

# Preparation of Polystyrene/Toluene-2,4-di-isocyanate-Modified Montmorillonite Hybrid

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**ABSTRACT:** A novel selective interlamellar modification of cetyltrimethylammonium bromide-exchanged montmorillonite (MMT) by toluene-2,4-di-isocyanate (TDI) has been successfully obtained, and a polystyrene/TDI-modified MMT hybrid has been prepared. After the interlamellar modification, TDI was grafted to hydroxyl groups of the MMT, and the orientation of cetyltrimethylammonium in the interlayer space changed from a bilayer lying flat structure to a double-layer inclined one. The structures of the TDI-modified MMT and the hybrid were characterized by Fourier transform infrared (FTIR) spectra, powder X-ray diffraction (XRD), and transmission electron microscopy (TEM) techniques. A schematic model of the TDI-modified MMT structure was also presented. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 2201–2205, 2000

**Key words:** hybrid; montmorillonite; toluene-2,4-di-isocyanate; polystyrene

## INTRODUCTION

Recently, polymer/clay hybrids have attracted significant attention due to their unusual physical properties, such as mechanical, thermal, and gas barrier properties, superior to the parent materials.<sup>1,2</sup> In preparation of polymer/clay hybrids, appropriate modification of clay is very important, because it enlarges the clay gallery to accommodate the monomer or polymer, renders clay surface hydrophilic to organophilic, lowers the surface energy of clay surface, and improves the compatibility between clay and the polymer or monomer.<sup>1,2</sup>

MMT is a commonly used clay. So far, interlamellar modifications of MMT with organic

surfactants, including organoammonium and organopyridinium surfactants, have been investigated extensively.<sup>3–6</sup> Other kinds of organic guests (such as poorly water-soluble nonionic organic contaminants,<sup>7</sup> cationic dye,<sup>8</sup> and photoactive chemical<sup>9</sup>), inorganic substances (such as FeCl<sub>3</sub><sup>10</sup>) and polymers<sup>1,2</sup> have also been reported. However, most of the previous interlamellar modifications were accomplished by ion exchange reaction, hydrogen bonding or ion-dipole interaction. Although some researchers reported the grafting of silanol groups of MMT,<sup>11–15</sup> sepiolite,<sup>16</sup> and chrysotile,<sup>17</sup> selective interlamellar grafting of hydroxyl groups of MMT with a chemical with high selective functional groups has not been found in our literature survey.

Toluene-2,4-di-isocyanate (TDI) has two —N=C=O groups, which can react with —OH groups with a rather high selectivity. Additionally, being a major industrial raw material, TDI

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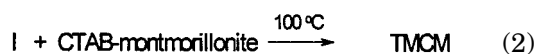
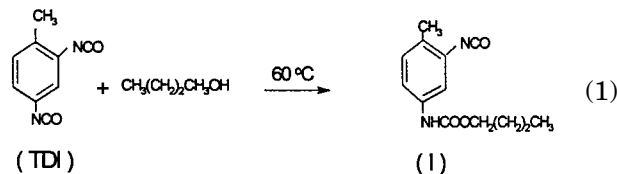
is cheap and commercially available. Therefore, if TDI can be grafted to layered materials, such as MMT, it may expand the surface modification chemistry of layered materials and promote the scientific research and industrial application of novel advanced inorganic-organic nanocomposites. In the present article, the grafting reaction of TDI with —OH groups of cetyltrimethylammonium bromide (CTAB)-exchanged MMT (CTAB-MMT) has successfully been achieved. The structure of the TDI-modified CTAB-MMT (TMCM) was confirmed by FTIR spectra and powder XRD techniques; the schematic outlines of the CTAB-MMT and the synthesized TMCM were illustrated as well. Further, the modification product, TMCM, was used to prepare a polystyrene/TMCM hybrid, the structure and morphology were characterized by XRD and TEM.

## EXPERIMENTAL

### Preparation of CTAB-MMT

CTAB-MMT was prepared by the conventional ion-exchange method, i.e., adding amounts of CTAB (AR grade) equivalent to the cation exchange capacity (CEC) of Na-montmorillonite (Swy-2 type, CEC = 92 mEq/100 g, generously provided by the Source Clay Repository, Department of Geology, University of Missouri, Columbia, MO) suspension, after stirring for 1 day, the suspension was filtered and washed three times with distilled water, then dried in a vacuum oven and ground.

