

# PRE-SWELLING PROCESS OF THE SURFACE MODIFIED MONTMORILLONITE (O-MMT) AS A STRATEGY TO ENHANCE EXFOLIATION AND DISPERSION

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**ABSTRACT:** The production of exfoliated polymer/clay based nanocomposites is crucial to obtain an actual benefit of nanoscale reinforcement in the polymer matrix. The objective of this study was to employ the pre-swelling process through the combination of magnetic stirring and ultra-sonication technique to produce more readily exfoliated O-MMT for the production of polymer nanocomposite. The effects of dispersant concentration on the thermal stability, structure and morphology of the pre-swelled O-MMT were studied. Results indicated that the pre-swelling process did not reduce the thermal stability of the O-MMT, showing that this method did not leach out or degrade the surface modifier of the O-MMT. Among all the pre-swelled O-MMTs, the one prepared using H<sub>2</sub>O/O-MMT ratio of 1:1 had the best thermal stability. As proved through the XRD analysis, this sample possesses larger basal spacing as compared to the origin O-MMT. FESEM analyses suggested that disorientation and misalignment of platelets occurred, forming 'house of card' structure. More porous and loosely packed platelets were obtained, which is predicted can allow better O-MMT dispersion and polymer chains intercalation during the formation of exfoliated polymer nanocomposite. Furthermore, the H<sub>2</sub>O/O-MMT ratio of 1:1 was selected as the best dispersant concentration to form the pre-swelled O-MMT.

**KEYWORDS:** *Montmorillonite; Pre-Swelling; Structure; Morphology; Exfoliation*

## 1.0 INTRODUCTION

Polymer nanocomposites, with dispersed nanoparticles, have been studied extensively due to their outstanding mechanical, physical, thermal, and barrier properties with very low nanoparticles loading of 1–5 wt% [1-3]. With regard to polymer nanocomposites, montmorillonite (MMT) and other smectite nanoclay particles have been used as nanofiller by many researchers [3-7]. With a structure of one dimension stacked platelets in the nanometer scale, MMT has a high aspect ratio and specific surface area when exfoliated. If the platelets are dispersed properly, its nano-size can provide a significant amount of interface between the clay and the matrix resin with only a small weight percentage of MMT, thus contributing to the excellent mechanical and physical properties of the nanocomposites [2, 8-10]. However, in order to disperse the MMT throughout the hydrophobic polymer matrix, its hydrophilic surface must be transformed into hydrophobic. The purpose is to improve compatibility and allow good interface bonding between the nanofiller and polymer matrix. The well-known method to allow this happens is called surface modification using organic surface modifier [2, 8]. Generally, this can be done through ion exchange reactions by replacing interlayer cations with quaternary alkylammonium or alkyl phosphonium cations [2, 9-11]. The resulting surface modified MMT is called O-MMT, in which 'O' stands for 'organic'.

There are many papers reporting the effects of O-MMT addition on the properties of the polymer nanocomposites. However, it was found that O-MMT cannot always improve the mechanical properties of the polymer nanocomposites, especially if the nanofiller was added in high content (greater than 3 wt%) [2, 8, 12]. The main reason is the reduction in degree of O-MMT dispersion due to over-crowding of the large clay platelets (tactoids) in the polymer matrix. These findings show that even when surface modified MMT is used, we cannot guarantee the production of well exfoliated MMT platelets in the polymer matrices. Lately, ultra-sonication, has been widely used as a technique to disperse nanomaterials in different types of liquid medium. When ultrasonic waves pass through a liquid medium, a large number of microbubbles form, grow, and collapse in very short times, about a few microseconds [13]. Ultra-sonication creates alternating high-pressure and low-pressure waves in liquids, lead to the development and

violent collapse of small vacuum bubbles. This phenomenon is called “cavitation”. It causes high-speed impinging liquid jets and strong hydrodynamic shear-forces [12, 14]. These effects are used for the de-agglomeration of nanometer-size materials. Besides, it can develop the material transfer at particle surfaces too, hence this resulting in improving surface functionalization of materials that possess a high specific surface area.

