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1 **Influence of montmorillonite/carbon nanotube hybrid nanofillers on the**  
2 **properties of poly(lactic acid)**

3

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25 ABSTRACT

26

27 Multi-walled carbon nanotube (MWCNT) and montmorillonite (Mt) are used as reinforcing  
28 fillers in polymers. Achieving homogeneous distribution of the reinforcing nanoparticles  
29 without agglomerates in polymeric matrices continues to be an important topic in materials  
30 science. In this study, hybrid Mt/MWCNT nanofiller was prepared after determining the most  
31 stable composition with the help of dynamic light scattering (DLS). The hybrid Mt/MWCNT  
32 was characterized via X-ray diffraction (XRD) and Fourier-transform infrared (FTIR)  
33 spectroscopy. The Mt/MWCNT hybrid fillers were incorporated in poly(lactic acid) (PLA) at  
34 concentrations of 0.5, 1 and 2 wt%, by a two-step procedure of solution and melt mixing, and  
35 their physicochemical, thermal, mechanical and morphological properties were evaluated.  
36 The physicochemical studies suggested strong hybrid-polymer interaction. The structural  
37 analyzes confirmed synergy between nanoclay and carbon nanotubes in achieving  
38 homogeneous dispersion of Mt/MWCNT nanoparticles in the PLA matrix. The thermal  
39 characterizations depicted that the Mt/MWCNT hybrid nanofillers synergistically restricted  
40 the PLA segment motions and promoted the crystallization of the polymer matrix. The  
41 mechanical properties of PLA/Mt/MWCNT nanocomposites were improved, confirming the  
42 reinforcing effect of the Mt/MWCNT hybrid on PLA matrix.

43

44 *Keywords:* Poly(lactic acid), montmorillonite, carbon nanotubes, nanocomposite, hybrid

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## 49 **1. Introduction**

50 Polymer nanocomposites gain increasing interest in advanced engineering applications  
51 such packaging, sports, military, energy and automobile, due to their multi-functional  
52 properties (Ramírez-Herrera et al., 2019). For ecological protection, more research attention  
53 is directed towards polymers that are biocompatible and biodegradable, like poly(lactic acid)  
54 (PLA). PLA is an aliphatic polyester, commercially sourced from renewable agricultural  
55 produce, and known for its easy processability by any of the conventional thermoplastic  
56 processing techniques, degradability to natural products and good mechanical properties (Liu  
57 et al., 2019; Yang et al., 2011; Katiyar et al., 2010). The use of nanoparticles in polymers to  
58 develop composites remains highly attractive because of their large interfacial area, low  
59 percolation threshold, and commensurate size scale between nanoparticles (Francisco et al.,  
60 2018). All these features translate to high mechanical properties, thermal and electrical  
61 conductivity, flame retardancy, chemical resistance and decreased permeability of  
62 nanocomposites, which are the desirable characteristics for engineering applications  
63 (Francisco et al., 2018; Bhattacharya, 2016). Within the previous decade, montmorillonite  
64 (Mt) and carbon nanotubes (MWCNTs) remain the leading and most studied nanofillers  
65 reported to impact superior properties in various polymeric matrices (Sanusi et al., 2020a;  
66 Anbusagar et al., 2018). Therefore, researchers explore the synergistic properties of Mt and  
67 MWCNT in polymers (Ma et al., 2007; Hapuarachchi and Peijs, 2010; Geng et al., 2012;  
68 Khajepour et al., 2014; Pandey et al., 2014; Song, 2016; Hosseini and Yousefi, 2017) and  
69 blends (Zhu et al., 2020; Al-Saleh, 2015; Chiu, 2017). This is to earnest both of their  
70 extraordinary individual properties, reducing the percolation threshold as well as addressing  
71 the limitation of each of the two prominent nanofillers (Bilotti et al., 2013). MWCNT  
72 typically forms stabilized aggregates attributed to high hydrophobicity, making its dispersion  
73 exceedingly difficult (Sianipar et al., 2017; Barrau et al., 2011), while the stacking of Mt

74 platelets and its incompatibility with common hydrophobic polymers are the common  
75 nanoclay challenges (Madaleno et al., 2013; Sibeko, 2012).

76 In some studies, the two nanofillers were physically added to polymers by solution mixing  
77 (Azam and Samad, 2018) or melt mixing (Al-Saleh, 2017; Stern et al., 2018). Yet,  
78 agglomerates of the nanofillers in the matrices persisted, related among others, to the increase  
79 of filler content in matrix (Azam and Samad, 2018). Recently, Mumtazah et al. (2019)  
80 prepared Mt/MWCNT hybrid nanofiller using a sol-gel method with strong acids, in elevated  
81 temperatures, to reinforce Chitosan/phthalic anhydride. Such a method constantly raises  
82 environmental and hazard concerns because of the acids and energy consumption involved  
83 (Koo, 2016).

84 Growth of MWCNT with catalytic chemical vapor deposition (CCVD) over metal ion-  
85 exchanged Mt platelets is another method of preparing preformed Mt/MWCNT hybrid filler  
86 to improve polymer properties (Manikandan et al., 2012). The growth of MWCNT over Mt  
87 leads to pre-exfoliation of the Mt's internal structure, which facilitates its dispersion in the  
88 polymer matrix (Madaleno et al., 2013). Thus, incorporation of CCVD Mt/MWCNT  
89 nanofillers in polymers attracts research gains. Santangelo et al. (2011) reinforced PLA with  
90 CCVD Mt/MWCNT and achieved enhanced sorption and electrical conductivity in 6-9 orders  
91 of magnitude. Gorrasi et al. (2013) reinforced PLA with CCVD Mt/MWCNT and reported  
92 less elastic modulus degradation against UV irradiation time compared with neat PLA.  
93 Madaleno et al. (2013) also utilized CCVD Mt/MWCNT to develop polyurethane  
94 nanocomposite foam, all the composites attained improved compressive strength and thermal  
95 stability over the neat matrix. Manikandan et al. (2012) utilized CCVD-prepared  
96 Mt/MWCNT fillers to achieve defect-free homogenous Nafion nanocomposite for fuel cell  
97 applications. Zhang et al. (2006) incorporated CCVD-prepared Mt/MWCNT into polyamide-  
98 6 (PA6), tensile modulus and strength were significantly enhanced by 289% and 153%,

99 respectively. Homogenous dispersion of CCVD Mt/MWCNT and strong adhesion with the  
100 polymer, resulting in enhanced mechanical properties of the nanocomposite, were reported.  
101 Gorrasi et al. (2014) reported thermal stability, mechanical and electrical properties  
102 enhancement in poly(ethylene terephthalate) reinforced with CCVD Mt/MWCNT. Enotiadis  
103 et al. (2013) also incorporated Mt/MWCNT in polystyrene-b-poly(isoprene)-b-polystyrene  
104 and improved mechanical properties were reported, compared to neat triblock polymer and  
105 clay/polymer nanocomposite. However, the CCVD Mt/MWCNT hybrid nanofillers is often  
106 said to accelerate thermal degradation rates in the resulting nanocomposites. Most of the  
107 studies attributed this drawback to the high thermal conductivity nature of metal particle  
108 residues that are usually utilized in exfoliating clay during CCVD (Madaleno et al., 2013;  
109 Terzopoulou et al., 2016; Sanusi et al., 2020a). Furthermore, CCVD requires high-energy  
110 consumption, use of harmful chemicals, and the process is quite complex (Madaleno et al.,  
111 2012; Manikandan et al., 2012; Manikandan et al., 2013).

112 Lately, Wang et al. (2009) dispersed MWCNT in Mt aqueous dispersion before adding  
113 poly(ethylene oxide) to form a ternary nanocomposite. Young's modulus, strength at break  
114 and elongation of the nanocomposite were reported to be significantly improved. Ma et al.  
115 (2019) adopted the same approach by dispersing MWCNT in Mt aqueous dispersion to form  
116 Mt/MWCNT hybrid solution. Hydrophobic poly(ether ether ketone) (PEEK) was then mixed  
117 with the hybrid aqueous dispersion to form a coating over the PEEK masterbatch. They  
118 reported 48% storage modulus enhancement but with reduction in toughness, which was  
119 attributed to lack of diffusion of the matrix into the interlayer space of Mt. Levchenko et al.  
120 (2011) adopted freeze-drying in preserving the swelling agent (cetyl-trimethyl ammonium  
121 bromide) within intercalated Mt, before physical incorporation of MWCNT in polypropylene  
122 by melt-mixing. Hence, lyophilization of Mt/MWCNT aqueous dispersions is an efficient and

123 simple method for preparing Mt/MWCNT hybrid nanoparticles, which improves the  
124 intercalation of polymeric chains into the layers of Mt.

125 Most recently, Bai et al. (2020) adopted the freeze-drying method to prepare different  
126 formulations of functionalized MWCNT:Mt hybrids ((1:1), (1:2), (1:4)) for reinforcing PLA.  
127 The elongation at break increased from 5.9% for PLA to 87.3% for PLA reinforced with  
128 MWCNT:Mt hybrid in proportion of 1:2 (PLA/MWCNT:Mt (1:2)). The maximum modulus  
129 and ultimate strength reached 4.3 GPa and 75.6 MPa, respectively, for the PLA/MWCNT:Mt  
130 (1:4) nanocomposite compared to the respective 3.2 GPa and 74.2 MPa for neat PLA.  
131 Meanwhile, only nanocomposite reinforced with 1:1 of MWCNT:Mt hybrid had significant  
132 enhancement in the thermal stability. Well distribution of the freeze-dried hybrid  
133 nanoparticles was reported to be responsible for the properties improvement.

