their dry state XRD patterns, no diffraction peak at 5.0°

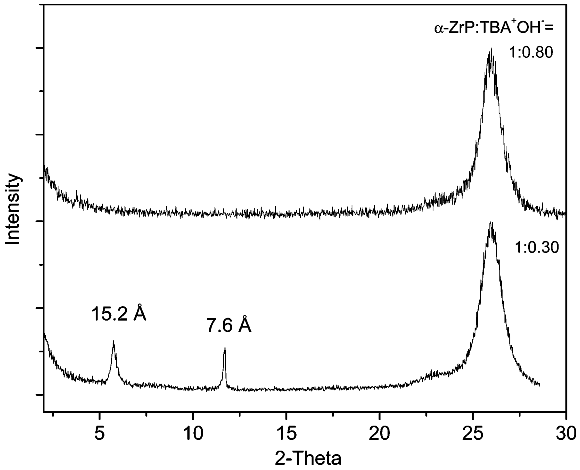

Figure 4. XRD patterns of α-ZrP intercalated/exfoliated by TBA^+OH^- at 0 °C in aqueous dispersion. Samples with a concentration of 5.0×10^{-3} mol/L α-ZrP were characterized directly in the liquid state.

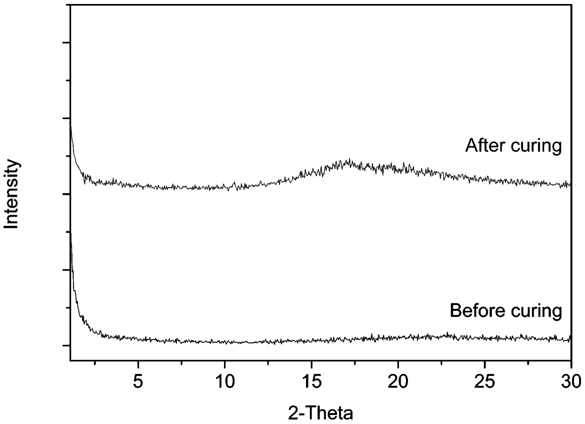

Figure 5. XRD patterns of α-ZrP/epoxy nanocomposites with 0.7 vol % α-ZrP.

position is observed from either of the two samples. For the system at an intercalation ratio of 1:0.30, it shows two peaks at 5.8° (15.2 Å) and 11.7° (7.6 Å) in its dried state XRD pattern. These two peaks are also present in its liquid-state XRD pattern. For the system at an intercalation ratio of 1:0.80, there is no peak presented in its liquid-state XRD pattern. This result again indicates that the peak at 5.0° (17.5 Å) in Figure 2 is from the restacked exfoliated α-ZrP nanoplatelets, while the peak at 5.8° (15.2 Å) is from the intercalated α-ZrP nanoplatelets. The large and broad peak at about 25.9° in the patterns is from the Mylar film.

It is found that the exfoliation of α-ZrP by TBA^+OH^- can be easily realized in an aqueous media, but not in polar organic solvents, such as methanol, acetone, tetrahydrofuran, and *N*,*N*-dimethylformamide. This is probably because TBA^+OH^- has a very high affinity with water, and the participation of water molecules is critical for the intercalation/exfoliation process by TBA^+OH^-. A similar phenomenon has also been observed when α-ZrP was treated with propylamine.[33] Unfortunately, most of the polymers are insoluble in water. To overcome this issue, but still take advantage of the convenience of intercalation and exfoliation by TBA^+OH^-, the well-exfoliated α-ZrP nanoplatelets in water were first centrifuged at 4400*g* force to collect exfoliated individual α-ZrP nanoplatelets. These exfoliated individual α-ZrP nanoplatelets were condensed to a gel form after centrifugation and the supernatant could then be easily removed. After the removal of supernatant, the same amount of water-miscible organic solvent, such as acetone, was mixed with the α-ZrP gel obtained from the previous process. The mixture was sonicated for 1 h and then shaken overnight to re-disperse α-ZrP nanoplatelets into acetone. This centrifugation and redispersion process was repeated three times to remove most of the water and to obtain exfoliated α-ZrP nanoplatelets in acetone. The supernatant separated after each of the three centrifugations was collected and heated in an oven at 110° to remove solvent and obtain a small amount of dried α-ZrP which was left in the supernatant. Thus, the exact amount of α-ZrP which was exchanged into acetone can be calculated. Generally, about 70% of the exfoliated α-ZrP nanoplatelets can be recovered after three cycles of centrifugation and redispersion process.

It should be noted that if the exfoliated α-ZrP nanoplatelets in aqueous dispersion are to be exchanged into any water-miscible organic solvent that has a boiling point much higher than that of water, then the organic solvent can be directly mixed with the α-ZrP nanoplatelets in water. Afterward, the water can be removed by heating the mixture at a temperature near 100 °C.[33] Subsequently, the exfoliated α-ZrP nanoplatelets in the organic solvent can be mixed with another soluble polymer or monomer directly to prepare fully exfoliated polymer nanocomposites.

