POLYMER-LAYER SILICATE NANOCOMPOSITES: LINEAR PEO AND HIGHLY BRANCHED DENDRIMER FOR ORGANIC WASTEWATER TREATMENT

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Abstract. Poly(amidoamine) (PAMAM) dendrimer, the polymer with highly-branched structure, was used in cooperation with montmorillonite (MMT), a smectite clay of high surface area in nanocomposite form which acts as an effective adsorbent in organic wastewater treatment applications. Due to the inorganic character of MMT, the organic adsorption ability of MMT was improved by replacing the exchangeable cations with octadecylamine and di(hydrogenated tallow)dimethylammonium chloride. The hyperbranched PAMAM/MMT nanocomposites were compared with poly(ethylene oxide)/MMTs, the nanocomposites with linear polymer molecules for organic waste adsorption. The ability to remove organic contaminants from aqueous solution, based on different molecular structures of organically modified clays, was evaluated using UV/VIS spectroscopy. The adsorption depend mostly on polarity and further enhanced by branching.

1. INTRODUCTION

Dendrimers have become a particular interest to the polymer science community in the past 20 years. A wide variety of dendrimers with different chemistries have been synthesized to present new and well-defined architectures with interesting properties and applications. Many of the potential applications make use of two important properties of dendrimers, both of which are a direct consequence of their architecture; the large number of end groups and the nanoporous nature of the interior at higher generations [1,2]. The example of the unique feature of dendrimer is 'dendritic box' which explored by Tomalia's group in 1997. The modified dendrimers Gn(C12) show the ability to host the hydrophobic dye in aqueous solution. Moreover, Bosman and coworkers, 1999 [3] proposed the micelles formed by hydrophilic dendrimers with hydrophobic functionalities on the periphery in organic solvents. Poly(amidoamine) hyperbranched is another example of dendritic materials. Due to its molecular structure, both hydrophilic and hydrophobic characters are represented in the molecules of poly(amidoamine) via ionic character of ammonium salt and methylene spacer length and this should be useful in the application of wastewater treatment.

Silicate clays are natural substances which have interesting geometry due to their surface area [4] and electronegative charge. As a consequence, thousands of positively charged ions are attracted to each colloidal crystal [5] (in expected – positive charge of ammonium salt of poly(amidoamine)). In addition, adsorptive surfaces of clays particles hold numerous water molecules that make up the clay micelle [5]. The property of these clays could be modified and used as an adsorbent for removing organic toxicants from wastewater by replacing the charge ions with different metal ions or attaching a different ions to the clays [6-8, 11]. In this work, the influence of polymeric molecular structure, linear and branch, poly(amidoamine) and their nanocomposites

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with modified silicate clay were prepared [9,10] and applied to aromatic organic solvents C7 and C8 (toluene and xylene). The ability to capture organic molecules was compared between linear PEO/clay and PAMAM/clay nanocomposites.

2. EXPERIMENTAL

2.1. Materials

Montmorillonite(Na-MMT) with cation exchange capacity of 119 meq/100 g was supplied by Kunimine Industrial Co., Ltd., Japan. Di(hydrogenated tallow)dimethylammonium chloride was kindly supplied by Unilever Thai Holding Co., Ltd. Poly(ethylene oxide) $M_v \sim$ 100,000 was perchased from Aldrich Chemical Company. The chemicals for modification of Na-MMT and organic solvent adsorption test, octadecylamine, n-hexane and cyclohexane were perchased from Fluka. Poly(amidoamine), PAMAM dendrimer with second generation in methyl alcohol (20 wt%) was perchased from Aldrich Chemical Company. All of the chemicals used in this work are used as received without further purification.

2.2. Sample Preparation

2.2.1. Preparation of Organically Modified Montmorillonite. Na-MMT (10 g) was stirred for 2 hours in 300 ml of distilled water and heated up at 80 °C for half an hour. At the same time, the solution of 1.5 equivalent alkylamine and 3 equivalent of HCl was heated at 80 °C for half an hour to give an alkylammonium solution. Then, the latter solution was gradually added into the Na-MMT suspension (at 80 °C) and mixed for another 2 hours with vigorous stirring. The sediment of organically modified MMT was collected by filtering and washing with 2 L of hot distilled water. The product was dried overnight at 80 °C, ground with mortar and was kept in a bottle.

