Synthesis of Disordered and Highly Exfoliated Epoxy/Clay Nanocomposites Using Organoclay with Catalytic Function via Acetone−Clay Slurry Method

Bin Chen,† Jia Liu, Haibin Chen, and Jingshen Wu*

Materials Research Group, Department of Mechanical Engineering, The Hong Kong University of Science and Technology, Kowloon, Hong Kong, China

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Polymer/clay nanocomposites have attracted considerable attention in recent decades[1−28] because of their unique properties compared with those of the conventional composites. Among those properties are higher strength and modulus,[1,3] better dimensional and thermal stabilities,[7,8] as well as improved barrier properties and chemical stability. [8,9] Polymer/clay nanocomposites can be generally classified into two groups. The intercalated polymer/clay nanocomposites have layered clay dispersed in a polymer matrix with polymer chains inserted into clay layers that retain their lateral order. The exfoliated ones consist of fully delaminated clay platelets dispersed individually in the matrix. Thus, each platelet interacts with the matrix and improves the properties of the nanocomposites more effectively. However, complete clay exfoliation in polymer matrixes is highly challenging. For instance, in the preparation of epoxy/clay nanocomposites, clay exfoliation is influenced by many factors, including curing agents[16,18] and conditions,[4,14,16] the cation-exchange capacity (CEC) of the clay,[15] and the property of clay modifier.[4,10,18] In particular, the authors of ref 4 pointed out that clay surface modifier has a significant effect on the clay exfoliation. They further proposed that use of a surfactant with catalytic function for epoxy curing as clay surface modifier could promote the curing reaction of the epoxy inside the clay gallery, leading to a high degree of clay exfoliation. On the other hand, it is also noted that many publications declared the achievement of exfoliated epoxy/clay nanocomposites. In most cases, the evidences given to support such declarations were either absence of d_{001} diffraction peak on XRD pattern and/or TEM images of a composite with clay layers parallel arranged in good order but with expanded gallery spacing. Recently, Mai et al.[29] reported a method for preparation of exfoliated epoxy/clay nanocomposites. The authors blended the water suspension of an epoxy-hardener-modified clay directly with epoxy. The water in the system was later removed by vaporization. Since water is difficult to remove completely from epoxy, the properties of the resultant composites may be poor.

A new method for nanocomposite preparation has been developed and is reported here. The new method has two characteristics. (1) An accelerator for epoxy curing, 2,4,6-tris-(dimethylaminomethyl) phenol (DMP-30), is employed for clay modification. The DMP-30 modified clay is expected to promote epoxy curing when it is mixed with epoxy resin and curing agent. (2) Acetone−clay slurry is used in sample preparation. After the modification of the pristine clay with DMP-30, the organoclay is precipitated from water. Instead of drying the organoclay, it is washed with hot acetone to replace the water. The acetone is kept in the clay and the acetone−clay slurry is added into epoxy resin followed by mixing and curing. Using this method, a highly exfoliated and disordered epoxy/clay nanocomposite was successfully prepared.

Pristine clay (10 g, CEC 92.6 meq/100 g, Southern Clay) was dispersed into 1500 mL of distilled water at 80 °C. DMP-30 was first protonated by dropping 70 mLof 0.2 N HCl solution (14 mmol) into 4.2 g (15 mmol) of DMP-30 in 100 mL of distilled water under stirring. The amount of DMP-30 was controlled to ensure that only one of the reactive groups on DMP-30 would be converted into a cation. The solution was then poured into the hot clay/water suspension and stirred vigorously for 2 h at 80 °C. A pale yellow precipitate formed and was isolated by filtration and washed several times with hot distilled water until no chloride was detected

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* Corresponding author. Tel: 852-2358-7200. Fax: 852-2358-1543. mejswu@ust.hk.

† On leave from Changchun Institute of Applied Chemistry, CAS.

[1] Messersmith, P.; Giannelis, E. P. *Chem. Mater.* **1994**, *6*, 1719.

[2] Wang, M. S.; Pinnavaia, T. J. *Chem. Mater.* **1994**, *6*, 468.

[3] Lan, T.; Pinnavaia, T. J. *Chem. Mater.* **1994**, *6*, 2216.

[4] Lan, T.; Kaviratna, P. D.; Pinnavaia, T. J. *Chem. Mater.* **1995**, *7*, 2144.