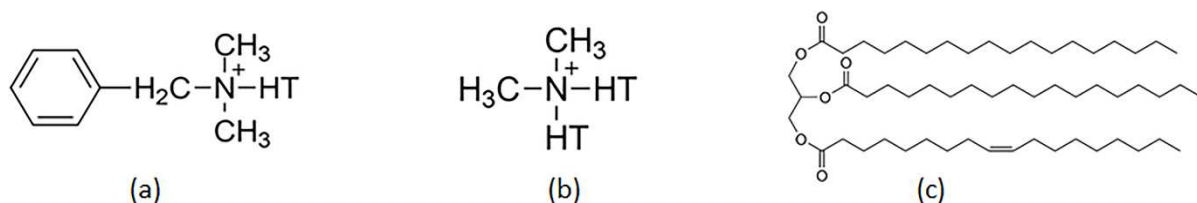
134 In this work, Mt/MWCNT hybrid nanofillers were prepared by ultrasonication and  
135 lyophilization technique, and then incorporated in poly(lactic acid) (PLA) via solution casting  
136 followed by melt mixing, to study their effects on the properties of PLA. To the best of our  
137 knowledge, besides the work by Bai et al. (2020) described above, PLA nanocomposites  
138 incorporated with freeze-dried Mt/MWCNT hybrid fillers are uniquely reported. Different  
139 from the work of Bai et al. (2020), it is worth noting that three kinds of Cloisite Mt (Mt Na<sup>+</sup>,  
140 Mt 10A and Mt 20A) and two MWCNT (pristine and functionalized) have been studied in  
141 this research, and the most stable Mt/MWCNT hybrid formulation has been selected in  
142 achieving nanocomposites. As against chemically functionalized MWCNT that may pose  
143 environmental hazard, this research identified the optimal Mt/MWCNT hybrid formulation  
144 using pristine MWCNT. In addition, this work presented a detailed structural characterization  
145 of the selected Mt/MWCNT hybrid treated by lyophilization in relation with its constituents.  
146 Thereafter, the influence of the mass fraction of the selected hybrid nanoparticles on the  
147 structure, physicochemical, crystallization, thermal and mechanical properties of PLA was

148 analyzed. Meanwhile, though thermal study was reported by Bai et al. (2020), the work  
 149 focused deeply on the relations between morphology and mechanical properties of PLA  
 150 reinforced with Mt/MWCNT hybrid, by varying concentration of surface compatibilized Mt  
 151 (1.34TCN Nanocor) over a fixed mass of carboxyl functionalized MWCNT.

## 152 2. Materials and methods

### 153 2.1. Materials

154 Poly(L-lactic acid) (PLA) (Ingeo™ Biopolymer 3052D) matrix used in the work was  
 155 supplied by Plastica Kritis S.A., with molecular weight  $M_w = 63.090$  g/mol and intrinsic  
 156 viscosity  $\eta = 1.055$  dL/g. Three different Cloisite® montmorillonite (Mt) nanoclay types  
 157 were used: Mt Na<sup>+</sup>, Mt 10A and Mt 20A, which correspond to unmodified Mt, dimethyl  
 158 benzyl hydrogenated tallow quaternary ammonium (2MBHT) modified Mt, and dimethyl  
 159 hydrogenated tallow quaternary ammonium (2MHT) modified Mt, respectively. These  
 160 nanoclays are produced by Southern Clay Products, Inc. Ganzales, USA. Fig. 1 presents the  
 161 structures of the modifiers for Mt 10A, Mt 20A and the structure of tallow. Multi-walled  
 162 carbon nanotubes (MWCNT) and functionalized multi-walled carbon nanotubes (MWCNT-f)  
 163 with 5% -NH<sub>2</sub> were used as the second nanofillers. The nanotubes are produced by Glonatech  
 164 SA, Athens, Greece with average diameter of  $15 \pm 5$  nm, length  $> 5$   $\mu$ m and bulk density of  
 165  $0.2$  g/cm<sup>3</sup>. Reagent-grade dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) was supplied by Scharlab S.L. Spain.



166 (a)  
 167 **Fig. 1.** Chemical structure of (a) dimethyl benzyl hydrogenated tallow quaternary ammonium  
 168 (2MBHT); (b) dimethyl hydrogenated tallow quaternary ammonium (2MHT); (c) HT -  
 169 tallow.



170 *2.2. Optimization of hybrid filler composition*

171 The stability and zeta potential ( $\zeta$ -potential) of different types of Mt (Mt Na<sup>+</sup>, Mt 10A and  
172 Mt 20A) and MWCNT (CNT, CNT-f) as well as different Mt/MWCNT mass ratios were  
173 examined to choose the optimum composition of the hybrid Mt/MWCNT nanofiller. First, an  
174 Mt aqueous dispersion was prepared by stirring and ultrasonication (UP100H Ultrasonic  
175 Processor Hielscher Ultrasound Technology, Germany) for 5 min. Afterwards, appropriate  
176 quantity of MWCNT was added in the Mt dispersion, stirred and ultrasonicated until there  
177 were no visible aggregates. The final concentration of the dispersions was 1 mg/mL and the  
178 Mt/MWCNT mass ratios tested were 1:1, 2:1 and 4:1 (Table 1). At varying time intervals,  
179 photographs of the sedimentation process were captured to monitor the suspension stability.  
180 The colloidal stability of the prepared Mt/MWCNT dispersions was evaluated 1 h after  
181 preparation by measuring the  $\zeta$ -potential with a Dynamic Light Scattering (DLS) apparatus,  
182 Zetasizer 5000, Malvern Instruments, UK.

183 *2.3. Preparation of Mt/MWCNT hybrid nanofiller*

184 The most stable Mt/MWCNT dispersion (section 2.2) was lyophilized with a Scanvac  
185 Coolsafe freeze dryer (Germany), equipped with vacuum pump (2.3/2.8 m<sup>3</sup>/h, 4.10<sup>-4</sup> mbar).  
186 The freeze-dried nanofiller, which is Mt/MWCNT hybrid produced by this lyophilization  
187 process, is referred to as hybrid and abbreviated as "hyb" throughout the rest of the  
188 manuscript.

189 *2.4. Preparation of PLA/hyb nanocomposites*

190 A two-step solution mixing and melt mixing method was adopted for the preparation of  
191 PLA/hyb nanocomposites. The first step was the preparation of masterbatch films via  
192 solution mixing. The composition of the masterbatch is 1 g of PLA and 0.05, 0.1 and 0.2 g of  
193 hyb dispersed by ultrasonication in dichloromethane (50 mL). The dispersion was under

194 continuous magnetic stirring until most of the solvent evaporated. The resulting slurry was  
 195 dried under vacuum at 50 °C to obtain the masterbatch film. Thereafter, the dried masterbatch  
 196 film and PLA were fed into a Haake-Buchler Reomixer (model 600) of 69 cm<sup>3</sup> volumetric  
 197 capacity, with twin-roller blades, at 180 °C and a speed 30 rpm for 5 min to prepare the  
 198 nanocomposites, according to the composition given in Table 2. The obtained  
 199 nanocomposites were molded into specimens, by compression at 180 °C, with a hot-pressing  
 200 machine (Paul-Otto Weber GmbH, Germany). Additionally, nanocomposite samples were  
 201 annealed at 120 °C for 1 h to crystallize them.

202 **Table 1**

203 Different amounts of Mt and MWCNT used to determine optimum stable Mt/MWCNT  
 204 hybrid nanofillers mass ratio

No.	Sample	Montmorillonite (mg)			Carbon nanotubes (mg)	
		Mt Na <sup>+</sup>	Mt 10A	Mt 20A	MWCNT	MWCNT-f
1	Mt Na <sup>+</sup>	30				
2	Mt 10A		30			
3	Mt 20A			30		
4	CNT				30	
5	CNT-f					30
6	Mt Na <sup>+</sup> /MWCNT 1:1	15			15	
7	Mt Na <sup>+</sup> /MWCNT 2:1	20			10	
8	Mt Na <sup>+</sup> /MWCNT 4:1	24			6	
9	Mt Na <sup>+</sup> /MWCNT-f 1:1	15				15
10	Mt Na <sup>+</sup> /MWCNT-f 2:1	20				10
11	Mt Na <sup>+</sup> /MWCNT-f 4:1	24				6
12	Mt 10A/MWCNT 1:1		15		15	
13	Mt 10A/MWCNT 2:1		20		10	
14	Mt 10A/MWCNT 4:1		24		6	
15	Mt 10A/MWCNT-f 1:1		15			15
16	Mt 10A/MWCNT-f 2:1		20			10
17	Mt 10A/MWCNT-f 4:1		24			6
18	Mt 20A/MWCNT 1:1			15	15	
19	Mt 20A/MWCNT 2:1			20	10	
20	Mt 20A/MWCNT 4:1			24	6	
21	Mt 20A/MWCNT-f 1:1			15		15
22	Mt 20A/MWCNT-f 2:1			20		10
23	Mt 20A/MWCNT-f 4:1			24		6

205

206 **Table 2**

207 Composition of the prepared nanocomposites.

No.	Sample	PLA (%wt)	Mt/MWCNT hybrid (%wt)
1	PLA	100	0
2	PLA0.5hyb	99.5	0.5
3	PLA1.0hyb	99	1
4	PLA2.0hyb	98	2

208 *2.5. Characterizations*

209 X-ray diffraction (XRD) analysis was carried out using a Rigaku MiniFlex II DESKTOP  
210 X-ray Diffractometer with Cu K $\alpha$  radiation ( $\lambda = 0.154$  nm). Measurements were performed  
211 over the ranges 2 - 10 $^\circ$  and 10 - 50 $^\circ$ , both with a step of 0.05  $^\circ$  and speed 1  $^\circ$ /min. The clay  
212 interlayer distance  $d$  was evaluated from the XRD patterns using Bragg's formula given by  
213 (Raji et al., 2018):

214 
$$2d \sin \theta = n\lambda \tag{1}$$

215 where  $\theta$ ,  $n$  and  $\lambda$  represent, diffraction angle, integer of the diffraction band order ( $n = 1$ )  
216 and wavelength of X-ray, respectively.

217 Fourier-transform infrared (FTIR) spectra were obtained using a Perkin-Elmer Spectrum  
218 One FT-IR, with a resolution of 4  $\text{cm}^{-1}$  and using 16 scans.

219 The dispersion state of Mt/MWCNT hybrid in the PLA was examined by transmission  
220 electron microscopy (TEM), using a Jeol JEM 1010 electron microscope operated at 100kV.  
221 The TEM specimens were prepared by cutting thin sections of the studied materials with a  
222 Leica UCT Ultracut ultramicrotome and collecting them on 400-mesh Au grids.

223 Differential scanning calorimetry (DSC) analyzes were conducted with a Perkin-Elmer  
224 Pyris 6 DSC, under 20 mL/min flow of nitrogen ( $\text{N}_2$ ). The experiments were conducted on  
225 samples mass of about 8 mg. In order to erase any thermal history, each sample was taken

226 through heating-cooling cycle twice, first heated from 20 to 190 °C at a rate of 10 °C/min,  
227 held for 1 min at 190°C, and then cooled from 190 °C to 20 °C at a rate of 10 °C/min. The  
228 crystallinity  $X_c$  of the neat PLA and its nanocomposites were calculated using equation (2)  
229 (Hu et al., 2017):

$$230 \quad X_c = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_m^o \times f} \times 100\% \quad (2)$$

231 where  $\Delta H_m$  and  $\Delta H_{cc}$  are melting and crystallization enthalpies,  $\Delta H_m^o$  is melting enthalpy for  
232 100% crystalline PLA (93.7J/g),  $f$  is the percentage weight of the PLA in the nanocomposite.