Both the α-ZrP-containing gels centrifuged from aqueous, and acetone dispersions (after 3 cycles) were screened by XRD. The samples were covered by a Mylar film during the characterization to minimize the evaporation of solvent. No peaks were present on the XRD patterns of either of the two gels, which indicate that no intercalated layered structure re-formed after centrifugation.

The exchanged α-ZrP nanoplatelets in acetone were mixed with epoxy monomer to achieve an α-ZrP loading of 0.7 vol % in the final composite. After moderate stirring and sonication to achieve a homogeneous dispersion, the acetone was removed with a rotavapor in a water bath at about 80 °C. Then, the curing agent DDS was added at a stoichiometric ratio. To be noted, after removal of the acetone, the viscosity of the mixture becomes much higher than the low aspect ratio (~100) case. And it becomes even higher after addition of DDS. It is necessary to increase the temperature to about 150 °C to reduce the viscosity and facilitate the mixing and processing. The resin mixture was finally cast into a preheated glass mold and cured in an oven at 180 °C for 2 h, followed by 2 h of postcure at 220 °C.

Figure 5 presents the XRD patterns of epoxy/α-ZrP nanocomposite containing 0.7 vol % of α-ZrP before and after curing. The XRD pattern of epoxy/α-ZrP nanocomposite before curing shows no peaks, indicating that α-ZrP nanoplatelets remain exfoliated after mixing with epoxy resin. In the case of cured epoxy/α-ZrP nanocomposite, the XRD pattern only exhibits a broad hump at around 18° in 2θ, which corresponds to the structure of the amorphous epoxy matrix.[24]

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(33) Casciola, M.; Alberti, G.; Donnadio, A.; Pica, M.; Marmottini, F.; Bottino, A.; Piaggio, P. *J. Mater. Chem.* **2005**, *15*, 4262−4267.

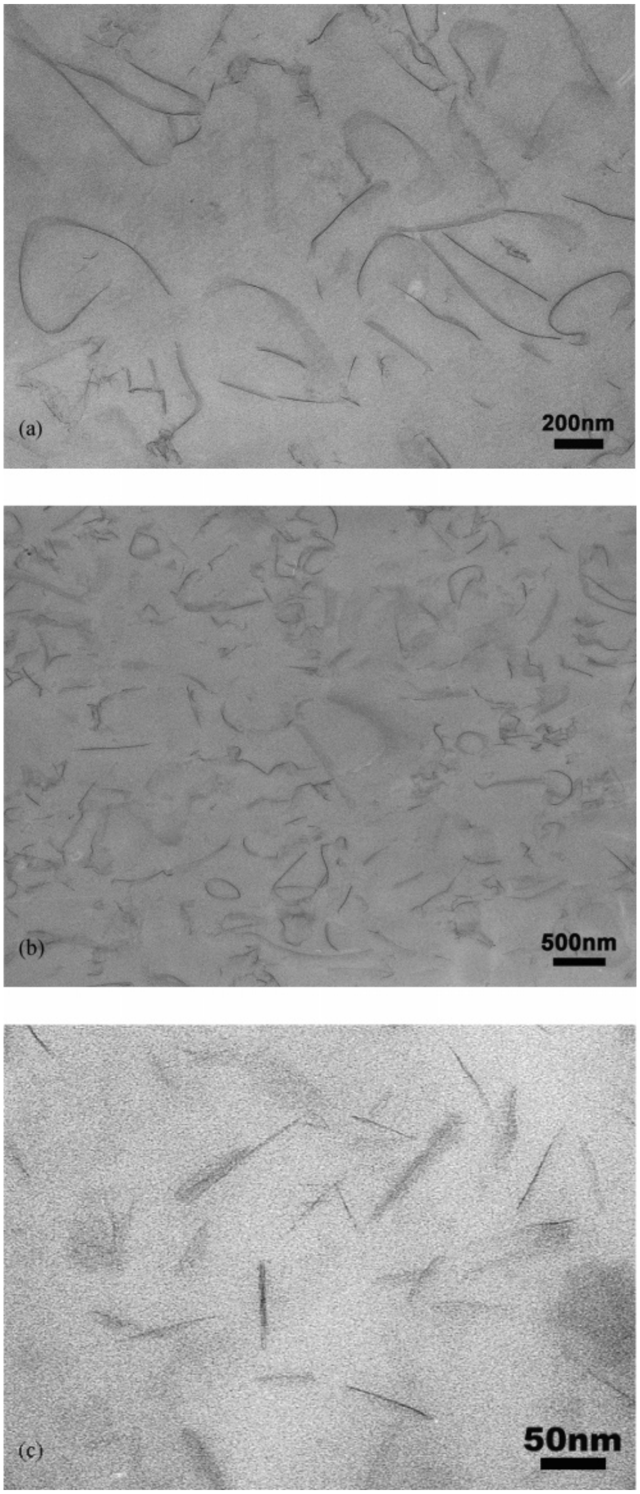

Figure 6. TEM of α-ZrP/epoxy nanocomposites with 0.7 vol % α-ZrP showing nanoplatelets with (a) high aspect ratio (high magnification), (b) high aspect ratio (low magnification), and (c) low aspect ratio.

