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Research paper

Effects of Ultrasonication Time on Thermal Stability and Swelling Behaviour of The Commercial Organo-Montmorillonite (O-MMT)

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Abstract

In this contribution, we report the effect of ultrasonication time on thermal stability and swelling of organically modified montmorillonite (O-MMT) upon ultrasonication in a water medium. In the production of well-exfoliated polymer/clay nanocomposite, ultrasonication was employed as a method to exfoliate and disperse organically modified montmorillonite (O-MMT) platelets prior to melt compounding with the polymer matrix. The suspension of distilled water and O-MMT was magnetically stirred for 2 hours and then ultrasonicated at the different sonicating time, namely, 2 minutes, 5 minutes, 10 minutes, 15 minutes and 20 minutes (min) at room temperature. Thermogravimetry analysis (TGA) suggested that dispersion of the O-MMT by ultrasonication for 5 minutes resulted in thermal stability enhancement without destruction of the organic surface modifier structure and bonding on the clay platelets. X-ray diffraction (XRD) also indicated that application of 5 minutes ultrasonication time has most obviously improved the swelling of the O-MMT platelets. This was further proved by Field emission scanning electron microscope (FeSEM) which revealed greater interlayer spacing within the O-MMT platelets was obtained.

***Keywords**: Ultrasonication; Organically modified montmorillonite; Sonicating time; Exfoliation; Dispersion.*

1. Introduction

Industry and academia have extensively studied and used smectite clays such as montmorillonite, hectorite, and saponite to improve the properties of the polymer [1-3]. The unique chemical and physical structures of these layered silicates have attracted the development of clay-based polymer nanocomposites. Among nanoclays, montmorillonite (MMT) stands out as the most commonly used filler material in polymers. MMT belongs to the general family of 2:1 layered or phyllosilicates. The thickness of an individual layer is around 1 nm, but the lateral dimensions of nano layers may vary from 100 nm to several microns [4]. An interesting behavior of MMT is its ability to swell in both polar and non-polar molecules, as their inter-galleries is sensitive to the absorption of both types of ancillary molecules [5,6]. In its pristine state, MMT possesses high surface area and surface reactivity of platelets. The platelets can extremely stack to form ‘tactoids’ and not easily exfoliated and dispersed when compounding with the polymer matrix. Surface modification of the MMT with the organic surface modifier can reduce the size of tactoids as the clay interlayer spacings can be increased due to the inclusion of the bulky surface modified molecules. Furthermore, MMT modified with the organic surface modifier is preferably miscible with the organic and polymeric materials due to the transformation of its hydrophilic surface into hydrophobic characteristic [7]. Therefore, the application of this organically modified MMT (O-MMT) as nanofiller in polymer matrices is more preferred compared to the pristine MMT. However, high-performance polymer/O-MMT nanocomposite can only be obtained if the organoclay is fully exfoliated within the host polymer structure. Unfortunately, the presence of organic surface modifiers could not guarantee the formation of fully exfoliated O-MMT in the polymer matrix [8,9]. The additional method might be needed to exfoliate and disperse the O-MMT prior to mixing with the polymers. However, it is important to ensure that this additional dispersing method would not leach out or degrade the surface modifier of the O-MMT, and subsequently decrease its thermal stability. This is because; thermal degradation of the organic surface modifier during high melt compounding process temperature can reduce the properties of the resultant polymer/O-MMT nanocomposites. Ultrasonication has been used as a technique to disperse nanomaterials without destruction of their chemical structure [10-12]. Yet, the efficiency of the ultrasonication in exfoliating the nano-size O-MMT platelets without degradation of surface modifier is still unknown. Therefore, in this work, we have employed ultrasonication method and investigated its capability in swelling/exfoliate the O-MMT, before this nanofiller is used to reinforce the polymer matrices. Herein, we report the effect of ultrasonication time on thermal stability and swelling behaviour of the organically modified montmorillonite (O-MMT) upon the dispersing process in a water medium.

2. Material

The organically modified montmorillonite (O-MMT) with the chemical formula $(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2{\cdot}nH_2O$ was supplied by Sigma-Aldrich (USA). This commercial organoclay known as Nanomer (types 1.44P) appears in off-white colour powder and was organically surface modified with 35-45% dimethyl dialkyl amine (C14–C18) as an organic surface modifier. Deionized water was used as a pre-dispersing medium to allow swelling of the O-MMT particles.

