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### ► To cite this version:

Dang Mao Nguyen, Thi Mai Loan Nguyen, Julien Colin, Patrick Perre, Trinh Duy Nguyen, et al.. Monoglyceride as an effective and friendly modification agent for nano-layered structure of Montmorillonite. Applied Clay Science, 2019, 179, pp.105100. 10.1016/j.clay.2019.04.008 . hal-02294222

**HAL Id: hal-02294222**

**<https://hal.science/hal-02294222v1>**

Submitted on 25 Oct 2021

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

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19

20 **Abstract**

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

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

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

#### 34 **1. Introduction**

35 Surface modification of clay minerals has received a great deal of attention because it can be  
36 used to create new materials and new applications (Borrego-Sánchez et al., 2018; Wang et al.,  
37 2018; Xu et al., 2018). The main focus of the surface modification of clays is to develop new  
38 polymer nanocomposites. This kind of material constitutes one of the most widely developed  
39 areas of nanotechnology (Beall and Goss, 2004; Jordan, 1949; Lucilene et al., 2008). The first  
40 attempt to chemically alter clay galleries with various organic molecules was reported in the late  
41 1940s (Jordan, 1949). Since then a substantial industry has been established to utilize these  
42 organically modified clays. Organoclays are also used in other applications such as adsorbents  
43 of organic pollutants in soil, water and air; oil well drilling fluids; paints; grease; cosmetics;  
44 refractory varnish; and personal care products (Beall and Goss, 2004; Jordan, 1949; Kumar et  
45 al., 2015; Lin et al., 2015; Lucilene et al., 2008; Olutoye et al., 2016; Xu et al., 2018; Zhuang et  
46 al., 2015).

47 Several techniques can be employed to modify clays such as adsorption, ion exchange with  
48 inorganic cations and organic cations, binding of inorganic and organic anions (mainly at the  
49 edges), rafting of organic compounds, reaction with acids, pillaring by different types of  
50 poly(hydroxo-metal) cations, intra-particle and inter-particle polymerization, dehydroxylation  
51 and calcination, delamination and re-aggregation of smectites, and lyophilization, ultrasound,  
52 and plasma (Bergaya and Lagaly, 2001; Ghiaci et al., 2011; Lucilene et al., 2008; Olutoye et al.,  
53 2016).

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

70 involves hydrogen bonding, either by the direct interaction between the adsorbed polymer and  
71 the oxygen (or hydroxyls) of the clay surface, or through a “water bridge” between the clay  
72 surface and the polymer (Rossi et al., 2003). Numerous studies have been conducted on the  
73 molecular association between montmorillonite (MMT) and organic species such as liquid  
74 aliphatic amine and polyamines (Alemdar et al., 2005; Lucilene et al., 2008; Pospisil et al.,  
75 2002; Xiao et al., 2003), acid and polyacids (Avom et al., 2001; Chou et al., 2005; Dentel et al.,  
76 1995; Ghiaci et al., 2011; Olutoye et al., 2016; Tran et al., 2005), alcohol, glycols (Chassin,  
77 1973; Lucilene et al., 2008; Pavlidou and Papaspyrides, 2008; Tran et al., 2006), polyglycols  
78 (Lucilene et al., 2008; Pavlidou and Papaspyrides, 2008; Shen et al., 2002; Strawhecker and  
79 Manias, 2000; Zhao et al., 1989) and polyglycol ethers (Lucilene et al., 2008). Analysis of these  
80 complexes has established that the amines are active in basic exchange, while glycerol and  
81 glycol enter the interlayer space without displacing cations (Lucilene et al., 2008; Pavlidou and  
82 Papaspyrides, 2008).

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

92 Longtime ago, we have done many projects on MMT and its products. For example;  
93 using several granulometric treatments and chemical processes to separate and purify  
94 montmorillonite (MMT) from the Vietnamese bentonite (Ha -Thuc et al., 2010) or many  
95 applications of organoclay in polymer nanocomposites (Ha-Thuc et al., 2014; Nguyen et al.,  
96 2016a; Nguyen et al., 2016b; Tran et al., 2012). We recognized the huge application of MMT in  
97 many areas such as cosmetics, water treatment, reinforcement and air permeability for  
98 packaging technology. However, to expand the application of MMT, its structure must be  
99 modified by biological agents to avoid affecting the health of users and the environment. Until  
100 now, there has been no report on the use of M-Gly for the modification of clay and based on the  
101 idea that these organic molecules can potentially form the self-assembled structure in the MMT  
102 interlayer. The present study focuses on the preparation of organoclays by intercalating the new  
103 modifying agent – M-Gly – into the MMT layers via the solution and melting intercalation  
104 methods.

## 105 **2. Experiment and materials**

### 106 **2.1. Materials**

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

113

114

115 **2.2. Modification of MMT using the solvent method**

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

122 **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 <sup>124</sup>	
	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

129

130 **2.3. Modification of MMT using the melting method**

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

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

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

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

#### 144 **2.4. Characterization of the modified specimens**

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

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

152 Thermogravimetric analyses (TGA) were conducted using a Netzsch STA 409C Thermo  
153 analyzer instrument. The pure and modified samples weighing 15 mg were heated from 25 to  
154 800°C at a heating rate of 10°C/min under nitrogen atmosphere to evaluate the amount of  
155 modifying agent inserted into the interlayer space of MMT and the thermal stability ability of  
156 the specimens.

157 The FT-IR spectra of the test specimens were recorded as KBr pellets in the spectral range  
158 4000–300  $\text{cm}^{-1}$  on a Perkin–Elmer 1725X FT-IR spectrometer in air at room temperature to  
159 identify the presence of M-Gly on the surface of MMT.

