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Surfactant monoglyceride as an effective and friendly modification agent for nano-layered structure of Montmorillonite

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Abstract

This study focused on the modification of montmorillonite (MMT) using the new modifying agent monoglyceride (M-Gly). M-Gly formed a self-assembled structure in MMT interlayers, which may be used for further study in polymer/clay nanocomposites and cosmetic additives.

The X-ray diffraction results showed the d-spacing of MMT increasing up to 16Å° in solvent and more than 60Å° in the melting method compared to 10Å° with neat MMT. This implies that when the melting method is applied using the internal thermomixer device with a high shear rate, the interlayer space of MMT is expanded considerably. The transmission electron microscopy results showed there was good dispersion of the organoclay layers in modified MMT. This means that the silicate layer structure was disordered with two- or three-layer stacks that were separated after modification. The thermogravimetric analysis also showed the thermal stability of the modified specimens in each method and evidenced the insertion and elimination of M-Gly from the interlayer space of MMT during the modification process.

Keywords: melting method; monoglyceride; multilayers; montmorillonite; organoclay.

1. Introduction

Surface modification of clay minerals has received a great deal of attention because it can be used to create new materials and new applications (Borrego-Sánchez et al., 2018; Wang et al., 2018; Xu et al., 2018). The main focus of the surface modification of clays is to develop new polymer nanocomposites. This kind of material constitutes one of the most widely developed areas of nanotechnology (Beall and Goss, 2004; Jordan, 1949; Lucilene et al., 2008). The first attempt to chemically alter clay galleries with various organic molecules was reported in the late 1940s (Jordan, 1949). Since then a substantial industry has been established to utilize these organically modified clays. Organoclays are also used in other applications such as adsorbents of organic pollutants in soil, water and air; oil well drilling fluids; paints; grease; cosmetics; refractory varnish; and personal care products (Beall and Goss, 2004; Jordan, 1949; Kumar et al., 2015; Lin et al., 2015; Lucilene et al., 2008; Olutoye et al., 2016; Xu et al., 2018; Zhuang et al., 2015).

Several techniques can be employed to modify clays such as adsorption, ion exchange with inorganic cations and organic cations, binding of inorganic and organic anions (mainly at the edges), rafting of organic compounds, reaction with acids, pillaring by different types of poly(hydroxo-metal) cations, intra-particle and inter-particle polymerization, dehydroxylation and calcination, delamination and re-aggregation of smectites, and lyophilization, ultrasound, and plasma (Bergaya and Lagaly, 2001; Ghiaci et al., 2011; Lucilene et al., 2008; Olutoye et al., 2016).

Ion exchange with alkylammonium ions is well known and is the preferential method to prepare organoclays (Lucilene et al., 2008). However, Beall and Goss (Beall and Goss, 2004) also reported that several limitations arise from using quaternary ammonium as a cation exchange medium, such as the toxicity of these compounds and the generation of decomposition polymer nanocomposites that impart an undesirable color, odor and taste, and also degrade the properties of the composite, as we have reported (Nguyen et al., 2016b) and as reported in the literature (Gao et al., 2001; Lucilene et al., 2008; Xie et al., 2002). In addition, with a wide variety of polymers, the commercial availability of quaternary ammonium chemicals, utilized mostly in the fabric-softener industry, does not meet the world's need for polymer nanocomposite elaboration, mainly due to thermodynamic compatibility between the modifying agent and the polymer. On the other hand, the use of organic surfactants that contain groups possessing partial negative charges has resulted in research attempting to find alternative methods to organically modify clays for use in producing polymer nanocomposites. The interaction of such molecules with the clay surface is possible through two mechanisms. The first involves ion-dipole interactions, where the saturating cation on the clay surface serves as an adsorption site for polar non-ionic molecules (Bizovská et al., 2018; Santos et al., 2018). The second type of interaction

involves hydrogen bonding, either by the direct interaction between the adsorbed polymer and the oxygen (or hydroxyls) of the clay surface, or through a “water bridge” between the clay surface and the polymer (Rossi et al., 2003). Numerous studies have been conducted on the molecular association between montmorillonite (MMT) and organic species such as liquid aliphatic amine and polyamines (Alemdar et al., 2005; Lucilene et al., 2008; Pospisil et al., 2002; Xiao et al., 2003), acid and polyacids (Avom et al., 2001; Chou et al., 2005; Dentel et al., 1995; Ghiaci et al., 2011; Olutoye et al., 2016; Tran et al., 2005), alcohol, glycols (Chassin, 1973; Lucilene et al., 2008; Pavlidou and Papaspyrides, 2008; Tran et al., 2006), polyglycols (Lucilene et al., 2008; Pavlidou and Papaspyrides, 2008; Shen et al., 2002; Strawhecker and Manias, 2000; Zhao et al., 1989) and polyglycol ethers (Lucilene et al., 2008). Analysis of these complexes has established that the amines are active in basic exchange, while glycerol and glycol enter the interlayer space without displacing cations (Lucilene et al., 2008; Pavlidou and Papaspyrides, 2008).

Glyceride was formed by the esterification reaction between a fat oil (vegetal oil) or fatty acid and glycerin. Glycerides were used in many food applications or dairy and oil-based products to control emulsion and foam stability. All these applications were based on the potential of M-gly to adsorb at interfaces, to crystallize and co-crystallize (Sagalowicz et al., 2006). In studying a successful application of M-Gly in drug delivery and for food, additional research (Sagalowicz et al., 2006) has shown that an intriguing characteristic of monoglycerides is their capacity to form various self-assembly structures, liquid crystalline phases, if in contact with water. These molecules spontaneously self-assemble into lamellar crystalline phase structures when present in an aqueous environment < 8 wt% of water and in the temperature range from 25 to 105°C.

Longtime ago, we have done many projects on MMT and its products. For example; using several granulometric treatments and chemical processes to separate and purify montmorillonite (MMT) from the Vietnamese bentonite (Ha -Thuc et al., 2010) or many applications of organoclay in polymer nanocomposites (Ha-Thuc et al., 2014; Nguyen et al., 2016a; Nguyen et al., 2016b; Tran et al., 2012). We recognized the huge application of MMT in many areas such as cosmetics, water treatment, reinforcement and air permeability for packaging technology. However, to expand the application of MMT, its structure must be modified by biological agents to avoid affecting the health of users and the environment. Until now, there has been no report on the use of M-Gly for the modification of clay and based on the idea that these organic molecules can potentially form the self-assembled structure in the MMT interlayer. The present study focuses on the preparation of organoclays by intercalating the new modifying agent – M-Gly – into the MMT layers via the solution and melting intercalation methods.