2.1. Sample Preparation

The suspension of distilled water and O-MMT in the ratio of 1:1 was firstly magnetically stirred for 2 hours at room temperature until homogeneous. The swelling process was continued using the ultrasonication probe with different sonicating time, namely, 2 min, 5 min, 10 min, 15 min and 20 min at room temperature under the 20 kHz amplitude with a pulse on at 10 seconds and pulse off at 2 seconds. Then, the suspension was allowed to fully dry in the oven for 48 hours. Finally, the resultant ultrasonicated powder was ground and sieved to diminish agglomeration.

3. Characterization

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3.1. Thermogravimetric Analysis (TGA)

Thermal stability of the specimens was studied by thermogravimetric analysis (TGA) using TGA Pyris Diamond Perkin Elmer analyzer. The TGA scans were recorded at a constant heating rate of 5 °C/min, under nitrogen flow and temperature from 30 to 700 °C.

3.2. X-ray diffraction (XRD)

The degree of O-MMT swelling (d-spacing), before and after the ultrasonication process was compared by X-ray diffraction (XRD). The analysis was carried out using a high-resolution X-ray Diffractometer (XRD) device model Phaser-D2 manufactured by Bruker company (X'Pert PRO). The experiment was run at room temperature with an angle range (2θ) from 10° to 30° at a scanning rate of 2° min^{-1} and step size of 0.02° using CuKα radiation operating at 45 kV and 40 mA.

3.3. Field Emission Scanning Electron Microscope (FeSEM) analysis

The morphology of the pristine and ultrasonicated O-MMT powder was observed using a (JOEL, JSM-7800F, Japan) field emission scanning electron microscope. The samples were examined at magnifications of 50 000x and 200 000x.

4. Results and Discussion

4.1. TGA

Thermal stability of the pristine and ultrasonicated O-MMT was determined using thermogravimetric analysis (TGA). The TGA and derivative thermogravimetry (DTG) curves of all the samples are shown in Figure 1(a) and 1(b), respectively, while the thermal degradation peak temperature (Tdmax) and percentage of mass loss are summarized in Table 1.

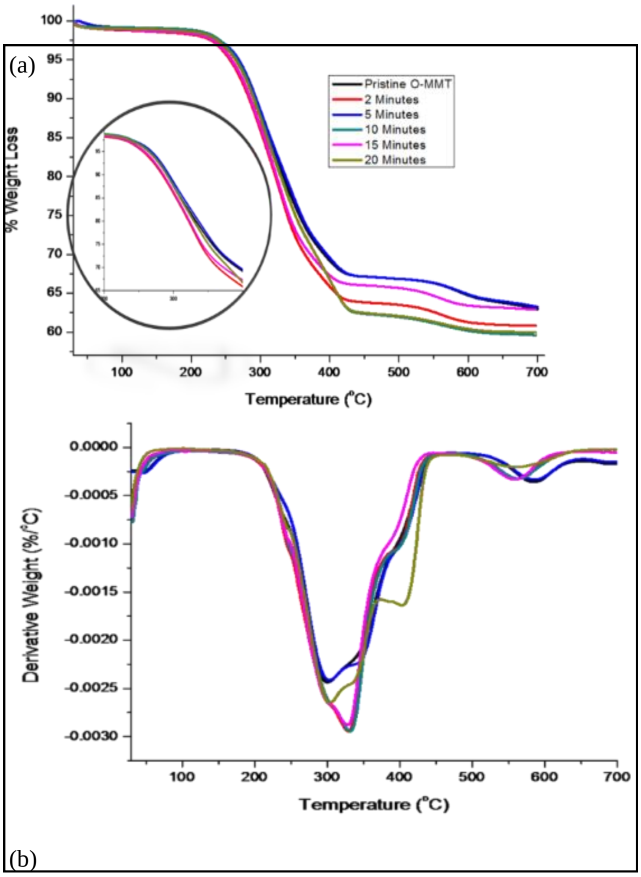


Figure 1: (a) TGA (b) DTG curves of the pristine O-MMT and ultrasonicated O-MMT with different sonicating time

Based on the analysis, the decomposition pattern of the pristine O-MMT and all the ultrasonicated O-MMTs is similar, where three well-defined degradations (mass loss) steps appeared. For all samples, the first step mass loss occurred at Tdmax of~45°C and could be related to the evolution of absorbed water and gases (which generally occurred below 150 °C). The second step mass loss was observable at Tdmax range of 290 to 326°C, and mainly occurred due to the chemical decomposition of the bonded structure of the organic surface modifier. Finally, the Tdmax for the third step mass loss appeared in the range of 549 to 552 °C due to dehydroxylation of structural ~OH units from the O-MMT layers [13].