[5] Messersmith, P.; Giannelis, E. P. *J. Polym. Sci., Part A: Polym. Chem.* **1995**, *33*, 1047.

[6] Shi, H.; Lan, T.; Pinnavaia, T. J. *Chem. Mater.* **1996**, *8*, 1584.

[7] Wang, Z.; Pinnavaia, T. J. *Chem. Mater.* **1998**, *10*, 1820.

[8] Massam, J.; Wang, Z.; Pinnavaia, T. J.; Lan, T.; Beall, G. *Polym. Mater. Sci. Eng.* **1998**, *78*, 274.

[9] Massam, J.; Pinnavaia, T. J. *Mater. Res. Soc. Symp. Proc.* **1998**, *520*, 223.

[10] Brown, J. M.; Curliss, D.; Vaia, R. A. *Chem. Mater.* **2000**, *12*, 3376.

[11] Ishida, H.; Campbell, S.; Blackwell, J. *Chem. Mater.* **2000**, *12*, 1260.

[12] Zilg, C.; Thomann, R.; Finter, J. *Macromol. Mater. Eng.* **2000**, *280/281*, 41.

[13] Chin, I. J.; Thurn, A. T.; Kim, H. C.; Russell, T. P. *Polym. Prepr.* **2000**, *41*, 591.

[14] Ke, Y. C.; Lu, J. K.; Yi, X. S.; Zhao, J.; Qi, Z. N. *J. Appl. Polym. Sci.* **2000**, *78*, 808.

[15] Kornmann, X.; Lindberg, H.; Berglund, L. A. *Polymer* **2001**, *42*, 1303.

[16] Kornmann, X.; Lindberg, H.; Berglund, L. A. *Polymer* **2001**, *42*, 4493.

[17] Chin, I. J.; Albrecht, T. T.; Kim, H. C.; Russell, T. P. *Polymer* **2001**, *42*, 5947.

[18] Lu, J. K.; Ke, Y. C.; Qi, Z. N. *J. Polym. Sci., Part B: Polym. Phys.* **2001**, *39*, 115.

[19] Zerda, A. S.; Lesser, A. J. *J. Polym. Sci., Part B: Polym. Phys.* **2001**, *39*, 1137.

[20] Chen, J. S.; Poliks, M. D.; Ober, C. K.; Zhang, Y.; Giannelis, E. *Polymer* **2002**, *43*, 4895.

[21] Chen, K. H.; Yang, S. M. *J. Appl. Polym. Sci.* **2002**, *86*, 414.

[22] Becker, O.; Varley, R.; Simon, G. *Polymer* **2002**, *43*, 4365.

[23] Xu, W. B.; Bao, S. P.; He, P. S. *J. Appl. Polym. Sci.* **2002**, *84*, 842.

[24] Kornmann, X.; Thomann, R.; Muhaupt, R. *J. Appl. Polym. Sci.* **2002**, *86*, 2643.

[25] Triantafillidis, C. S.; LeBaron, P. C.; Pinnavaia, T. J. *Chem. Mater.* **2002**, *14*, 4088.

[26] Kong, D.; Park, C. E. *Chem. Mater.* **2003**, *15*, 419.

[27] Becker, O.; Cheng, Y. B.; Varley, R. J.; Simon, G. P. *Macromolecules* **2003**, *36*, 1616.

[28] Park, J. H.; Jana, S. C. *Macromolecules* **2003**, *36*, 2758.

[29] Ma, J.; Yu, Z. Z.; Zhang, Q. X.; Xie, X. L.; Mai, Y. W.; Luck, I. *Chem. Mater.* **2004**, *16*, 757.