In this study, enhancement in exfoliation and dispersion capability of organically modified montmorillonite (O-MMT) nanofiller in the polymer matrix was aimed through processing strategies. Pre-swelling technique was studied as additional process to assist the exfoliation and dispersion of O-MMT during the melt compounding process between the nanofiller and the host polymer. The purpose was to obtain an optimise polymer nanocomposite system with improved mechanical properties and thermal properties when both low and high O-MMT loadings are used. The work involved the use of magnetic stirring and ultra-sonication to pre-swell the O-MMT prior to the melt compounding process, in order to improve its dispersion and exfoliation capability. The effect of dispersant concentration on the morphology and structure of the O-MMT was studied to optimize the pre-swelling process.

## **2.0 METHODOLOGY**

### **2.1 Materials**

A commercial montmorillonite, which was surface modified with 35-45 wt% dimethyl dialkyl (C14–C18) amine was chosen for this ‘pre-swelling’ study. It is known as Nanomer (types 1.44P) and herein referred to as organo-montmorillonite (O-MMT). This O-MMT was manufactured by Nanocor, (Hoffman Estates, IL, USA) and supplied by Sigma-Aldrich (USA). The average length of O-MMT particles, as demonstrated by the supplier, was approximately below  $\leq 20$  microns with the bulk density ranges from  $200 \text{ kg/m}^3$  to  $500 \text{ kg/m}^3$ . This O-MMT was used as such without any further purification. Dionized water was used as pre-swelling medium for the O-MMT due to its low cost, non-toxic and suitability for bulk industrial production.

## 2.2 Sample Preparation

The dispersant concentrations (H<sub>2</sub>O: O-MMT) of 5:1, 5:2, 5:3 5:4 and 5:5 (1:1) were used for the pre-swelling process through combination of magnetic stirring and ultra-sonication techniques. The suspension was stirred magnetically for 2 hours to obtain a homogenous mixture. To allow great swelling of the O-MMT, the suspension was subjected to ultra-sonication process using Branson Digital Ultrasonic Distruptor/Homogenizer, Model 450D. The suspension was ultrasonicated under 20 kHz amplitude for 5 minutes (10 seconds pulse on and 2 seconds pulse off). The obtained white precipitate was collected by suction filtration and placed in the oven at 50 °C for 48 hours to ensure complete drying. Finally, the dried powder was ground and sieved to de-agglomerate the clay. It was stored in desiccators to ensure dry atmosphere. The process parameters were summarized in Table 1.

Table 1: Pre-swelling parameters of O-MMT prepared through the combination of magnetic stirring and ultra-sonication technique

Dispersant Concentration H <sub>2</sub> O : O-MMT	Time for Magnetic stirrer	Time for Probe Sonication (minutes)	Magnitude for Probe Sonication (kHz)	Sample Acronym
5 : 1	2 hours	5 min	20	P1
5 : 2	2 hours	5 min	20	P2
5 : 3	2 hours	5 min	20	P3
5 : 4	2 hours	5 min	20	P4
1 : 1	2 hours	5 min	20	P5

## 2.3 Thermal Analysis

Thermogravimetric Analysis (TGA) was applied to assess both the thermal stability of O-MMT and weight loss arising from degradation of organic surface modifier and silicate (before and after the pre-swelling process). This analysis was run by TGA Pyris Diamond Perkin Elmer analyzer. About five to seven milligrams of O-MMT powder was placed in an aluminium pan and heated to 700 °C at a constant heating rate of 5 °C/min under nitrogen flow. The thermogravimetric (TG) and differential thermogravimetry (DTG) curves were interpreted as the percentage of weight loss versus the function of temperature.

## **2.4 Material Characterization**

X-Ray Diffraction (XRD) was used to examine the efficiency of the pre-swelling technique to increase the basal spacing of the O-MMT nanoclay platelets. XRD experiment was conducted by High resolution X-ray Diffractometer (XRD) device model Phaser-D2 by Bruker company (X'Pert PRO). The testing was run at a diffraction angle ( $2\theta$ ) of  $3^\circ$  to  $30^\circ$ , using a step size of  $0.02^\circ$  and scanning rate of  $1^\circ\text{min}^{-1}$ . The XRD equipment used  $\text{CuK}\alpha$  radiation operated at 40 mA and 45 kV for the testing. Powder samples were packed in horizontally held trays. The XRD data were analysed using high score plus software. The basal spacing of the O-MMT was calculated based on the peak position ( $2\theta$ ) and peak width at half maximum height in the XRD spectra by utilizing Bragg's law such as

$$\sin \theta = \frac{n\lambda}{2d} \quad (1)$$

where  $\theta$  is the angle between the incident x-ray and the surface of the crystal lattice,  $\lambda$  is the wavelength of x-ray radiation, while  $d$  is the spacing between layers in the clay lattice used in the diffraction experiments.

