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A Novel Method for Preparation of Disorderly Exfoliated Epoxy/Clay Nanocomposite

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Epoxy/clay nanocomposites were studied extensively on the intercalation and exfoliation of the clay structures.[1−25] However, merely intercalated or orderly exfoliated structures were obtained on epoxy/clay nanocomposites to date. Despite disordered exfoliation has been reported for several polymer matrixes, such as polyimide,[26] polyaniline,[27] and nylon,[28] it seems still impossible to make clay layers exfoliated disorderly in epoxy resin at present. Recent trend is to explore reactive group-contained ammonium surfactants to modify clay, by which the interaction among the monomer, the surfactant, and the clay surface is tailored and hence the exfoliated structure is obtained. The active groups might include styryl group for PS,[29] vinyl group for PMMA,[30] benzidine for PU,[31] and others. For example, Tyan and Wei prepared orderly exfoliated polyimide/clay nanocomposite by solution compounding poly(amic acid) with MMT modified by reactive surfactants, including *p*-phenylenediamine.[32,33] In our work, a commonly used hardener, M-xylylenediamine (MXD),

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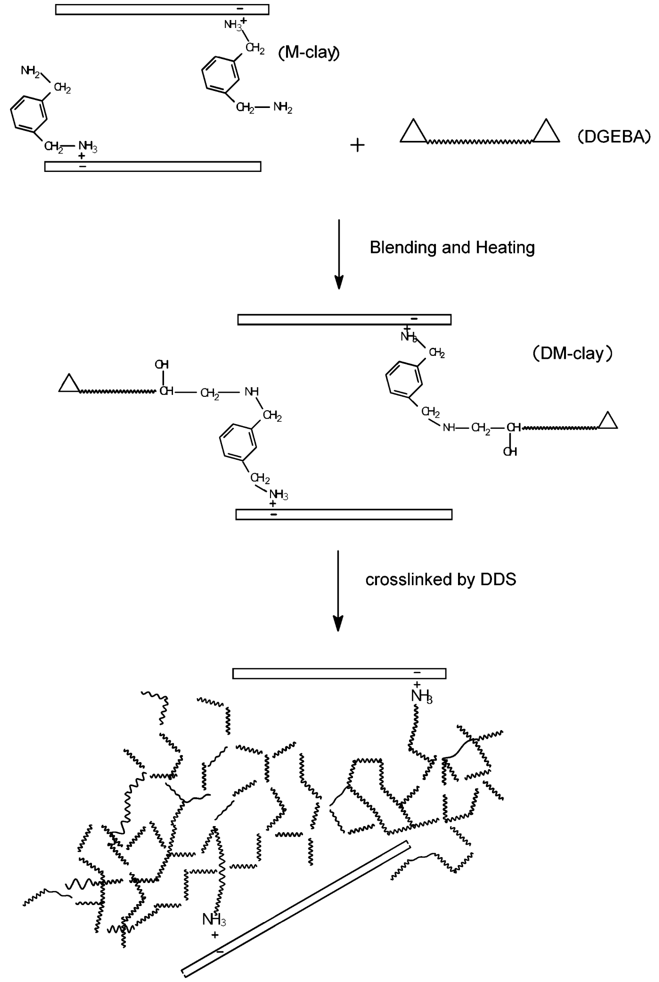

Figure 1. Schematic of reaction mechanisms.

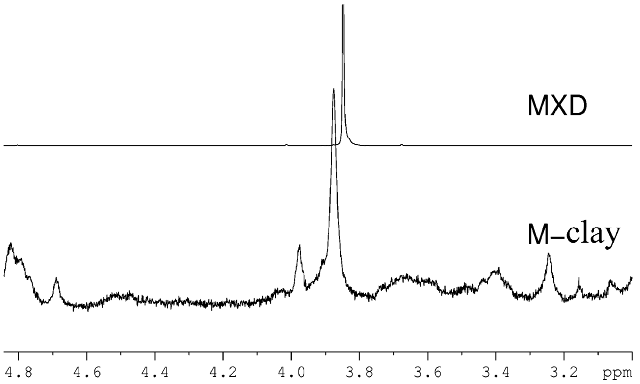

Figure 2. ^{1}H NMR spectra of MXD and M-clay.