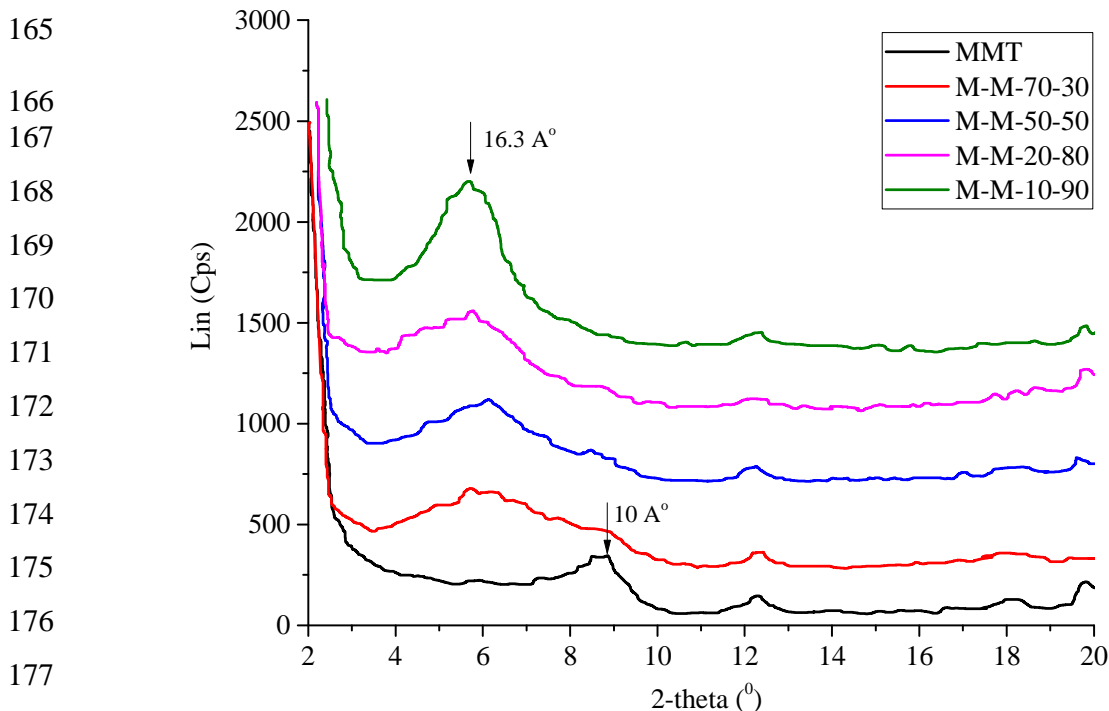
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161 **3. Results and discussion**

162 **3.1. Structural investigation of MMT modified using the solvent method**

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

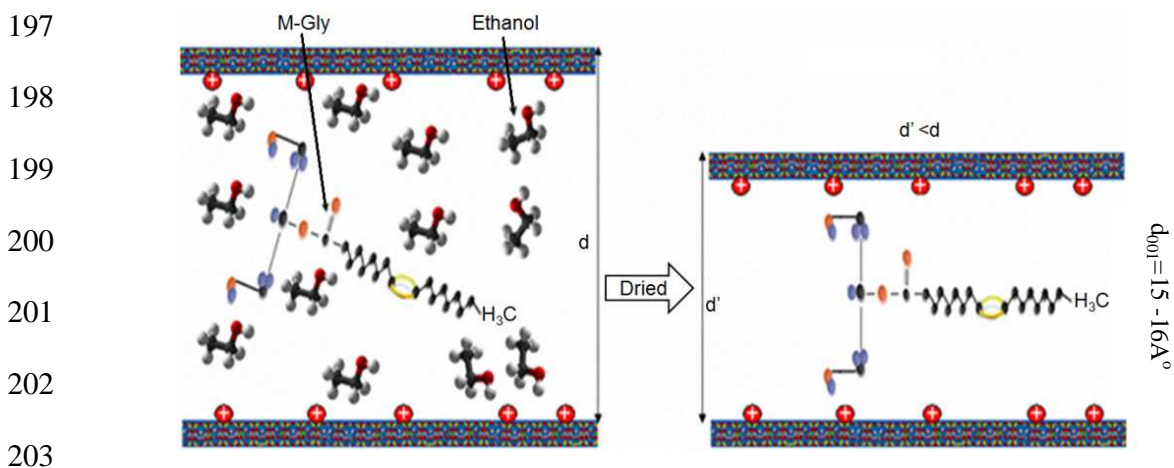


179 **Figure 1:** XRD pattern of monoglyceride modified MMT by solvent method according to  
180 various ratios of MMT/M-Gly: 100/0 (MMT); 70/30; 50/50; 20/80; and 10/90.

181

182 Montmorillonite is characterized by the heterogeneous interlayers, the  $d_{001}$ -spacing values is  
183 basal spacing or layer stacking in a phyllosilicate. In this study, the interlayer spacing increased  
184 from 10 A° ( $2\theta \sim 9^\circ$ ) of neat MMT to a maximum value of 16 A° ( $2\theta \sim 6^\circ$ ) at sample M-M-10-90  
185 (90 wt% M-Gly). This result showed a progressive disappearance of the 10 A° structure and the  
186 progressive increase of the distance, with a whole distribution between 10 A° and 16 A° and a  
187 stabilization of all structures at 16A° when the Gly content is enough. This could be proved by  
188 the peak shifted to a narrow angle range when the content of M-Gly increased, but the d-spacing

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

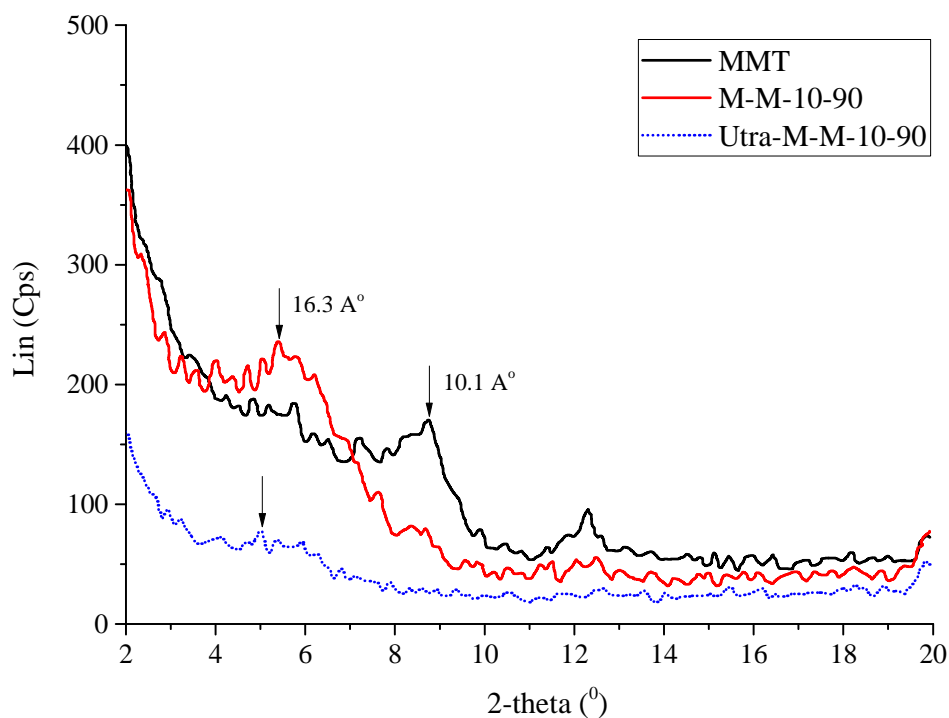


204 **Figure 2:** Models localization of monoglyceride molecules in the interlayer space of MMT after  
 205 the solvent modification

