Effect of Twice-Functionalized Montmorillonite to the Morphological Properties of PMMA/MMT Nanoco mposites

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Abstract: Sodium montmorillonite (MMT) was modified to org anophilic montmorillonite (OMMT) by exchanging Na+ ion in MMT with trihexyltetradecylphosphonium (THTDP) ion by cation-exchange method. The OMMT was then underwent second modification involving silane coupling agent of aminopropyltrimethoxylsilane (APTMS) to produce twice-functionalized clay (grafted-OMMT). The resulting OMMT and grafted-OMMT were characterized by Fourier transform infrared (FT-IR), nitrogen adsorption-desorption and X-ray diffraction (XRD) analyses. Addition of grafted-OMMT to PMMA matrix resulted in stronger polymer-clay interaction by forming exfoliated and intercalated types nanocomposites compared to OMMT which formed conventional type composite.

Index Terms: Organo-Montmorillonite, Twice-Functionalized Montmorillonite, Modified Clay,

I. INTRODUCTION

Clays are alumino silicates or hydrous silicates and are basically containing silicon, aluminium or magnesium, oxygen and hydroxyl with various associated cations. Cations and OH groups are structured into two dimensional structures as sheets. Among the different type of clay minerals, montmorillonite (MMT) is the most commonly used clay for the preparation of polymer clay nanocomposites [1]. MMT consists of platelets with an inner octahedral layer sandwiched between two silicate tetrahedral layers [2]. It is naturally abundant, non-toxic, inexpensive, chemically and thermally stable and can act as reinforcing material. Layered silicates of MMT are one of the ideal nano reinforcements for polymers because of its high intercalation chemistry, high aspect ratio, ease of availability and low cost [3]. Naturally, MMT exists as stacks of many platelets with Na^+ ions in between the platelets. It has hydrophilic character due to the ability of Na^+ ions to undergo hydration thus MMT will not easily disperse in polymer matrix such as poly(methyl metacrylate), PMMA which are hydrophobic. Incompatibility of MMT and PMMA influenced the polymer-clay interaction in composite.

Therefore, MMT has to undergo surface modification to promote uniform dispersion of MMT into the polymer matrix. One of the well-known method used to modify hydrophilic clay is cation-exchange reaction that involve cationic surfactant to form organo-modified MMT (OMMT). OMMT can be synthesized by replacing the naturally exist Na^+ ion between interlayer of MMT by cationic organic surfactant [4]. However, the presence of reactive hydroxyl group at the edge of OMMT clay platelets causes it to have slight hydrophilic character. Hence, the grafting reaction of hydrophobic groups into the layer surfaces has been attracted great attention. It is usually performed through the grafting reaction between silane coupling agents and the reactive hydroxyl group which are located at the broken edges of the clay platelets and at the structural defects located at the interlayer and external surface of layered silicates.

In this study, the MMT will undergo twice modification which are first cation-exchange reaction and followed by modification via silane grafting reaction to form grafted-OMMT. Melt intercalation technique was used to prepare the polymer-modified clay nanocomposite to study their compatibility.

II. MATERIALS AND METHODS

2.1 Cation –exchange Modidfication

25 g of MMT was dispersed into 2.5 L of hot distilled water by mechanical stirrer. 1 L of diethyl ether solution containing trihexyltetradecyl phosphonium chloride (THTDP) equivalent to the cation exchange capacity (CEC) of montmorillonite was added into MMT dispersion. The dispersion was moderately mixed for 12 hours, then the mixture heated to 60ºC to evaporate the diethyl ether until it becomes sticky solid OMMT precipitate. The precipitate underwent filtration and rinsed with distilled water then dispersed in hot water (80ºC). OMMT was then manually mixed with 200 ml of petroleum ether. After evaporation of petroleum ether by rota-evaporator, it was dried at 80ºC in an oven. Dried sample was then ground into fine powder.

a. Silane Grafting Reaction

5g of OMMT was dispersed in 400 ml of ethanol: water solution (75:25 by volume). 4 ml of 3-aminopropyltrimethoxysilane (APTMS) was added to the mixture and refluxed for 6 hours at 80ºC with constant stirring. The obtained grafted-OMMT was filtered and dried at 60ºC in an oven.