2.2.2. Preparation of PEO/MMT Nanocomposites. PEO/MMT nanocomposites were accomplished by heating PEO with MMTs at 80 °C. Both components were thoroughly mixed in an agate mortar, formed into a pellet using hydraulic press and a pressure of 70 MPa, and heated at 80 °C in ambient atmosphere for 2 hours. The amount of MMTs was varied between 1-60 wt%.

2.2.3. Preparation of PAMAM/MMT Nanocomposites. PAMAM/MMT nanocomposites were prepared by introducing 10 wt% of MMTs to PAMAM dispersed in methyl alcohol for MMT and 1-butanol for OC-MMT and OH-MMT. The mixture was stirred in ambient atmosphere at 50 °C with a magnetic stirrer for two hours. After drying in air for two days at 80 °C, the resulting viscous gel was transferred to a vacuum oven at 110 °C for another one day.

2.3. Wide-angle X-ray Diffraction Measurements

XRD spectra were recorded by using a D/MAX-2000 series of Rigaku/X-ray Diffractometer that provides X-ray of Cu K-alpha at 40 kV/30 mA. The glass sample holders were applied to the composite pellets. The experiment was operated in the 2θ range of 2-30 degrees at the scan speed of 5 degrees/min and 0.02 degree of scan step.

2.4. Adsorption Test Using UV/VIS Spectroscopy

The amount of remaining organic solvent in wastewater after treated with the nanocomposite was determined by using Lambda 10 UV/VIS spectrophotometer of Perkin Elmer. The nanocomposites were applied to 100 ml of wastewater with 10 vol% of two organic solvents (toluene and mixed xylene) varied in amount of the nanocomposites. The mixture was stirred for 1 day to allow equilibrium to be achieved and the aggregate was isolated from the slurry by centifuging at 10,000 rpm for 10 minutes. The organic fraction was extracted by using n-hexane for toluene and cyclohexane for xylene and the adsorbate concentration was analysed by using UV\VIS spectrometer. The amount of organic adsorbate uptake was then calculated by using mass balance equation.

3. RESULTS AND DISCUSSION

3.1. Characterization of PEO/MMT Nanocomposites

The obtained PEO/Na-MMT nanocomposites prepared by melt technique were characterized by XRD. It could be clearly observed from Fig. 1 that the XRD spectra of PEO/Na-MMT nanocomposites prepared by melt technique showed the shift in peak position of Na-MMT from around 7.1 degree (12.40 Å) to 6.0-5.4 degree (14.71-16.35 Å) for every ratio. The diffraction peaks at high 2θ angle (>15°) are belong to PEO crystalline. The results suggested that by mixing PEO with Na-MMT in the pristine form, the distance between silicate layers of Na-MMT was increased. Consequently, intercalated nanocomposites of Na-MMT and PEO were obtained by the melt technique. On the other hand, crystalline peaks of PEO are diminished as Na-MMT content in-
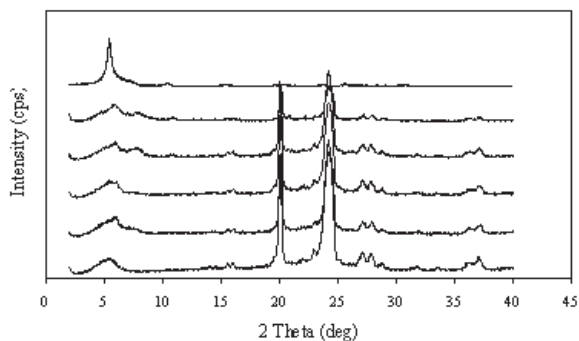
Fig. 1. XRD spectra of PEO/Na-MMT nanocomposites with various amount of Na-MMT.
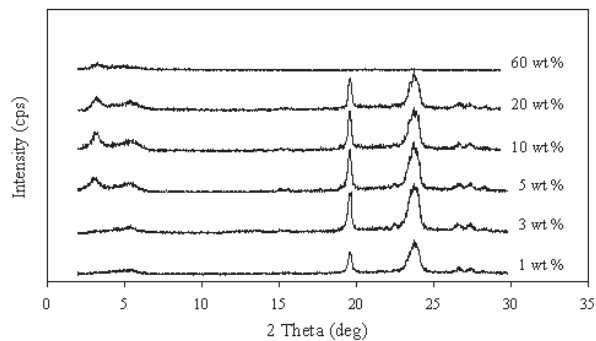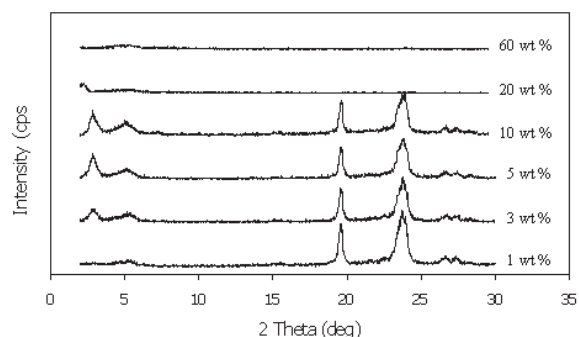

