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Simultaneous Occurrence of Self-Assembling Silicate Skeletons to Wormlike Microarrays and Epoxy Ring-Opening Polymerization

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The occurrence of self-assembled structures in nano- to micrometer scale is ubiquitous in nature including deoxyribonucleic acid (DNA) double-helix[1−3] and unique structures of seashells,[4,5] bones,[6,7] and nacres.[8] The existence of naturally occurring nanostructures is inspiring for scientists in different disciplinary areas. Recent efforts have been emphasized on "bottom-up" synthesis of new self-assemblages, applications, and scientific understanding of their formation mechanism. Examples include inorganic nanoparticles such as quantum dots for optoelectronic devices[9] and silver particles in various shapes.[10,11] In addition, organic polymers such as di- and triblock copolymers were well-known for their phase separation into domains of structurally well-defined shapes. Self-assembly mechanisms and controlling geometric shapes is often the main theme of the syntheses and is generally a thermodynamically driven process involving noncovalent bonding forces—electrostatic charge attraction,[12] hydrogen bonding,[13] van der Waals forces,[14,15] and hydrophobic effect.[16,17]

The self-assembling phenomenon may occur for the inorganic ionic platelets of clay. These natural clays have a generic aluminosilicate structure of multiple layers in stacks and 2:1 tetrahedron-to-octahedron ratio sandwiched structure for each layer. The clay stacks had a strong tendency to swell in water and form a colloidal dispersion.[18−20] At low concentrations, the swelling clays are in a state of exfoliation and exhibit liquid crystal behaviors due to their self-alignment. When dispersed in polymer matrices, the silicate platelets may improve material properties such as enhancing thermal stability,[21−23] hardness,[21] lowering coefficient of thermal expansion,[21−24] and barring gas permeation.[23] For these applications, the inherently hydrophilic clays are modified to be hydrophobic and compatible with organic polymers. The organic modification is generally achieved by ionic exchange reaction with fatty quaternary ammonium salts or other surfactants. Recently, we have reported a method to manipulate the clay-layered structures by using a family of poly(oxyalkylene)diamine salts (POP-amine) of M_w 230−4000 g/mol.[25−30] For example, the intercalation of the POP salts into sodium montmorillonite (MMT) and mica could modify their hydrophobicity. In addition, the organic exchange with the counterions in the clay gallery could also expand the clays' interlayer spacing in the range of 5.8−9.2 nm by XRD analysis. By modifying both the organic embedment and platelet spacing, we can control the hydrophobicity and tailor its amphiphilic nature. It was reported that such an organoclay enables self-assembly into orderly structures such as rodlike arrays of 100−800 nm diameter and 2−40 μm in length.[29,30] The self-assembly was controllable by selecting the amphiphilic POP/clay hybrids under water-evaporating conditions. The process is mainly a thermodynamically driven process of unit aggregation through noncovalent bonding interaction.

The modified clays are easily dispersed in hydrophobic epoxy resins and demonstrate the successful synthesis of nanocomposites when cured with a second component of amine curing agents.[21−24] In our recent studies on the compatibility of organoclays with epoxy resin, it was found that the intercalated amine−salt in clay may very well initiate a rapid epoxy polymerization.[31] However, a low molecular weight and brittle powder material was often produced. In the literature, there are limited reports on one-component epoxy curing for making clay nanocomposites.[32−35] The Pinnavaia group demonstrated the utilization of acidic derivatives of the naturally occurring silicate clays as the inorganic catalysts for spontaneous epoxy polymerization. Since the epoxy resin is highly hydrophobic, fine dispersions of organoclay in such a polymer may be difficult. However, the problem of forming clay aggregates in the epoxy material was interesting to us. By utilizing different aspects of clays, particularly the large size of mica as the initiator, the DGEBA epoxy self-polymerization is studied. It appeared that the layered silicate structure can initiate epoxy monomer propagation but, at the same time, generate the noncompatible aggregates.