2. Experiment and materials

2.1. Materials

Vietnamese MMT minerals with 86 milliequivalent (meq)/100 g exchange capacity was obtained from the Clay Minerals Depository Hiep Phu, Lam Dong province (southern Vietnam) according to the purification process reported in our previous study (Ha -Thuc et al., 2010). The modifying agent (M-Gly) used in this study is a commercial glycerin 1-monostearate (> 95 wt%) called distilled monoglycerides supplied by Rikemal® Co., Germany (solid form). This product was used as received without further purification.

2.2. Modification of MMT using the solvent method

In the solvent method experiment, the M-Gly and MMT were weighed according to the designated ratio as seen in (Table 1). Ethanol was used as a solvent to dissolve the M-Gly. An accurately weighed quantity of MMT (1 g) was dispersed in a certain volume of M-Gly/ethanol solution at 40°C, for 4 h using a mechanical stirrer at 1000 rpm. The solid sample was collected by centrifugation and carefully dried under vacuum at 80°C in 24 h before further characterization.

Table 1: Content of monoglyceride used for modification of MMT

Material	Modification ratio in percentage of weight		Melting method using magnetic stirrer	Solvent method	Melting method using Haake thermomixer	
	MMT (wt%)	Monoglyceride (wt%)				
M-M-90-10	90	10	---	---	✓	125
M-M-70-30	70	30	✓	✓	✓	
M-M-50-50	50	50	✓	✓	✓	126
M-M-40-60	40	60	---	---	✓	
M-M-30-70	30	70	---	---	✓	127
M-M-20-80	20	80	✓	✓	✓	
M-M-10-90	10	90	✓	✓	---	128

2.3. Modification of MMT using the melting method

The melting method was applied to modify the MMT by mixing it directly with the modifying agent without using solvent. Since it is in liquid form above 70°C, the M-Gly was agitated with MMT at 80°C for 4 h using a magnetic stirrer at an agitation speed of 350 rpm, at the same ratios as the solvent method (Table 1).

The special method in this study was the melting modification process performed at 80°C using a Haake internal mixing option. In this typical experiment, the MMT and M-Gly were weighed according to the various ratios (Table 1) and loaded in the mixing chamber. A mixing process

was run at the defined speed of 120 rpm with a high shear rate for 15 min. Then the modified MMT was washed once in ethanol before drying under vacuum at 80°C for further characterization.

The content of M-Gly intercalated in the interlayer space of MMT and the presence of M-Gly on the surface of MMT were determined to investigate the structural change of modified specimens and evaluate the effectiveness of each modified method.

2.4. Characterization of the modified specimens

The structural change of the MMT-Gly samples in both modified methods was investigated by XRD in a 2θ range of 0.5–20° using a D8 Advance diffractometer (Burker, Germany) with Ni-filtered CuK_α radiation ($k = 1.54^\circ\text{\AA}$) at 40 kV and 40 mA. The scanning was performed with a resolution of 0.2°/s.

Transmission electron microscope (TEM) images were obtained using TEM equipment, the JEOL model JEM-1400 with an acceleration voltage of 120 kV. Powder samples are thinly dispersed on the carbon film coating TEM grids before observation.

Thermogravimetric analyses (TGA) were conducted using a Netzsch STA 409C Thermo analyzer instrument. The pure and modified samples weighing 15 mg were heated from 25 to 800°C at a heating rate of 10°C/min under nitrogen atmosphere to evaluate the amount of modifying agent inserted into the interlayer space of MMT and the thermal stability ability of the specimens.

The FT-IR spectra of the test specimens were recorded as KBr pellets in the spectral range 4000–300 cm^{-1} on a Perkin–Elmer 1725X FT-IR spectrometer in air at room temperature to identify the presence of M-Gly on the surface of MMT.

3. Results and discussion

3.1. Structural investigation of MMT modified using the solvent method

The XRD pattern (Fig. 1) shows the d_{001} -spacing of MMT modified at different contents in weight of M-Gly via the solvent method.

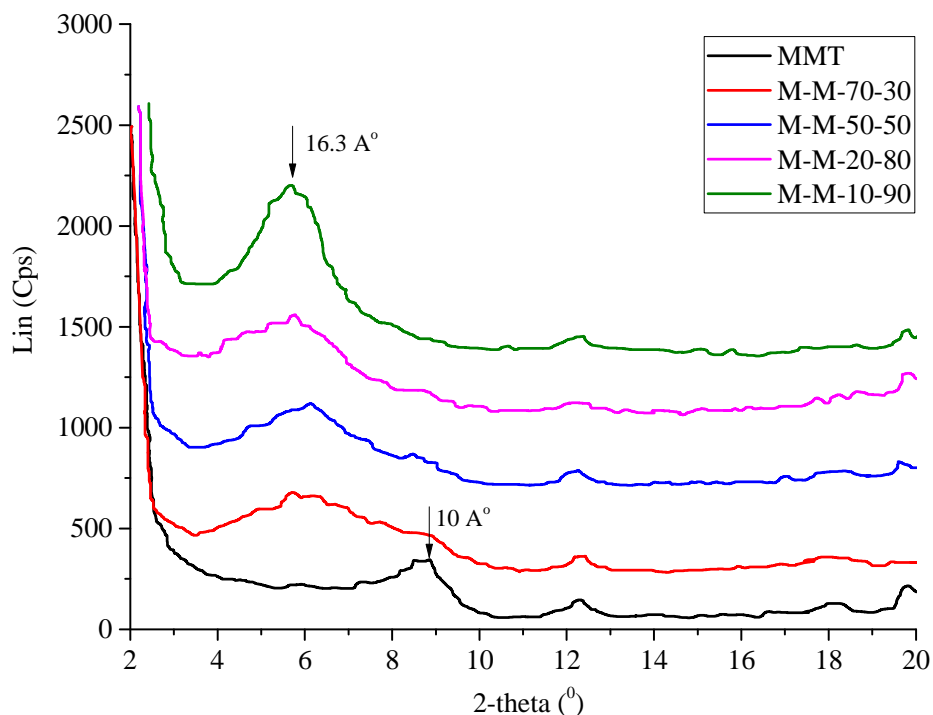


Figure 1: XRD pattern of monoglyceride modified MMT by solvent method according to various ratios of MMT/M-Gly: 100/0 (MMT); 70/30; 50/50; 20/80; and 10/90.