Table 1: Thermal degradation peak temperature (T_{dmax}) of pristine and ultrasonicated O-MMT

Nanoclay	First step mass loss		Second Step mass loss		Third Step mass loss	
	T_{dmax} (°C)	% Weight Loss	T_{dmax} (°C)	% Weight Loss	T_{dmax} (°C)	% Weight Loss
Pristine O-MMT	~ 45-46	~ 0.5	290	10	568	34
2 minutes			322	19	555	37
5 minutes			299	11	580	35
10 minutes			302	17	563	38
15 minutes			326	18	550	36
20 minutes			304	22	557	38

Among all the samples, O-MMT ultrasonicated in 5 minutes appears to be the most thermally stable clay as its Tdmax of the third step mass loss was the highest. Furthermore, the percentage of weight loss during second step mass loss achieved the lowest value among all the ultrasonicated O-MMTs and it is almost similar to the pristine O-MMT. This shows that the organic surface modifier has not detached and degraded upon 5 mins of ultrasonication process in water. The increase in the percentage of second step weight loss in other ultrasonicated O-MMT samples showing that greater number of surface modifier chains have detached and thermally degraded at elevated temperatures. Long ultrasonication time could reduce the bonding forces between the surface modifier and the MMT, therefore heating process can degrade the organic chains more easily. The higher amount of degraded organic substances resulted in increased weight loss in the 250-400°C region. Obviously, the results suggest that 5 minutes of ultrasonication did not reduce the thermal stability of the O-MMT because the process can maintain the integrity of the surface modifier and its bonding forces with the MMT.

4.2. XRD

The crystallographic microstructure of the pristine and ultrasonicated O-MMT was characterized using XRD analysis. Figure 2 displays XRD patterns of the pristine O-MMT and ultrasonicated O-MMT with different sonicating time, namely 2 minutes, 5 minutes, 10 minutes, 15 minutes and 20 minutes. Table 2 summarizes the diffraction peak and d-spacing of these samples.

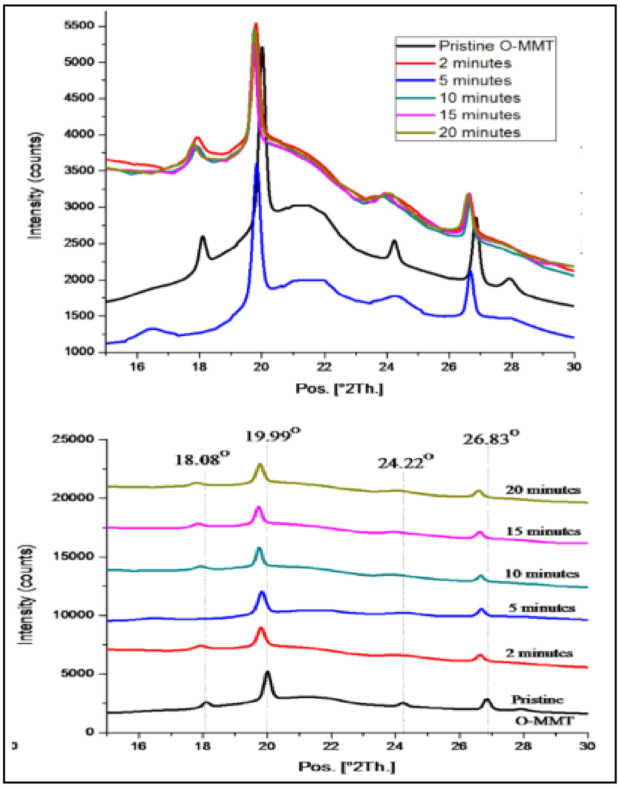


Figure 2: XRD patterns of the pristine O-MMT and ultrasonicated O-MMT with different sonicating time