Experimentally, the requisite organoclays were prepared by the ionic exchange reaction of poly(oxypropylene)amine HCl salt of M_w 2000 g/mol (POP2000) with the mica clay and analyzed by XRD, as described elsewhere. The maximum exchange[27] (cationic exchange capacity = 85 mequiv/100 g) and organic incorporation allowed the preparation of organo-mica with a d spacing of 5.2 nm (Figure 1b), expanded from the original 1.2 nm (Figure 1a). The basal spacing ($n = 1$) was assigned from the apparent peaks or calculated according to Bragg's equation ($n\lambda = 2d \sin \theta$) through the observed peaks of $n = 1, 2, 3$, etc. Widening the interlayer spacing also incorporated the organic species at 65 wt %, making it highly compatible with the epoxy. The resultant hybrid is actually highly dispersible in both water and toluene. When mixing the organo-mica in the epoxy (i.e., 3−10 wt % mica-POP2000 in DGEBA) at room temperature, the silicate was slightly expanded to 5.6 nm (Figure 1c), indicating the accessibility of the clay gallery for the incoming epoxy monomer. At the heating to 180 °C, the reaction occurred dramatically and transformed the liquid monomers into powder materials. Apparently, the POP-amine-salt in the mica gallery initiated the epoxy ring-opening polymerization in an exceedingly fast rate at the elevated temperature. The sudden formation of the powder materials from liquid form of epoxy monomers within 1 min period of time was recorded on a movie (provided in the Supporting Information Figure S1 and Movie MS1). The powder was analyzed by XRD and showed no Bragg's peak (Figure 1d), implying a large basal spacing beyond the detection limit (> 10 nm) or a randomization of the layered structure. In the case of 3 wt % of the organo-mica (or mica/POP2000/epoxy at 3.0/5.6/91.4 as the actual composition for each component), the reaction afforded a cured material of brittle and loose powder, as shown in Figure 2. For comparison, with the addition of organo-mica, the two-component DGEBA and Jeffamine-T403 amine agent produced a transparent and hard material with a hardness of 5 H, increased from the pristine 2 H without clay.[36,37]

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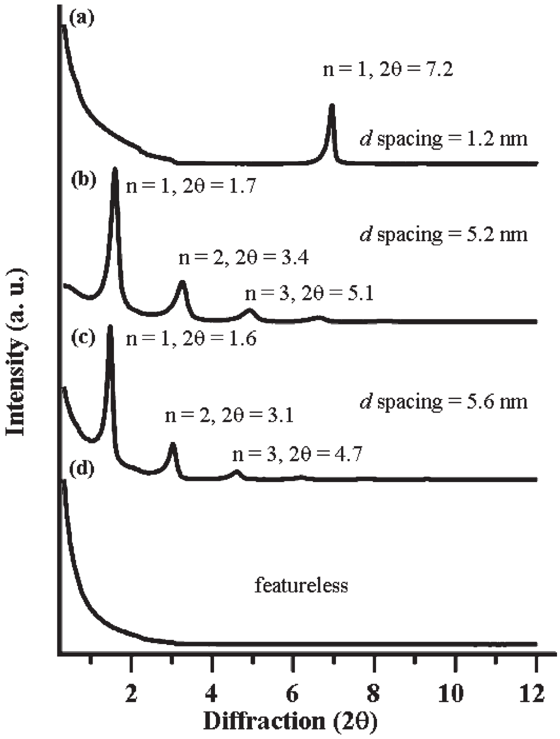

Figure 1. X-ray diffraction patterns of (a) pristine mica, (b) mica-POP2000, (c) 3 wt % mica-POP2000 in epoxy hybrid before the intensive heating, and (d) 3 wt % mica-POP2000 cured epoxy powder material after 180 °C.

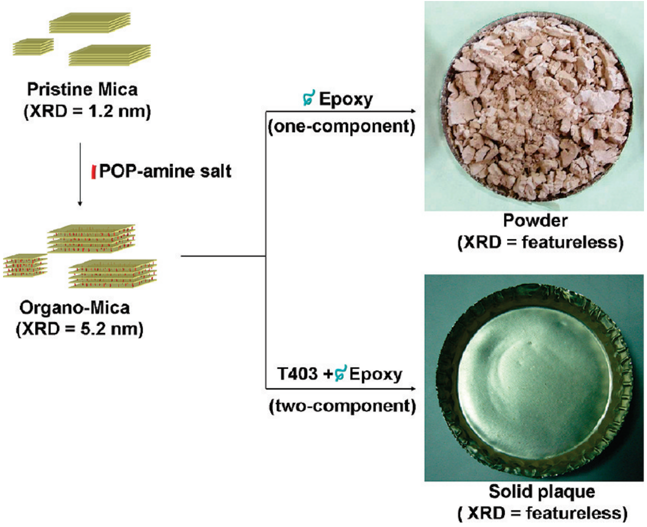

Figure 2. Conceptual illustration for the epoxy curing in the presence of 3 wt % organo-mica: (a) loose powder material (under one-component DGEBA curing) and (b) transparent and hard solid with smooth surface (under two-component curing with DGEBA and Jeffamine T403).