Fig. 2. XRD spectra of PEO/OC-MMT nanocomposites with various amount of OC-MMT.
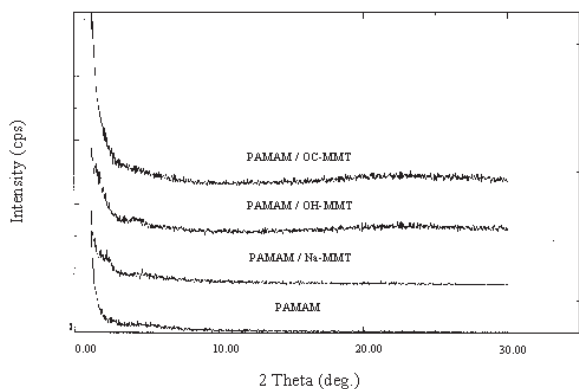
creases indicating that Na-MMT acts to disturb and inhibit the formation of crystalline structure.

For PEO/OC-MMT nanocomposites, the results were different from nanocomposites using Na-MMT as shown in Fig. 2. It could be observed that at lower amount of OC-MMT (< 5 wt%), there was no peak presented in the position of OC-MMT. This in-

Fig. 3. XRD spectra of PEO/OH-MMT nanocomposites with various amount of OH-MMT.


Fig. 4. XRD spectra of PAMAM/Na-MMT, PAMAM/OC-MMT and PAMAM/OH-MMT nanocomposites containing 10 wt% MMTs.

dicated that silicate layers of OC-MMT were separated into individual layer and relatively far from each other revealing the insertion of large amount of PEO. Consequently, exfoliated nanocomposites could be generated. In contrast, for higher amount of OC-MMT up to 20 wt%, the slightly shift in peak position of OC-MMT to lower degree was observed from 3.36 degree (26.27Å) to 3.32-2.96 degree (26.59-29.82 Å). This suggested that among these ratios, intercalated nanocomposites were dominated. At 60 wt% OC-MMT, however, the exfoliation was occured again coincidently with the disappearance of PEO crystalline structure such that the layer silicate has better chance and less constraint to exfoliate in amorphous matrix. The exfoliation of PEO/OC-MMT nanocomposite containing 60 wt% OC-MMT are apparent due to the larger basal spacing of OC-MMT (14.51 Å), the higher possibility of insertion of PEO. As well as PEO/OC-MMT nanocomposites, PEO/OH-MMT nanocomposites showed similar trend as that of PEO/OC-MMT as shown in Fig. 3.

3.2. Characterization of PAMAM/MMT Nanocomposites

The XRD spectra of PAMAM/MMT nanocomposites with 10 wt% MMTs are shown in Fig. 4. It could be observed that the corresponding peaks of Na-MMT, OC-MMT and OH-MMT were disappeared and exfoliation was confirmed to dominate.
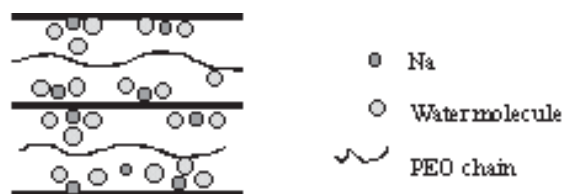
3.3. Adsorption Test