Montmorillonite is characterized by the heterogeneous interlayers, the d_{001} -spacing values is basal spacing or layer stacking in a phyllosilicate. In this study, the interlayer spacing increased from 10 \AA° ($2\theta \sim 9^\circ$) of neat MMT to a maximum value of 16 \AA° ($2\theta \sim 6^\circ$) at sample M-M-10-90 (90 wt% M-Gly). This result showed a progressive disappearance of the 10 \AA° structure and the progressive increase of the distance, with a whole distribution between 10 \AA° and 16 \AA° and a stabilization of all structures at 16 \AA° when the Gly content is enough. This could be proved by the peak shifted to a narrow angle range when the content of M-Gly increased, but the d-spacing

value changed little. In this case, it was suggested that the M-Gly molecules had penetrated into the interlayer space of MMT and arranged in the interlayer, forming the monolayer conformation with the thickness of about 5-6 Å, as suggested in Fig. 2. According to the study of how clay was modified by the alkyl ammonium agent (Beall and Goss, 2004), the authors reported that the d_{001} -spacing of MMT did not depend on the length but rather on the thickness of these alkyl chains of the modifying agent. Therefore, with the 3.8-Å thickness of the modifier carbon chains (Beall and Goss, 2004), the d_{001} -spacing gained about 15–16 Å, corresponding to only one layer of M-Gly (Fig. 2).

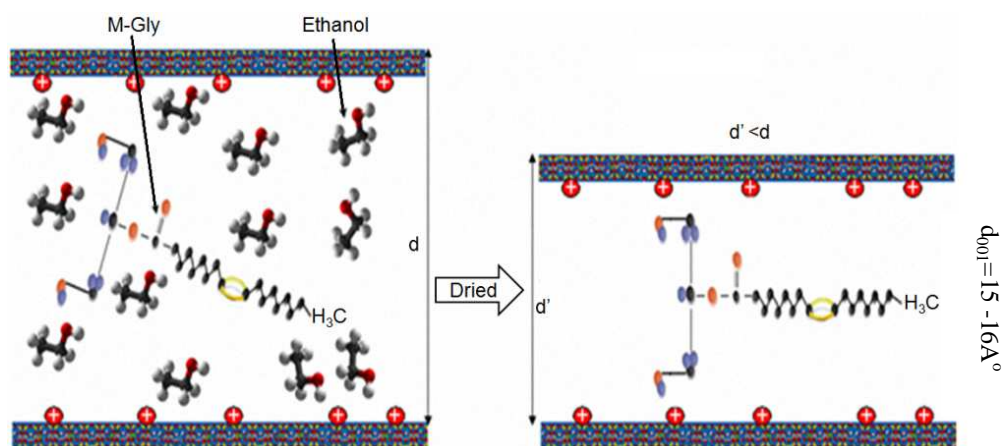


Figure 2: Models localization of monoglyceride molecules in the interlayer space of MMT after the solvent modification

The main reason for the small amount of M-Gly intercalated in the interlayer space was a competing factor of ethanol in the interlayer space of MMT. These molecules will hinder the interaction between the modifying agent and the MMT surface or the exchanged cations in the interlayer space. Consequently, as illustrated in Fig. 2, the intercalation of M-Gly into MMT was restricted. After the sample was dried, solvent molecules were evaporated, reducing the MMT interlayer space. This result was observed in other clay modification studies using ionic

or non-ionic modifying agents (Nakas and Kaynak, 2008; Shen et al., 2003; Strawhecker and Manias, 2000).

To improve the M-Gly intercalation into the layer structure of MMT, the ultrasonic treatment during the modified process was also used at a 40-Hz frequency in 15 min for the MMT/M-Gly mixture (10/90), called (Ultra-M-M-10-90). The XRD results (Fig. 3) show the peak of d_{001} -spacing was not clearly observed and the intensity decreased remarkably as compared to neat MMT and modified MMT with no ultrasonic treatment (M-M-10-90). This phenomenon may come from the effect of ultrasonic oscillation, which causes the MMT lamellar disordering and better dispersion in solution (Guo et al., 2007), resulting in improved intercalation of M-Gly in the interlayer space of MMT. It also reduced the crystalline layer structure of the MMT.

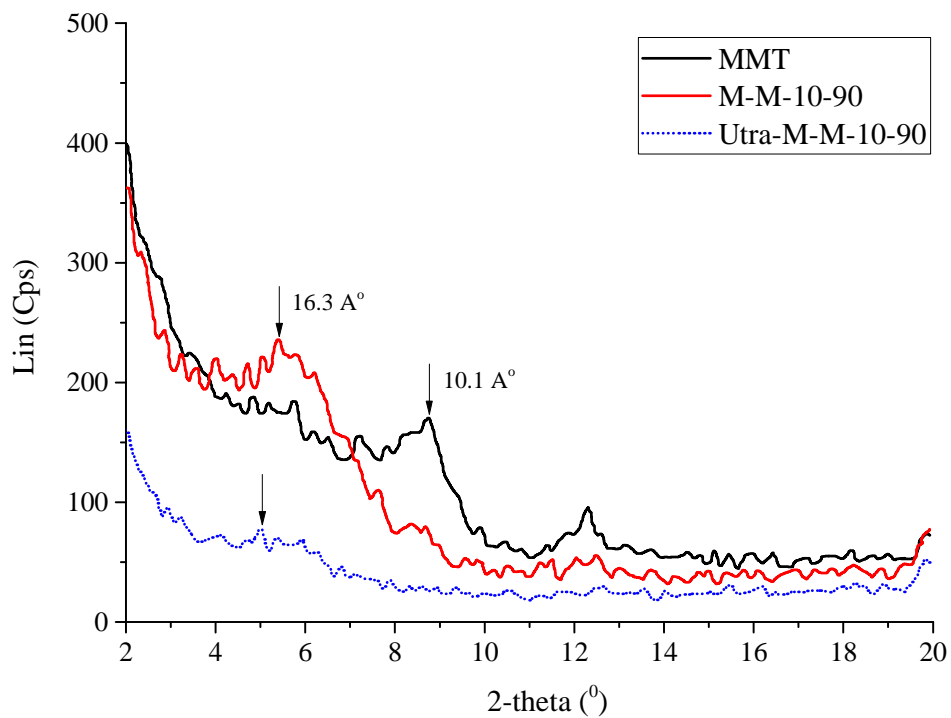


Figure 3: XRD patterns of MMT, and M-Gly modified MMT at ratio 10/90 (M-M-10-90) and treatment of ultrasound (Ultra-M-M-10-90)

3.2. Structural investigation of MMT modified by the melting method

3.2.1. MMT modified by M-Gly using a magnetic stirrer

Using a magnetic stirrer at high temperature, MMT was modified by M-Gly via the melting method according to various ratios, as shown in Table 1. The XRD results (Fig. 4) of the modified samples were not as expected and were similar to those of the solvent method. Even at a MMT/M-Gly ratio (10/90) (M-M-10-90) with a high M-Gly content, the d_{001} distance could only increase to about 14 \AA , corresponding to the single layer of M-Gly molecules lying in the interlayer space of MMT (Avom et al., 2001; Beall and Goss, 2004).