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b. Preparation of nanocomposites

Nanocomposites of PMMA/MMT, PMMA/OMMT and PMMA/grafted-OMMT were prepared via melt mixing technique at predetermined ratio (1 to 4 wt% clay loadings) using Haake Internal Mixer operating at 180ºC for 15 minutes with screw speed at 50 rpm.

c. Characterizations

All clay samples were characterised by Fourier transform infrared spectroscopy (FTIR) on a Perkin Elmer Spectrum 100. The infrared analysis was done by using potassium bromide (KBr) pressed pellet method. The IR spectra were recorded with 16 scans for each measurement over the spectral range of 400-4000 cm^{-1}.

Nitrogen adsorption and desorption analysis was carried out for all clay samples at -196ºC by using Micromeritics ASAP 2020M instrument. The specific surface area and total pore volume were calculated by Branauer-Emmett-Teller (BET) method and Barrett-Joyner-Halenda (BJH) respectively for confirmation of ion exchange and silanization reactions.

Powder X-ray diffraction analysis was performed for all samples using X-Ray Diffractometer Rigaku Mini Flex II with a scan rate in 2º/min over a range of 2θ = 2 – 10º.

III. RESULTS AND DISCUSSION

Peak around 3630 cm^{-1} appears in FTIR spectra (Figure 1) of all samples is assigned to the stretching vibration of the structural hydroxyl groups that bonded to the silicon in MMT and this Si-OH is responsible for the reaction with the silane coupling reagent [5]. Also, the broad bands around 3400 cm^{-1} and 1640 cm^{-1} correspond to the the -OH stretching and bending vibration of adsorbed water [6]. The bands in the region between 1000 and 1100 cm^{-1} are related to the Si-O-Si functional group in MMT.

The MMT modified with THTDP (Figure 1(b)) shows the existence of three new peaks at 2927, 2856, 1467 and 1412 cm^{-1}. Peaks at 2927 and 2856 cm^{-1} are assigned to C-H aliphatic stretching whereas peaks at 1467 and 1412 cm^{-1} are attributed to C-H bending of CH$_2$ group of THTDP. The presence of these new peaks indicates the successful cation-exchange of Na$^+$ ion in MMT with THTDP forming OMMT. As compared to MMT, grafted-OMMT exhibit new bands in FTIR spectrum depicted in Figure 1(c). The absorption peaks at 2927 and 1467 cm^{-1} in grafted-OMMT spectrum show the C-H aliphatic stretching and C-H bending of CH$_2$ from the silane coupling agent (APTMS) confirm the successful of grafting and functionalization of organosilane onto the MMT surface. This observation was also reported by previous researchers [7-9].
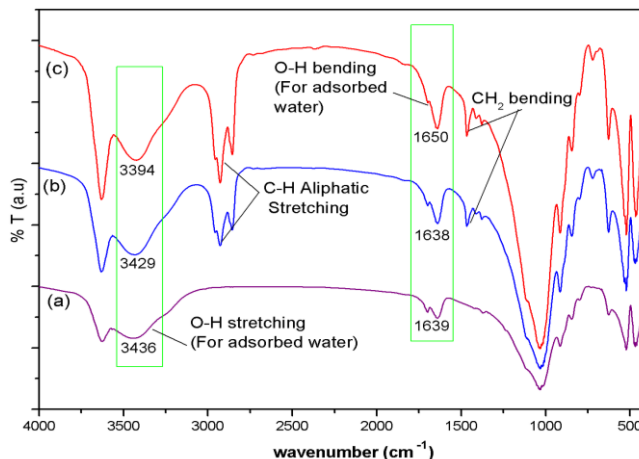

Figure 1. FTIR spectra of (a) MMT, (b) OMMT and (c) grafted-OMMT.