3.3.1. PEO/MMT Nanocomposites. The intercalated nanocomposites found at 10 wt% PEO/MMTs were selected for the study of adsorption in comparison to PAMAM/MMT nanocom-posites at 10 wt% with exfoliated structure. At 10 wt%, basal
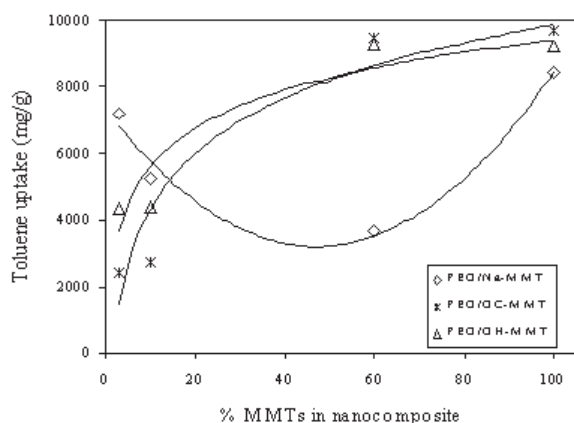
Fig. 5. Amount of toluene adsorb onto nanocomposites at various compositions (initial toluene concentration 86.7 mg/ml at constant concentration of nanocomposite 0.1g/100ml).

Fig. 6. Schematic illustration of hydrated Na$^+$ by water in PEO/Na-MMT nanocomposite.

Fig. 7. Schematic illustration of bridging flocculation occurs in polymer nanocomposite in the presence of high molecular weight polymer.

spacing of PEO/OC-MMT and PEO/OH-MMT are 29.82 and 30.87 Å, respectively. Fig. 5 shows the amount of toluene adsorbed onto the PEO/Na-MMT, PEO/OC-MMT and PEO/OH-MMT nanocomposites at various compositions. It is seen that the ability to adsorb toluene is enhanced by the increase in amount of OC-MMT and OH-MMT in the nanocomposites and OH-MMT shows greater toluene adsorption than OC-MMT at low MMT content. In case of organoclays (at 100 % Na-MMT, OC-MMT and OH-MMT), the introduction of long alkyl chains to the structure of MMT improved the toluene adsorption ability and OC-MMT gives the highest toluene absorption. Wibulswas also reported that the modified MMT with quaternary ammonium cation could improve the sorbent property of MMT for organic molecules [7]. At low MMT content, Na-MMT and OH-MMT show higher toluene absorption than OC-MMT. This is contributed to higher polarity of OH leading to greater swelling in water and thus greater adsorption. Contrary to PEO/Na-MMT nanocomposite systems, Sodium montmorillonite show reduced adsorption with increased clay content in the nanocomposites. The inorganic exchangeable cations (Na$^+$) between the layer of MMT are strongly hydrated by water. Consequently, the adsorption of nonionic organic compounds (NOCs), such as benzene, alkylbenzenes and chlorinated phenols [11], by MMT is reduced in the presence of water because NOCs cannot effectively compete with highly polar water molecules for adsorption sites on the MMT surface (see Fig. 6). Therefore, increasing in amount of Na-MMT led to decrease in ability

of the nanocomposite to adsorb toluene. The improvement in toluene adsorption of PEO/organoclay compared with PEO/Na-MMT nanocomposites is around 60% (from 38 to 98% adsorption) at 60 wt% MMTs. However, at 100% Na-MMT and modified MMT, the adsorption becomes the highest. This might be explained that at this composition, there is no effect of bridging flocculation [12]. This effect is occurred by the presence of high-molecular-weight polymer (PEO) which supposes that the two ends of a PEO chain adsorb onto both MMT surfaces and thereby draw them together and induces a reduction of the interlayer spacing results in the reduction of adsorption of toluene (see Fig. 7). Moreover, Na-MMT has high degree of swelling in water that could lead to higher adsorption of toluene.

