

**PRE-DISPERSING PROCESS USING THE COMBINATION OF
MAGNETIC STIRRING AND ULTRA-SONICATION TECHNIQUE: THE
EFFECTS ON STRUCTURE AND MORPHOLOGY OF THE ORGANICALLY
MODIFIED MONTMORILLONITE**

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ABSTRACT: Organically modified montmorillonite (O-MMT) can be effective nanofiller in enhancing the performance of the polymer nanocomposite if their nanoplatelets are well dispersed throughout the matrix. In this research, pre-dispersing process of the O-MMT was done to obtain more loosely packed and readily dispersed platelets, prior to melt compounding process with the polymeric matrix. The 'pre-dispersed O-MMT' could allow greater polymer chain intercalation in between the loosely packed platelets, thereby improving its level of dispersion inside the polymer matrix. Well-dispersed O-MMT platelets were targeted in order to optimize the properties of the resultant polymer nanocomposite. In this work, the pre-dispersing process was done through the combination of magnetic stirring and ultra-sonication technique. The effects of dispersant concentration on the structure and morphology of the pre-dispersed O-MMT were studied. Among all the pre-dispersed O-MMTs, the one prepared using the H₂O/O-MMT ratio of 1:1 had the best exfoliation characteristic. BET and FeSEM analyses suggested that disorientation and misalignment of platelets occurred, forming 'house of card' structure. More porous and loosely packed platelets were obtained. This particular morphology benefits in facilitating the intercalation of polymer chains in between the O-MMT platelets and improving the O-MMT dispersion during the compounding process with the polymer resin.

KEYWORDS: *Organically modified montmorillonite; Pre-dispersing; Morphology; Structure; Brunauer–Emmett–Teller (BET)*

1.0 INTRODUCTION

The successful of polymer nanocomposite is much depends on the degree of nanofiller dispersion in the matrix material. Therefore, scientific research on the optimization of the nanofiller dispersion is crucial. Nanoclay attracts much attention as high aspect ratio nanofiller. However, dispersion of native clays in most polymeric matrices is not easily achieved due to the intrinsic incompatibility of the hydrophilic clays and hydrophobic synthetic engineering polymers (Osman et al., 2017; Wang & Mao, 2012). Moreover, the high surface area and energy of the nanoclays may highly induce the formation of platelet stacking or tactoids, thus inhibit the full function of nanoclay as the reinforcing nanofiller. In order to successfully develop polymer-clay based nanocomposites, it is necessary to chemically modify natural clay so that it can be compatible with a chosen polymer matrix. Therefore, surface modification of the clay nanofiller using organic surface modifiers is commonly applied to render the clay surface hydrophobic and subsequently enhance the compatibility between the nanoclay and the hydrophobic polymer matrix. Generally, this can be done through ion exchange

reactions by replacing interlayer cations with quaternary alkylammonium or alkyl phosphonium cations (Theng, 2012). The resultant organically modified clay or 'organoclay' material can be better nanofiller to reinforce the synthetic, hydrophobic polymers. In this study, the commercially available surface modified MMT was used as nanofiller. It contains dimethyl dialkyl (C14–C18) amine surface modifier, which make it compatible with the synthetic hydrophobic polymer.

Even though the use of surface modified MMT can solve the problem regarding compatibility, to obtain the highly exfoliated organoclay in the polymer matrix is not really an easy task. Large number of publications indicated that the application of surface modification alone could not promise the production of thoroughly exfoliated organoclay as dispersed phase in host polymer (Kotal & Bhowmick, 2015; Osman et al., 2016; Osman, Alakrach, Kalo, Azmi, & Hashim, 2015; Michael, Khalid, Walvekar, Ratnam, Ramarad, Siddiqui, & Hoque, 2016). Dispersion of nanofiller in host polymer has become critical issue in most polymer/clay based nanocomposite systems, including ethylene vinyl acetate (EVA)/MMT nanocomposite. Previous work revealed that the incorporation of O-MMT had resulted in significant improvement in tensile properties and biostability of the EVA matrix when low loading (1 wt%) of this nanofiller was employed (Osman et al., 2017). However, when higher loading of O-MMT was added (5 wt%), the reduction in both properties was observed (Osman, Alakrach, Kalo, Azmi, & Hashim, 2015). The leading cause of this phenomenon was due to the reduced quality of O-MMT dispersion and exfoliation in the EVA matrix. Therefore, additional procedure might be needed to further assist the exfoliation of the organoclay into individual clay platelets and improve their dispersion quality inside the host materials. In conjunction with this matter, this present work deals with a pre-dispersing technique using magnetic stirring and ultra-sonication to improve the dispersion and exfoliation capability of the O-MMT nanofiller. The effect of dispersant concentration on the morphology and structure of the O-MMT and the resultant polymer nanocomposite was studied to optimize the pre-dispersing process.