### Selective Interlamellar Modification of CTAB-MMT with TDI



6.0 mmol 1-butanol (AR grade, dried with  $\text{MgSO}_4$  before use) and 0.80 g toluene (dried with  $\text{MgSO}_4$ ) were added into 6.0 mmol TDI (with a purity of higher than 99.0%). The mixture was

stirred vigorously, reacted at 60°C for 4 h and I was formed as in eq. (1). Then, 1.50 g CTAB-MMT was added to 60 mL toluene, dispersed fully, and refluxed for 20 min, removing the interlayer water. Finally, the synthesized product I and one drop of catalyst were added into the CTAB-MMT/toluene system and reacted at 100°C for 6 h. The interlamellar grafting process was accomplished as shown in eq. (2).

### Synthesis of the Polystyrene/TMCM Hybrid

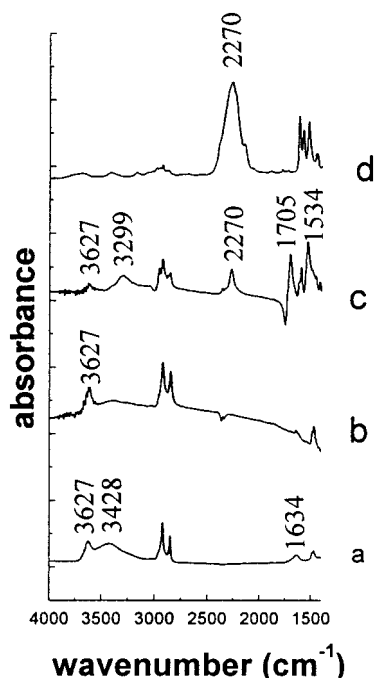
0.75 g of TMCM powder, 35 mL of distilled water, 0.1 g of ammonium persulfate ( $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ), 0.3 g of sodium dodecyl sulphate, and 15 mL styrene monomer were placed in a 200-mL glass flask. The mixture was stirred at room temperature until a stable, transparent system was obtained. Then, it was polymerized at 80°C for 5 h, resulting in the polystyrene/TMCM hybrid. Finally, the hybrid was crushed and dried in a vacuum overnight.

### Characterization

FTIR spectra were performed in the transmission mode on a Perkin-Elmer System 2000 IR spectrometer at room temperature. KBr pellets were employed for powder samples, and solution spectra were obtained using a Perkin-Elmer demountable liquid cell. XRD spectra was collected on a Rigaku D/max 2400 X-ray diffractometer, using  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.154$  nm). The voltage and current of the X-ray tubes were 40 kV and 100 mA, respectively. Transmission electron micrographs were obtained using a HITACHI H-800 electron microscope, operated at an acceleration voltage of 100 kV. The powder sample of polystyrene/TMCM nanocomposite was mounted in epoxy before sectioned.

## RESULTS AND DISCUSSION

The interlayer water in the CTAB-MMT can react with TDI, and is harmful to the interlayer grafting reaction. The FTIR spectra in Figure 1 show the effectiveness of removing the interlayer water by toluene. The wide absorption bands at 3428 and 1634  $\text{cm}^{-1}$  are due to the stretching vibration and deformation vibration of the interlayer water, respectively. Comparing with (a) and (b) in Figure 1, it can be seen that after codistilled with toluene, the absorption bands at 3428 and 1634  $\text{cm}^{-1}$  disappear in Figure 1(b), and no other obvious



**Figure 1** FTIR spectra of (a) CTAB-montmorillonite (predistilled), (b) CTAB-montmorillonite (after removing water with toluene), (c) TMCM, and (d) TDI.

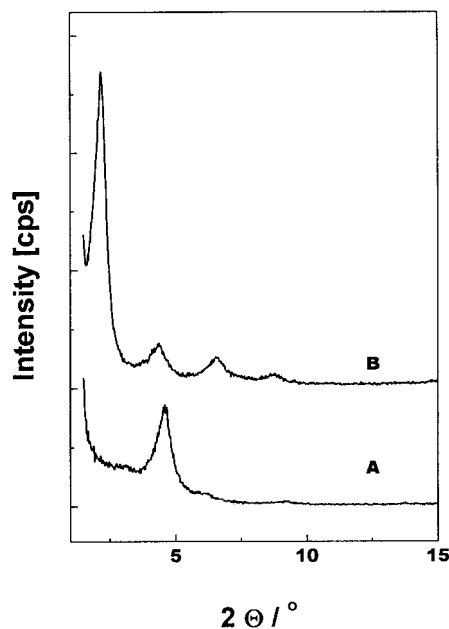
changes between Figure 1(a) and (b) are discernible, indicating that the interlayer water can be removed by distilled with toluene. This is a simple but rapid technique, compared with traditional heating method, to remove interlayer water of layered silicates.

