

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

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Olawale Monsur Sanusi, Abdelkibir Benelfellah, Lazaros Papadopoulos, Zoi Terzopoulou, Lamprini Malletzidou, et al.. Influence of montmorillonite/carbon nanotube hybrid nanofillers on the properties of poly(lactic acid). Applied Clay Science, 2021, 201, pp.105925. 10.1016/j.clay.2020.105925 . hal-03605260

# HAL Id: hal-03605260 https://hal.science/hal-03605260

Submitted on 3 Feb 2023

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Version of Record: https://www.sciencedirect.com/science/article/pii/S0169131720304907 Manuscript e851269a2515e7ff80ddb088a01c7c79

# 1 Influence of montmorillonite/carbon nanotube hybrid nanofillers on the

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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 homogeneous dispersion of Mt/MWCNT nanoparticles in the PLA matrix. The thermal 38 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.

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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 Khajehpour 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 the limitation of each of the two prominent nanofillers (Bilotti et al., 2013). MWCNT 71 72 typically forms stabilized aggregates attributed to high hydrophobicity, making its dispersion exceedingly difficult (Sianipar et al., 2017; Barrau et al., 2011), while the stacking of Mt 73

platelets and its incompatibility with common hydrophobic polymers are the common
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, agglomerates of the nanofillers in the matrices persisted, related among others, to the increase 78 79 of filler content in matrix (Azam and Samad, 2018). Recently, Mumtazah et al. (2019) prepared Mt/MWCNT hybrid nanofiller using a sol-gel method with strong acids, in elevated 80 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 leads to pre-exfoliation of the Mt's internal structure, which facilitates its dispersion in the 87 polymer matrix (Madaleno et al., 2013). Thus, incorporation of CCVD Mt/MWCNT 88 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. Madaleno et al. (2013) also utilized CCVD Mt/MWCNT to develop polyurethane 93 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-6 (PA6), tensile modulus and strength were significantly enhanced by 289% and 153%, 98

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. Gorrasi et al. (2014) reported thermal stability, mechanical and electrical properties 101 102 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 clay/polymer nanocomposite. However, the CCVD Mt/MWCNT hybrid nanofillers is often 105 106 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. (2019) adopted the same approach by dispersing MWCNT in Mt aqueous dispersion to form 115 116 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 simple method for preparing Mt/MWCNT hybrid nanoparticles, which improves theintercalation 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. The elongation at break increased from 5.9% for PLA to 87.3% for PLA reinforced with 127 128 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. Meanwhile, only nanocomposite reinforced with 1:1 of MWCNT:Mt hybrid had significant 131 132 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 from the work of Bai et al. (2020), it is worth noting that three kinds of Cloisite Mt (Mt Na<sup>+</sup>, 139 140 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 of the selected Mt/MWCNT hybrid treated by lyophilization in relation with its constituents. 145 146 Thereafter, the influence of the mass fraction of the selected hybrid nanoparticles on the structure, physicochemical, crystallization, thermal and mechanical properties of PLA was 147

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

#### 152 **2. Materials and methods**

153 2.1. Materials

Poly(L-lactic acid) (PLA) (Ingeo<sup>TM</sup> Biopolymer 3052D) matrix used in the work was 154 supplied by Plastika Kritis S.A., with molecular weight Mw = 63.090 g/mol and intrinsic 155 viscosity  $\eta = 1.055$  dL/g. Three different Cloisite<sup>®</sup> montmorillonite (Mt) nanoclay types 156 157 were used: Mt Na<sup>+</sup>, Mt 10A and Mt 20A, which correspond to unmodified Mt, dimethyl benzyl hydrogenated tallow quaternary ammonium (2MBHT) modified Mt, and dimethyl 158 hydrogenated tallow quaternary ammonium (2MHT) modified Mt, respectively. These 159 160 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 SA, Athens, Greece with average diameter of  $15\pm 5$  nm, length > 5  $\mu$ m and bulk density of 164 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. 165



Fig. 1. Chemical structure of (a) dimethyl benzyl hydrogenated tallow quaternary ammonium
 (2MBHT); (b) dimethyl hydrogenated tallow quaternary ammonium (2MHT); (c) HT tallow.