## **2.5 Morphological Analysis**

Field Emission Scanning Electron Microscope, (FESEM) (JOEL, JSM-7800F, Japan) were used to evaluate and observed the surface morphology of the O-MMTs (in origin state and pre-swelled) powder. Samples were placed on the aluminium casing with a carbon nanotape followed by a sputter coating with platinum at an accelerating voltage of 20 kV to make them conductive and reduce the effect of charging before FESEM analysis. The magnifications of the sample were set at  $50,000\times$  and  $200,000\times$ , respectively.

## **3.0 RESULTS AND DISCUSSION**

### **3.1 Thermal Analysis**

TGA analysis provides the information about the thermal stability behaviour of the origin O-MMT and the pre-swelled O-MMT which was prepared using the combination of magnetic stirring and ultrasonication processes. Figure 1(a) expresses the weight loss (as a function of temperature) of the O-MMT and pre-swelled O-MMT.

Figure 1(b) display the DTG curves of all the materials. Their thermal degradation peak temperature ( $T_{dmax}$ ) and percentage of mass loss are summarized in Table 2.  $T_{dmax}$  refers to decomposition temperature where the maximum mass loss is observed. Based on the analysis, the decomposition pattern of the pristine O-MMT and all the pre-swelled O-MMTs is similar, where three well-defined degradations (mass loss) steps appeared. The first step of mass loss which is attributed to removal of absorbed water and gases occurred in the  $T_{dmax}$  around 65 °C. The second step mass loss which correlated to the chemical decomposition of the organic surface modifier (dimethyl dialkyl amine) was observable at  $T_{dmax}$  range of 290 °C to 323 °C. Finally, the  $T_{dmax}$  for the third step mass loss appeared in the range of 545 °C to 580 °C due to dehydroxylation of structural ~OH units from the O-MMT layers. This finding is similar as reported by Hamid and Osman [12], Xi et al. [15] and Cárdenas et al. [16].

Among all the samples, O-MMT which underwent pre-swelling process using H<sub>2</sub>O/O-MMT ratio of 1:1 (samples P5) appears to be the most thermally stable clay as its  $T_{dmax}$  of the third step mass loss was the highest. Furthermore, the percentage of weight loss during the second step degradation process was similar to the origin O-MMT, showing that the organic surface modifier has not further decomposed upon the pre-swelling process. Due to this result, we further analyse the pre-swelled O-MMT which prepared using greater O-MMT concentration (H<sub>2</sub>O/O-MMT ratio equal to 5:6). This was done to allow the determination of the best dispersant concentration for enhancing the thermal stability of the O-MMT. The sample referred as P6. The data summarized in Figure 1 and Table 2 confirmed that the thermal stability of the P6 was the lowest among all the O-MMTs. Therefore, further analysis on this sample was not performed. Obviously, the results suggest that pre-swelling process through the combination technique did not reduce the thermal stability of the surface modifier if the ratio of O-MMT was similar or lower than water. Higher ratio of O-MMT used in the pre-dispersing medium would reduce the thermal stability of the O-MMT. In the P5 sample, it seems that the platelets arrangement upon the pre-dispersing process did not allow more heat being absorbed into the clay inter-gallery and broke the surface modifier's bonds. Therefore, the thermal stability of the surface modifier maintained.