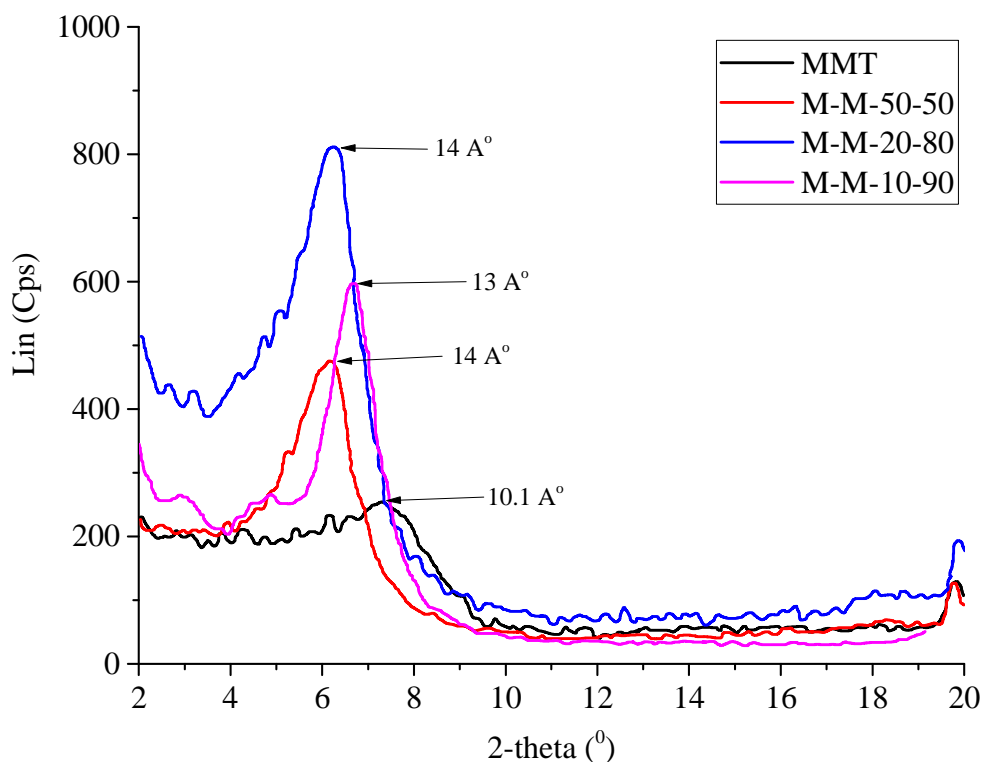


Figure 4: XRD patterns of M-Gly modified MMT by magnetic stirrer according to various ratios of MMT/M-Gly:100/0 (MMT); 50/50 (M-M-50-50); 20/80 (M-M-20-80) and 10/90 (M-M-10-90).

The XRD results may be due to the high viscosity of the M-Gly modifying agent at 80°C ($T_m \sim 70^\circ\text{C}$); thus the agitation force by the magnetic stirrer was not enough to make M-Gly molecules intercalate into the interlayer space of MMT. At a higher modification temperature, the M-Gly modifying agent starts to be degraded, evidenced by a changed color and smell. Therefore, in this method, the results showed the interlayer structure of MMT, which was inserted by a single parallel layer of M-Gly, which increases the d_{001} -spacing to 14 Å.

3.2.2. MMT modified by M-Gly using the Haake thermomixer

The modification of MMT by M-Gly, with or without solvent, did not effectively increase the d_{001} -spacing of MMT, as shown in the above-reported results. Another method for the modification of MMT by melting was based on the Haake internal mixer. This method was used in creating the high shear rate during mixing at a defined speed, which will enhance the dynamic mobility of the M-Gly molecules and result in a better interaction with MMT platelets. This will help M-Gly penetrate into interlayer space of MMT much more easily. The XRD results (Fig. 5) showed the d_{001} -spacing of modified MMT using the Haake internal mixer. The M-M-90-10 sample was about 13.6 Å and nearly identical to that of modified clay using the solvent method and the melting method using magnetic stirring. Meanwhile, the XRD results of the M-M-70-30 and M-M-50-50 samples did not show the d_{001} peak clearly. There was only a broadened mound of a peak observed in 2θ at $4-8^\circ$ with low intensity. It could be concluded that, as the M-Gly content increases, the high shear rate force created by the rollers of the internal mixer plays a greater role that enhances the friction force between M-Gly and MMT and makes the layer structure of MMT become unstable and disordered.

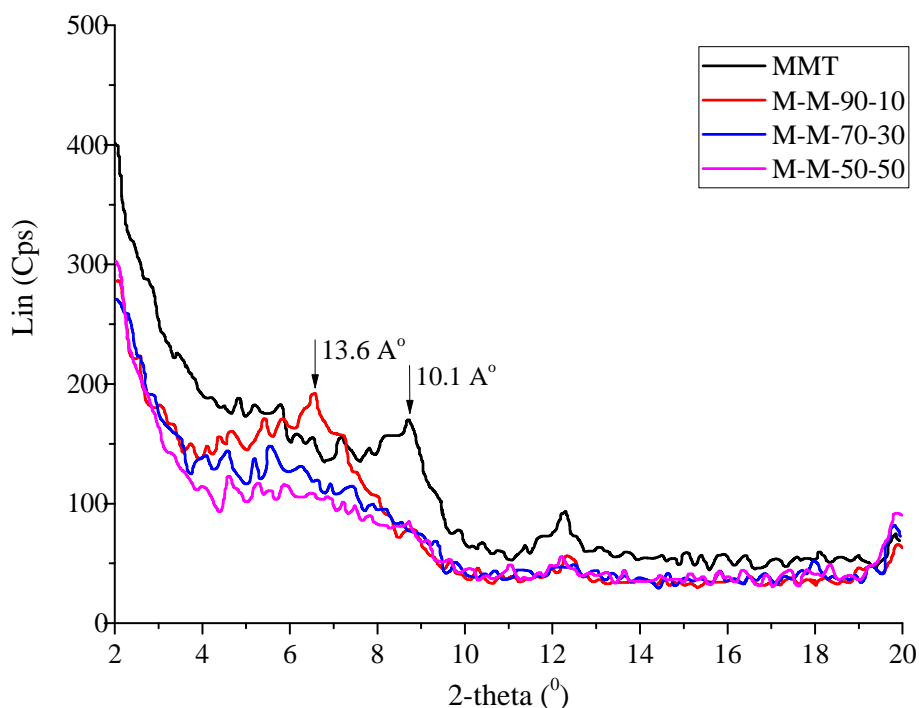


Figure 5: XRD patterns of MMT modified by M-Gly at different ratios of MMT/M-Gly: 100/0; 90/10 (M-M-90-10); 70:30 (M-M-70-30) and 50/50 (M-M-50-50)

When the content of M-Gly used was higher than 30 wt% (from 50 to 80 wt%), a broad diffraction peak was clearly observed in the small angle of X-ray diffraction (Fig. 6). On the other hand, the synchrotron X-ray diffraction pattern obtained at 28°C (Fig. 7) evidenced the presence of diffraction peaks that can be ascribed to the presence of monoglyceride crystals organized in bilayers.