In case of xylene which is more hydrophobic than toluene, the results from adsorption were relatively similar to that of toluene as shown in Fig. 8. The capacity of xylene adsorbed onto PEO/MMT nanocomposites increases with increasing organoclay and show higher increment than the system of PEO/Na-MMT nanocomposites (the adsorption is improved from 22% adsorption of PEO/Na-MMT to 97% adsorption of PEO/organoclay). This result confirms the proposed concept of using organoclay as an adsorbent for the removal of organic molecules from aqueous solution. The schematic illustrations of toluene and xylene adsorption of PEO/organoclay nanocomposites with high and low percentage of organoclay are shown in Fig. 9. It is likely that PEO/OH-MMT can adsorb both toluene and xylene better than PEO/OC-MMT. Thus,
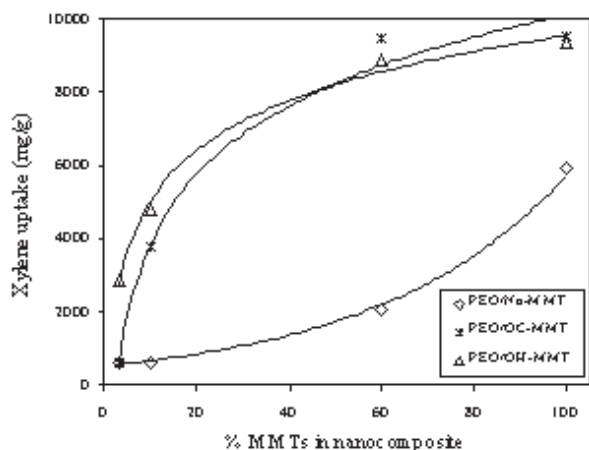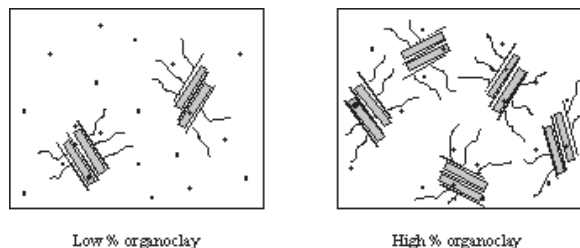
Fig. 8. Amount of xylene adsorb onto nanocomposites at various compositions (initial xylene concentration 86.0 mg/ml at constant concentration of nanocomposite 0.1g/100ml).
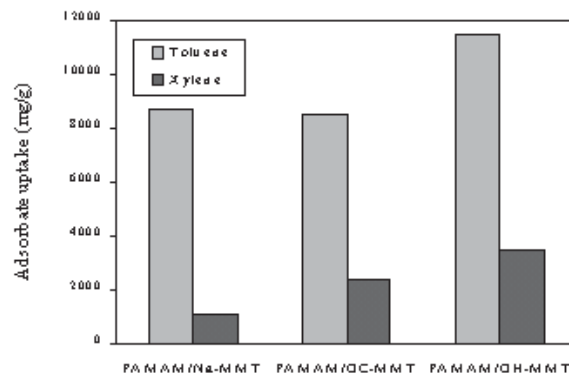

Fig. 9. Schematic illustration of toluene and xylene adsorption of PEO/organoclay nanocomposites.

Fig. 10. Toluene and xylene adsorption of PAMAM/MMT nanocomposites containing 10 wt% MMTs.

the adsorption can be contributed to comparable polarity of the adsorbent and adsorbate and the gallery spacing (OH-MMT > OC-MMT).

3.3.2. PAMAM/MMT Nanocomposites. At the compoistion of 10 wt% MMTs, PAMAM/MMT nanocomposites show majority of exfoliated structure. Fig. 10 shows the comparison of the ability of toluene and xylene adsorption by PAMAM/MMT nanocomposites containing 10 wt% of MMTs. It is clearly seen from the figure that the amount of toluene uptake by PAMAM/MMT nanocomposites is much greater than that of xylene for all types of clay. This implies that the nanocomposites of poly(amidoamine) and MMTs have higher affinity for toluene than that of xylene. This can be due to structure hindrance, i.e. two methyl groups on xylene molecules indicate more bulkiness and more hydrophobic than toluene; thus may not allow xylene to adsorb well on PAMAM/MMT nanocomposites.