233 Thermogravimetric analyzes (TGA) were performed with a Setaram SETSYS TG-DTA  
234 16/18 instrument. Samples of  $3 \pm 0.5$  mg were placed in alumina crucibles and were measured  
235 in dynamic conditions, in the temperature range from 26 to 600 °C, with a heating rate of 20  
236 °C/min, with a 50 mL/min N<sub>2</sub> flow. In addition, TGA under kinetic conditions were  
237 performed, with the additional heating rates of 5, 10 and 15 °C/min, using the NETZSCH  
238 Kinetics Neo software, version 2.4.6. For this test, samples of the same mass and under the  
239 same aforementioned conditions were adopted.

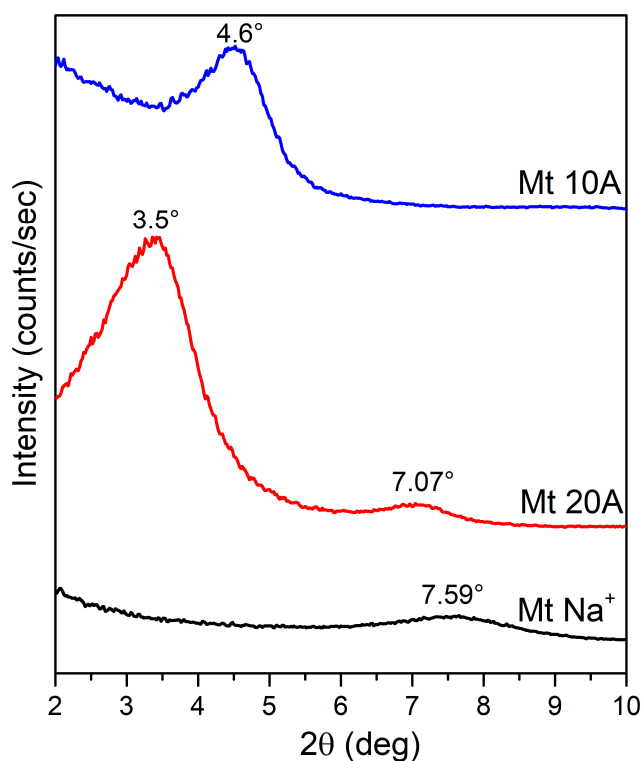
240 The mechanical tensile tests were achieved using an Instron 3344 dynamometer (USA),  
241 according to ASTM D638, at a crosshead speed of 2 mm/min. Average of three dumbbell-  
242 shaped samples were tested for each kind of material to determine the mechanical  
243 characteristics of the studied neat PLA and nanocomposites.

### 244 **3. Results and discussion**

#### 245 *3.1. Structures of the montmorillonite nanoclays*

246 The Small Angle X-ray diffraction (SAXD) results of the crystallographic structures of Mt  
247 Na<sup>+</sup>, Mt 10A and Mt 20A are presented in Fig. 2. The unmodified Mt Na<sup>+</sup>, that contains  
248 primarily Na<sup>+</sup> exchangeable cations recorded  $2\theta = 7.59^\circ$  equivalent to 1.163 nm basal  $d$ -

249 *value*. The result is consistent with literature (Tunç and Duman, 2011; 2010). The modified  
250 nanoclays Mt 10A and Mt 20A featured sharp diffraction peaks at lower positions compared  
251 to unmodified Mt Na<sup>+</sup>, i.e. at  $2\theta = 4.6^\circ$  and  $2\theta = 3.5^\circ$ , corresponding respectively to the  
252 interlayer distances  $d = 1.918$  nm and  $d = 2.521$  nm. This suggests that the quaternary  
253 ammonium ions intercalated into the modified clays Mt 10A and Mt 20A layers resulted in  
254 the expansion of basal spacing (Qin et al., 2018). However, the diffractograms of Mt 20A  
255 shows additional smaller peak around  $7.07^\circ$  ( $d = 1.249$  nm) which is not attributed to  $d_{002}$   
256 but close to crystallographic *d-value* of Mt Na<sup>+</sup> ( $d = 1.163$  nm). This implies that Mt 20A  
257 contains some amount of tactoids that have nanoclays platelets intercalated with Na<sup>+</sup> cations  
258 (Timochenco et al., 2010). This second peak, at  $7.07^\circ$ , also suggests an insignificant edge  
259 grafting or interlayer of 2MHT ammonium molecules within the Mt 20A layers (Raji et al.,  
260 2018). Moreover, by comparing the intensities and shapes of Mt 10A and Mt 20A, it can be  
261 agreed that Mt 10A presented the more disordered layer-structure while the very sharp and  
262 high peak of Mt 20A shows higher ordered layer-structure (Zhuang et al., 2015; Qin et al.,  
263 2018). Thus, from the above, we can conclude that the disordered layer-structure in Mt 10A  
264 is probably an advantage, over other clays, for easier intercalation of other phases.



265

266

**Fig. 2.** Small angle X-ray diffractograms of Mt Na<sup>+</sup>, Mt 20A and Mt 10A.

267 *3.2. Evaluation of dispersion quality of the nanoparticles in water*

268 The sedimentation photographs of different Mts, MWCNTs and combinations of  
 269 Mt/MWCNT hybrid suspensions are shown in Figs. 3 and 4; after 1 h, 24 h and 1 week of  
 270 suspension. Single dispersion of Mt Na<sup>+</sup> or Mt 10A in aqueous solution by agitation showed  
 271 significant level of the nanoclays stability in the aqueous solution up to 24 h, thereafter,  
 272 sediments begun to grow at the bottom of the vial with time (Fig. 3). In contrary, for Mt 20A  
 273 suspension, significant amount of sediments was obtained after 1 h, at the bottom of the vial,  
 274 leaving almost clear solution at the top. Pristine Mt Na<sup>+</sup> is greatly hydrophilic because of the  
 275 rich Na<sup>+</sup> cations in the clays, which are easily hydrated, and that makes it disperses fine in  
 276 water on agitation (Narro-Céspedes et al., 2018). Likewise, the modifying agent 2MBHT on  
 277 Mt 10A was suspected to provide good interaction with water molecules that promoted the  
 278 nanoclay suspension in the solution. Ha (2006) reported that the replacement of an  
 279 hydrogenated tallow group with a benzyl group gives Mt 10A a moderate hydrophobicity as

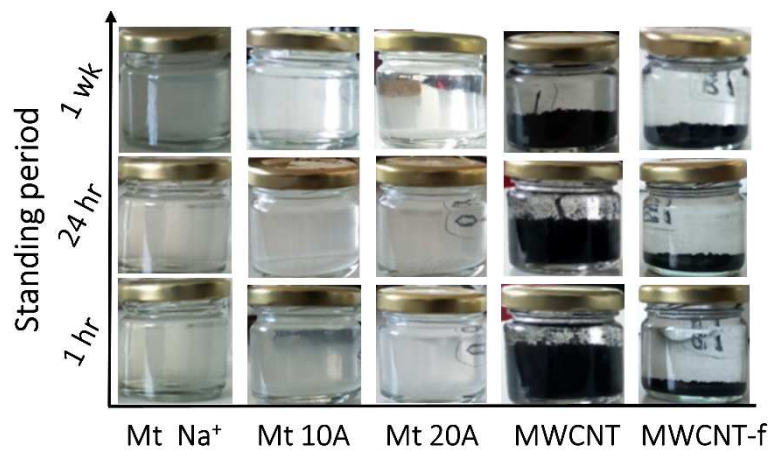
280 well as compatibility with poly(butylene terephthalate). However, Mt 20A is modified with  
281 only hydrogenated tallow group. After 1 h of the solution preparation, singly prepared  
282 pristine MWCNT or MWCNT-f suspension settled towards the bottom of the of vial leaving  
283 few MWCNT suspension at the top (Fig. 3), and the sediment increased rapidly with time.  
284 This is attributed to the inherent high force of attraction between the MWCNT nanoparticles.

285 With varying ratio of Mt Na<sup>+</sup> over MWCNT (Fig. 4a), the dispersions remained black  
286 solution beyond 1 h. However, after 24 h, sediments began to build-up leaving dark but a bit  
287 transparent solution at the top of the vial and this progressed with time. The samples with Mt  
288 Na<sup>+</sup>/MWCNT-f (Fig. 4b) maintain black aqueous solution until 24 h, when the solution  
289 turned transparent-brownish with black sediments after 1 week. The fair maintenance of dark  
290 solution before the clear separation shows little level of stability, that is, weak promotion of  
291 MWCNT suspension and dispersion in water as result of Mt Na<sup>+</sup> incorporation.

292 On addition of Mt 10A with MWCNT (Fig. 4c) or MWCNT-f (Fig. 4d), the entire sample  
293 ratios showed high level of stable black aqueous solutions beyond 24 h, with insignificant  
294 sedimentation after a week. This suggests that Mt 10A greatly support the dispersion of both  
295 pristine and functionalized MWCNT, independently of the standing period and irrespective of  
296 the nanofillers ratio, when compared with Mt Na<sup>+</sup>.