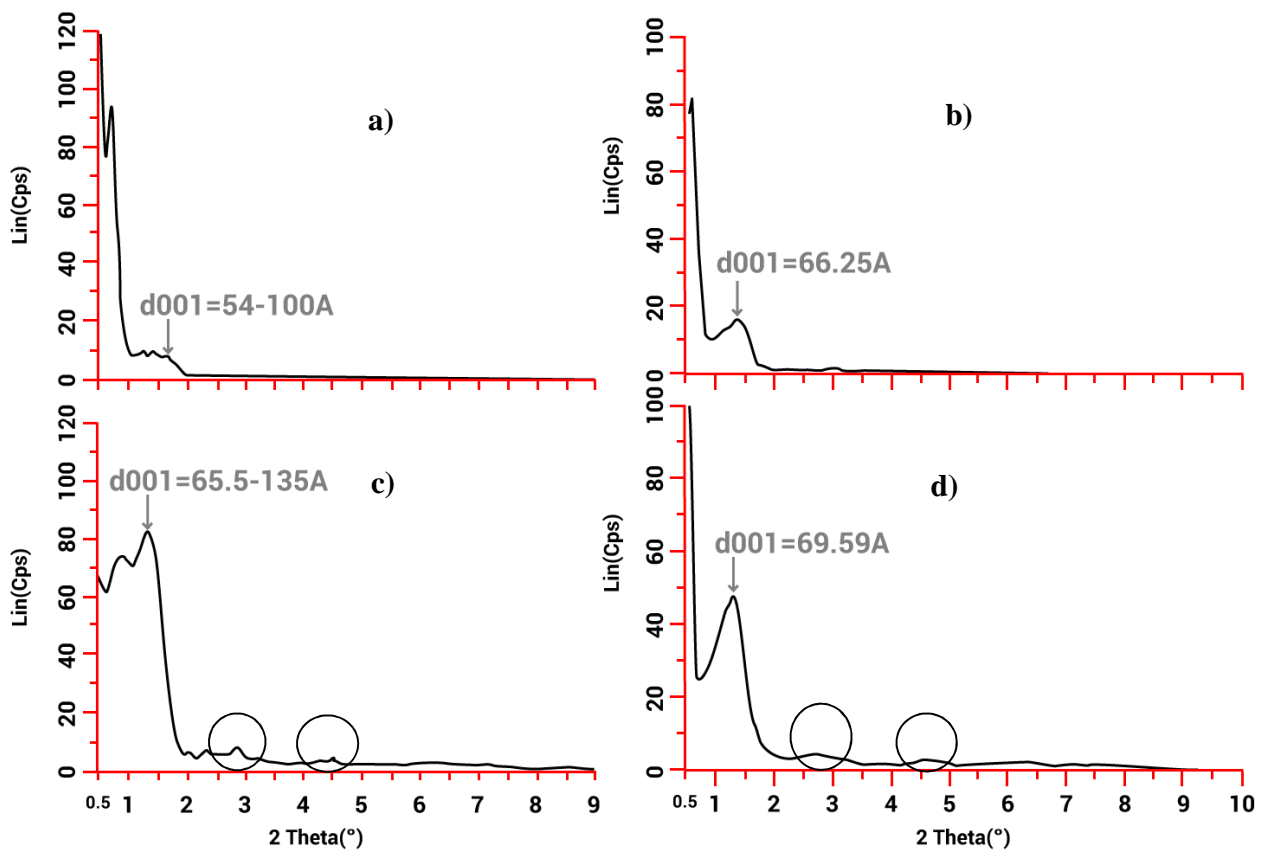


Figure 6: Small Angle XRD patterns of mixture MMT/ M-Gly at ratio: (a) 20/80 (M-M-20-80); (b) 30/70 (M-M-30-70); (c) 40:60 (M-M-40-60); (d) 50:50 (M-M-50-50).

In particular, wide-angle peaks at 3.81, 4.31 and 4.54 Å and a narrow-angle peak at 48.35 Å can be associated with the formation of the M-Gly lamellar L β phase (Anese et al., 2011). Thus, for all modification cases (Fig. 6), this large diffraction peak at 54–70 Å ($1-1.5^\circ$, 2θ) might correspond to the d_{001} -spacing of the expanded MMT layer structure after being modified and to M-Gly crystals on the MMT surface. At the modifying agent content of 50 and 60 wt% (Fig. 6d and 6c), a very small broad peak in the zone from 2 to 3° , 2θ was also observed, indicating the d_{001} -spacing (about 20–30 Å) of the intercalated MMT layer.

When the M-Gly content increased further (70 and 80 wt%) (Fig. 6b and 6a), the d_{001} peak of the modified MMT in the wide-angle diffraction was no longer observed. This indicates that at a

higher content, under the high shear mixing force of the thermomixer, the modifying agent was easily intercalated and expanded the layer structure of clay, and results in the disappearance of characteristics at the wide-angle diffraction (from 2 to 3⁰, 2 θ). Especially at 80 wt% of M-Gly, the diffraction peak at small angles was broadened, which might have been caused by the high ratio of the expanded MMT layer structure (> 60 Å) and have affected the crystal size of M-Gly.