The absorption band at  $3627\text{ cm}^{-1}$  is ascribed to the surface  $\text{—OH}$  groups of the CTAB-MMT. The absorption at  $2270\text{ cm}^{-1}$  is characteristic of the  $\text{—N=C=O}$  group of TDI, which can be observed in Figure 1(d). Figure 1(c) shows that, after the grafting reaction, the absorption of  $\text{—N=C=O}$  is very weak, and the absorption band of the surface hydroxyl group almost disappears, suggesting the completeness of the grafting reaction. The absorption bands at 3299, 1534, and  $1705\text{ cm}^{-1}$  are due to the stretching and deformation vibrations of  $\text{—NH—}$ , and carbonyl, respectively, also suggesting the interlamellar grafting reaction.

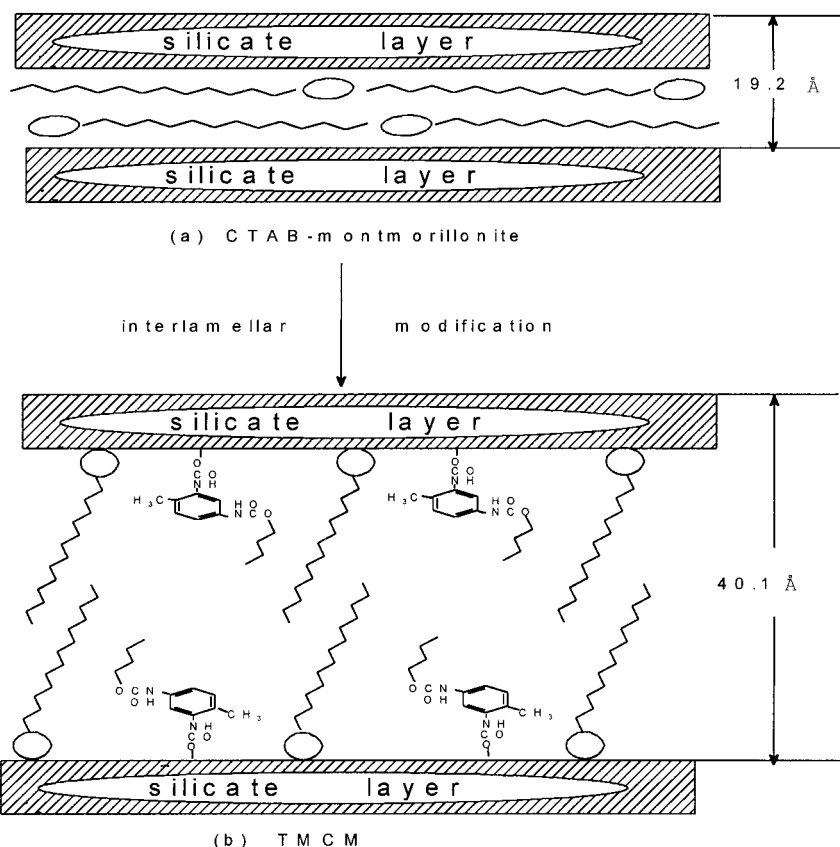
Figure 2 presents the powder XRD patterns, wherein A and B represent the diffractograms of CTAB-MMT and the synthesized TMCM, respectively. The  $d_{001}$  spacing of CTAB-MMT is  $19.2\text{ \AA}$ , which is consistent with our previous results.<sup>3</sup> According to the summarization of Jaynes and Boyd,<sup>18</sup> CTAB may pack as bilayers lying flat in

the interlayer of MMT parallel to the adjacent silicate lamellae, as shown in Figure 3(a). It can be seen from Figure 2(B) that the  $d_{001}$  spacing of TMCM increases to  $40.1\text{ \AA}$ . If we subtract the thickness of an individual three-layer silicate lamella, about  $9.6\text{ \AA}$ ,<sup>19</sup> the net intergallery distance increases from  $9.6$  to  $30.5\text{ \AA}$ , larger than three times. The XRD results further indicate that I reacted with the interlayer  $\text{—OH}$  groups of CTAB-MMT and greatly increased the interlayer distance of MMT.

It may be deduced that the increase of the interlayer distance is due to the introduction of TDI; it occupies part of the interlayer surface area, and may change the CTAB orientation. As for surfactant-MMT intercalation system, Jaynes and Boyd<sup>18</sup> pointed out that alkylammonium surfactant packed as paraffin complexes in the interlayer space when  $d_{001}$  value was larger than  $22\text{ \AA}$ . Calculation from Walker's formulae<sup>19</sup> of *n*-alkylammonium ions in layer silicates suggests that the basal spacings of double-layer and single-layer packed structure (inclined to surface) of cetylammmonium bromide are about  $46.1$  and  $22.7\text{ \AA}$ , respectively. Considering of the volume effect of the part of TMCM (II) that bonded to CTAB MMT, the interaction of II with CTAB and the possible experimental errors, CTAB might follow a double-layer inclined packed structure, as suggested in Figure 3(b).