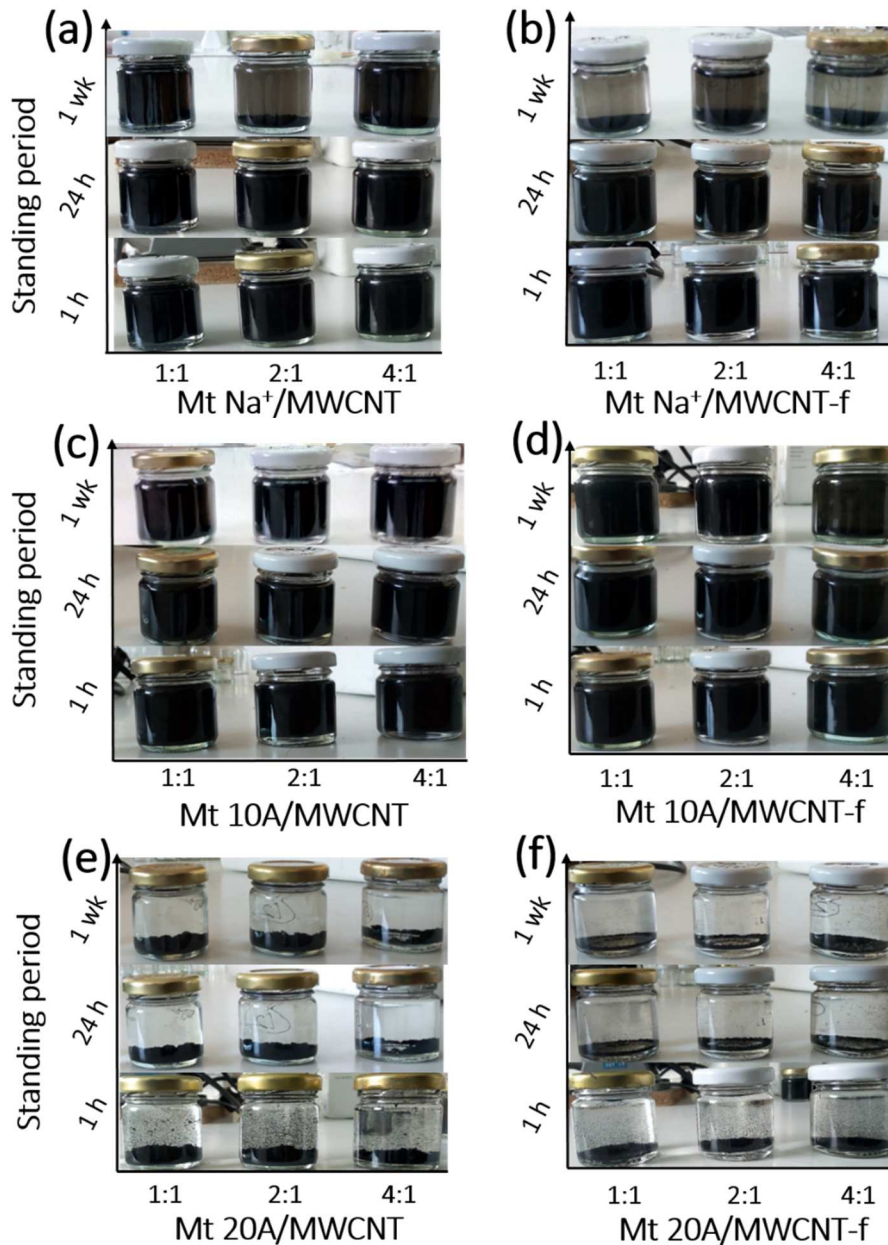
297 As seen in Fig. 4e and 4f, the presence of Mt 20A did not keep either the MWCNT or  
298 MWCNT-f particles suspended in the solution. The consistent inability of Mt 20A to  
299 influence MWCNT suspension in the aqueous solution suggests that the 2MHT ion over Mt  
300 20A does not interact with neither of the MWCNTs nor the aqueous medium. As earlier  
301 identified in the SAXD pattern of Mt 20A, insignificant edge grafting or interlayer of 2MHT  
302 ammonium molecules within the Mt 20A layers, may have prevented the MWCNT  
303 intercalation into the clay platelets. Thus, the two nanoparticles discretely settled rapidly.

304 Conclusively, absence of clay in any of the vials brings about complete sedimentation of  
305 MWCNT owing to strong van der Waals forces between the MWCNT particles and deficient  
306 chemical affinity with the aqueous medium (Lee et al., 2007; Wang et al., 2009). Garcia et al.  
307 (2015) remarked that chemical modification of phyllosilicate Mt raises its hydrophobicity,  
308 and Mt 20A is more than Mt 10A. The 2MHT ammonium cation of Mt 20A has a high  
309 density and hydrophobicity because of its tallow chains (Galimberti et al., 2015), hence, its  
310 rapid sedimentation in solution and the least compatibility with MWCNT. Re-aggregation of  
311 dispersed MWCNT, due to van der Waals force resulting from high surface energy, seemed  
312 to be mostly prevented by the platelets of Mt 10A nanoclay type. This presents Mt 10A to be  
313 of higher compatibility with either of the two carbon nanotubes.



314  
315 **Fig. 3.** Sedimentation of Mt Na<sup>+</sup>, Mt 10A, Mt 20A, MWCNT and MWCNT-f at different  
316 periods.





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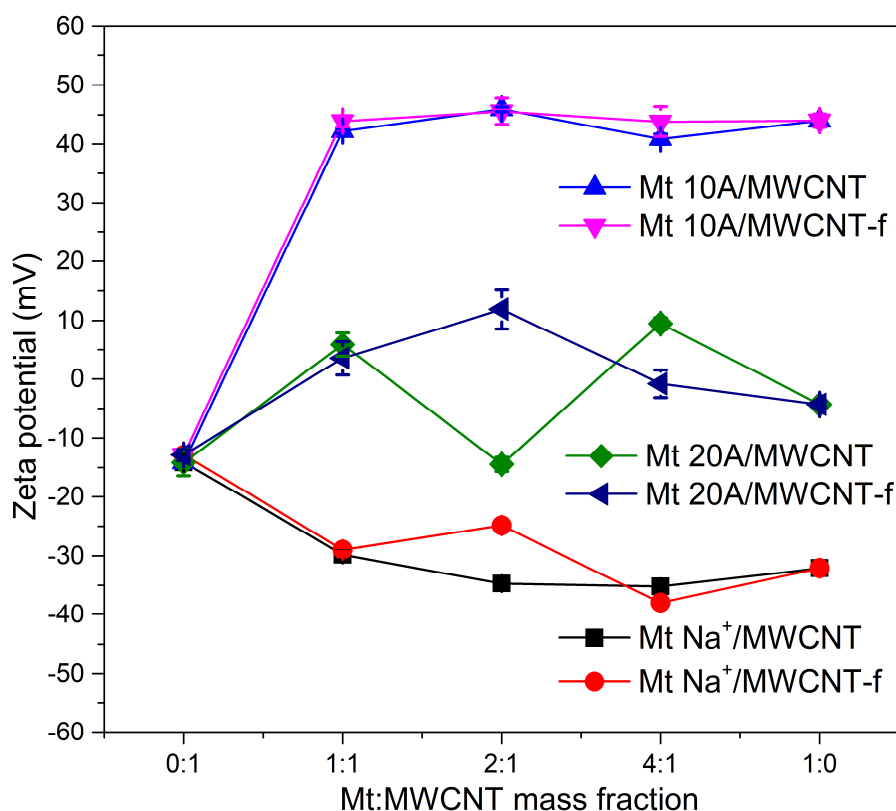
318 **Fig. 4.** Sedimentation of different ratios of (a) Mt Na<sup>+</sup>/MWCNT; (b) Mt Na<sup>+</sup>/MWCNT-f; (c)  
 319 Mt 10A/MWCNT; (d) Mt 10A/MWCNT-f; (e) Mt 20A/MWCNT; (f) Mt 20A/MWCNT-f at  
 320 different standing periods.

321  $\zeta$ -potential can evaluate the synergetic interactions between two different nanofillers  
 322 (Galimberti et al., 2015). The dividing line between stable and unstable suspensions is  
 323 generally taken at either 30 mV or -30 mV. Particles having the zeta potentials higher than  
 324 +30 mV or lower than -30 mV is normally considered as stable particles (Duman and Tunç,  
 325 2009). Nanoparticles with  $\zeta$ -potential more than +30 mV are regarded as strongly cationic (or

326 less than -30 mV as strongly anionic) (Abouelhag et al., 2017), that is, the particles are stable  
327 on dispersion in solution. Fig. 5 presents the plots of the  $\zeta$ -potential values for the various  
328 hybrids of nanoclays and carbon nanotubes, measured with DLS. The  $\zeta$ -potentials of single  
329 MWCNT or MWCNT-f is approximately -13 mV that indicates poor stability. This is in  
330 conformity with the results found in sedimentation experiment, and agrees with the  
331 bibliography (Chu et al., 2012). Single Mt 20A solution recorded -4 mV. In combination with  
332 any of the MWCNTs, absolute  $\zeta$ -potential values of Mt 20A/MWCNT hybrid nanofillers  
333 were ~14 mV, suggesting high tendency of aggregation, as observed in the sedimentation  
334 results.

335 Meanwhile, the  $\zeta$ -potential values of Mt 10/MWCNT or Mt 10/MWCNT-f were greater  
336 than those of Mt Na<sup>+</sup>/MWCNT or Mt Na<sup>+</sup>/MWCNT-f, with highest value of about 46 mV,  
337 observed for the ratio 2:1. This supposes good stability or low tendency of the particles to  
338 aggregate (Jain, 2012; Ma et al., 2019). Consequently, Mt 10A and MWCNT with a mass  
339 ratio 2:1 were selected for the preparation of the Mt/MWCNT nanohybrid particles. Pristine  
340 MWCNT was chosen over functionalized MWCNT for economic and environmental reasons,  
341 as well as the sustenance of carbon nanotube structural integrity, which may be affected by  
342 functionalization (Guadagno et al., 2011; Vennerberg et al., 2014; Alshammari and  
343 Wilkinson, 2016).

344



345

346

**Fig. 5.** Zeta potential values against Mt/MWCNT hybrid mass fraction ratio.

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### 3.3. Structural characterization of the Mt/MWCNT hybrid

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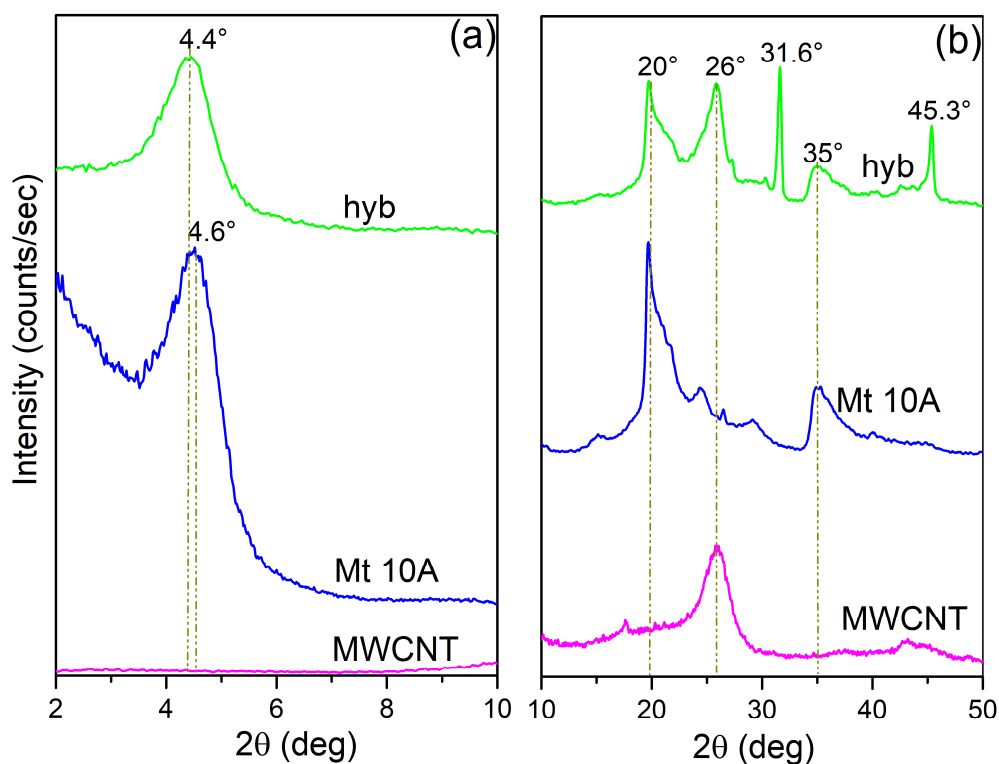
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The prepared Mt/MWCNT hybrid was characterized by XRD and FTIR, which are presented in Fig.6 and Fig.7, respectively. The XRD peak of Mt became broader and shifted from  $2\theta = 4.6^\circ$  (Mt 10A;  $d_{100} = 1.918$  nm) to  $4.4^\circ$  (hyb;  $d_{100} = 2.006$  nm) after its hybridization with MWCNT. The shift in the diffraction peak position is caused by the increase in the basal spacing in the clays from 1.918 nm in Mt 10A to 2.006 nm in hyb. This suggests intercalation of MWCNT in the clay platelets, which could prevent the re-aggregation of MWCNT, as the nanoclays do prevent the formation of van der Waals forces between the nanotubes (Zhuang et al., 2015; Qin et al., 2018). The diffraction peak of MWCNT at  $26^\circ$  corresponds to the (002) plane of graphitized multi-walled carbon nanotubes (Gorrasi et al., 2013; Mumtazah et al., 2019), and it is present in the Mt/MWCNT hybrid at the same angle. Similarly, the diffraction peaks of Mt at  $20^\circ$  and  $35^\circ$  correspond to