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

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

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

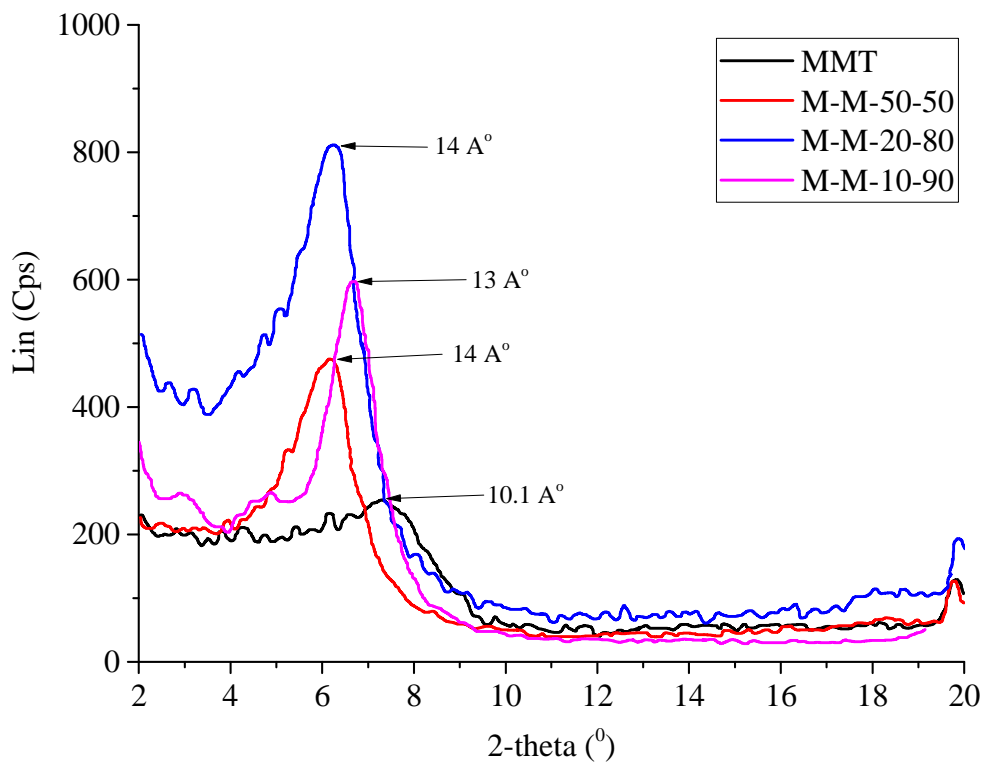


233 **Figure 3:** XRD patterns of MMT, and M-Gly modified MMT at ratio 10/90 (M-M-10-90) and  
234 treatment of ultrasound (Ultra-M-M-10-90)

235 **3.2. Structural investigation of MMT modified by the melting method**

236 **3.2.1. MMT modified by M-Gly using a magnetic stirrer**

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



254 **Figure 4:** XRD patterns of M-Gly modified MMT by magnetic stirrer according to various ratios  
255 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-  
256 90).

257 The XRD results may be due to the high viscosity of the M-Gly modifying agent at 80°C ( $T_m \sim$   
258 70°C); thus the agitation force by the magnetic stirrer was not enough to make M-Gly  
259 molecules intercalate into the interlayer space of MMT. At a higher modification temperature,  
260 the M-Gly modifying agent starts to be degraded, evidenced by a changed color and smell.  
261 Therefore, in this method, the results showed the interlayer structure of MMT, which was  
262 inserted by a single parallel layer of M-Gly, which increases the  $d_{001}$ -spacing to 14 Å.

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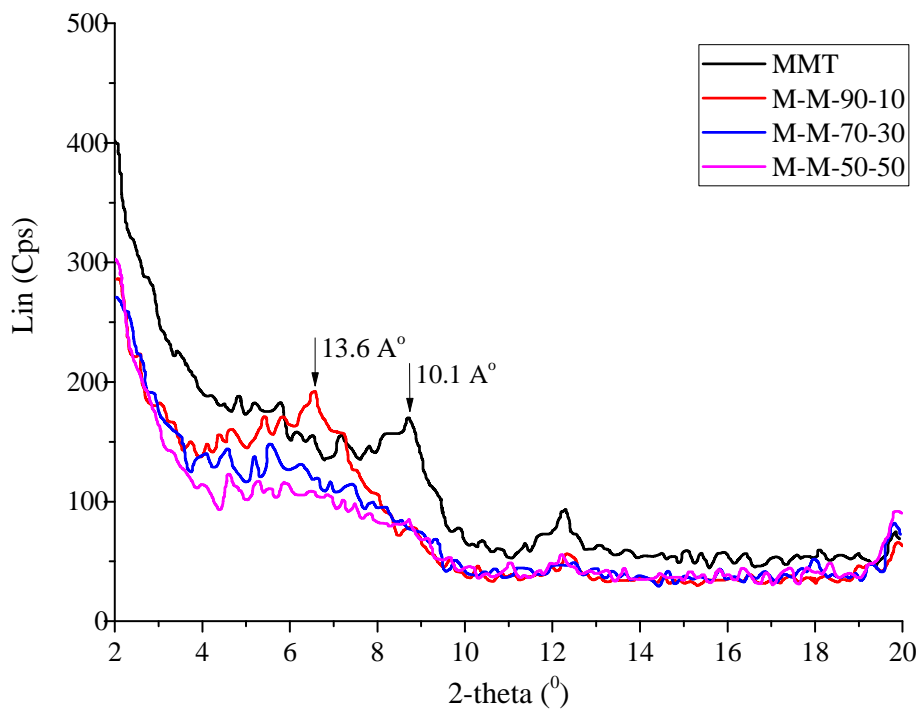
### 264 **3.2.2. MMT modified by M-Gly using the Haake thermomixer**

265 The modification of MMT by M-Gly, with or without solvent, did not effectively increase the  
266  $d_{001}$ -spacing of MMT, as shown in the above-reported results. Another method for the  
267 modification of MMT by melting was based on the Haake internal mixer. This method was used  
268 in creating the high shear rate during mixing at a defined speed, which will enhance the  
269 dynamic mobility of the M-Gly molecules and result in a better interaction with MMT platelets.  
270 This will help M-Gly penetrate into interlayer space of MMT much more easily. The XRD  
271 results (Fig. 5) showed the  $d_{001}$ -spacing of modified MMT using the Haake internal mixer.

272 The M-M-90-10 sample was about 13.6 Å and nearly identical to that of modified clay using  
273 the solvent method and the melting method using magnetic stirring. Meanwhile, the XRD  
274 results of the M-M-70-30 and M-M-50-50 samples did not show the  $d_{001}$  peak clearly. There  
275 was only a broadened mound of a peak observed in  $2\theta$  at  $4-8^\circ$  with low intensity. It could be  
276 concluded that, as the M-Gly content increases, the high shear rate force created by the rollers  
277 of the internal mixer plays a greater role that enhances the friction force between M-Gly and  
278 MMT and makes the layer structure of MMT become unstable and disordered.