2.0 MATERIALS AND METHOD

The commercial nanoclay used was montmorillonite surface modified with 35-45 wt% dimethyl dialkyl (C14–C18) amine and is herein referred to as organo-montmorillonite (O-MMT). This O-MMT known as Nanomer (types 1.44P) was manufactured by Nanocor (Hoffman Estates, IL, USA) and supplied by Sigma-Aldrich (USA). Deionized water was used as pre-dispersing medium to allow swelling of the O-MMT due to its low cost, non-toxic and suitability for bulk industrial production. The dispersant concentrations (H₂O: O-MMT) of 5:1, 5:2, 5:3, 5:4 and 5:5 (1:1) were used for the pre-dispersing process by magnetic stirring + ultrasonication. The procedures were explained elsewhere (Hamid & Osman, 2018). The pre-dispersing process parameters using this route were summarized in Table 1.

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

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

3.0 RESULTS AND DISCUSSION

Figure 1 (a) showed the N₂ adsorption-desorption curves of the pristine O-MMT, P1, P2, P3, P4 and P5 while Figure 1 (b) showed their distribution of pore size. The results of the BET analysis were summarized in Table 2.

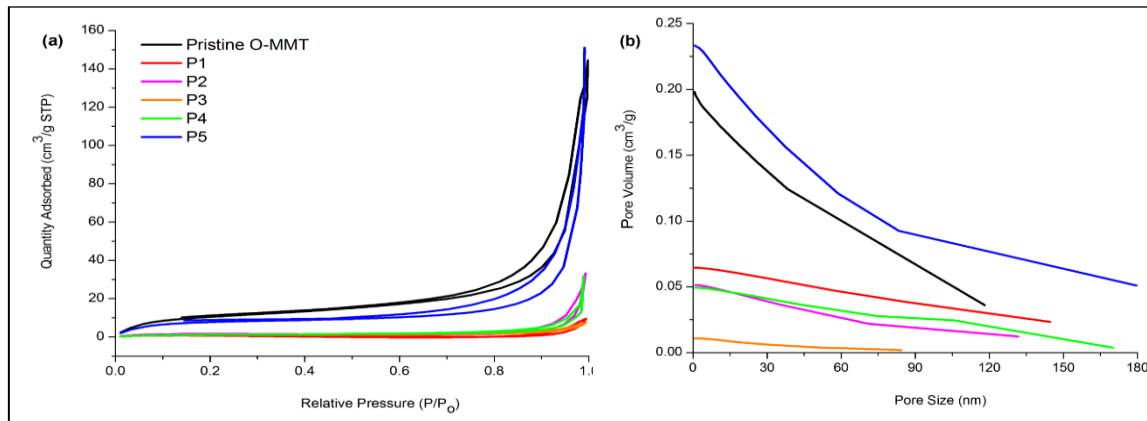


Figure 1: (a) N₂ adsorption-desorption curves; (b) distribution of mesopores size for the Pristine O-MMT and pre-dispersed O-MMTs (P1, P2, P3, P4 and P5)

Table 2: Specific surface areas calculated by BET Isotherm, Pore Volume and Pore Size for the Pristine O-MMT and pre-dispersed O-MMTs (P1, P2, P3, P4 and P5)

