Layered-Clay-Skeleton Initiated Epoxy Polymerization and Formation of Unique Silicate/Polymer Hybrid Assemblies

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INTRODUCTION

The fabrication of nanomaterials, including nano-wires, -rods, -belts, -balls and -tubes have been widely reported, but still remains a challenging task. It is also well-known that the presence of inorganic silicates in organic polymers may reinforce the composite's properties. Among many inorganic fillers, layered silicate clays such as montmorillonite (MMT) and fluorinated mica (Mica) have been intensively studied in preparing nanocomposites. The naturally occurring layered silicates are conventionally applied in catalysts, and metal chelating agents. For utilizing these silicate clays, generally,organic onium salts have been incorporated into the layered structure, including ammonium, pyridinium, and phosphonium salts. Furthermore, the inorganic clay salts may be used as catalysts, such as zeolite, Mangesium/aluminum synthetic anionic clay, and modified MMT clay.[1] Again, the naturally occurring clays are of hydrophilic character and require a modification by intercalating with amino acids, alkylammonium or phosphonium salts to become organically compatible. The modified clays are actually organically encapsulated with a widened interlayer spacing up to 30 Å.

Previously, we have reported the use of high-molecular-weight (2000–4000 g/mol) polyoxyalkylene-backboned quaternary ammonium salts as intercalating agents for enlarging the clay interlayer space as wide as 58–92 Å.[2,3] The sufficient interlayer widening is the key for homogeneously dispersing silicate platelets. More recently, we have focused on the manipulation of inorganic smectite clays through self-organization processes[4,5] from their nanoscale primary units. Among the different degree of poly(oxypropylene)amine intercalations, the modified clays with a specific range of 16–67 wt % organic encapsulation demonstrate a self-aligning property to form a rod-like array. In this report, we study the one-component composites by using Mica/POP-D2000 as the inorganic catalysts for the spontaneous epoxy self-polymerization and their self-assembled morphologies of these clays. We observed the formation of unique arrays, from the clay with poly(oxyalkylene)amines intercalated / exfoliated during the epoxy self-curing polymerization. The self-assemblages are worm-like or coliseum-shape, derived from the layered silicate skeleton of large-platelet Mica.

EXPERIMENTAL

The POP-amines (polyoxyalkylene-backboned) of 2000 M_w (abbreviated as POP-D2000,) and diglycidyl ether of bisphenol-A (DGEBA, trade name BE-188) were used. The procedures are described as an example.[2–5] The hybrid of 3 wt % clay content epoxy (weight ratios of Mica/POP-D2000/epoxy = 3.0/5.6/91.4), was complete swelled. The well suspended organoclays (8.6 g, inorganic/organic = 35/65 based on TGA) within epoxy (91.4 g), and vigorously stirred by using a mechanical stirrer for an additional 1 h, and then thermal curing in an oven at an elevated temperature of 80 °C, 120 °C, 150 °C, and 180 °C each for 1 h. A 3 wt % clay content one component epoxy composite was obtained as a resultant powder.

The delamination of the clay is confirmed by X-ray diffraction (XRD) measurement, was recorded on a Schimadzu SD-D1 diffractometer with Cu target (k = 1.54 Å) at 35kV, 30mA). The basal spacing (n = 1) was assigned from the apparent peak or calculated according to Bragg's equation ($n\lambda = 2d\sin\theta$) through the observed peaks of n = 2, 3, etc. The organic fractions were estimated by using a thermal gravimetric analyzer (TGA, Perkin Elmer Pyris 1), with a temperature gradient that ramped from room temperature to 800 °C at a rate of 10 °C /min. The isolation of random silicate platelet was characterized by using a Transmission electronic microscopy (TEM) was performed on a Zeiss EM 902A and operated at 80 kV. A scanning electronic microscope (SEM), operated at 15 kV, was used to examine the morphology of the powder formation.

RESULTS and DISCUSSION

For the Mica/POP-D2000, the resultant clay exhibited X-ray *d* spacing of 5.2 nm (Figure 1B) from 1.2 nm for the pristine Mica (Figure 1A). In contrast to the 3 wt % Mica/POP-D2000 in epoxies, the X-ray *d* spacing is evidenced about 5.6 nm (Figure 1C) and only slightly different from the ordinary Mica/POP-D2000, indicated some epoxies are diffusely enlarging the clay interlayer by a vigorously stirring and heating, but the primary stacking platelets unit is still remain. Furthermore, after at an elevated temperature of 80 °C, 120 °C, 150 °C, and 180 °C each for 1 h, the 3 wt % Mica/POP-D2000 in epoxies become to powder from a liquid slurry via a violently exploded phenomenon and the X-ray pattern is evidenced featureless (Figure 1D). The results implied the primary stacking platelets unit may be destroyed or exfoliated to a huge *d* spacing over the XRD detecting limit, the detail picture of silicate platelet dispersion can be further revealed by using the analysis of TEM.