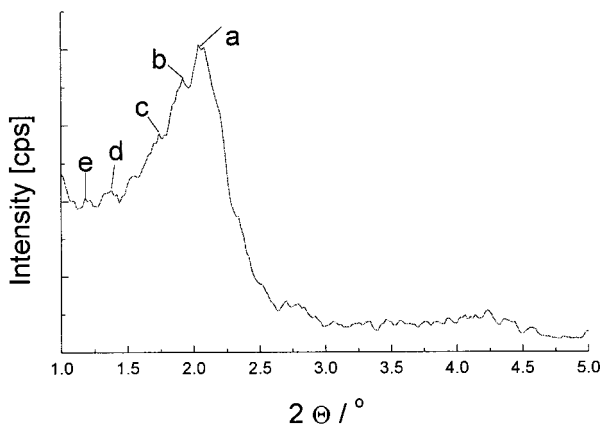


**Figure 2** X-ray powder diffraction patterns of (A) CTAB-montmorillonite, (B) TMCM.



**Figure 3** Schematic outlines of (a) CTAB-montmorillonite and (b) TCMC.

After the interlamellar modification, a polystyrene/TCMC hybrid was prepared by the emulsion polymerization method. If polystyrene did intercalate into the interlayer space, the basal spacing of TCMC should be enlarged. The XRD results in Figure 4 and Table I present the interlayer dis-



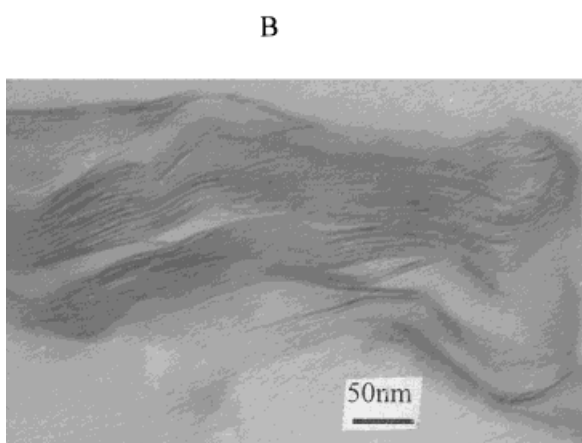
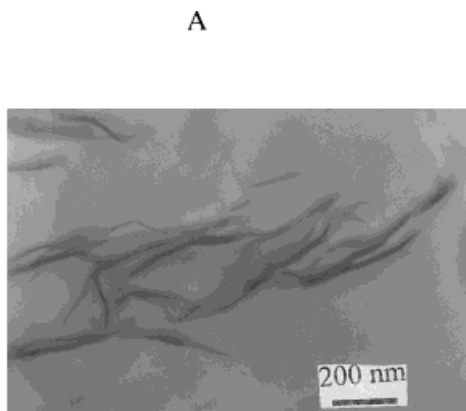
**Figure 4** X-ray powder diffraction pattern of the polystyrene/TCMC hybrid.

tances of the polystyrene/TCMC hybrid. The results reveal that the intergallery distances of the polystyrene/TCMC hybrid, including a, b, c, d, and e, are higher than that of TCMC, 40.1 Å. This indicates that the polystyrene intercalated into the TCMC galleries during the polymerization process.

Figure 5 shows bright field TEM images of the polystyrene/TCMC hybrid. In Figure 5(A), the dark bands and the light regions stand for the polymer and the silicate primary particles, respectively. Figure 5(A) reveals that the particle size of the clay silicate in the PS matrix is reduced from the original 40–70 μm to 20–50 nm in a lateral dimension during the polymerization process. The narrow, dark lines and the light regions

**Table I** Interlayer Distances of the Polystyrene/TCMC Hybrid

	a	b	c	d	e
$2\theta/^\circ$	2.08	1.92	1.74	1.34	1.18
$d/\text{Å}$	42.4	46.0	50.7	65.9	74.8



**Figure 5** Bright-field TEM images of the polystyrene/TMCM hybrid, with magnification: A,  $\times 45,000$ ; B,  $\times 180,000$ .

in Figure 5(B) represent the individual silicate layers and the polymer, respectively. It can be observed that the interlayer distances are approximately 4–10 nm, which is also consistent with the results determined by XRD. These results indicate that a polystyrene/clay hybrid was successfully prepared. Its physical properties are still under way, and will be published later.

## CONCLUSION

Toluene-2,4-di-isocyanate (TDI) can be selectively grafted to hydroxyl groups of montmorillonite (MMT). After the interlamellar modification, the orientation of cetyltrimethylammonium bromide in the interlayer space changed from a bilayer structure parallel to adjacent silicate layers to a double layer-inclined structure. The XRD and TEM results suggest that the TDI-modified MMT can be used to synthesize a polystyrene/TDI-modified MMT hybrid.

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