Sample	BET Surface Area (m ² /g)	Micropore Volume (cm ³ /g)	Total Pore Volume (cm ³ /g)	Average Pore Size (nm)
Pristine O-MMT	40.94	-0.003	0.163	15.96
P1	5.12	0.002	0.018	14.69
P2	5.43	0.001	0.017	12.60
P3	3.88	0.0002	0.008	7.82
P4	4.18	-0.0002	0.016	14.83
P5	21.2	-0.0002	0.068	12.83

The N₂ adsorption-desorption isotherms of the BET has strongly implied the distribution of different types of pore in the tested particles which can be categorized as micropores (0 nm to 2 nm), mesopores (between 2 nm to 50 nm) and macropores (more than 50 nm) (Zainal Abidin, Mohamad, Bani Hashim & Adbullah, 2016). Furthermore, the shape of the isotherm curve indicates the qualitative assessment of the porous materials. As referred to Figure 1(a), the pristine O-MMT powder showed a significant mesopores Type IV nitrogen isotherm plot with H3 hysteresis loops, indicating the presence of slit-like pores. This pristine O-MMT also possesses steep slopes in the relative pressure range (p/p_0) of 0.80–1.00. Based on the adsorption-desorption pattern (Figure 1a), all the prepared samples showed a small distribution area of the isotherm curves (hysteresis). This small area obtained suggested that the number of N₂ gas molecules adhered to the surface (not desorbed) of the O-MMT powder is small due to presence of organic surface modifier's chains in the inter-gallery of the O-MMT platelets. The pristine O-MMT shows higher adsorption peak and larger hysteresis loop than the P1, P2, P3 and P4 samples, suggesting that it contains higher surface area platelets. The BET surface area of the pristine O-MMT is 40.9 m²/g but reduced when it is pre-dispersed by the combination of magnetic stirring and ultrasonication processes. As clearly seen in Table 2, P3 sample shows the smallest surface area which is 3.88 m²/g. Among all the pre-dispersed O-MMTs, P5 shows the highest value of surface area, which is 21.2 m²/g. The BET data also suggest that the pristine O-MMT contains mesopores with a diameter of 15.96 nm, whilst its total pore volume is 0.163 cm³/g. In contrary, the pre-dispersed samples (P1, P2,

P3 and P4) show smaller pore diameter with lower pore volume. Referring to Figure 1b, the O-MMT possesses large difference in the pore size distribution upon the pre-dispersing process. Apparently, the P1, P2, P3 and P4 samples exhibit smaller pore size and pore size distribution than the pristine O-MMT. Interestingly, the P5 sample shows different pore characteristic. Eventhough the P5 shows smaller pore size than the pristine O-MMT, its pore size distribution is greater. As illustrated in Figure 2, this could be due to the misalignment and disordering of its platelets arrangement, which affect the measurement of its surface area and pore size. The ultra-sonication process had provided high energy sonic waves to reduce the O-MMT interlayer electrostatic bonding energy and subsequently disrupt the ordering and orientation of the OMMT platelets. As a result, the platelets turned into 'house of card' arrangement, having smaller surface area but deeper pore underneath. In some soils, the clay minerals are arranged in random fashion, with much pore space between the individual platelets. This is often referred to as a "house of cards" structure (Mirghasemi, & Bayesteh, 2015).