10.1021/cm048922e CCC: $27.50

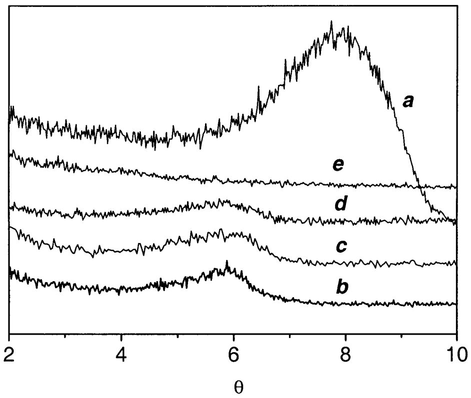


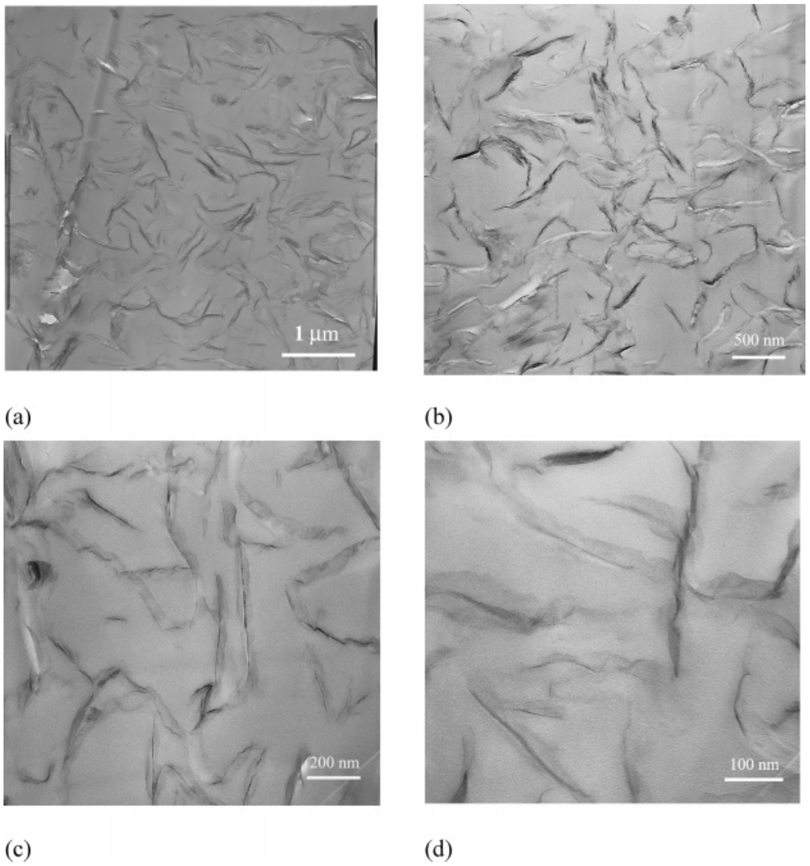
Figure 1. XRD patterns of (a) pristine clayl (b) DMP-clay washed with distilled water; (c) DMP-clay washed with acetone; (d) epoxy/DMP-Clay (5 wt %) without curing; (e) epoxy/DMP-clay (5 wt %) nanocomposite cured by MeTHPA.

in the filtration by one drop of 0.1 N $AgNO_3$ solution. The modified clay (DMP-clay) was filtered to remove water and washed with hot acetone 3× to replace the residual water in the DMP-clay. The acetone−DMP-clay slurry was added into epoxy resin (EPON 828, Shell Co.), with stirring at 75 °C for 2 h. Most of the acetone was evaporated during the mixing. A stoichiometric amount of curing agent, methyltetrahydrophthalic anhydride (MeTHPA) from Puyang Huicheng Chemicals Co., China, was added. The mixture of epoxy/DMP-clay/MeTHPA was outgassed in a vacuum oven at 60 °C,; cured at 100 °C for 2 h, and post-cured at 160 °C for 3 h.

Microstructures of the epoxy/DMP-clay composite were characterized by XRD and TEM. XRD results in Figure 1 show that the pristine clay (curve *a*) has a peak at about $2\theta = 8$ while the water-washed DMP-clay (curve *b*) presents a weak, broad peak at about $2\theta = 5.8$, indicating that the clay galleries were expanded after DMP-30 modification. The acetone-treated DMP-clay shows a slightly broader peak on curve *c* at the same location as on curve *b*. After mixing with epoxy resin, the peak of the epoxy/acetone/DMP-clay mixture became much broader and weaker (curve *d*), suggesting that the clay galleries were further expanded by epoxy penetration and the order of the clay platelets was partially violated. After adding curing agent and finishing the curing reaction, the peak disappeared completely (curve *e*), meaning that the clay in the epoxy/DMP-clay nanocomposite was highly exfoliated.