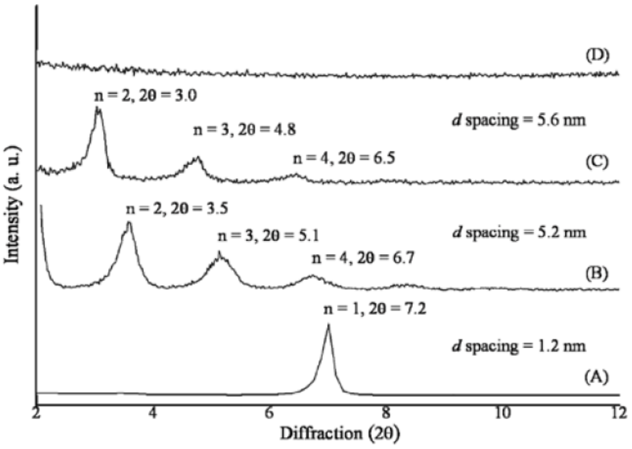

Figure 1. X-ray diffraction patterns of (A) pristine Mica (B) Mica/POP-D2000 (C) 3 wt % Mica/POP-D2000 in epoxies (D) 3 wt % Mica/POP-D2000 curing epoxies powder.

The side view of TEM images with a diameter of 80–100 nm and the primary unit (8–10 stacking platelets) of the MMT platelets are randomly destroyed as exhibited in Figure 2A and 2B. We clearly estimated the enlarged layers with a huge *d* spacing of 36–96 nm are exfoliated from the ordinary MMT/POP-D2000 (5.8 nm) in epoxies. In comparison, Figure 2C and 3D are clearly proved a various sizes of diameter of 0.1–1 μm, and the isolation Mica platelets are also exfoliated with a huge *d* spacing. Particularly, the appearance of a radial conformation in the same location and asymmetric *d* spacing of 0.12–0.61 μm are enlarged from the ordinary Mica/POP-2000 (5.2 nm) as exhibited in Figure 2D. The completed explanation is attributed to high aspect ratio and large surface area of the Mica silicates, relatively compared with two different silicates, the MMT silicates have a wide-defined structure of approximately 80–100 nm wide, 1 nm thick for each layer and average 8–10 stacking platelets as a primary unit, on the other hand, the Mica silicates are 100–1000 nm wide, 1 nm thick and average 4–6 stacking platelets as a primary unit. In the epoxy-surrounded matrix, a competitive reaction of inter- and extra- layers is occurred while at a heating, due to Mica has a greater diameter and is harder to enlarge layers than MMT, the layered structure promote a strong interaction and the interlayer space is filled with the organic polymers between the neighboring platelets maintains the stacking primary structure and hence a frequently observed in the shape of radial conformation, as shown as dotted line in Figure 2C and 2D. Consequently, by the direct observation of the TEM images reveals unambiguous evidence for the MMT platelets are random distribution

(Figure 2A and 2B) and the maximal interlayer expansion can be possibly achieved has not been reported in the literatures.

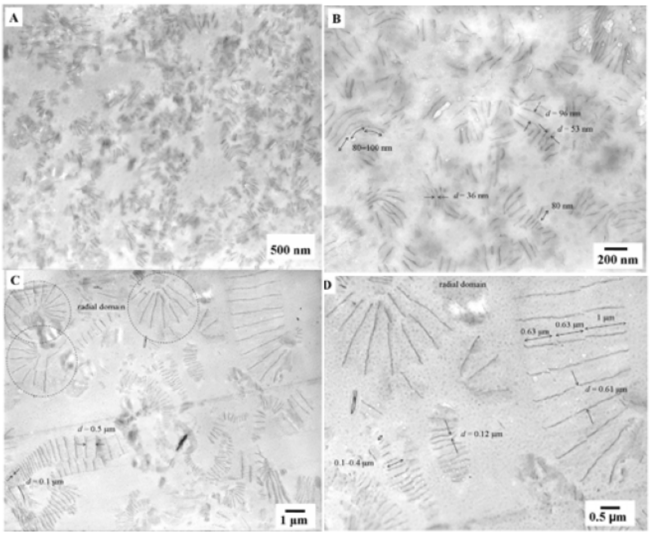

Figure 2. (A) TEM images of (A and B) 3 wt % MMT/POP-D2000 curing epoxies powder and (C and D) 3 wt % Mica/POP-D2000 curing epoxies powder.

