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Modification of Montmorillonite through Intercalative Polymerization

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Abstract: Montmorillonite (MMT) was modified through intercalative polymerization of phenol and formaldehyde catalyzed by oxalic acid. The modified montmorillonite was delaminated at large, as demonstrated by XRD and TEM studies. It can disperse easily in epoxy resin to form exfoliated nanocomposites. The nanoscale silicate platelets dispersed in water can be metallized by silver deposition.

Keywords: Montmorillonite, intercalative polymerization, novolac resin, nanocomposites.

Montmorillonite (MMT) possesses a 2-to-1 layered structure with an octahedral aluminum layer located between two layers of silicon tetrahedral[1]. Each layered sheet is about 1 nm thick with lateral dimensions of 100-1000nm. Recently, MMT was used in the preparation of nanocomposites with polymers[1-4]. In these cases, the platelets were nanoscale reinforcement for the polymer matrix. On the other hand, intercalative polymerization can be utilized to make the layered silicate easy to exfoliate. Here we describe the modification of MMT through intercalative polymerization of phenol and formaldehyde catalyzed by oxalic acid.

The intercalative polymerization was carried out as follows: 94.1 g phenol, 69.0 g formaldehyde (37%) and 5.0 g Na-MMT were mixed in a 500 mL three-necked flask, and stirred mechanically at room temperature for 1 h. The mixture was heated to 80°C. Then, 0.25 g oxalic acid was added; thereby the temperature was immediately raised to 95°C. The reaction was carried on until the complete consumption of formaldehyde.

The upper aqueous layer was discarded. In order to separate the modified MMT, 200 mL acetone was added to dissolve the novolac resin. After stirring for 20 min, the solution was set aside for one day. The upper clear solution was removed, and another 50 mL acetone was added to extract the precipitate. The solid was filtered, washed with acetone repeatedly, and finally dried at 50°C to yield 4.2 g modified MMT.

The modified MMT did not show any crystallographic order of clay layers. In the X-ray diffraction pattern for the pristine Na-MMT, the 2θ value for the 001 reflection of Na-MMT was 7.0^{o} (trace *a* in **Figure 1**), which corresponded to a basal space of 1.25 nm

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according to the Bragg equation. For the modified clay prepared in the above way, however, the 001 reflection vanished (trace *b* in **Figure 1**). That is to say, the order of clay layers disappeared.

It was indicated by FT-IR analysis that in the modified MMT, some kind of organic substance was firmly adsorbed by MMT, which could not be washed away by acetone. In the IR spectrum for the modified MMT (**Figure 2**), the band at 1507 cm^{-1} was characteristic of novolac resin. In addition to the bands for Si-O-Si at 1038cm^{-1} (stretching) and 466 cm^{-1} (bending)[5], a strong absorption at 1695 cm^{-1} was found. This band did not appear in the spectrum for novolac resin. It is likely that novolac resin on the clay surface was severely oxidized to form quinoid structure.

Figure 1 XRD patterns of (a) pristine Na-MMT and (b) modified MMT.

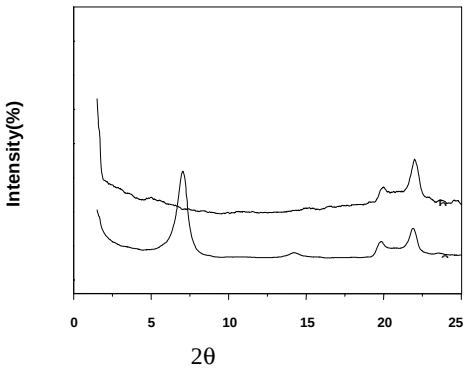
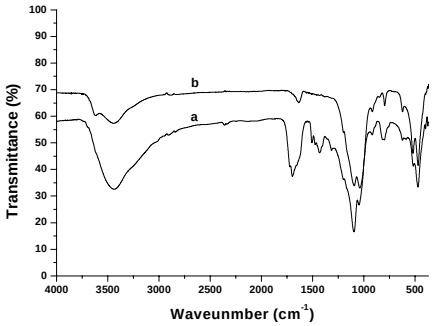


Figure 2 FT-IR spectra of (a) modified montmorillonite and (b) pristine sodium montmorillonite.



The modified clay powder was blended with epoxy resin (Epon812-dodecyl succinic anhydride-DMP-30) and cured at 30°C, 45°C and 60°C for each 12 h. Ultra thin sections were microtomed for TEM studies. It is shown in the TEM image that the modified clay was exfoliated in the epoxy matrix (**Figure 3**).

Figure 3 TEM micrograph of ultra thin section of modified MMT dispersed in the epoxy matrix.

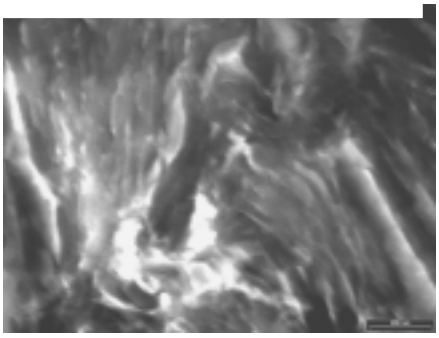
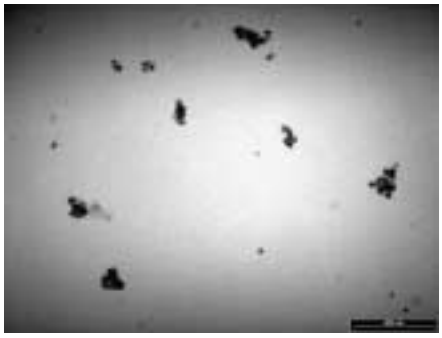


Figure 4 TEM image of MMT platelets deposited with silver nano-particles.



The clay modified through intercalative polymerization was very easy to delaminate in water or other polar organic liquids. For example, 50 mg modified MMT was dispersed in 100 mL water with the aid of ultrasonic irradiation. In a glass test tube containing 5 mL MMT dispersion, two drops of formaldehyde (wt-36%) was introduced. Then 0.5 mL of the silver-amine solution was added. The homogeneous mixture turned to light brown after staying at room temperature for 3 h. A drop of the above solution was dried on a carbon-covered copper grid for TEM studies. It is seen in the micrograph that the silicate platelets are separated from each other, and most of the silver particles are deposited on the surface of the MMT platelets (**Figure 4**).

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