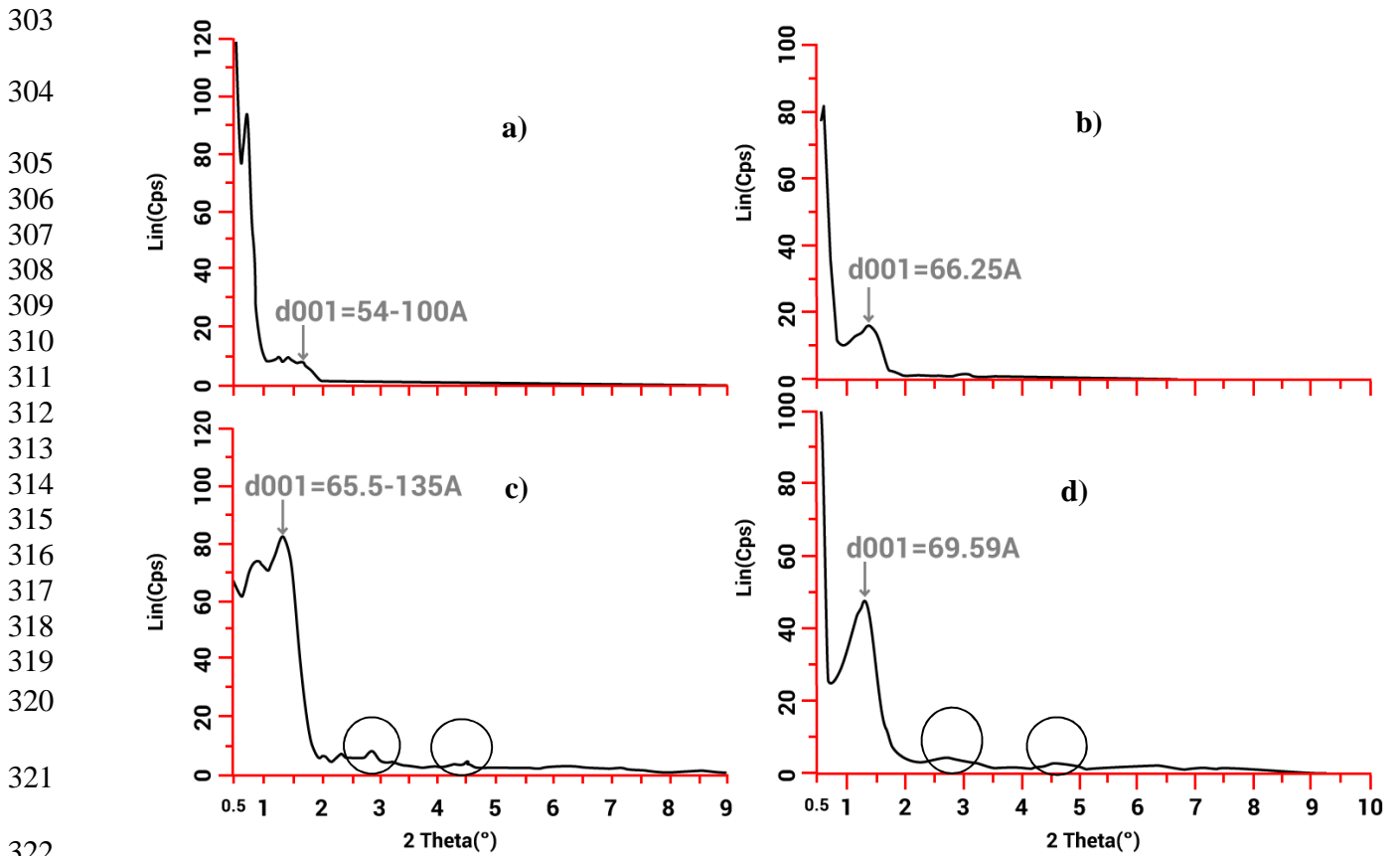
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**Figure 5:** XRD patterns of MMT modified by M-Gly at different ratios of MMT/M-Gly: 100/0; 90/10 (M-M-90-10); 70:30 (M-M-70-30) and 50/50 (M-M-50-50)

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.

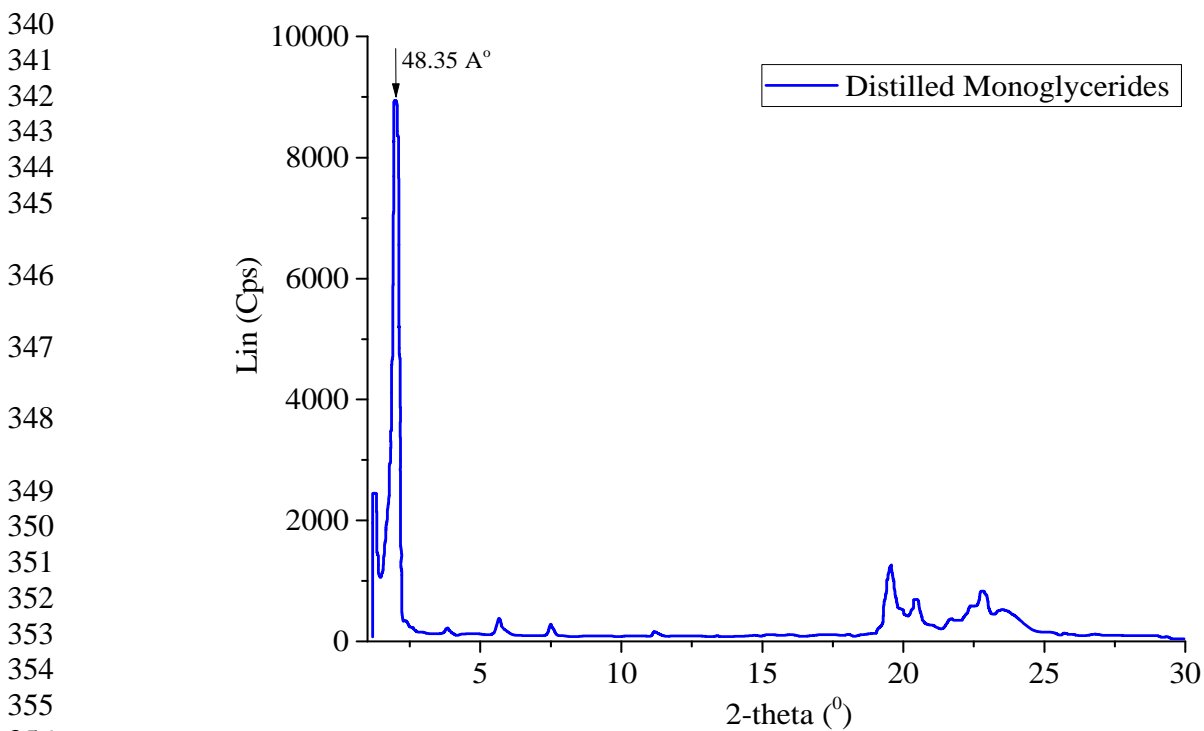


323 **Figure 6:** Small Angle XRD patterns of mixture MMT/ M-Gly at ratio: (a) 20/80 (M-M-20-80);  
 324 (b) 30/70 (M-M-30-70); (c) 40:60 (M-M-40-60); (d) 50:50 (M-M-50-50).