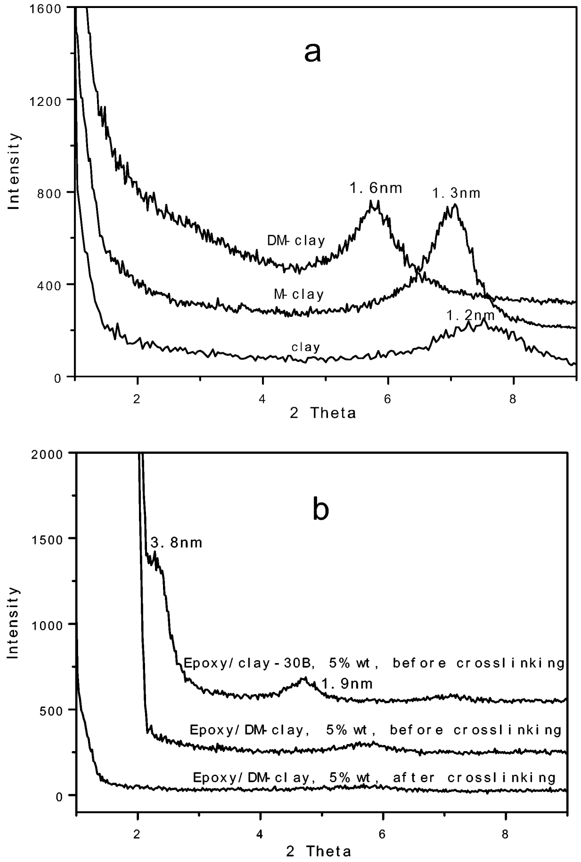

Figure 3. XRD patterns of (a) clay, M-clay, and DM-clay and (b) epoxy/clay-30B and epoxy/DM-clay nanocomposites.

containing two amine groups, was chosen as the surfactant for modification of sodium clay (montmorillonite with a CEC of 120 mequiv/100 g, provided by Southern Clay Products, Inc). After converting one reactive group of the hardener into a cation, Figure 1, this cation (functional group) can form an ionic bond with the negatively charged silicate layers, and then the clay was grafted and intercalated by the hardener. Disorderly exfoliated structure was easily obtained finally because of the large cross-linked epoxy molecules connected to the clay platelet via the hardener grafted on the platelet surface.

The disorderly exfoliated epoxy/clay nanocomposite was prepared following the three steps below: (1) Modification of clay. Ten grams of clay was added to 5 kg of boiling water, mixed, and heated for 10 min. MXD was dissolved in 500 g of water and then a given quantity of hydrochloric acid was added to protonate only one amine function per MXD molecule. The solution was added slowly to the clay suspension and then the blend was vigorously stirred for 15 min at 80−90 °C. After modification, the clay suspension was repeatedly washed with deionized water until no chloride ion was detected by $AgNO_3$. Then, the suspension was condensed to 1000 mL by heating and denoted as "M-clay". (2) Further modification of clay. The desired amount of M-clay suspension was added to 100 g of diglycidyl ether of bisphenol A (DGEBA) and the mixture was vigorously stirred in a 500-mL beaker at 75 °C for 2 min to form an opaque emulsion. The beaker was covered by aluminum foil with a 10-mm-diameter hole in the center. The temperature was raised to vaporize the water and mixing continued until the emulsion became transparent. Then, the mixture was placed in a highly degassed oven at 105 °C to remove the remnant water. The modified clay obtained in this step was called "DM-clay". (3) Epoxy/DM-clay nanocomposites were formed by curing the above blend with stoichiometric 4-aminophenyl sulfone (DDS).

Figure 2 shows ^{1}H NMR spectra of the hardener (MXD) and extracted M-clay. In the free MXD molecule the methylene protons are chemically equivalent and appear as a single resonance at 3.85 ppm. Upon grafting MXD to the clay layer surface via one quaternary ammonium center, the methylene units would no longer

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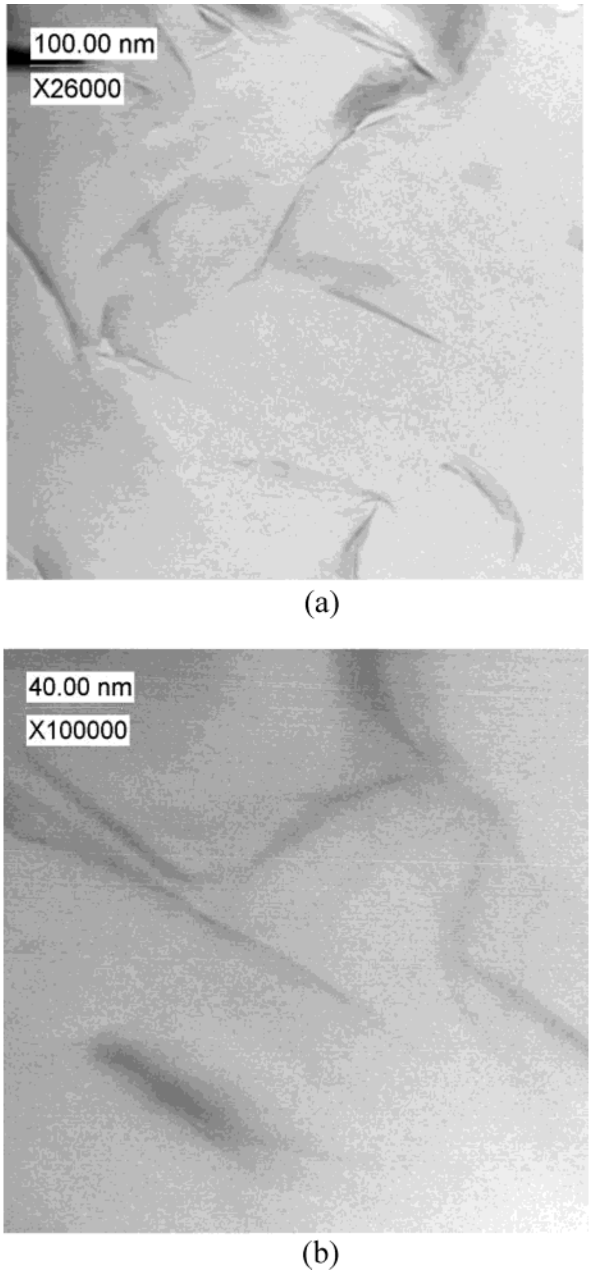