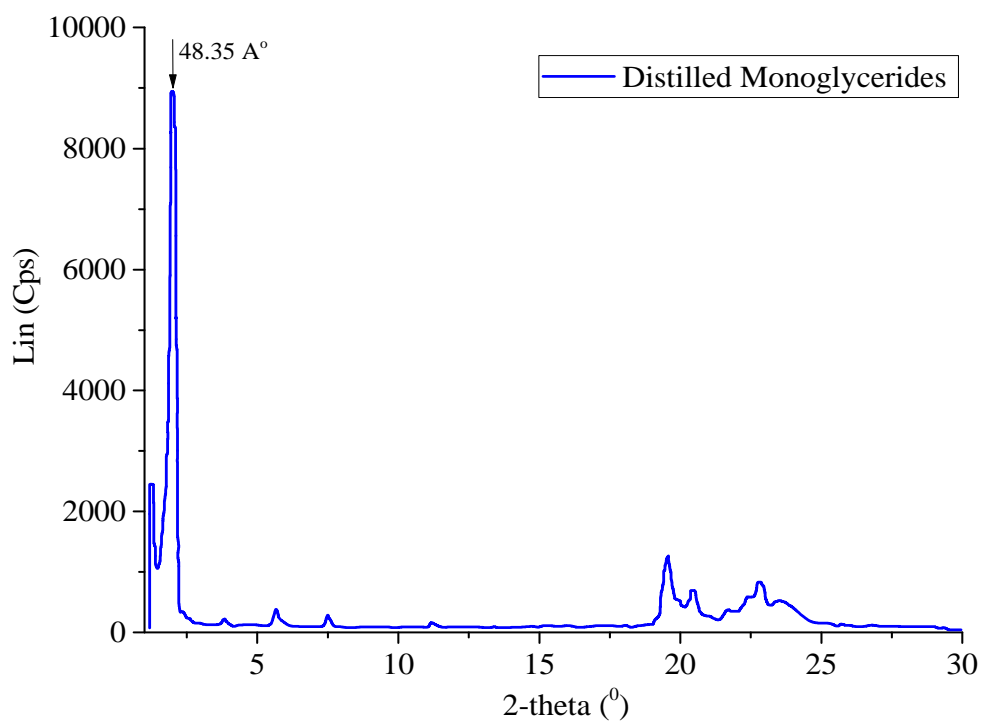


Figure 7: XRD pattern of commercial Distilled Monoglycerides

The very high d_{001} -spacing values (> 60 Å) were obtained by assuming that M-Gly molecules are self-arranged via hydrogen linking and assembled vertically, as a bilayer, to the MMT layer, as suggested (Fig. 8). These results were explained based on the previous studies of M-Gly structure formation (Anese et al., 2011; Beall and Goss, 2004). According to the structure model of M-Gly proposed (Fig. 8), under the high shear rate force and high content of a modifying

agent, the electrostatic interaction between layers of clay became weaker and easily disordered. Thus the modifying agent penetrated easily and expanded the galleries of clay noticeably.

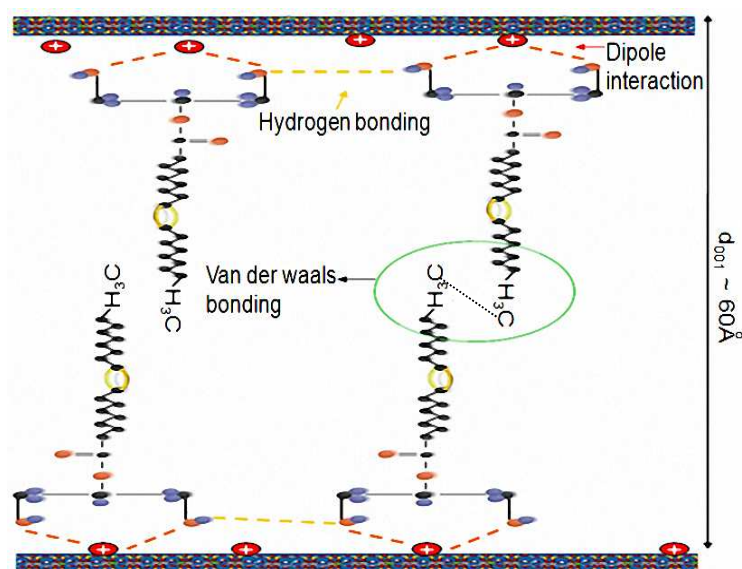


Figure 8: Illustration of self-assembly molecular structure of M-Gly in clay gallery after being modified by Haake method

The layer structure organization of MMT-modified M-Gly with the Haake internal mixer was also investigated by transmittance electronic microscopy (TEM). The TEM images (Fig. 9) showed the layer structure of modified MMT with some ranges appearing as three or five layers of clay stacked together but disordered as compared to the original structure of unmodified MMT. There were also zones showing the single- or double-layer form distributed incoherently and separately. These results confirm the change of d_{001} peak formation and its movement toward the low angles in XRD patterns.

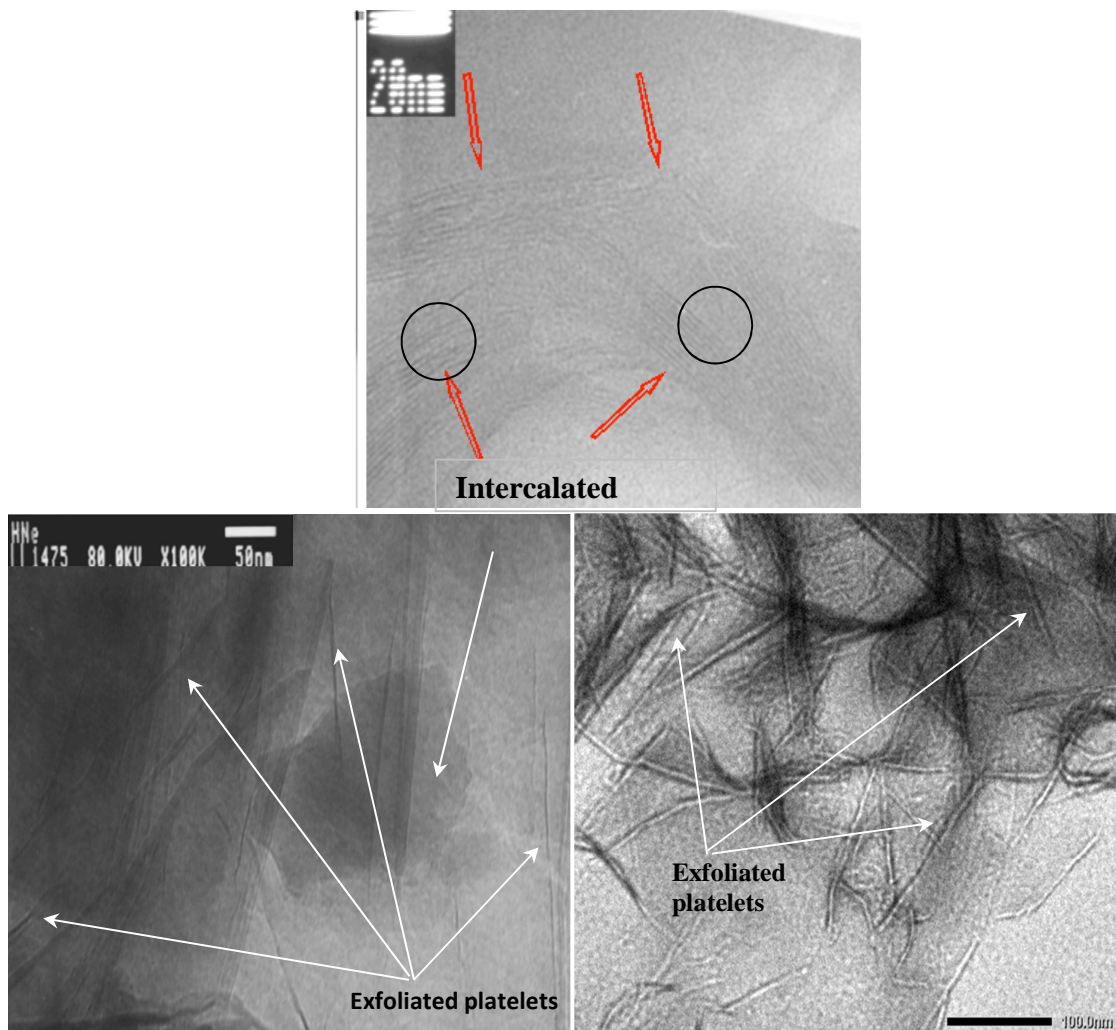


Figure 9: TEM images of organoclay modified by 50 wt% of monoglyceride agent (M-M-50-50) via Haake method