A detailed analysis of the powder was examined by using a TEM, which observed the side view of silicate platelets. As shown in Figure 3, the cluster formation of these platelets was ca. 8–60 layers in one cluster. The spacing between two neighboring platelets is quite large, such as 100, 120, 610, or mostly 500 nm (Figure 3a,b). The spacing between the neighboring platelets over 100 nm is far beyond the XRD detection limit (~10 nm). In these TEM micrograms, the existence of platelet clusters in a radial or fanlike arrangement, as shown the dotted circles were observed (Figure 3b). The interlayer spacing (120–610 nm) is much larger than that of the mica-POP2000 organoclay (5.2 nm). Moreover, the formation of parallel or fanlike shape for the platelet units rather than a simple randomization implies a new mechanism for the platelet expansion. Presumably, during the clay surface initiated epoxy ring-opening polymerization, the epoxy monomers in the surrounding may compete differently for the amine–salt reactive sites. Opening up the layered structure and expanding the platelet spacing could occur simultaneously but unevenly and cause the formation of fanlike shapes for the platelet stacks (Figure 3a,b). A random distribution of the platelets or an exceptionally large interlayer expansion was found in some areas. Widely spaced, but still parallel, formation is informative in determining the formation mechanism. Furthermore, a greater than 60 layer parallel formation with a considerable regularity was seen in the micrographs (Figure 3c,d). The individual mica units are comprised of only 4–6 platelets (in the Supporting Information Figure S2), the high number of platelets in the array must be derived from a self-assembly of the clay primary units into secondary structures. The occurrence in TEM micrograms was only observed only for the mica clay (100–1000 nm in dimension). For comparison, the analogous MMT with the dimension of 80–100 nm was intercalated by POP2000-amine salt and cured with DGEBA epoxy but showed none of the radial or fanlike morphology. Similarly, the two-component curing (epoxy and amine curing agent) in the presence of the same organoclay was only generating well-distributed and randomized platelets in the polymer matrix. The self-organized mica platelet formation is unique for the epoxy ring-opening polymerization.

The surface morphology was then examined by using SEM and shown in Figure 4. The microstructures of three-dimensional multilayered morphologies such as foreign worms (Figure 4b,c) and semicoliseum (Figure 4d,e) were observed, in some areas, at 8–10 μm in length (estimated ca. 46 layers of platelets) and 5–6 μm in height. It is noted that these arrays may contain fundamental units of 1000 nm in length (Figure 4c,d), similar to the average dimension of the pristine mica.[27] These formations are attributed to the piling of the primary mica stacks through platelet vertical "face-to-face" direction and horizontal "edge-to-edge" alignment. In some formations, the piling was not straight but rather twisted into curvatures (Figure 4f), seen as artifacts.

The mechanism of forming these self-organized microstructures is proposed. First of all, the amount of the organo-mica in the epoxy in the range of 3–10 wt % silicates was the optimal content for the epoxy ring-opening polymerization to form the clay–polymer heterogeneous powder. Through the polymer end cross-linking, the tethered silicate units were aligned into multiple unit piling into the observed morphologies. The piling of the primary clay units under the pulling forces of epoxy monomer propagation occurred at the elevated temperature of 180 °C. It was observed the transformation of liquid epoxy into powder in a rapid and exothermic manner. At lower temperatures (80–150 °C), the epoxy monomers could only diffuse into the interlayer and form a sticky liquid. Presumably, the formation of a curved structure was spontaneously accompanied by the appearance of powder material. Several examples of detail structures showing straight and bent formations are illustrated in Figure 5 to support the viewpoint of epoxy polymer cross-linking in assisting the clay unit self-organization. Furthermore, the existence of fanlike units and their contribution to the piling through vertical, horizontal, and bending directions can be correlated to the inserted TEM and SEM micrographs. For the formation of bending arrays, the smaller clay units appear to serve as the bending and unit interconnecting sites, as indicated in Figure 5b.