Figure 4. TEM image of epoxy/DM-clay nanocomposite prepared by the novel method, revealing, for the first time, the disorderly exfoliated silicate layer structure in epoxy.

be equivalent, and a downfield shift in resonance would be expected for the methylene moiety adjacent to the grafted ammonium center. The ^{1}H NMR spectrum for M-clay exhibits two distinct resonances at 3.87 and 3.98 ppm, and this implies that the two ammonium groups on the MXD molecule are in different chemical environments, with one ammonium group grafted onto the clay layer surface and the other unchanged. This result confirms the reaction of the DGEBA with the dangling ammonium group. When the clay was further modified with epoxy, abundant epoxy signal in ^{1}HNMR (not shown here) was found because of a large amount of DGEBA grafted to clay via MXD.

In Figure 3a, the XRD pattern of the untreated clay shows a primary silicate (001) reflection at about 7.5°, corresponding to an interlayer space of about 1.2 nm. A single and large peak at around 7.0° was found for M-clay, corresponding to an interlayer space of 1.3 nm. The increase from 1.2 to 1.3 nm is due to the MXD grafted onto the clay layer surface via ion exchange, in agreement with the analyses of NMR. The XRD pattern of DM-clay shows a Bragg reflection peak at 5.7° or so, corresponding to an interlayer separation of approximately 1.6 nm. The increase of the layer space of M-clay from 1.3 to 1.6 nm is caused by the grafting reaction of the DGEBA with the dangling ammonium group of MXD, consistent with the NMR result.

In Figure 3b, the uncured epoxy/DM-clay shows no peak between 2° and 9°, indicating it is fully intercalated (at least 4.4 nm of layer separation) or even possibly exfoliated. Also, the cured nanocomposite shows no peak between 1° and 9°, meaning it is fully intercalated (at least 8.9 nm of layer separation) or even possibly exfoliated. It is reported that clay (e.g., clay-30B) modified by surfactants containing hydroxy groups could be orderly exfoliated in epoxy.[10,12] As a comparison benchmark, we prepared and characterized epoxy/clay-30B (Southern Clay Products, Inc.) nanocomposites before cross-linking according to ref 12. Two peaks were found in Figure 3b. One shoulder peak is at 2.3°, corresponding to a layer space of about 3.8 nm, and the other is at 4.7°, indicating a layer space of 1.9 nm. Both peaks could be assigned to the (001) lattice spacing of clay and their appearance might show the structural or chemical modification discontinuity of clay-30B. However, the uncured epoxy/DM-clay nanocomposite shows no peak, suggesting that epoxy/DM-clay nanocomposite prepared by this novel method is completely different from previously reported epoxy/clay nanocomposites.

Transmission electron microscopy (TEM) is often used to differentiate two classes of relative separation of clay layers in the exfoliated state: disorderly exfoliated structure[26−28] and orderly exfoliated structure.[1,2−13] In Figure 4, the silicate layers were found to be not only exfoliated but also disorderly dispersed at the monolayer level, which is totally different from all previously reported orderly exfoliated structures.[2−6,8−13,24] The platelet thickness in Figure 4b appears to be approximately 3 nm or over while the average length is about 100−200 nm. The thickness deduced from these photomicrographs is somewhat higher than that of a single MMT platelet. This could be caused by tilted platelets that are inclined obliquely to the sectioned plane as shown in our previous work.[34]

The disorderly exfoliated epoxy/clay nanocomposite prepared by this novel method should open up the range of applications of this new material. We are continuing to study the strengthening mechanisms and barrier properties of the nanocomposite.

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