3.3. Stability investigation of modified MMT layers

To investigate the modifying agent content in the sample using 50 wt% and 80 wt% of M-Gly (M-M-50-50 and M-M-20-80, respectively), the Soxhlet extraction process was performed for 48 h in ethanol solvent at 80°C. The XRD results (Fig. 10) show that after extraction of the M-M-50-50 sample, the obvious diffraction peak at the low-angle region had disappeared and there was only the d_{001} peak of intercalated MMT distributed at two ranges of 20 Å° and 30 Å°. In the

case of the M-M-20-80 sample, there was no longer a diffraction peak observed in the XRD pattern. This demonstrates that a part of M-Gly was washed out from the MMT layer structure by solvent, resulting in the disordering of the layer structure of modified clay, which could not be found as a d_{001} -spacing peak in the XRD pattern.

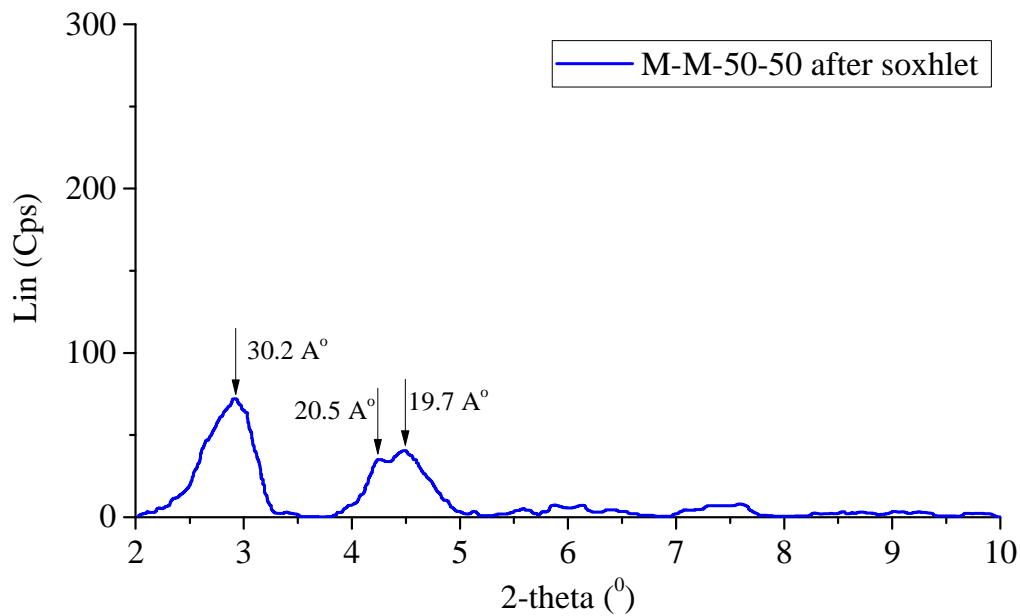


Figure 10: Small Angle XRD pattern of M-Gly modified MMT (50 wt%, M-M-50-50; Haake method) after soxhlet extraction process during 48 h

Furthermore, the M-Gly content existing in the layer structure was also investigated by thermal gravimetric analysis (TGA). The results from Fig. 11 showed that the decomposition temperature of M-Gly occurred from 150°C to 470°C. With unmodified MMT, the mass loss occurred at the temperature range from 40°C to 120°C, corresponding to the evaporation of water molecules existing in the MMT structure. Meanwhile, before and after being extracted by ethanol, the M-M-50-50 (Haake method) did not show this weight loss. It was suggested that after being modified, MMT became more hydrophobic and remarkably reduced the inherent moisture absorption ability of MMT. The nearly 50% weight loss in the M-M-50-50 (Haake

method) sample from 150 to 420°C corresponds to the appropriate M-Gly content used to modify MMT. Consistently, since the M-Gly was mixed and intercalated into the layer structure of MMT, the mass loss of the modified MMT corresponds to the corresponding proportion of the pure M-Gly curve.

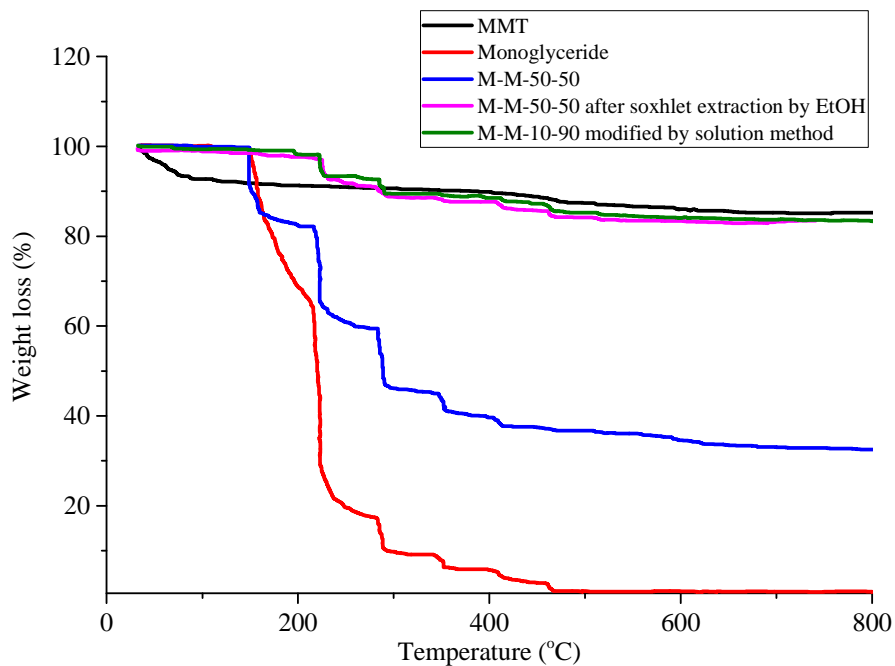


Figure 11: TGA curves of modified MMT: MMT; Monoglyceride (M-Gly); M-M-50-50 (Haake method); M-M-50-50 (Haake method) soxhlet extraction; and M-M-10-90 (solution method). After Soxhlet extraction; the TGA curve of the sample was different, the mass loss rate decreased remarkably, and the degradation temperature was also higher as compared to the previous cases. This could be explained by the fact that after being extracted by ethanol solvent, a large amount of the modifying agent was washed out of the MMT surface and galleries. In addition, only a small content of M-Gly, which exists in the d-spacing zone of 20 and 30 Å (Fig. 10), remains in the sample and undergoes a weight loss from 213°C to 466°C. Similarly, MMT modified by M-Gly using the solution method (M-M-10-90) showed nearly 16% weight