359 montmorillonite (110) and (105) planes (Manikandan et al., 2012; Galimberti et al., 2015)  
 360 and these two peaks are also present in the prepared hybrid but with lower intensities,  
 361 suggesting improved exfoliation of Mt 10 platelets (Manikandan et al., 2012; Raji et al.,  
 362 2016). Hence, the SAXD and WAXD studies on Mt/MWCNT hybrid shows adequate  
 363 interactions occurred between the MWCNT and Mt nanoparticles that resulted in an  
 364 intercalated structure. Furthermore, two new characteristic peaks at  $45.4^\circ$  and  $31.6^\circ$  are  
 365 identified. The peak at  $45.4^\circ$  corresponds to the (100) reflection of graphite, along with the  
 366 (002) plane at  $26^\circ$ , which is believed to arise from high quality multi-walled MWCNTs (Zhu  
 367 et al., 2004; Wu et al., 2019). The peak at  $31.6^\circ$  is likely to be impurity of iron catalyst on  
 368 MWCNT during its synthesis (Hapuarachchi and Peijs, 2010; Norazlina et al., 2019). Finally,  
 369 since there are no shifts in the peak positions of both Mt 10A and MWCNT, it can be implied  
 370 that their structures were preserved (Kumar et al., 2018).



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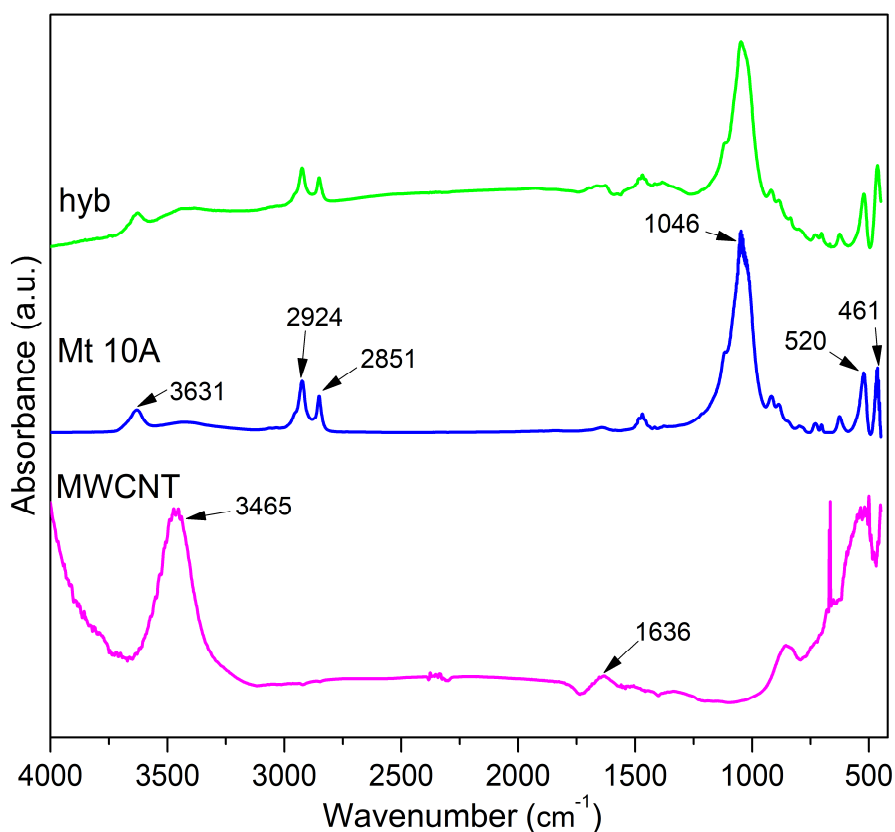
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373

**Fig. 6.** (a) SAXD and (b) WAXD of MWCNT, Mt 10A and the lyophilized Mt 10A/MWCNT hybrid nanofillers.

374 The FTIR spectra of the nanofillers are presented in Fig. 7. For Mt 10A, the absorption  
375 band at  $3631\text{ cm}^{-1}$  represents the -OH stretching of Si-OH and Al-OH (Shabanian et al.,  
376 2016). The band at  $1046\text{ cm}^{-1}$  is ascribed to Si-O-Si stretching vibration of Mt (Pan et al.,  
377 2014). The two peaks at  $516$  and  $462\text{ cm}^{-1}$  correspond to stretching vibration of the Al-O and  
378 bending vibration of Si-O in Mt, respectively (Zhang et al., 2003; Arjmandi et al., 2014;  
379 Arjmandi et al., 2015b). The strong bands of MWCNT at  $3465\text{ cm}^{-1}$  indicates isolated surface  
380 stretching vibrations of -OH group and/or carboxyl group (Montanheiro et al., 2015), while  
381  $1636\text{ cm}^{-1}$  is assigned to aromatic ring stretching, of the backbone of MWCNT, that indicates  
382 the presence of graphitic structure (Zhou et al., 2018). The hybrid filler (hyb) shows all the  
383 peaks of Mt 10A at the same wavenumbers, but the main peaks of MWCNT are absent. This  
384 could be partially related to the greater amount of Mt 10A (Mt/CNT 2:1 mass ratio) in the  
385 hybrid formulation (Santangelo et al., 2011). Besides, as concluded from XRD, MWCNT  
386 intercalated between the clay platelets, which might limit its detection by FTIR.

387

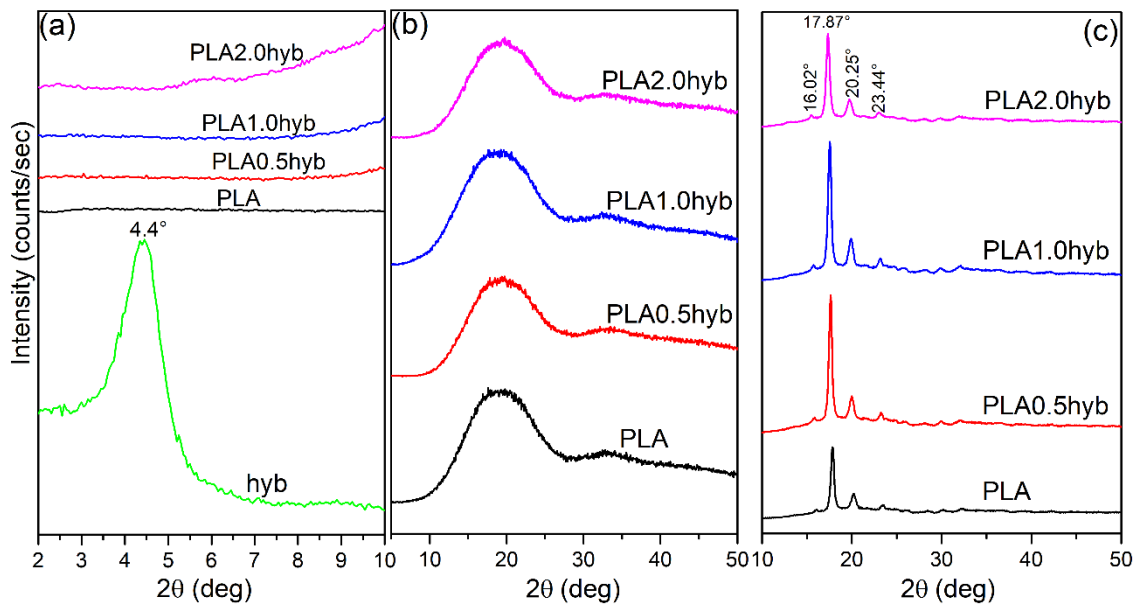


388  
389 **Fig. 7.** FTIR spectra of MWCNT, Mt 10A and their hybrid (hyb).

390 *3.4. Structural and morphological characterizations of PLA/hyb nanocomposites*

391 The XRD diffractograms of PLA/hyb nanocomposites are presented in Fig. 8. The  
392 diffraction peak related to the nanoclay ( $2\theta = 4.4^\circ$ ) in the Mt /MWCNT hybrid disappeared  
393 in the diffractogram of PLA/hyb nanocomposites (Fig. 8a), which suggests the exfoliation of  
394 the Mt layered silicate in the polymer matrix (Gorrasi et al., 2013; Shabanian et al., 2016).  
395 From the diffractograms of Fig. 8b, PLA/hyb nanocomposites displayed no other peaks aside  
396 the PLA amorphous halo, which implies good dispersion of hyb in the nanocomposites.  
397 Therefore, one could conclude that there is a synergy, between the nanoclay and MWCNT  
398 particles, that helps in the exfoliation of clay platelets. This observed structure in the  
399 PLA/hyb nanocomposite supports the discussed intercalation of Mt by the MWCNT in the  
400 prepared Mt/MWCNT hybrid particles (section 3.3), which now translate to almost complete  
401 exfoliation of the nanoclay platelets within the PLA matrix (Fig. 8a). Similarly, no obvious

402 peak of graphitic carbon is detected (Fig. 8b), substantiating the hypothesis that the even  
 403 dispersion of clay in Mt/MWCNT hybrid is sustained, and as such prevents any re-  
 404 agglomeration of MWCNT particles due to van da Waal attraction forces in the PLA matrix.  
 405 This PLA-hyb interaction is assumed to translate into improved properties in the ternary bulk  
 406 nanocomposites. After annealing, the three peaks ( $17.87^\circ$ ,  $20.25^\circ$  and  $23.44^\circ$ ) emerge on the  
 407 diffractogram of PLA (Fig. 8c) and correspond to the orthorhombic crystalline  $\alpha$ -PLA form  
 408 (Jia et al., 2019). They are all retained in the diffractograms of the nanocomposites, which  
 409 implies that the crystalline structure of PLA is not altered by the incorporation of lyophilized  
 410 Mt/MWCNT hybrid nanofillers (Barrau et al., 2011).