According to structural effect, the efficiency of the adsorbent PAMAM/MMT nanocomposites are compared with PEO/MMT nanocomposites in aqueous system as shown in Fig. 11. It could be seen that PAMAM/MMT nanocomposites show much higher toluene adsorption than that of PEO/MMT nanocomposites for all types of MMT and much beyond those of pristine clay and organoclays. The higher efficiency of PAMAM/MMT nanocomposites as an adsorbent for organic solvents, i.e. toluene and xylene, is due to the structure of second generation PAMAM with highly branching alkyl chains that could improve the affinity for toluene. In addi-

tion, bulky molecules of PAMAM incorporated to MMTs structure provided higher d-spacing (or exfoliation) than PEO/MMT nanocomposites as well as declined the possibility of cage formation and thus resulted in higher ability for adsorption. However, this characteristic was not observed in the case of xylene adsorption (see Fig. 12). Pure Na-MMT which has high polarity shows much reduction to adsorb more hydrophobic xylene while adsorption by organoclay show slightly change. This suggests that the polarity of the adsorbent and adsorbate are dominant. The adsorption by the PEO and PAMAM/MMT nanocomposites were much lower than those of pure MMTs. In case of the nanocomposites, PEO/OC-MMT and PEO/OH-MMT nanocomposites showed higher efficiency for xylene adsorption than PAMAM/MMT nanocomposites because of the lower in polarity of xylene than that of toluene and PEO is less polar than PAMAM. OC-MMT is slightly poorer than OH-MMT nanocomposites despite of its higher hydrophobicity due to more hydrophobicity or less polarity of octadecylamine (aliphatic amine) compared to the adsorbate (aromatic). This could be implied that PAMAM/MMT nanocomposites at 10 wt% MMTs have a degree of selectivity for toluene and xylene.
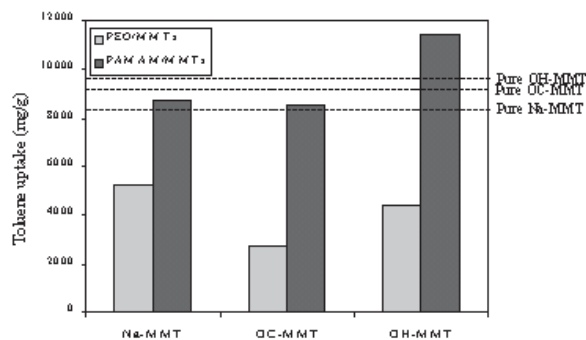
Fig. 11. Toluene adsorption of PEO/MMTs and PAMAM/MMT nanocomposites containing 10 wt% MMTs.
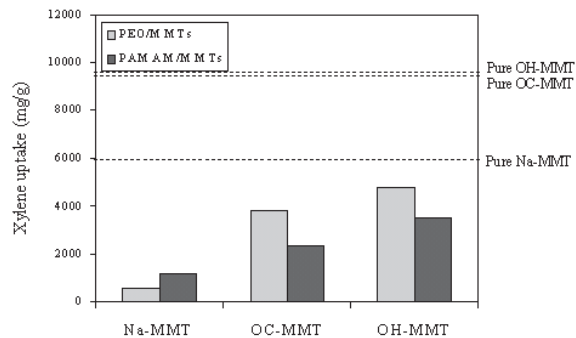
Fig. 12. Xylene adsorption of PEO/MMTs and PAMAM/MMT nanocomposites containing 10 wt% MMTs.

4. CONCLUSION

Polymer nanocomposite of PEO/MMTs and PAMAM/MMTs can be used as adsorbent for wastewater treatment application. The ability of the nanocomposites to adsorb organic impurities can be improved by using organically modified montmorrillonite especially at 60 wt% MMTs of PEO/MMT nanocomposites the adsorption are improved from 38% to 98% for toluene and from 22% to 97% for xylene. The organoclay which were prepared by ion-exchange reaction using octadecylamine and di(hydrogenated tallow)dimethylammonium chloride have higher degree of basal spacing expansion than the unmodified form. Consequently, the probability of polymer to incorporate into the clay structure is higher and the organophillic site is created between the layer of clay. Moreover, incorporation of PAMAM dendrimer with organoclay has improvement in the ability to capture organic molecules due to highly branched structure with alkyl chain of PAMAM. The difference in ability to adsorb toluene and xylene molecules of PEO/MMTs and PAMAM/MMT nanocomposite is mainly based on the polarity and the molecular structure of both adsorbent and adsorbate.

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