XRD diffractograms of MMT, OMMT and grafted-OMMT (Figure 2) were used to compare the d$_{001}$ diffraction plane which indicate the interlayer distance of platelets before and after modification process.

In both cases, incorporation of THTDP (red line) and APTMS (yellow line) shifted the peak corresponding to the d$_{001}$ diffraction plane of MMT to the left (lower 2θ value). In OMMT, the peak shifted from 5.94º to 3.50º corresponds to the interlayer distance of platelets from 1.49 nm to 2.52 nm. The increase of OMMT basal spacing is assigned to the presence of THTDP surfactant that successfully intercalated into the interlayer of MMT. Meanwhile, the characteristics peak of grafted-OMMT change from 5.94º to 4.23º shows an increase of basal spacing from 1.49 nm to 2.08 nm. This indicates that the silane molecules (APTMS) were intercalated in the galleries or grafted at the broken edges of the clay. The OMMT shows expansion of interlayer spacing greater than grafted-OMMT because most of the aminosilane grafted on the edges and only small amount of aminosilane inserted and co-existed with THTDP in the interlayer. This phenomenon lead to slight increase in interlayer distance of platelets after silanization [5, 10-11].
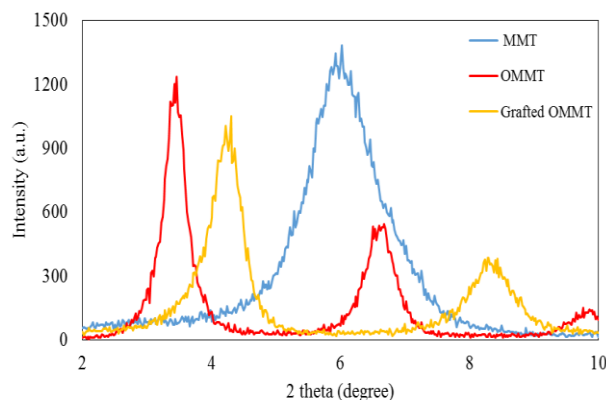

Figure 2. XRD diffractogram for MMT, OMMT and grafted-OMMT.

Since interaction between polymer and filler was influenced by the surface area of filler, therefore unmodified clay and modified clay were undergone nitrogen adsorption and desorption analysis to calculate the BET surface areas and BJH pore volumes of the clay.

Table 1. BET surface area and BJH pore volume of MMT, OMMT and grafted-OMMT

Samples	BET surface area (m^2/g)	BJH pore volume (cm^3/g)
MMT	9.5	0.032
OMMT	0.6	0.003
Grafted-OMMT	4.7	0.022

BET surface area of OMMT declined after cation-exchange reaction with THTDP ions however it increase after the surface functionalization with APTMS, forming grafted-OMMT. This happens due to successful intercalation of THTDP into the galleries of MMT samples, and grafting of APTMS at the broken edges of the clay which proved by reduction of pore volumes [6,12]. Grafting of organo-silane compounds associated with the shrinkage of structure in the twice-functionalized MMT (grafted-OMMT) which lead to a significant decrease in the surface area area [13-15]. OMMT shows drastic decrease of BET surface area over grafted-OMMT after modification indicates that higher amount of surfactant deposited on the OMMT layer   compared with grafted-OMMT which give marginally   decrease of surface area ascribed to the limited entry to the interior porosity of clays [16].

Figures 3 and 4 illustrate XRD patterns of PMMA composites containing different amount of OMMT and grafted-OMMT produced by melt intercalation, with OMMT and grafted-OMMT diffractograms in yellow color as reference.
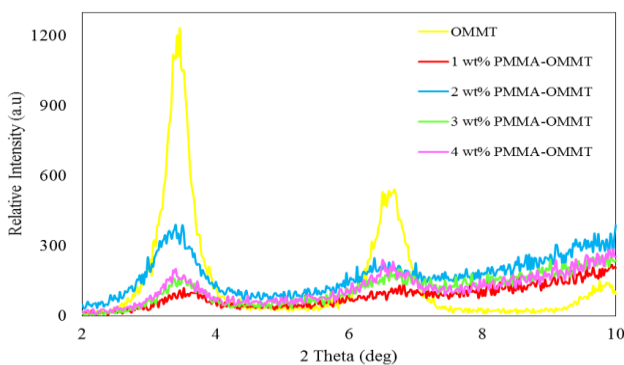