To confirm the state of exfoliation and the aspect ratio of α-ZrP nanoplatelets in epoxy matrix, TEM imaging was performed. The TEM images in Figure 6 clearly show a high degree of exfoliation of α-ZrP nanoplatelets in epoxy. The dispersion of α-ZrP nanoplatelets in epoxy matrix is uniform throughout the sample. The aspect ratio of the α-ZrP nanoplatelets can be estimated by dividing the observed length of α-ZrP nanoplatelets by the thickness of the α-ZrP layer (ca. 0.68 nm).[30] The estimated aspect ratios of α-ZrP nanoplatelets range from about 800 to 1500, which is about 10 times larger than the clay-based polymer nanocomposites.

It is interesting to note that the high aspect ratio α-ZrP nanoplatelets exhibit severe curling. This finding is different from our previous studies, which indicate that the exfoliated α-ZrP nanoplatelets appear to be straight if their aspect ratios are ca. 100.[24,26] A number of reasons may result in the observed curvature when aspect ratio is greater than 1000, including (1) the lowered buckling stress of α-ZrP nanoplatelets as the aspect ratio increases, (2) inhomogeneous stress distribution and shear within the sample during curing, and (3) possible defects in the α-ZrP nanoplatelets. Molecular dynamics modeling is currently being pursued to gain insights into the possible causes for such a phenomenon. For comparison purposes, the epoxy/α-ZrP with aspect ratio of ca. 100 was also prepared and imaged by TEM (Figure 6c). These low aspect ratio nanoplatelets are straight and show no sign of curling.

A small amount of nanoplatelets with lower aspect ratio were also observed in the TEM images. These nanoplatelets may be formed due to the TEM thin sectioning process since the thickness of the thin sections is about 70−100 nm, which is much smaller than the lateral dimension of the α-ZrP nanoplatelets. Another possibility is the presence of small sizes of the α-ZrP crystals. Nevertheless, on an average, the aspect ratio of the α-ZrP nanoplatelets prepared in this study is still an order of magnitude higher than clay nanoplatelets and those prepared based on low-crystallinity α-ZrP.

In comparison with the polymer nanocomposites investigated in the past, the aspect ratio of the nanoplatelets prepared in this study is an order of magnitude higher. This kind of high aspect ratio nanoplatelets should be much more effective in improving the physical and mechanical properties of polymers. To be noted, even larger α-ZrP crystals can be synthesized[34] to prepare polymer nanocomposites with even higher aspect ratios. However, some modeling work has suggested that too high an aspect ratio cannot bring about dramatic improvements in modulus due to the significantly reduced volume fraction that high aspect ratio nanoplatelets can be incorporated in a polymer matrix.[14] Another negative impact from the use of high aspect ratio nanoplatelets is the unacceptable increase in viscosity for the polymer system.[17]

Meanwhile, based on what has been observed in this study, increased aspect ratio may introduce significant curvature of the nanoplatelets. Such a curvature may greatly affect the efficiency of fully exfoliated nanoplatelets in reinforcing the composite properties. Therefore, under such a scenario, in addition to the importance of aspect ratio, nanoplatelet curvature and shape should also be considered in establishing structure−property relationship of polymer nanocomposites. The higher aspect ratio nanoplatelets may not necessarily correspond to improved mechanical and physical properties proportionally. In future modeling work, both aspect ratio and curvature should be taken into account to better address the structure−property relationship of polymer nanocomposites. The study on how the aspect ratio of the nanoplatelets

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(34) Alberti, G.; Costantino, U.; Allulli, S.; Massucci, M. A. *J. Inorg. Nucl. Chem.* **1975**, *37*, 1779−1786.

affects physical and mechanical properties is currently underway and will be reported in the near future.

4. Conclusions

An approach to prepare polymer nanocomposites containing high aspect ratio nanoplatelets from pre-exfoliated nanoplatelets has been developed via a centrifugation and re-dispersion process. Based on the above approach, epoxy nanocomposites containing well-exfoliated high aspect ratio α-ZrP nanoplatelets have been successfully prepared. These high aspect ratio α-ZrP nanoplatelets show an interesting curvature characteristic, which is not observed in low aspect ratio α-ZrP systems. This new finding implies that the aspect ratio of nanoplatelets is no longer an independent parameter for studying physical and mechanical properties of nanocomposites if the aspect ratio is high. The aspect ratio issue should be considered together with the corresponding curvature. The curvature of the nanoplatelets may affect the efficiency of both load transfer and barrier layer formation. Thus, in a certain aspect ratio range, the higher aspect ratio nanofillers may not necessarily be superior to lower aspect ratio ones in improving physical and mechanical properties of polymer nanocomposites.

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