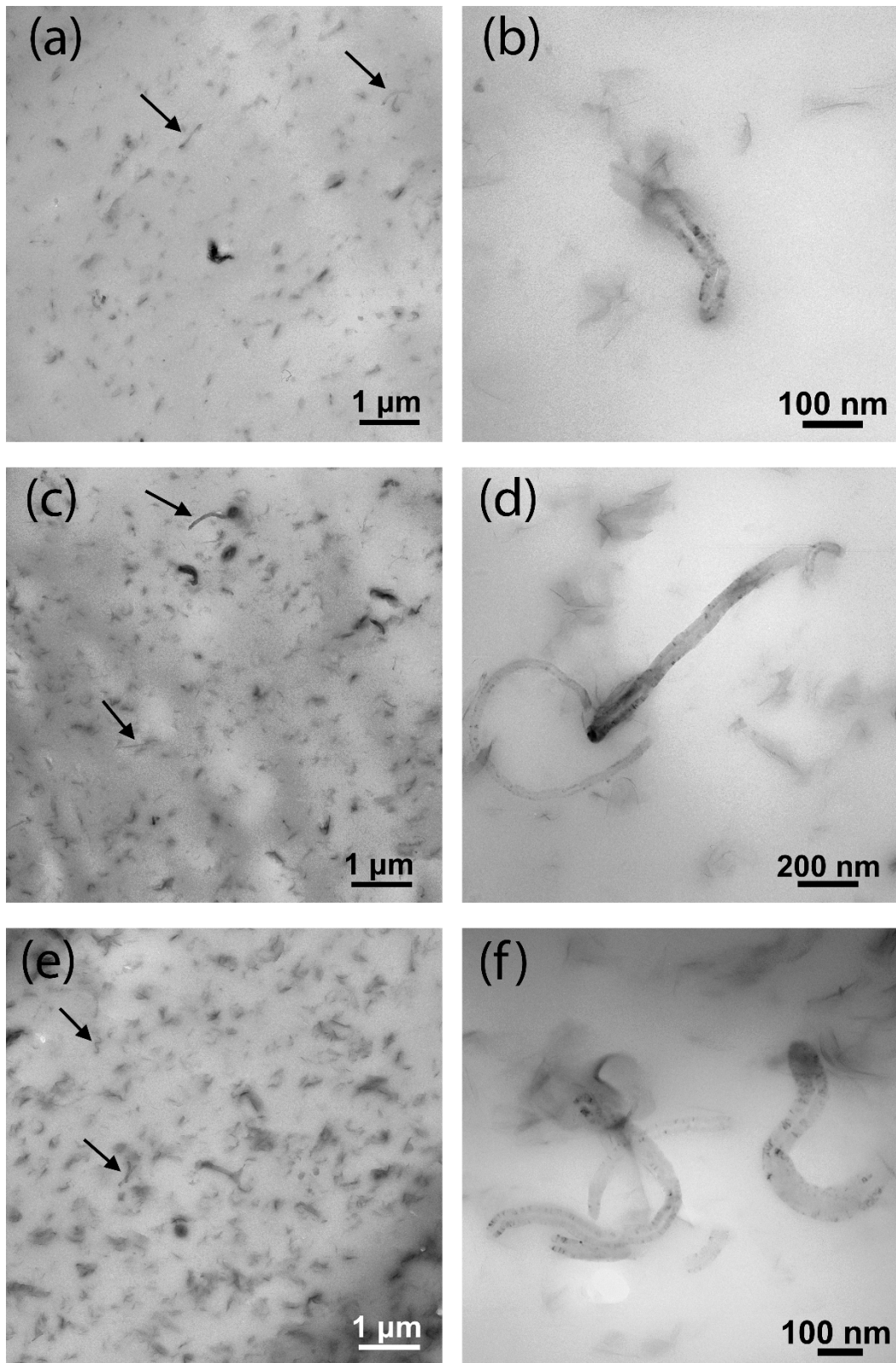


411  
 412 **Fig. 8.** XRD diffractograms of neat PLA and PLA/hyb nanocomposites (a) in small angles,  
 413 (b) wide angles, (c) annealed PLA and PLA nanocomposites at  $120^\circ\text{C}$  for 1 h.

414 Fig. 9 (a-f) represent the TEM images of PLA0.5hyb (a and b), PLA1.0hyb (c and d) and  
 415 PLA2.0hyb (e and f). These images reveal that MWCNT and Mt particles are homogenously  
 416 dispersed in all the samples, which corroborate the XRD analyzes, and agree with the  
 417 findings of Bai et al. (2020) and Ma et al. (2007). This result suggests that the hybridization  
 418 of Mt and CNT promotes the dispersion of the nanoparticles and prevents CNT aggregation.

419 From Fig. 9 (a, c and e), the densification of the particle distribution is observed with the  
420 increase of the fillers concentration. The arrows in Fig. 9 (a, c and e) indicate individual  
421 dispersed MWCNT. Fig. 9 (b, d and f) highlights single carbon nanotubes in connection with  
422 exfoliated Mt platelets, which depicts that each of the two nanofillers influences the  
423 dispersibility of the other, i.e. synergetic interactions seem to occur between the two different  
424 nanofillers. Finally, from the TEM results presented above, one may conclude that the  
425 lyophilization treatment and the nanocomposites preparation process have positive effect on  
426 the distribution of the hybrid nanoparticles in PLA matrix.





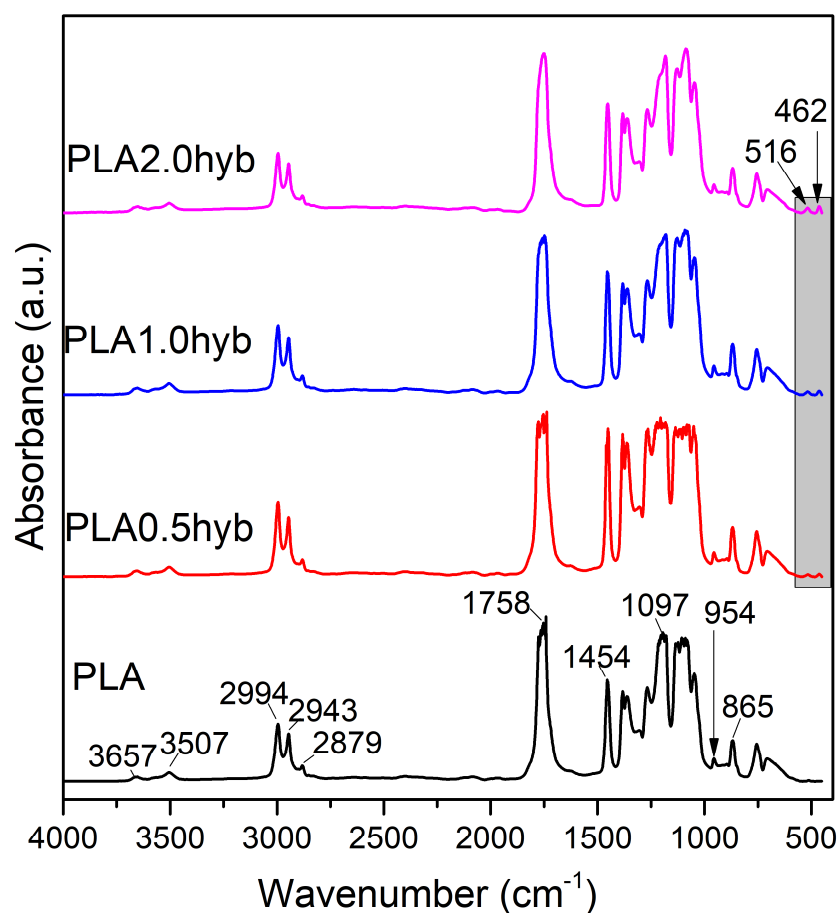
427

428 **Fig. 9.** TEM images of PLA0.5hyb (a and b), PLA1.0hyb (c and d) and PLA2.0hyb (e and f).

429

430 In the FTIR spectrum of neat PLA (Fig. 10), the peaks at 3657 and 3507  $\text{cm}^{-1}$  correspond  
431 to  $-\text{OH}$  stretching vibrations (Arjmandi et al., 2014; Shabanian et al., 2016). Both peaks at  
432 2994 and 2943  $\text{cm}^{-1}$  are attributed to the aliphatic asymmetric stretching vibration of the  $-\text{CH}$   
433 moiety (Arjmandi et al., 2015a; Shabanian et al., 2016). The carbonyl ( $\text{C}=\text{O}$ ) group stretching  
434 vibration appears at 1757  $\text{cm}^{-1}$  as a sharp peak (Fu et al., 2018; Huang et al., 2020). The  
435 characteristics bands at 1454 and 1047  $\text{cm}^{-1}$  are the bending groups of  $-\text{CH}_3$  and  $-\text{OH}$ ,  
436 respectively, while 1361  $\text{cm}^{-1}$  represents the bending vibrations of  $-\text{CH}_2$  (Choksi and Desai,  
437 2017; Fu et al., 2018). The band at 1097  $\text{cm}^{-1}$  corresponds to the C-O stretching vibration  
438 (Arjmandi et al., 2015a; Hu et al., 2017). The C-C stretching vibrations are reflected at 954  
439 and 865  $\text{cm}^{-1}$  (Arjmandi et al., 2014; Y. Liu et al., 2019).

440 It is obvious from Fig. 10 that all characteristics peaks of PLA are also in the spectra of the  
441 PLA/hyb nanocomposites. In addition, the spectra of the PLA/hyb nanocomposites show two  
442 new weak peaks at 516 and 462  $\text{cm}^{-1}$  that represent the stretching vibrations of Al-O and  
443 bending vibrations of Si-O from the nanohybrid (Zhang et al., 2003; Arjmandi et al., 2014;  
444 Arjmandi et al., 2015b), perhaps owing to the larger amount of Mt in the hybrid nanofillers  
445 (i.e., Mt:MWCNT 2:1). The weak intensity of the Si-O peak suggests high degree exfoliation  
446 of the nanoclay (Molinaro et al., 2013), as also implied by the XRD results. Mt has a high  
447 number of uniformly distributed polar sites along its structure, which support hydrogen  
448 bonding with PLA (Arjmandi et al., 2015b). However, because of the low mass fraction of  
449 the Mt/MWCNT hybrid nanofillers in the nanocomposite, the detection of other features from  
450 interacting moieties may be difficult (Terzopoulou et al., 2016).