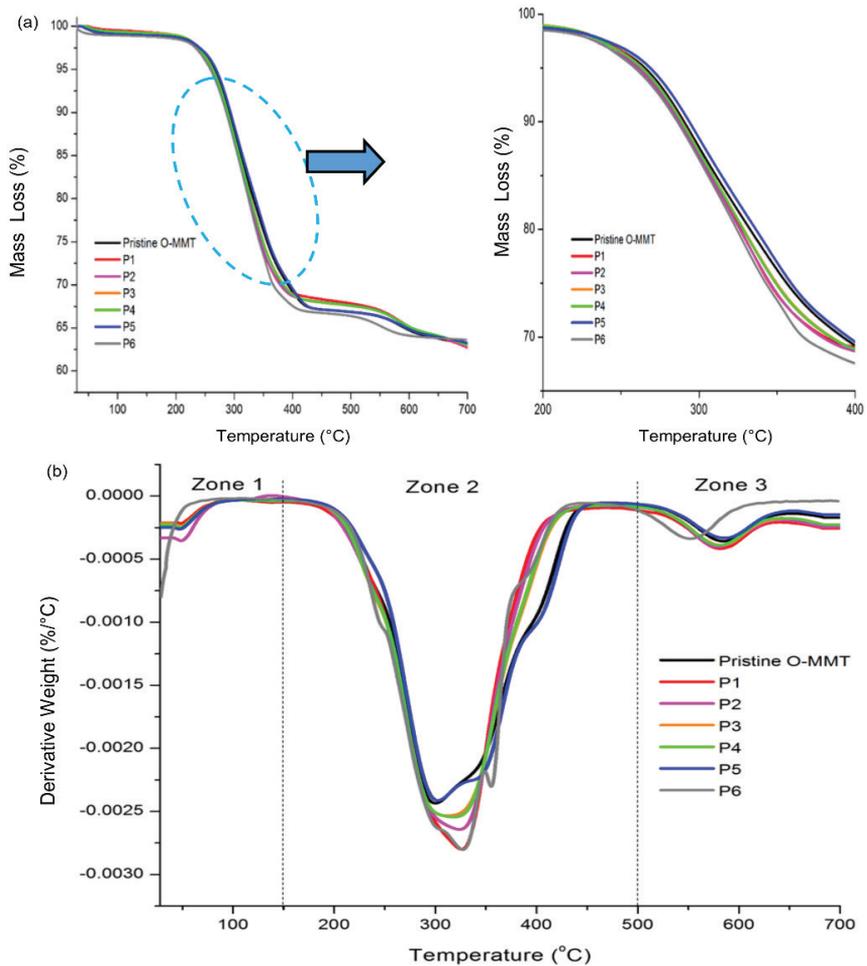


Figure 1: (a) Thermogravimetric curves and (b) Derivative thermogravimetry (DTG) curves of the O-MMT and pre-swelled O-MMTs

Table 2: Thermal degradation peak temperature (T<sub>dmax</sub>) of the Pristine O-MMT and pre-swelled O-MMTs (P1, P2, P3, P4, P5 and P6)

Nanoclay	1 <sup>st</sup> step mass loss		2 <sup>nd</sup> Step mass loss		3 <sup>rd</sup> Step mass loss	
	T <sub>dmax1</sub> (°C)	% Mass Loss	T <sub>dmax2</sub> (°C)	% Mass Loss	T <sub>dmax3</sub> (°C)	% Mass Loss
Pristine O-MMT	~65	~0.5	290	10	570	34
P1			322	19	577	34
P2			320	18	574	34
P3			308	15	577	34
P4			311	16	575	34
P5			298	10	580	35
P6			323	20	545	35

### 3.2 Analysis on Phase and Crystallite Size

XRD was performed to analyse changes in basal spacing of the O-MMT upon the pre-dispersing process by the combination of magnetic stirring and ultra-sonication technique. Figure 2 displays the XRD pattern of the origin O-MMT, P1, P2, P3, P4 and P5. Table 3 summarized the basal spacing  $d_{001}$  values of all the materials. It can be seen that the pristine O-MMT exhibits diffraction peaks at  $2\theta = 3.35^\circ$ ,  $6.90^\circ$ ,  $19.61^\circ$  and  $26.52^\circ$ , which correspond to basal spacing's of 2.6 nm, 1.3 nm, 0.4 nm and 0.3 nm, respectively. To allow clear comparison on the  $d_{001}$  basal spacing of the pristine and pre-swelled O-MMTs, the diffraction region between  $2\theta = 3^\circ$  to  $10^\circ$  was focused. Generally, the XRD patterns of P1, P2, P3, P4 and P5 are similar with the pristine O-MMT [12, 17]. However, it is clearly observed that the  $d_{001}$  peak of the P5 sample was shifted to lower  $2\theta$  angle as compared to the  $d_{001}$  peak of the pristine O-MMT. It is generally understood that an increase in the interlayer distance of the O-MMT leads to a shift of the diffraction to lower diffraction angles [2]. Therefore, greater  $d_{001}$  basal spacing is observed in the P5 sample, with a value of 2.9 nm (Table 3).