In summary, we report the formation of self-organized silicate skeleton morphologies in the epoxy matrix. The POP-intercalated mica enabled the initiation of the epoxy ring-opening and in

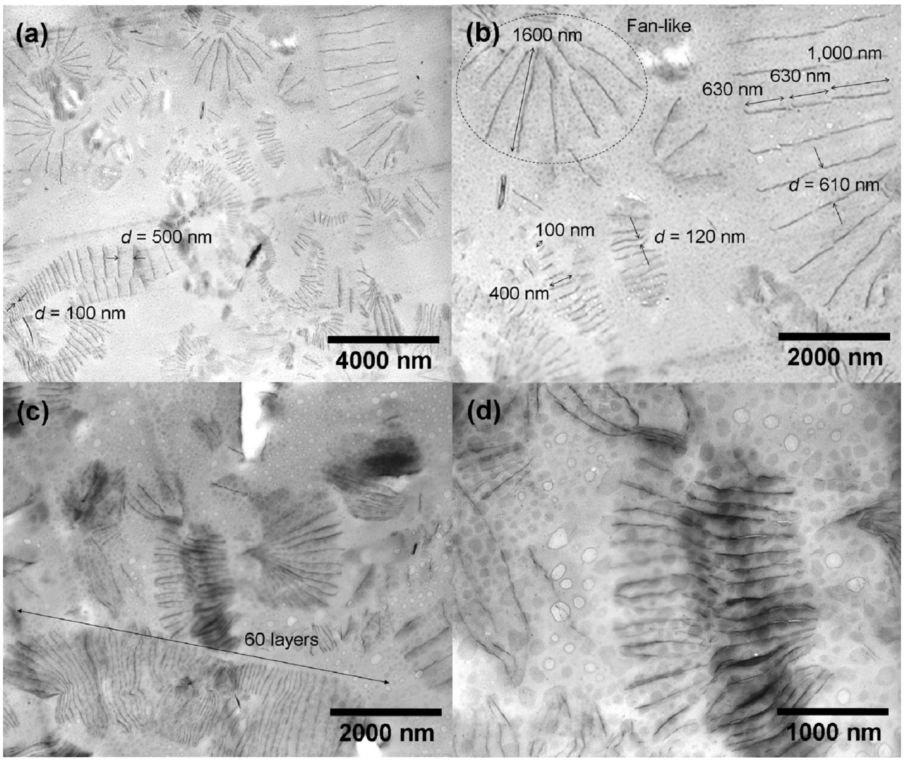

Figure 3. TEM images of 3 wt % mica-POP2000 cured epoxy powder material.