451

452

**Fig. 10.** FTIR spectra of neat PLA and PLA nanocomposites.

### 453 3.5. Thermal properties of PLA/hyb nanocomposites

454 The DSC second heating thermograms of the PLA and its nanocomposites, shown in Fig.

455 11, were used for the thermal analysis, as the first scan was to reduce thermal history. The

456 glass transition temperature ( $T_g$ ), cold crystallization temperature ( $T_{cc}$ ) and melting

457 temperature ( $T_m$ ), crystallization enthalpy ( $\Delta H_{cc}$ ), melting enthalpy ( $\Delta H_m$ ) and crystallinity

458 ( $X_c$ ) were obtained and summarized in Table 3. For neat PLA,  $T_g$  was identified at 63.6 °C.

459 The exothermic peak corresponding to  $T_{cc}$  appeared at 119.6 °C, while the endothermic peak

460 at 149.9 °C represents the PLA melting point. The results are in accord with those found in

461 literature (Choksi and Desai, 2017; Terzopoulou et al., 2019a; Pires et al., 2020). The  $T_g$  of

462 the nanocomposites are approximately unchanged, while  $T_m$  of these nanocomposites slightly

463 increased compared to the neat PLA. Chattopadhyay et al. (2009) reported similar little

464 change in  $T_g$  and related it to the possibility of more prominent filler-filler interaction than  
465 the polymer-filler interaction. The bimodal  $T_g$  peaks recorded on PLA2.0hyb can be related  
466 to several factors such as crystal structures, processing conditions (Pires et al., 2020). The  
467 observed minor changes in  $T_m$  may be traced to perturbation of the PLA stereoregularity that  
468 is defined by enthalpy or entropy of the isomer units causing the PLA crystal structure to  
469 show minute melting temperature changes (Molinaro et al., 2013). The slight increase in  
470 melting temperature can also be attributed to the rearrangement of polymer chain that  
471 becomes more effective owing to the nanofillers high surface energy (Vukić et al., 2019).

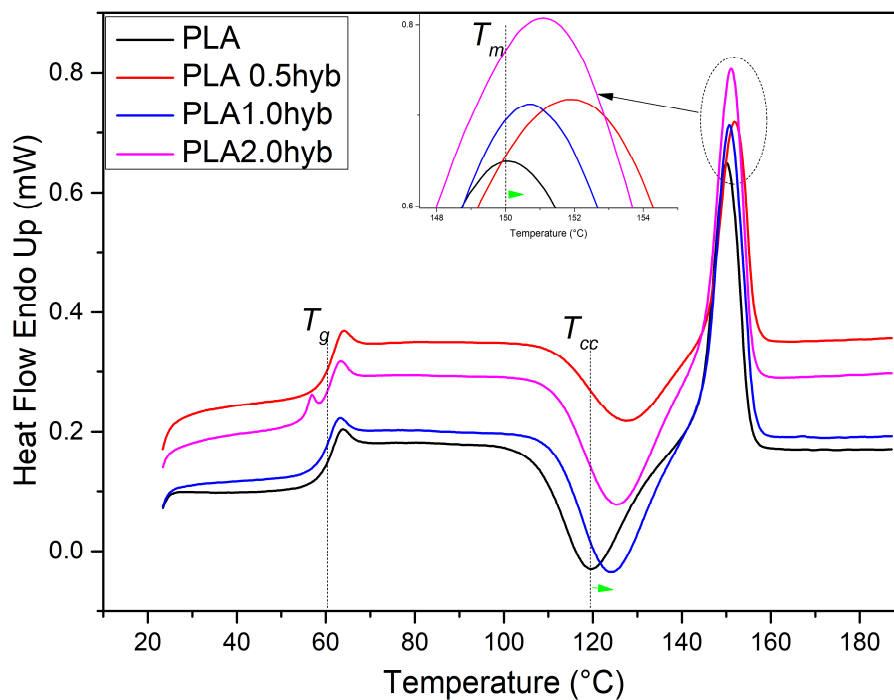
472 The PLA/hyb nanocomposites show significant increase in the crystallization temperature  
473 compared to neat PLA; determined in the range of 124 - 128 °C. The observed significant  
474 increase of the crystallization temperature for all the nanocomposites supports that there is a  
475 strong interaction between the PLA matrix and the incorporated lyophilized nanohybrid  
476 (Sibeko, 2012). Furthermore, the obvious increase in the nanocomposites  $T_{cc}$  compared to  
477 neat PLA (119.57°C) connotes that the PLA-hyb interaction restricted the PLA molecular  
478 motion (Hu et al., 2017). Notably, the nanocomposite with the least filler loading  
479 (PLA0.5hyb; 0.5 %wt Mt/MWCNT) shows the most significant  $T_{cc}$  and  $T_m$  increase. Except  
480 for PLA0.5hyb with reduced  $X_c$ , it was found that crystallinity grows with the hyb  
481 concentration significantly (Table 3). The observed crystallinity reduction at lower  
482 concentration may be associated with the crystal growth limitation as well as imperfect  
483 crystal structure (Shayan et al., 2019). In other words, the initial  $X_c$  depression may be due to  
484 two competing effects of hyb in restricting PLA chain motion and its nucleating effect that  
485 promoted the crystallization kinetics of the matrix (Sanusi et al., 2020b)(Hu et al., 2017).  
486 Meanwhile, the subsequent crystallinity improvement can be due to uniform dispersion  
487 revealed by the TEM images, and increased active nucleation sites generated by the  
488 Mt/MWCNT hybrid (Chu et al., 2012). Mt (Jia et al., 2019) and MWCNT (Vukić et al.,

2019) are revealed sometimes to be a nucleating agent, so their incorporation as components of Mt/MWCNT is suspected to play a synergistic role of improving  $X_c$  in PLA. Hence, it can be inferred that the lyophilized Mt/MWCNT hybrid increased the amount of crystallinity in the matrix, and thus reinforced the matrix.

**Table 3**

Thermal properties of PLA and PLA/hyb nanocomposites.

Sample	$T_g$ (°C)	$T_{cc}$ (°C)	$\Delta H_{cc}$ (J/g)	$T_m$ (°C)	$\Delta H_m$ (J/g)	$X_c$
PLA	63.60	119.57	20.44	149.94	21.21	44.78
PLA0.5hyb	64.10	128.19	14.54	151.93	14.79	33.19
PLA1.0hyb	63.22	124.73	27.61	150.79	19.83	56.67
PLA2.0hyb	63.60	126.22	29.37	151.12	17.22	62.61



**Fig. 11.** DSC thermograms of PLA and nanocomposites obtained during second heating cycle at 10 °C/min.

### 3.6. Thermal stability

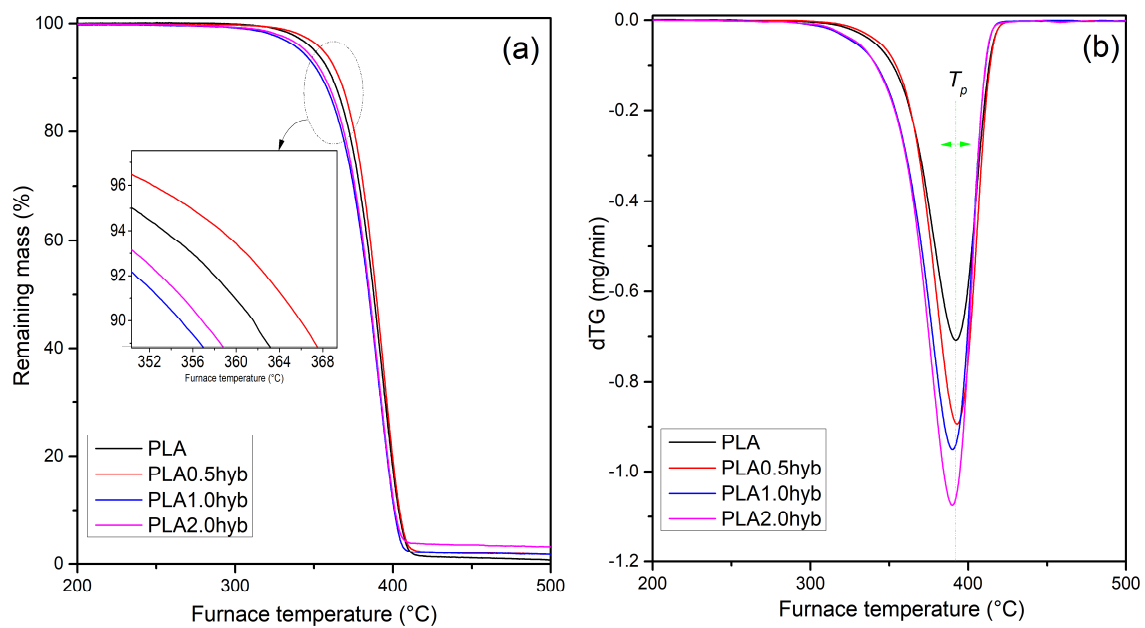
Thermal stability of polymer is critical, as the property is considered as the limiting factor for processing as well as for end-use applications (Terzopoulou et al., 2019b). Fig. 12 shows

501 the TGA thermograms of the PLA and its nanocomposites; while Table 4 presents the  
502 summary of the thermal performance i.e., the initial, 10% mass loss, maximum mass loss and  
503 final degradation temperatures as  $T_{onset}$ ,  $T_{d,10\%}$ ,  $T_p$  and  $T_{comp}$ , respectively. The PLA/hyb  
504 nanocomposite reinforced with lyophilized Mt/MWCNT particles gained improved thermal  
505 stability properties at the least nanofillers concentration of 0.5 wt% (PLA0.5hyb), as shown  
506 in Table 4 and Fig. 12. Beyond this loading, the thermal stability of the PLA/hyb  
507 nanocomposites fall, samples PLA1.0hyb and PLA2.0hyb almost have similar decrease in the  
508 characteristics degradation temperatures. Malkappa et al. (2018) reported that promotion of  
509 PLA degradation, due to reduced  $T_{d,10\%}$  at lower temperature, forms thermally insulating  
510 char quicker and prevents further degradation of polymer. Another explanation can be the  
511 attainment of percolation threshold point at 0.5 %wt loading of the Mt/MWCNT (hyb) in the  
512 PLA matrix. Thus, at higher loading, the 3D percolation structure seems to be well  
513 established thereby creating a physical network of interaction with the volatile component  
514 and conduction of heat that results in promotion of decomposition process (Chu et al., 2012;  
515 Pandey et al., 2014; Shayan et al., 2019). Similarly, the TEM images (section 3.4) support the  
516 fact that there are interactions between Mt and MWCNT nanoparticles, which are  
517 homogenously distributed in PLA and could lead to the formation of 3D network of the  
518 Mt/MWCNT hybrid in the matrix.