Table 3: The diffraction peaks and associated basal spacing of the origin O-MMT and pre-swelled O-MMTs (P1, P2, P3, P4 and P5)

Sample	$2\theta$ (degree)	$d_{001}$ (nm)	$2\theta$ (degree)	$d_{002}$ (nm)	$2\theta$ (degree)	$d_{003}$ (nm)	$2\theta$ (degree)	$d_{004}$ (nm)
O-MMT	3.35	2.6	6.90	1.3	19.61	0.4	26.52	0.3
P1	3.39	2.6	6.97	1.3	19.77	0.4	26.62	0.3
P2	3.43	2.6	6.92	1.3	19.68	0.4	26.54	0.3
P3	3.48	2.6	7.14	1.2	19.89	0.4	26.66	0.3
P4	3.48	2.6	-	-	19.53	0.4	26.44	0.3
P5	3.24	2.9	6.92	1.4	19.60	0.4	26.64	0.3

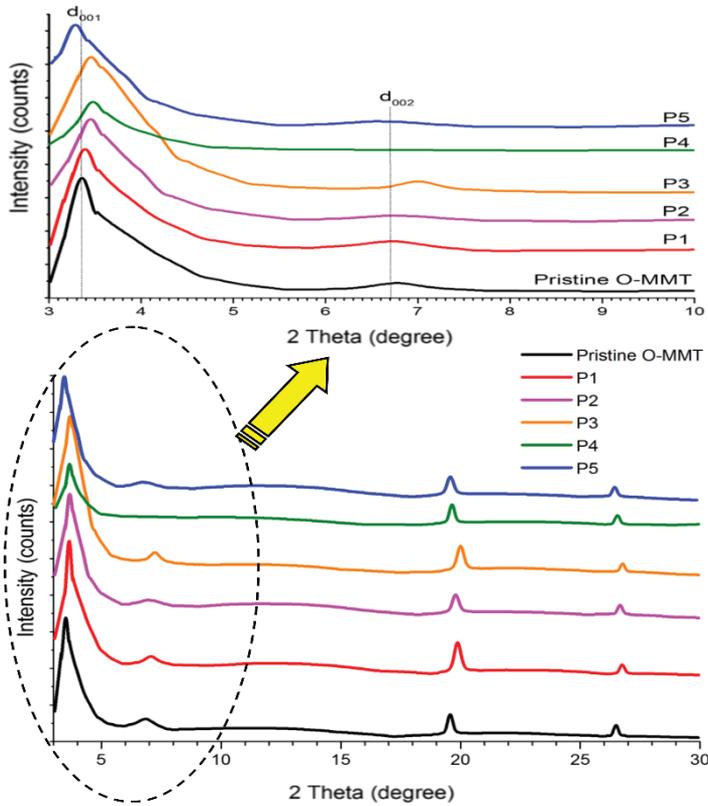


Figure 2: X-ray diffraction patterns of the pristine O-MMT and pre-swelled O-MMTs (P1, P2, P3, P4 and P5)

This indicates that the basal spacing of the O-MMT increased upon the pre-dispersing process using the combination of magnetic stirring and ultra-sonication in water medium ( $H_2O/O\text{-MMT}$  ratio = 1:1). Using other  $H_2O/O\text{-MMT}$  ratios could not efficiently enhanced the exfoliation of the O-MMT. As seen in the XRD data, other pre-swelled O-MMTs (P1, P2, P3 and P4) have similar  $d_{001}$  basal spacing with the pristine O-MMT.

From the XRD analysis, it is clear that the P5 sample possesses the largest basal expansion among all the pre-swelled samples. These indicate that the ultra-sonication process improved the effectiveness in dispersing and exfoliating clay platelets when combined with the magnetic stirring. This was because; the ultra-sonication process involved the high-speed impinging liquid jets and strong hydrodynamic shear-force [18-19]. As illustrated in Figure 3, the

ultrasound propagated in the form of attenuated waves and entering the stacked clay platelets (tactoids) through development of small vacuum bubbles known as “cavitation”. The tactoids were then “peeled off” into loosely packed nano-platelets, thus the clay galleries (interlayer spacing) opened. These effects would disrupt the ordering and orientation of the OMMT platelets.