325 In particular, wide-angle peaks at 3.81, 4.31 and 4.54 Å<sup>o</sup> and a narrow-angle peak at 48.35 Å<sup>o</sup>  
 326 can be associated with the formation of the M-Gly lamellar Lβ phase (Anese et al., 2011). Thus,  
 327 for all modification cases (Fig. 6), this large diffraction peak at 54–70 Å<sup>o</sup> (1–1.5<sup>o</sup>, 2θ) might  
 328 correspond to the d<sub>001</sub>-spacing of the expanded MMT layer structure after being modified and to  
 329 M-Gly crystals on the MMT surface. At the modifying agent content of 50 and 60 wt% (Fig. 6d  
 330 and 6c), a very small broad peak in the zone from 2 to 3<sup>o</sup>, 2θ was also observed, indicating the  
 331 d<sub>001</sub>-spacing (about 20–30 Å<sup>o</sup>) of the intercalated MMT layer.

332 When the M-Gly content increased further (70 and 80 wt%) (Fig. 6b and 6a), the d<sub>001</sub> peak of  
 333 the modified MMT in the wide-angle diffraction was no longer observed. This indicates that at a

334 higher content, under the high shear mixing force of the thermomixer, the modifying agent was  
335 easily intercalated and expanded the layer structure of clay, and results in the disappearance of  
336 characteristics at the wide-angle diffraction (from 2 to 3<sup>0</sup>, 2 $\theta$ ). Especially at 80 wt% of M-Gly,  
337 the diffraction peak at small angles was broadened, which might have been caused by the high  
338 ratio of the expanded MMT layer structure (> 60 A<sup>o</sup>) and have affected the crystal size of M-  
339 Gly.



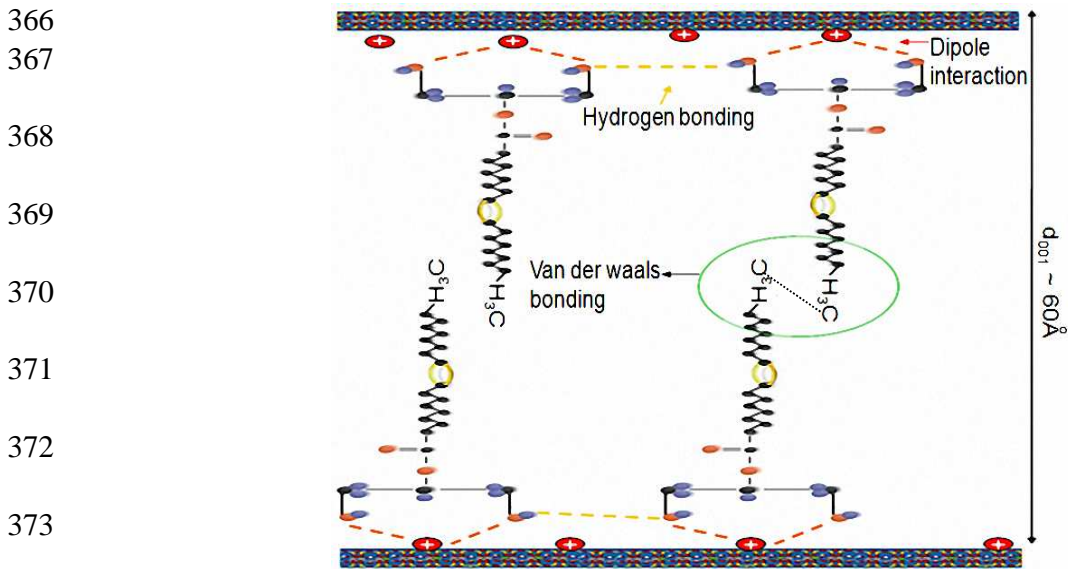
357 **Figure 7:** XRD pattern of commercial Distilled Monoglycerides

358  
359 The very high  $d_{001}$ -spacing values (> 60 A<sup>o</sup>) were obtained by assuming that M-Gly molecules  
360 are self-arranged via hydrogen linking and assembled vertically, as a bilayer, to the MMT layer,  
361 as suggested (Fig. 8). These results were explained based on the previous studies of M-Gly  
362 structure formation (Anese et al., 2011; Beall and Goss, 2004). According to the structure model  
363 of M-Gly proposed (Fig. 8), under the high shear rate force and high content of a modifying



364 agent, the electrostatic interaction between layers of clay became weaker and easily disordered.

365 Thus the modifying agent penetrated easily and expanded the galleries of clay noticeably.



374

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

377 The layer structure organization of MMT-modified M-Gly with the Haake internal mixer was

378 also investigated by transmittance electronic microscopy (TEM). The TEM images (Fig. 9)

379 showed the layer structure of modified MMT with some ranges appearing as three or five layers

380 of clay stacked together but disordered as compared to the original structure of unmodified

381 MMT. There were also zones showing the single- or double-layer form distributed incoherently

382 and separately. These results confirm the change of  $d_{001}$  peak formation and its movement

383 toward the low angles in XRD patterns.