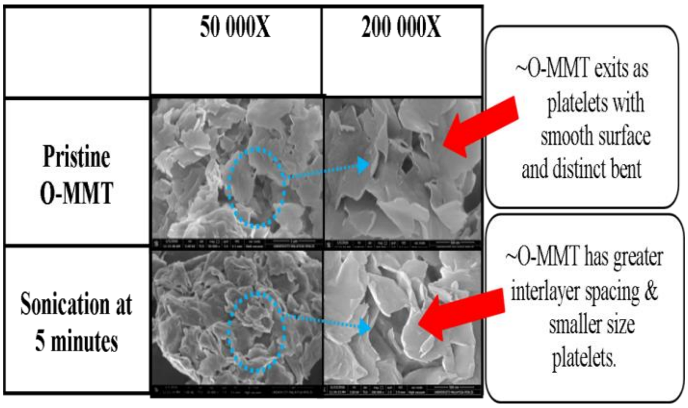
From the XRD results, we can see that the pristine and ultrasonicated O-MMT show several diffraction peaks. Four diffraction peaks were observable at 2θ = 18.08°, 19.99°, 24.22° and 26.83° in the pristine OMMT sample. Mostly, the diffraction peaks for all the ultrasonicated O-MMT were shifted to lower 2θ angles, indicating expansion of the basal spacing due to swelling of the clay platelets. Interestingly, the O-MMT ultrasonicated for 5 mins exhibits the largest basal expansion among all the samples. In addition, more diffuse and less intense diffraction peaks were observed. These results indicate that the ultrasonication process has reduced the OMMT tactoid size by swelling and disrupting the ordering of the OMMT platelets. These effects were obtained through 'destabilization' of the O-MMT interlayer cohesive energy by high energy sonic waves [3,7].

Table 2: The diffraction peak and d-spacing of pristine O-MMT and pre-dispersing of O-MMT with different sonicating time

	[d_{001}]		[d_{002}]		[d_{003}]		[d_{004}]	
	2θ (deg)	d-spacing (nm)	2θ (deg)	d-spacing (nm)	2θ (deg)	d-spacing (nm)	2θ (deg)	d-spacing (nm)
OMMT	18.08	0.49	19.99	0.44	24.22	0.37	26.83	0.33
2 Minutes	17.09	0.49	19.79	0.45	24.19	0.37	26.61	0.33
5 Minutes	16.43	0.54	19.81	0.45	24.30	0.37	26.66	0.33
10 Minutes	17.91	0.50	19.73	0.45	23.82	0.37	26.63	0.33
15 Minutes	17.82	0.50	19.71	0.45	23.92	0.37	26.61	0.34
20 Minutes	17.77	0.50	19.76	0.45	24.07	0.37	26.58	0.34

4.3. FeSEM

FeSEM analysis (Figure 3) was performed to image the structure and ordering of the O-MMT platelets, before and after 5 minutes of ultrasonication. It is clearly evident that the pristine O-MMT exists as platelets with a smooth surface and distinct bent edges [14]. The ultrasonicated O-MMT exhibits nanosize platelets with greater interlayer spacing. During ultrasonication, some of the surface modifier ions and H_2O molecules were driven into the interlayer space. Under the influence of high-speed impinging liquid jets and strong hydrodynamic shear-forces, the platelets were exfoliated at greater interlayer spaces/distances. It is believed that this phenomenon termed as "cavitation" which facilitates the exfoliation of the O-MMT tactoids into thinner tactoids.



~O-MMT exits as platelets with smooth surface and distinct bent

~O-MMT has greater interlayer spacing & smaller size platelets.

Figure 3: FeSEM morphology of pristine and ultrasonicated O-MMT (5 mins) at 50000x and 200000x magnification

5. Conclusion

This paper presents the effects of ultrasonication time on thermal stability and swelling of the commercial O-MMT nanofiller. Optimum ultrasonication time for the O-MMT was found to be 5 mins, where more thermally stable and swelled clay powder was obtained. Disruption in platelets ordering upon the ultrasonication process resulted in smaller tactoid size and more loosely packed OMMT platelets.

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