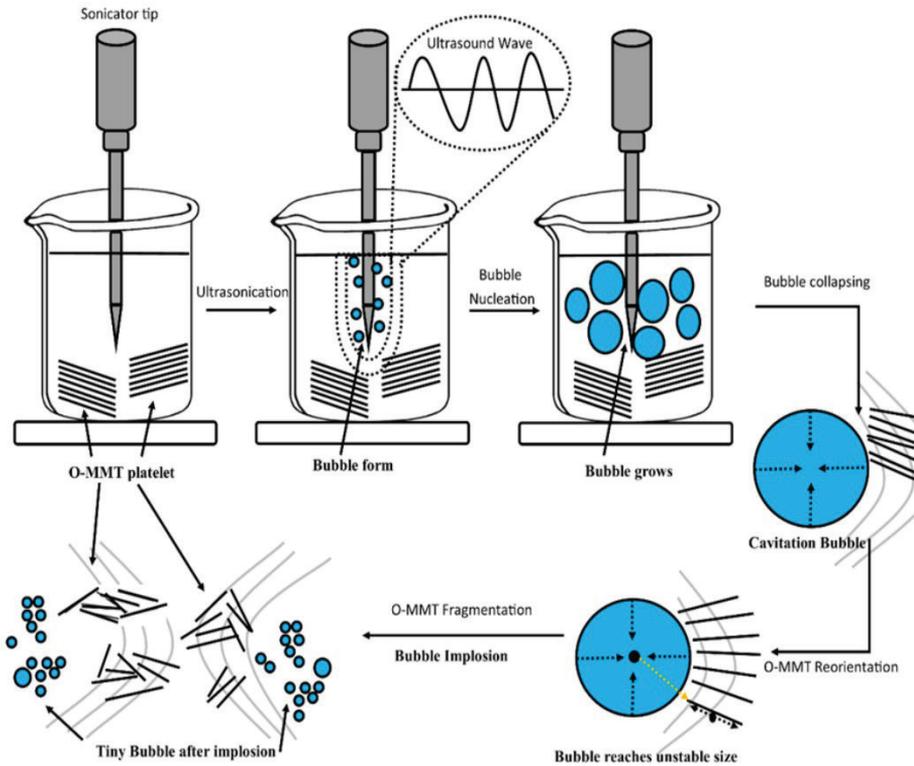


Figure 3: The proposed mechanism on how ultra-sonication can assist for the O-MMT exfoliation/dispersion during the pre-swelling process

### 3.3 Exfoliation Properties

The FESEM images of the pristine O-MMT and the pre-swelled O-MMTs (P5) are shown in Figure 4. The ultra-sonicated O-MMT has formed porous-agglomerated structure due to enhancement in platelet spacing and disorganization of the platelets. These showed successful improvements in the nano-platelet exfoliation. The FESEM data of the P5 sample is consistent with its XRD and TGA results, where greater interlayer spacing and deeper pore underneath was obtained due to the formation of the ‘house of card’ structure [20].