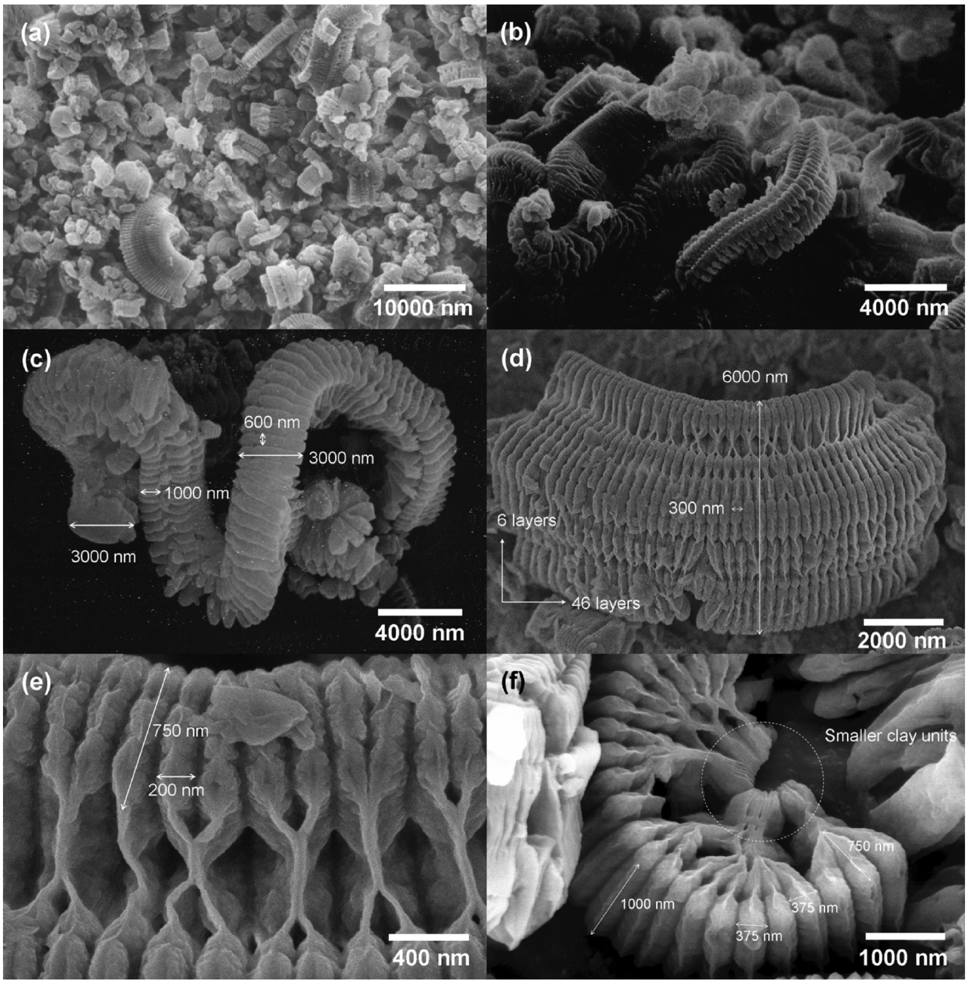

Figure 4. SEM images of 3 wt % mica-POP2000 cured epoxy powder material.

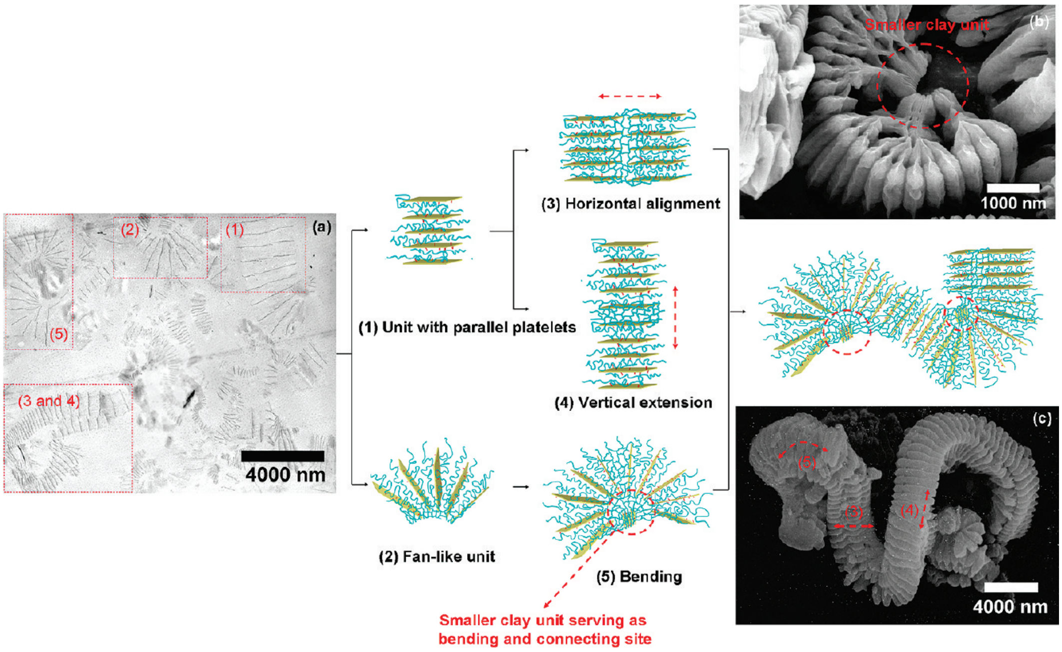

Figure 5. Schematic illustration of the self-assembling mechanism through two types of clay units (1) parallel platelets and (2) fanlike and units alignment via (3) horizontal, (4) vertical, and (5) bending direction, corresponding to TEM micrograph (a) and SEM morphologies (b, c).

situ produce multilayered microstructures with a parallel platelet distance of over 100 nm. TEM micrographs further revealed the mica clay unit (originally 4−6 platelets in average) underwent a self-piling into fanlike or radial-shape arrays and self-assembling to 60 layers. Surface examination by SEM exhibited a number of foreign multilayered arrays. The formation mechanism is attributed to the covalent bonding force during the epoxy ring-opening polymerization and subsequent chain cross-linking. The chain growth of epoxy propagation simultaneously expanded the layered structures and forced them to self-pile into lengthy arrays. The epoxy self-polymerization occurred rapidly at 180 °C like a mini-scaled version of a "volcano explosion", witnessed by the naked eye. The instant formation of such silicate skeleton arrays during the dynamic epoxy self-polymerization is unprecedented.

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Supporting Information Available: Experimental details; a movie of "volcano explosion" and powder formation; SEM images of pristine mica; SEM and the corresponding TEM images of organo-mica cured epoxy powder materials; SEM images of self-assembling silicate skeletons. This material is available free of charge via the Internet at http://pubs.acs.org.

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