519 Influence of heating rate is another vital factor that affects thermal degradation process,  
520 for instance, the conversion and thermal distribution (Lv et al., 2019). In Fig. 13, the mass  
521 loss thermograms of the neat PLA and PLA1.0hyb are shown, for four different heating rates  
522 of 5, 10, 15 and 20 °C/min. It is clear that the mass loss curves of the samples degradation  
523 properties similarly shift towards higher temperature regions with the heating rate increment.  
524 This can be due to the heat flow rate variations inside the studied samples (Lv et al., 2019);  
525 and thermal lag (i.e. temperature gradient) across the materials sections as a result of the

526 different heating rates (Mishra and Mohanty, 2018). At lower heating rate, temperature  
 527 profile in the sample cross-section is presumed to be linear because the inner and outer cores  
 528 of the material achieve the same temperature at a given time as there exists enough time for  
 529 heating; while higher heating rate generates reduced heat distribution and poorer heat transfer  
 530 efficiency (Niu et al., 2017; Lv et al., 2019).

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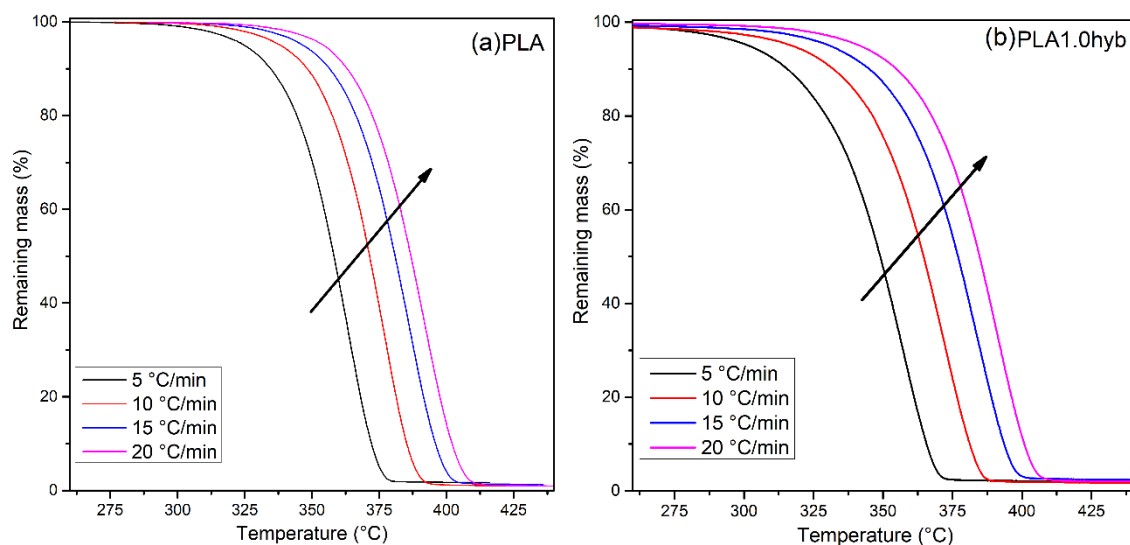
**Fig. 12.** (a) TGA thermograms; (b) dTG curves.

534 **Table 4**

535 Characteristics thermal degradation temperatures of PLA and its nanocomposites.

Sample	$T_{onset}$ (°C)	$T_{d,10\%}$ (°C)	$T_{comp}$ (°C)	$T_p$ (°C)
PLA	368.3	361.5	406.4	392.4
PLA0.5hyb	371.7	365.8	406.2	393.0
PLA1.0hyb	363.0	354.8	405.5	390.0
PLA2.0hyb	363.0	356.8	405.5	390.0

536



537

538 **Fig. 13.** Mass loss curves of (a) PLA; (b) PLA1.0hyb for four different heating rates of 5, 10,

539 15 and 20 °C/min. The arrow indicates the increase of heating rate.

### 540 3.7. Mechanical properties

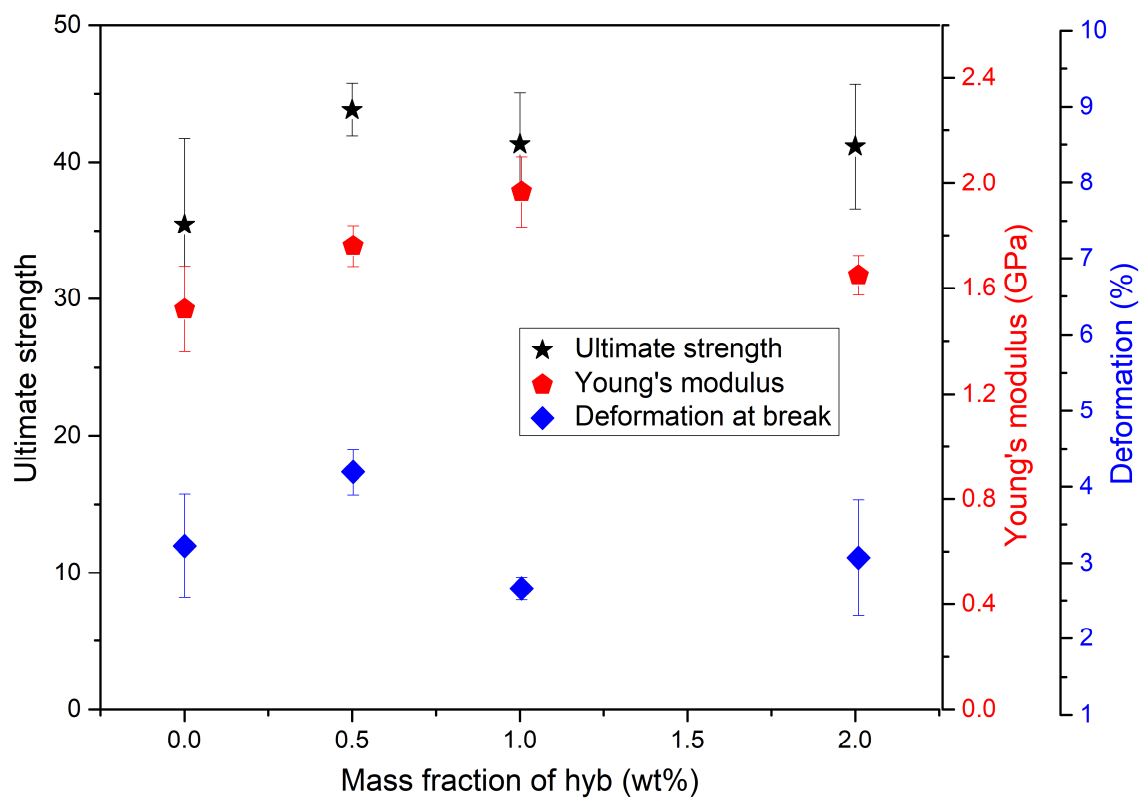
541 The Young's modulus, ultimate tensile strength and deformation at break of PLA and the  
 542 PLA/hyb nanocomposites were evaluated and summarized in Fig. 14. The elastic modulus of  
 543 PLA0.5hyb, PLA1.0hyb and PLA2.0hyb are 1.76, 2.0 and 1.65 GPa, respectively, compared  
 544 to 1.52 GPa in neat PLA. The modulus enhancement in all the nanocomposite samples can be  
 545 attributed to the reinforcing effect of Mt/MWCNT and stress transfer mechanism from the  
 546 matrix to the dispersed hybrid nanoparticles (Chiu, 2017; Arjmandi et al., 2015a). The slight  
 547 reduction of modulus at 2.0 wt% Mt/MWCNT may be due to self-aggregation of hybrid  
 548 nanoparticles (Zhou et al., 2018), as the percolation threshold was reached earlier at 1.0 wt%  
 549 (maximum modulus).

550 The tensile strength increased from 35.5 MPa for PLA to 43.8 MPa for nanocomposite  
 551 reinforced with 0.5 wt% of Mt/MWCNT, and the values slightly reduced at higher  
 552 concentrations. The results are in consonant with literature (Zhou et al., 2018; Arjmandi et  
 553 al., 2015a). It also signified that the Mt/MWCNT particles reduced the mobility of PLA  
 554 chains (Keshavarzi et al., 2019). The deformation at break also recorded its peak value at 0.5



555 wt% of Mt/MWCNT, followed by the property reduction at higher concentrations of  
556 Mt/MWCNT. Both ultimate tensile strength and deformation at break indicate 0.5 wt%  
557 Mt/MWCNT as the percolation threshold which agrees with the value indicated by the DSC  
558 and TGA results.

559 Summarily, since the Young's modulus indicates 1.0 wt% as percolation threshold point,  
560 while other material properties (DSC, TGA, strength and deformation at break) suggest it to  
561 be at 0.5 wt%, one can conclude that the percolation threshold should be really found  
562 between 0.5 and 1.0 wt% Mt/MWCNT.



563

564 **Fig. 14.** Mechanical properties of PLA and PLA/hyb nanocomposites.

#### 565 4. Conclusion

566 Hybrid of montmorillonite (Mt) and multi-walled carbon nanotubes (MWCNT) was  
567 successfully prepared by adopting lyophilization method. The most stable Mt/MWCNT  
568 formulation was identified from varying combinations of different types of Mt and MWCNT,

569 in addition to finding the optimum Mt-MWCNT concentration ratio. Through the XRD and  
570 FTIR characterizations, the hybrid was determined to have been successfully prepared with  
571 improved nanoclay exfoliation and dispersed MWCNT, while the lyophilization approach  
572 was simple and "green". Thereafter, the synthesized Mt/MWCNT hybrid filler was  
573 incorporated in poly(lactic acid) (PLA) to study its influence in improving the polymer  
574 matrix properties. The nanocomposites prepared by a two-step approach (solution and melt  
575 mixing) were fully characterized by XRD, FTIR, TEM, DSC, TGA and mechanical  
576 techniques. The physicochemical studies revealed structural interaction between the  
577 Mt/MWCNT hybrid and polymer without altering the PLA structure. Moreover, the  
578 incorporation of the lyophilized Mt/MWCNT nanoparticles in PLA led to the augmentation  
579 in the crystallinity, crystallization and melting temperatures, and mechanical properties of the  
580 nanocomposites beyond the neat PLA. This indicates the suitability of the lyophilized  
581 Mt/MWCNT hybrid as a nanomaterial for reinforcing polymer matrices. The improvement in  
582 material properties is related to homogeneous dispersion of Mt/MWCNT hybrid  
583 nanoparticles in the PLA matrix. This homogeneous distribution was confirmed by TEM  
584 analysis and partially attributed to the synergy between nanoclay particles and carbon  
585 nanotubes. Finally, at low loading of Mt/MWCNT, PLA0.5hyb nanocomposite, the thermal  
586 degradation performance was enhanced, while higher concentration of the nanohybrid  
587 suggests a well-established percolation network in the nanocomposite, which might serve as a  
588 good thermal conductive material.

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