Figure 3. XRD diffractogram of OMMT and PMMA/OMMT nanocomposite

Single-modified clay, OMMT shows a characteristic peak at 3.50º, with the interlayer distance of 2.52 nm. The d_{001} diffraction plane of PMMA-OMMT were insignificantly change and remain around 2.52 nm and suggesting the formation of conventional composites which indicate poor interaction between PMMA and OMMT.

In Figure 4 the grafted-OMMT that undergone twice modification (yellow line) shows a peak around 4.24º, corresponding to basal spacing of 2.08 nm. In this study, complete disappearance of characteristic peak of PMMA

composites containing grafted OMMT produced by melt intercalation method except composites with 4 wt% clay loading. It is suggested that these products are mainly exfoliated structure whereas 4 wt% PMMA-grafted OMMT composite shows intercalated structure. This observation is merely match with the result obtained by other researcher by pointing out that an exfoliated system is more feasible with lower clay content (around 1 wt %), whereas at high load of clay content an intercalated structure frequently observed[17].
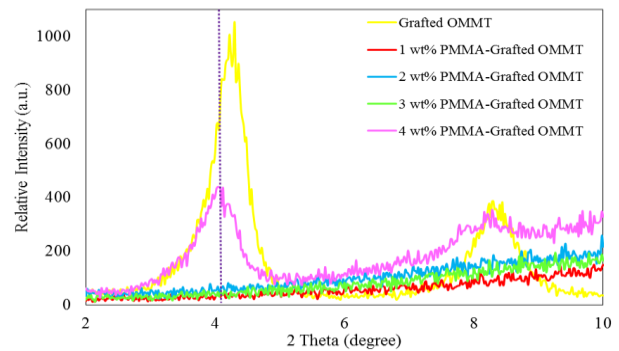

Figure 4. XRD diffractograms of grafted OMMT and PMMA/Grafted-OMMT nanocomposite.

Based on XRD results of PMMA composites, we can conclude that in spite of quaternary alkyl phosphonium ion in OMMT when compared to small size of aminosilane in grafted-OMMT present as the intercalating moiety, the twice-functionalized clay display better dispersion inside the PMMA matrix [17]. This is attributed to the THTDP and silane coupling agent (APTMS) successfully expanded the inter-galleries of layered silicates for polymer penetration as evidenced by higher interlayer spacing owned by grafted-OMMT filled composites. Furthermore, the aminosilane and alkyl phosphonium ion grafted on the edges of the clay improve the miscibility and hydrophobicity of clay and thus lead to better compatibility between clay that undergo double modification and polymer matrix [18].

Table 2. XRD results for MMT and its nanocomposites

Composites	Clay loading (wt %)	2θ value (°)	d-spacing (nm)
OMMT (reference)		3.50	2.52
	1	3.49	2.53
PMMA-OMMT	2	3.35	2.63
composites	3	3.50	2.52
	4	3.44	2.56
Grafted OMMT (reference)		4.24	2.08
	1	-	-
PMMA-Grafted	2	-	-
OMMT composites	3	-	-
	4	4.08	2.16

IV. CONCLUSION

Montmorillonite was successfully modified by THTDP and APTMS by means of cation exchange method and silane grafting method, respectively. This achievement was confirmed by FTIR spectroscopy and XRD analysis depict that the THTDP intercalated into the clay layers of OMMT whilst silylation of APTMS were predominantly took place on the edges of grafted OMMT.

In case of compatibility, PMMA/OMMT nanocomposite exhibited conventional types of composite. However, the absence of d_{001} diffraction plane in PMMA/grafted-OMMT indicates the formation of exfoliated nanocomposites. It implies that grafted-OMMT have better compatibility with PMMA resulted in stronger polymer-clay interaction.

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