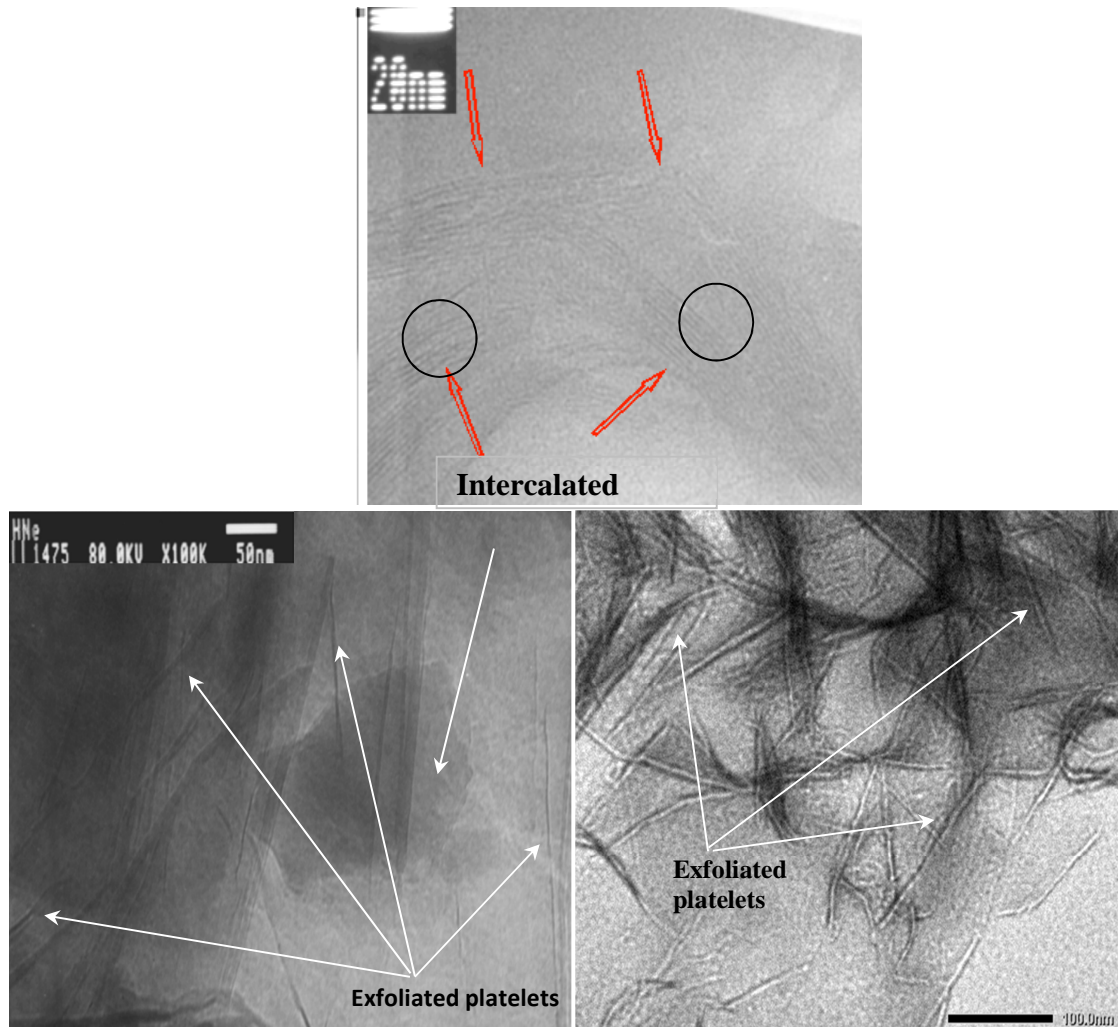
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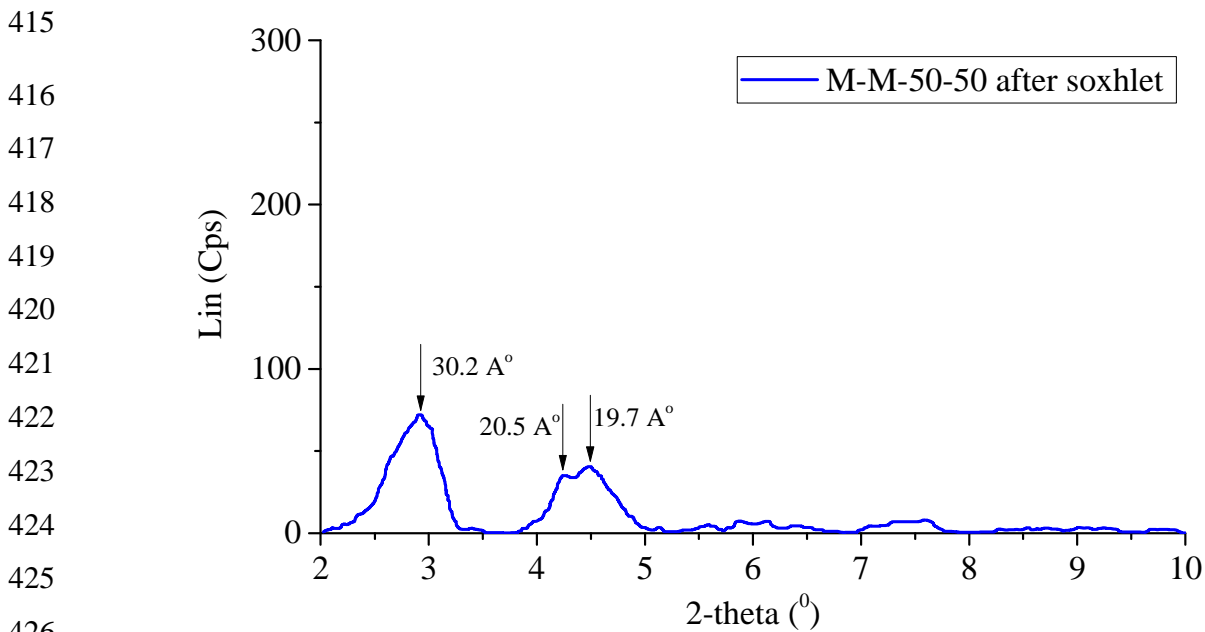
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**Figure 9:** TEM images of organoclay modified by 50 wt% of monoglyceride agent (M-M-50-50) via Haake method

### 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

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

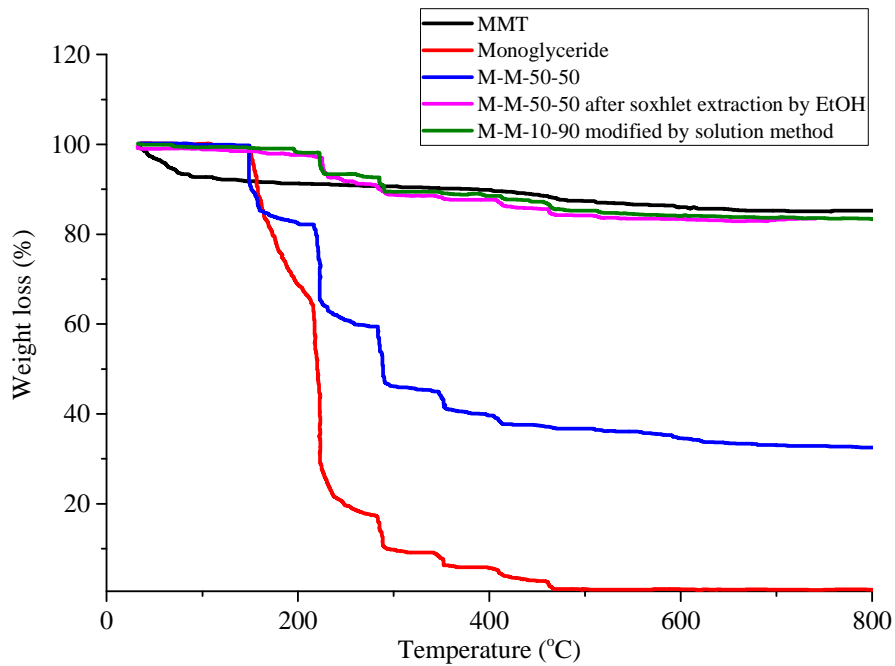


427 **Figure 10:** Small Angle XRD pattern of M-Gly modified MMT (50 wt%, M-M-50-50; Haake  
428 method) after soxhlet extraction process during 48 h

429

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

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



452 **Figure 11:** TGA curves of modified MMT: MMT; Monoglyceride (M-Gly); M-M-50-50 (Haake  
453 method); M-M-50-50 (Haake method) soxhlet extraction; and M-M-10-90 (solution method).