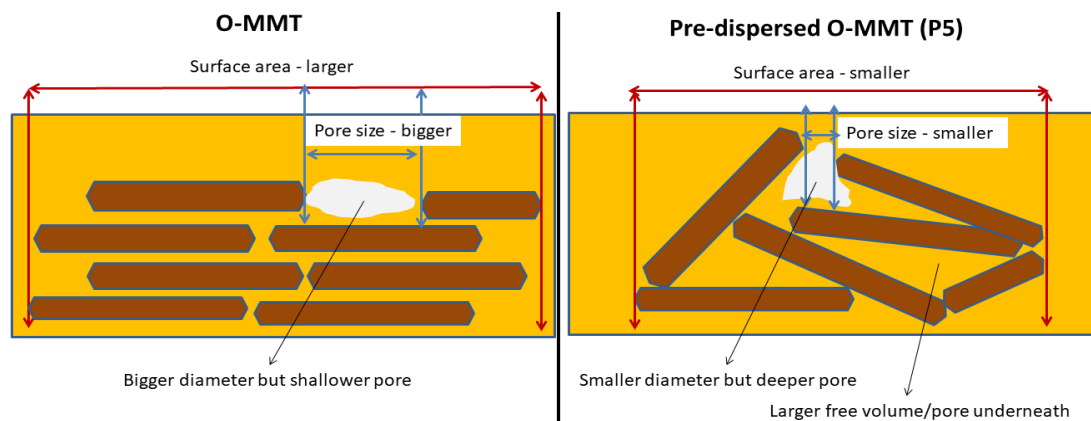


Figure 2: O-MMT nanoplatelets arrangement in the pristine O-MMT and Pre-dispersed O-MMT (P5)

The FeSEM images of the pristine O-MMT and the pre-dispersed O-MMTs (P5) are shown in Figure 3.

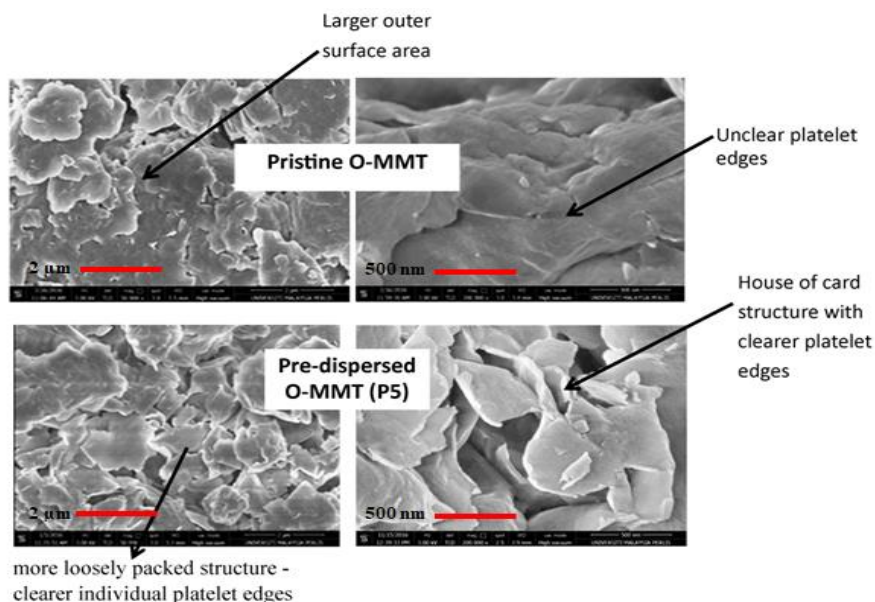


Figure 3: FeSEM images of the pristine O-MMT and pre-dispersed O-MMT (P5) taken at 50,000x (left) and 200,000x (right) magnification.

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 nanoplatelet exfoliation. The FeSEM data of the P5 sample is consistent with its BET results, where greater

interlayer spacing and deeper pore underneath was obtained due to the formation of the 'house of card' structure.

4.0 CONCLUSION

The O-MMT has been pre-dispersed using the combination of magnetic stirring and ultra-sonication technique. The BET results suggest that the 'outer' surface area of the O-MMT nanoplatelets (P5 sample) reduced due to their resultant 'house of card' structure formation upon the ultra-sonication process. This structure reduced the 'surface pore size' but enhanced the 'underneath pore size' of the O-MMT. In agreement with the BET results, FESEM images show rougher powder surface in P5 sample due to disorientation/misalignment of the platelets, forming 'house of card' structure. Furthermore, more loosely packed platelets were observed. In summary, the best O-MMT exfoliation characteristic was obtained when dispersant concentration ($H_2O/O\text{-MMT}$ ratio) = 1:1 was employed.

5.0 REFERENCES

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