loss of the modifying agent in the same degradation zone. Since it is in the clay interlayer, the modifying agent degrades, in the last two cases, more slowly than that of M-M-50-50 (Haake method) and M-Gly, because of the thermal insulation effect. The TGA results are completely similar to those of the XRD analysis.

The results of XRD and TGA have shown that in modifying MMT using the Haake thermal mixer, M-Gly has penetrated easily into the interlayer space and expanded the d_{001} spacing of MMT. This led the layer structure of MMT to become unstable because the interaction between the layers of clay weakened. This was the reason that the platelet structure of MMT could not be held when using extraction by ethanol solvent causing the modifying agent to be easily washed out of clay galleries during extraction. With TGA analysis, the remaining content of the M-Gly modifying agent, after ethanol extraction, is about 15.5 wt% inside the MMT layer. Therefore, this phenomenon will be an advantage in the application of the polymer/clay nanocomposite preparation where the polymer matrix could be easily inserted into clay's weaker layer structure to easily obtain the good dispersion state of the clay in the material.

To identify the presence of M-Gly on the MMT surface after modifying by extraction, FT-IR analysis (Fig. 12) shows the vibration of the different specific functional groups of M-Gly existing in modified clay. It showed the characteristic peaks of bonding vibrations, such as $-\text{CH}_2$ and $-\text{C}=\text{O}$ bonding vibration at $2900\text{--}3000\text{ cm}^{-1}$ and 1720 cm^{-1} , respectively. The intensity of these peaks was relative low, because the content of M-Gly was arranged in a single layer (solvent method) or double layer (melting method using the magnetic stirrer) in the sample. With M-Gly-modified MMT by the Haake thermal mixer, the intensity of the peaks was high and clearly shown (Fig. 12d). These characteristic peaks confirmed again that this Haake method allowed the substantial content of M-Gly to be easily intercalated into the layer

structure of MMT as compared to the other methods used. After the Soxhlet extraction using ethanol solvent, the intensity of the peaks decreased considerably, indicating a significant amount of modifying agent, which was washed out of the clay structure by solvent.

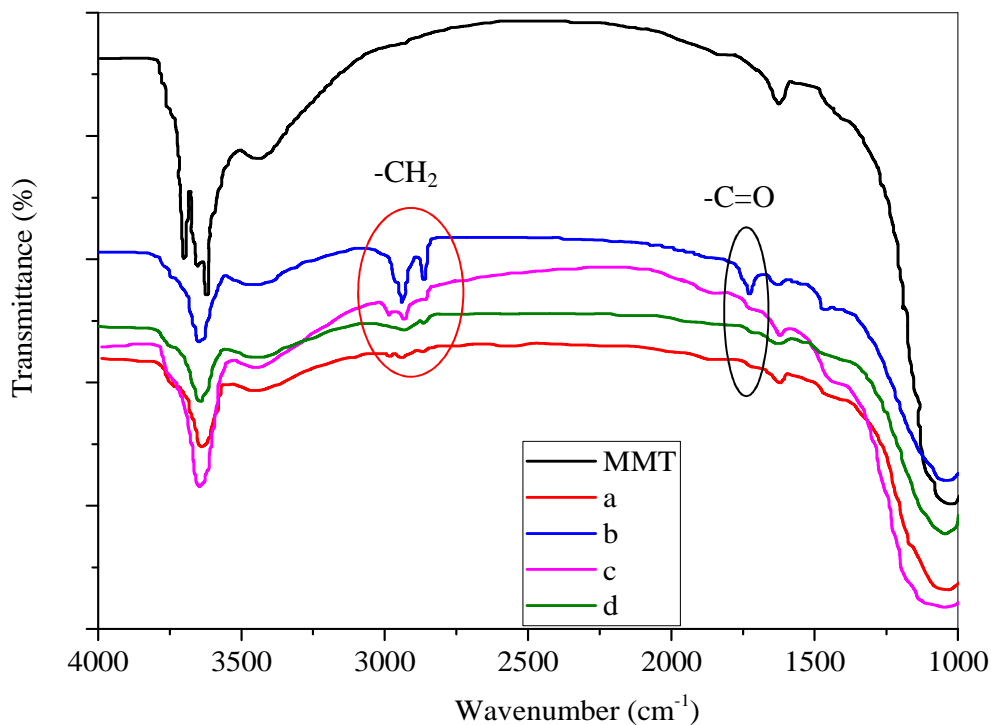


Figure 12: FT-IR spectra of M-Gly modified MMT (50/50 wt%) by different methods: (a) M-Gly modified MMT by solvent method, (b) M-Gly modified MMT by Haake method after soxhlet process, (c) M-Gly modified MMT by magnetic stirring, (d) M-Gly modified MMT by Haake method

4. Conclusion

Montmorillonite was modified by commercial monoglyceride (M-Gly) using the solvent method and the melting method. In the solvent method, the modifying agent intercalated into the interlayer space and formed the double layers parallel to MMT platelets, which increased the d_{001} -spacing of MMT from 10 Å to 16 Å. From the melting method using a magnetic stirrer,

only one layer of M-Gly was intercalated into the interlayer space of MMT, resulting in 14 Å of clay d_{001} -spacing. With the high content of M-Gly (>30 wt%), the modification process of MMT using the Haake internal thermomixer increased the d_{001} -spacing of MMT impressively (from 54 to 100 Å), making the distribution of the MMT layer structure more disordered. The extraction of modified clay by ethanol has proved that the M-Gly inside the expanded MMT galleries was easily washed out and then the layer structure was partially loss. This phenomenon indicates that in such expanded MMT galleries, the electrostatic force between the MMT layers becomes very weak and easily loses the crystalline layer structure if there is a sufficiently high shear force applied. This point will be an advantage in the use of this modified MMT in the polymer nanocomposite field.

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Graphical abstract