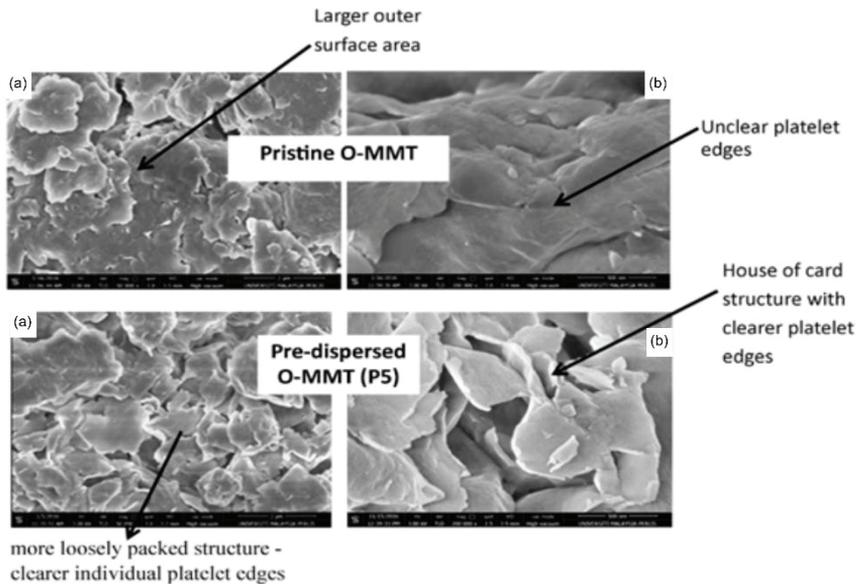


Figure 4: FESEM images of the Pristine O-MMT and pre-swelled O-MMT (P5) taken at (a) 50,000 $\times$  and (b) 200,000 $\times$  magnification

As illustrated in Figure 5, there are two possibilities of O-MMT structure and platelets arrangement after underwent pre-dispersing process by the combination of magnetic stirring and ultra-sonication process: i) Upon pre-dispersing in water medium ( $H_2O/O\text{-MMT}$  ratio = 1:1), the platelets might be tilted/misaligned/disoriented, forming house of card structure. Slight increase in the average basal spacing can be obtained. ii) Upon pre-dispersing in water medium ( $H_2O/O\text{-MMT}$  ratio = 5:1, 5:2, 5:3 and 5:4) the platelets might be tilted, misaligned/disoriented in few degrees due to the stirring and ultra-sonication effect. However, the average basal spacing/distance remains the same. The results suggest that the dispersant (water) concentration affect greatly the exfoliation behaviour and disorganization of the O-MMT platelets. The most ideal composition of pre-dispersing medium is  $H_2O/O\text{-MMT}$  ratio equal to 1:1 because in such condition, the disorientation and disorganization of platelets can most easily occur.

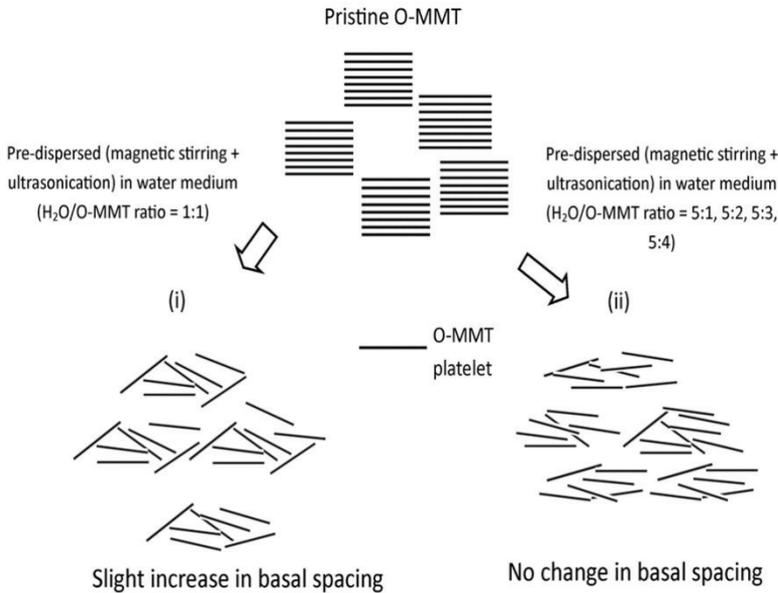


Figure 5: Possibility of O-MMT platelets arrangement and delamination upon pre-dispersing process by the combination of magnetic stirring and ultra-sonication

#### 4.0 CONCLUSION

The effects of dispersant concentration on the structure and morphology of the O-MMT was studied in order to optimize the pre-swelling process of the O-MMT, to prepare it as readily exfoliated nanoclay filler for polymer nanocomposite production. Among all the pre-swelled O-MMTs, the one prepared using the  $H_2O/O\text{-MMT}$  ratio of 1:1 had the best thermal stability. As proved through the XRD analysis, this sample possesses larger basal spacing as compared to the pristine O-MMT and FESEM analyses suggested that disorientation and misalignment of platelets occurred, forming 'house of card' structure. This type of structure is beneficial in terms of assisting polymer chains intercalation in between the O-MMT platelets and thereby, promoting greater platelets exfoliation and dispersion during the nanocomposite formation.

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