TEM micrographs of the epoxy/DMP-clay nanocomposite are presented in Figure 2a−d. It is clear at lower magnification (Figure 2a) that the exfoliated clay platelets are distributed in the matrix homogeneously and randomly. The size of the clay layers is ~3 nm thick and ~300−500 nm long (Figure 2b). At higher magnification (Figure 2c), it is revealed that some of the clay domains actually consist of 3−5 layers, indicating that the clay exfoliation did not reach the single-layer-exfoliation condition. This is probably because the charge of the pristine clay layer is not locally constant but varies from layer to layer.[30] Moreover, some of the fully exfoliated clay platelets seem to be folded or curled up, as can be seen in Figure 2d.

The exfoliation mechanisms are proposed as follows. The water in the DMP-clay galleries is replaced by acetone in the acetone washing process. Therefore, the clay galleries are full of acetone when the acetone−clay



(a) (b) (c) (d)

Figure 2. TEM micrographs of epoxy/DMP-clay (5 wt %) nanocomposite cured by MeTHPA at various magnifications.

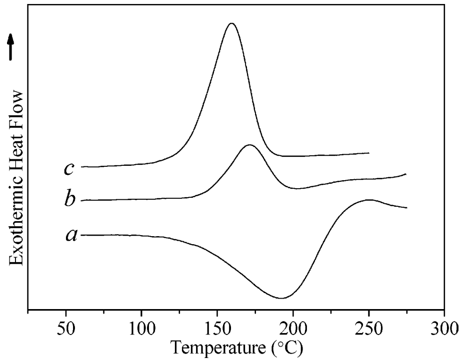


Figure 3. DSC curves of various epoxy−MeTHPA mixtures: (a) only epoxy and MeTHPA, (b) with 1 wt % DMP-30 added ,and (c) with 5 wt % DMP-clay added.

slurry is being mixed with epoxy. Since acetone is a good solvent for epoxy, the epoxy monomers can easily penetrate into the clay galleries, which had been expanded by water and preoccupied by acetone molecules. When the acetone is removed by heating, epoxy monomers remain inside the galleries. After curing agent is added, epoxy curing will take place both inside and outside the clay galleries. Since the clay is modified by DMP-30 which can accelerate the curing reaction (supporting evidences are given in the text below), the curing rate inside the galleries would be higher than that outside. As a result of the difference in reaction kinetics inside and outside, the monomers outside will be pulled into the galleries as the curing reaction is taking place, resulting in a further expanded *d*-space. The clay exfoliation mechanism discussed above is in agreement with that proposed in ref 4.

The accelerating function of DMP-clay to epoxy curing was supported by our DSC study. The DSC results in Figure 3 suggest that without DMP-30, a curing reaction between epoxy and MeTHPA did not take place. No curing reaction peak, but only an endothermic peak due to the MeTHPA evaporation, is found on curve *a*. After adding 1 wt % DMP-30 into the epoxy-MeTHPA system, curing reaction took place readily with the peak curing temperature at about 171 °C (curve *b*). Similarly, the curing reaction occurred in the presence of 5 wt % DMP-clay and the peak curing temperature was at 160 °C (curve *c*). Obviously, the DMP-clay has the same function to promote the epoxy-MeTHPA curing reaction as DMP-30. Since the DMP-30 resides mostly inside the clay galleries, the intra-gallery curing would be faster than the extra-gallery one. The monomer concentration gradient, caused by the reaction rate difference inside and outside the clay gallery, pulls the monomer into the clay galleries, leading to further exfoliation of the clay.

A new method for epoxy/clay nanocomposite preparation is developed. It has two characteristics, i.e., to modify pristine clay with an epoxy curing accelerator and to use acetone-treated organoclay, instead of dried organoclay, in compounding. It is proposed that acetone replaces the water in the clay galleries and facilitates epoxy penetration into the gallery space. It is confirmed that the clay modifier DMP-30 acts as a compatibilizer as well as a catalyst for epoxy curing. Its catalytic function accelerates epoxy curing inside the clay galleries, and hence, encourages further exfoliation of the clay. A highly exfoliated and disordered epoxy/clay nanocomposite was successfully made via the new method.

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(30) Alexandre, M.; Dubois, P. *Mater. Sci. Eng.* **2000**, *28*, 1.