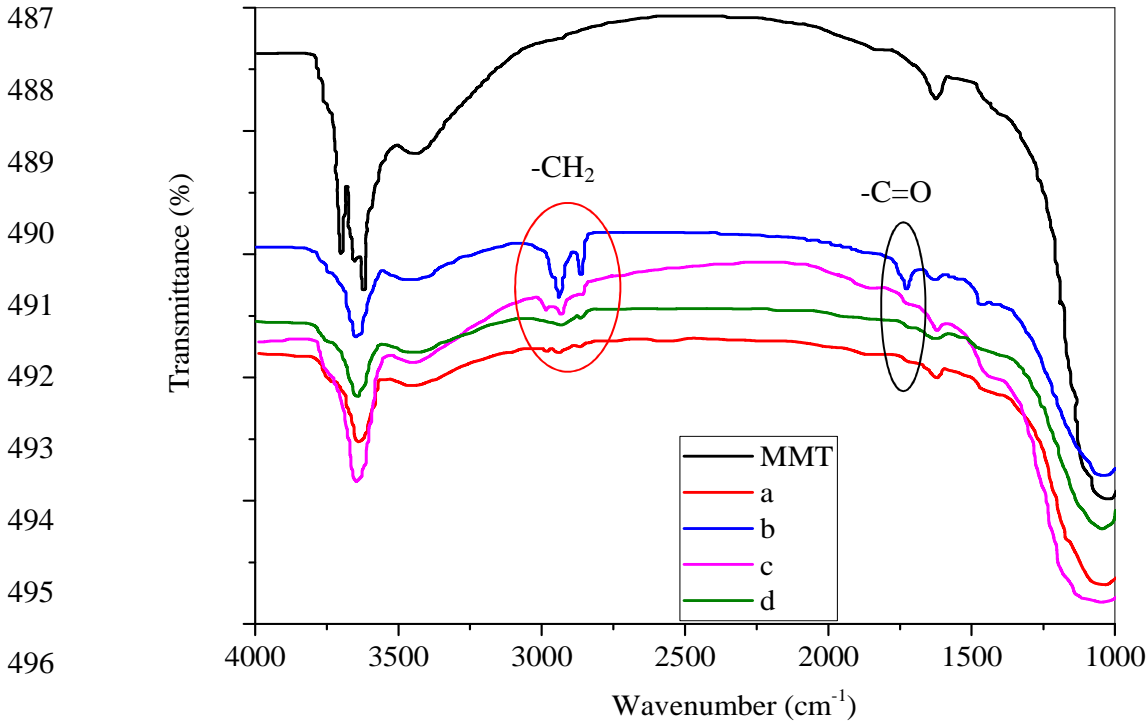
454 After Soxhlet extraction; the TGA curve of the sample was different, the mass loss rate  
455 decreased remarkably, and the degradation temperature was also higher as compared to the  
456 previous cases. This could be explained by the fact that after being extracted by ethanol solvent,  
457 a large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

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

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

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

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



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

#### 502 4. Conclusion

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

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

#### 517 **Acknowledgements**

518 This research was supported by Faculty of Material Science, University of Science, Viet Nam  
519 National University Ho Chi Minh city, Viet Nam and CentraleSupélec, Université Paris-Saclay,  
520 Centre Européen de Biotechnologie et de Bioéconomie (CEBB), 3 rue des Rouges Terres, 51  
521 110, Pomacle, France.

#### 522 **References**

523 Alemdar, A., Oztekin, N., Gungor, N., Ece, O.I., Erim, F.B., 2005. Effects of polyethyleneimine  
524 adsorption on the rheological properties of purified bentonite suspensions. *Colloids and Surfaces*  
525 *A: Physicochem. Eng. Aspects* 252, 95–98.  
526 Anese, M., Quarta, B., Peloux, L., Calligaris, S., 2011. Effect of formulation on the capacity of l-  
527 asparaginase to minimize acrylamide formation in short dough biscuits. *Food Research*  
528 *International* 44, 2837–2842.

529 Avom, J., Mbadcam, J.K., Matip, M.R.L., Germain, P., 2001. Adsorption isotherme de l'acide  
530 acétique par des charbons d'origine végétale. *African Journal of Science and Technology* 2, 1-7.

531 Beall, G.W., Goss, M., 2004. Self-assembly of organic molecules on montmorillonite. *Applied*  
532 *Clay Science* 27, 179– 186.

533 Bergaya, F., Lagaly, G., 2001. Surface modifications of clay minerals. *Applied Clay Science* 19,  
534 1–3.

535 Bizovská, V., Jankovič, L., Madejová, J., 2018. Montmorillonite modified with unconventional  
536 surfactants from the series of octylammonium-based cations: Structural characterization and  
537 hydration properties. *Applied Clay Science* 158, 102-112.

538 Borrego-Sánchez, A., Gómez-Pantoja, G., Morillo, E., Undabeytia, T., Sainz-Díaz, C.I., 2018.  
539 Adsorption of the tallow amine ethoxylate surfactant Ethomeen T/15 on montmorillonite.  
540 *Applied Clay Science*, Volume 161, 533-543.

541 Chassin, P., 1973. Etude de L'hydratation de la Montmorillonite Calcique en Présence  
542 d'Ethylène-glycol. *Ann. Agron* 24, 425-436.

543 Chou, C.C., Chiang, M.L., Lin, J.-J., 2005. Unusual Intercalation of Cationic Smectite Clays  
544 with Detergent-Ranged Carboxylic Ions. *Macromol. Rapid Commun* 26, 1841–1845.

545 Dentel, S.K., Bottero, J.Y., Khatib, K., Demougeot, H., Duguet, J.P., Anselme, C., 1995.  
546 Sorption of Tannic Acid, Phenol and 2, 4, 5-Trichlorophenol on organoclays *Wat. Res.* 29, 1273-  
547 1280.

548 Gao, X.W., Liu, K.Z., Pan, W.-P., Vaia, R., Hunter, D., Singh, A., 2001. Thermal  
549 characterization of organically modified montmorillonite. *Thermochimica Acta* 367–368, 339–  
550 350.



551 Ghiaci, M., Aghabarari, B., Gil, A., 2011. Production of biodiesel by esterification of natural  
552 fatty acids over modified organoclay catalysts. *Fuel* 90, 3382–3389.

553 Guo, H., Jing, X., Zhang, L., Wang, J., 2007. Preparation of inorganic–organic pillared  
554 montmorillonite using ultrasonic treatment. *Journal of Materials Science* 42, 6951-6955.

555 Ha-Thuc, C.N., Cao, H.T., Nguyen, D.M., Grillet, A.C., 2014. Preparation and Characterization  
556 of Polyurethane Nanocomposites Using Vietnamese Montmorillonite Modified by Polyol  
557 Surfactants. *Journal of Nanomaterials* 2014, 302735.