For the pristine Mica SEM images (Figure 3A), the Mica platelets are revealed in a various sizes of diameter correlate well with the TEM images in Figure 2C, some of them are over 1 *μ*m because the pristine Mica is a huge amount of stacking platelets units through the platelet face-to-face direction and edge-to-edge aggregation. Surprisingly, the novel formation of worm-like arrays is appeared for 3 wt % Mica/POP-D2000 in epoxies powder (Figure 3B–3D). These observations disclose the importance of Mica has a large layer dimension and high aspect ratio, resulting in easily self-aligned a high degree of regular morphologies, such as gyroidal formations (as doted line in Figure 3B) or worm-like arrays (Figure 3C) or a Colosseum (Figure 3D). In contrast to the MMT/epoxy hybrids with a relatively simple processing, is revealed a common morphology (Figure 3E and 3F), only in the present of uniform arrays about 100–400 nm diameter but most of them are amorphous. The reasonable explanation is corresponding to the TEM images (Figure 2A and 2B), the primary units of the MMT platelets are randomly destroyed and a small layer dimension results in a random layered aggregation without gyroidal formations through the epoxies polymerization rearrangement.

The striking similarity of the silicate clay skeletons covered with epoxies can be seen by comparing the TEM and SEM images at different wt % Mica loadings as shown in Figure 4, the self-assembly appears to be a facile process and most of the surface is covered with epoxies in a huge *d* spacing and high regular arrangement. The use of different wt % of Mica loadings as the self-assembled materials are shown to have a similar skeleton to the precursor clay units as appeared, indicating the Mica stacking platelet units performed the most important role for the fundamental building block and particularly, with a 3 wt % Mica loading (Figure 4A and 4B) had formed the self-assembled microstructure with a larger dimension, in summary, the regular arrays disappear as the Mica loadings increased.

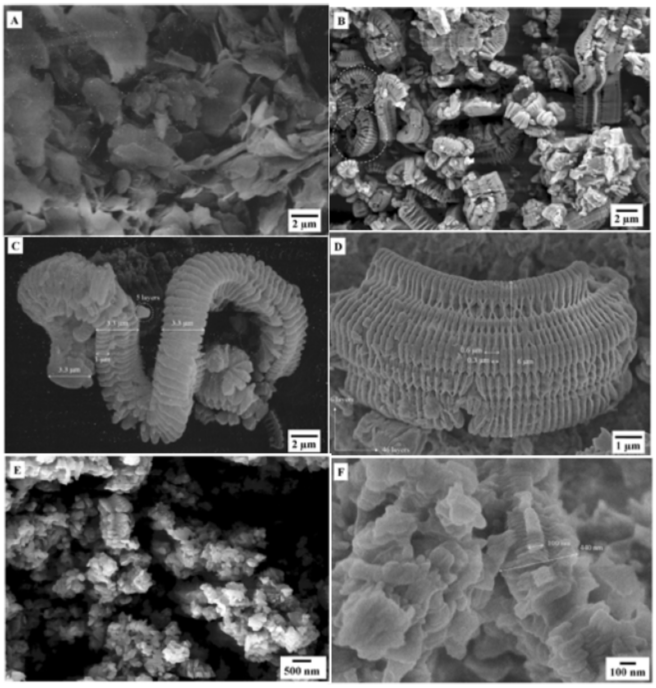

Figure 3. SEM images of (A) pristine Mica (B, C, and D) 3 wt % Mica/POP-D2000 curing epoxies powder (E and F) 3 wt % MMT/POP-D2000 curing epoxies powder.

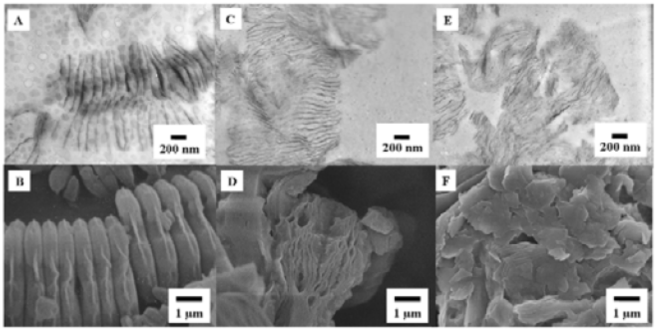

Figure 4. Relatively compare TEM with SEM images of (A with B) 3 wt % (C with D) 5 wt % (E with F) 10 wt % Mica/POP-D2000 in epoxies powder.

CONCLUSIONS

It is found that organoclays from a space-enlarged clay with an approximate 52–58 Å *d* spacing can be the catalysts for the epoxy self-cured polymerization. Furthermore, the organoclays could undergo the self-assembling process to grow into a series of three dimensional multi-storey arrays, especially at 3 wt % of Mica/POP-D2000 in epoxies. The observation of worm-like arrays with unique dimensional characteristics brings up several interesting aspects and such alignment is particularly important for applications.

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