558 Ha -Thuc, C.N., Grillet, A.-C., Duclaux, L., Reinert, L., Ha-Thuc, H., 2010. Separation and  
559 purification of montmorillonite and polyethylene oxide modified montmorillonite from  
560 Vietnamese bentonites *Applied Clay Science* 49, 229-238.

561 Jordan, J.W., 1949. Organophilic bentonites: I. Swelling in organic liquids. *Journal of Physical  
562 and Colloid Chemistry* 53, 294– 306.

563 Kumar, J.P., Ramacharyulu, P.V.R.K., Prasad, B.S., Singh, B., 2015. Montmorillonites  
564 supported with metal oxide nanoparticles for decontamination of sulfur mustard. *Applied Clay  
565 Science* 116-117, 263–272.

566 Lin, F., Zhu, G., Shen, Y., Zhang, Z., Dong, B., 2015. Study on the modified montmorillonite for  
567 adsorbing formaldehyde. *Applied Surface Science* 356, 150–156.

568 Lucilene, B.P., Ana Rita Morales, A.R., Francisco, R.V.D., 2008. Organoclays: Properties,  
569 preparation and applications. *Applied Clay Science* 42, 8–24.

570 Nakas, G.I., Kaynak, C., 2008. Use of different alkylammonium salts in clay surface  
571 modification for epoxy-based nanocomposites *Polymer Composites* 30, 357–363.

572 Nguyen, D.M., Tran, D.T., Nguyen, T.T., Grillet, A.-C., Kim, N.H., Lee, J.H., 2016a. Enhanced  
573 Mechanical and Thermal Properties of Recycled ABS/Nitrile Rubber/Nanofil N15  
574 Nanocomposites. *Composites Part B: Engineering* 93, 280-288.

575 Nguyen, D.M., Vu, T.T., Grillet, A.C., Ha-Thuc, H., Ha-Thuc, C.N., 2016b. Effect of organoclay  
576 on morphology and properties of linear lowdensity polyethylene and Vietnamese cassava starch  
577 biobased blend. *Carbohydrate Polymers* 136, 163–170.

578 Olutoye, M.A., Wong, S.W., Chin, L.H., Amani, H., Asif, M., Hamee, B.H., 2016. Synthesis of  
579 fatty acid methyl esters via the transesterification of waste cooking oil by methanol with a  
580 barium-modified montmorillonite K10 catalyst. *Renewable Energy* 86, 392-398.

581 Pavlidou, S., Papaspyrides, C.D., 2008. A review on polymer-layered silicate nanocomposites.  
582 *Progress in Polymer Science* 33, 1119–1198.

583 Pospisil, M., Capková, P., Weiss, Z., Malac, Y.Z., Simonik, J., 2002. Intercalation of  
584 Octadecylamine into Montmorillonite: Molecular Simulations and XRD Analysis. *Journal of*  
585 *Colloid and Interface Science* 245, 126–132.

586 Rossi, S., Luckham, P.F., Green, N., Cosgrove, T., 2003. NMR solvent relaxation studies of Na-  
587 montmorillonite clay suspensions containing non-ionic polymers *Colloids and Surfaces A:*  
588 *Physicochemical and Engineering Aspects* 215, 11 -24.

589 Sagalowicz, L., Leser, M.E., Watzke, H.J., Michel, M., 2006. Monoglyceride selfassembly  
590 structures as delivery vehicles. *Trends in Food Science & Technology* 17, 204–214.

591 Santos, A.D., Viante, M.F., Pochapski, D.J., Downs, A.J., Almeida, C.A.P., 2018. Enhanced  
592 removal of p-nitrophenol from aqueous media by montmorillonite clay modified with a cationic  
593 surfactant. *Journal of Hazardous Materials* 355, 136-144.

594 Shen, Z., Simon, G.P., Cheng, Y.-B., 2002. Comparison of solution intercalation and melt  
595 intercalation of polymer-clay nanocomposite. *Polymer* 43, 4251-4260.

596 Shen, Z., Simon, G.P., Cheng, Y.-B., 2003. Saturation ratio of Poly(ethylene oxide) to silicate in  
597 melt intercalated nanocomposites. *European Polymer Journal* 39, 1917–1924.

598 Strawhecker, K.E., Manias, E., 2000. Structure and Properties of Poly(vinyl  
599 alcohol)/Na+Montmorillonite Nanocomposites. *Chemistry of Materials* 12, 2943-2949.

600 Tran, D.T., Nguyen, D.M., Nguyen, T.K.N., Ha -Thuc, C.N., 2012. Study structure and  
601 properties of nanocomposite material based on Unsaturated polyester with clay modified by poly  
602 (ethylene oxide). *Journal of Nanomaterials* 2012, 841813.

603 Tran, N.H., Dennis, G.R., Milev, A.S., Kannangara, G.S.K., Williams, P., Wilson, M.A., Lamb,  
604 R.N., 2005. Interactions of sodium montmorillonite with poly(acrylic acid). *Journal of Colloid  
605 and Interface Science* 290, 392–396.

606 Tran, N.H., Dennis, G.R., Milev, A.S., Kannangara, G.S.K., Williams, P., Wilson, M.A., Lamb,  
607 R.N., 2006. Dispersion of organically modified clays within n-alcohols *Journal of Colloid and  
608 Interface Science* 297, 541–545.

609 Wang, G., Lian, C., Xi, Y., Sun, Z., Zheng, S., 2018. Evaluation of nonionic surfactant modified  
610 montmorillonite as mycotoxins adsorbent for aflatoxin B1 and zearalenone. *Journal of Colloid  
611 and Interface Science* 518, 48-56.

612 Xiao, W., Zhan, M., Li, Z., 2003. Organically modifying and modeling analysis of  
613 montmorillonites. *Materials and Design* 24, 455–462.

614 Xie, W., Xie, R., Pan, W.-P., Hunter, D., Koene, B., Tan, L.-S., Vaia, R., 2002. Thermal stability  
615 of quaternary phosphonium modified montmorillonite. *Chemistry of Materials* 14, 4837– 4845.

616 Xu, Y., Khan, M.A.K., Wang, F., Xia, M., Lei, W., 2018. Novel multi amine-containing Gemini  
617 surfactant modified montmorillonite as adsorbents for removal of phenols. *Applied Clay Science*  
618 162 204-213.

619 Zhao, X., Urano, K., Ogasawara, S., 1989. Adsorption of Polyethylene glycol from Aqueous  
620 Solution on Montmorillonite Clays. *Colloid and Polymer Science* 267, 899-906.

621 Zhuang, G., Zhang, Z., Fu, M., Ye, X., Liao, L., 2015. Comparative study on the use of cationic-  
622 nonionic-organo-montmorillonite in oil-based drilling fluids. *Applied Clay Science* 116-117,  
623 257-262.

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# Graphical abstract