#### 170 2.2. Optimization of hybrid filler composition

The stability and zeta potential ( $\zeta$ -potential) of different types of Mt (Mt Na<sup>+</sup>, Mt 10A and 171 172 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 quantity of MWCNT was added in the Mt dispersion, stirred and ultrasonicated until there 176 177 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, Zetasizer 5000, Malvern Instruments, UK. 182

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

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

#### 189 2.4. Preparation of PLA/hyb nanocomposites

A two-step solution mixing and melt mixing method was adopted for the preparation of PLA/hyb nanocomposites. The first step was the preparation of masterbatch films via solution mixing. The composition of the masterbatch is 1 g of PLA and 0.05, 0.1 and 0.2 g of 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 film and PLA were fed into a Haake-Buchler Reomixer (model 600) of 69 cm<sup>3</sup> volumetric 196 197 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			Carbon nanotubes	
		(mg)			(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**

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

207 Composition of the prepared nanocomposites.

#### 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° and 10 - 50°, both with a step of 0.05 ° and speed 1 °/min. The clay 212 interlayer distance *d* was evaluated from the XRD patterns using Bragg's formula given by 213 (Raji et al., 2018):

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

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

Fourier-transform infrared (FTIR) spectra were obtained using a Perkin-Elmer Spectrum
One FT-IR, with a resolution of 4 cm<sup>-1</sup> and using 16 scans.

The dispersion state of Mt/MWCNT hybrid in the PLA was examined by transmission electron microscopy (TEM), using a Jeol JEM 1010 electron microscope operated at 100kV. 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.

Differential scanning calorimetry (DSC) analyzes were conducted with a Perkin-Elmer Pyris 6 DSC, under 20 mL/min flow of nitrogen ( $N_2$ ). The experiments were conducted on samples mass of about 8 mg. In order to erase any thermal history, each sample was taken through heating-cooling cycle twice, first heated from 20 to 190 °C at a rate of 10 °C/min, held for 1 min at 190°C, and then cooled from 190 °C to 20 °C at a rate of 10 °C/min. The crystallinity  $X_c$  of the neat PLA and its nanocomposites were calculated using equation (2) (Hu et al., 2017):

230 
$$X_c = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_m^0 \times f} \times 100\%$$
(2)

where  $\Delta H_m$  and  $\Delta H_{cc}$  are melting and crystallization enthalpies,  $\Delta H_m^o$  is melting enthalpy for 231 100% crystalline PLA (93.7J/g), f is the percentage weight of the PLA in the nanocomposite. 232 233 Thermogravimetric analyzes (TGA) were performed with a Setaram SETSYS TG-DTA 234 16/18 instrument. Samples of  $3\pm0.5$  mg were placed in alumina crucibles and were measured in dynamic conditions, in the temperature range from 26 to 600 °C, with a heating rate of 20 235 236 °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.

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

- 244 **3. Results and discussion**
- 245 3.1. Structures of the montmorillonite nanoclays

The Small Angle X-ray diffraction (SAXD) results of the crystallographic structures of Mt Na<sup>+</sup>, Mt 10A and Mt 20A are presented in Fig. 2. The unmodified Mt Na<sup>+</sup>, that contains 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 to unmodified Mt Na<sup>+</sup>, i.e. at  $2\theta = 4.6^{\circ}$  and  $2\theta = 3.5^{\circ}$ , corresponding respectively to the 251 252 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° (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 (Timochenco et al., 2010). This second peak, at 7.07°, also suggests an insignificant edge 258 259 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.







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 hydrogenated tallow group with a benzyl group gives Mt 10A a moderate hydrophobicity as 279

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

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

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

As seen in Fig. 4e and 4f, the presence of Mt 20A did not keep either the MWCNT or MWCNT-f particles suspended in the solution. The consistent inability of Mt 20A to influence MWCNT suspension in the aqueous solution suggests that the 2MHT ion over Mt 20A does not interact with neither of the MWCNTs nor the aqueous medium. As earlier identified in the SAXD pattern of Mt 20A, insignificant edge grafting or interlayer of 2MHT ammonium molecules within the Mt 20A layers, may have prevented the MWCNT 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 dal Waal 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 dispersed MWCNT, due to van der Waals force resulting from high surface energy, seemed 311 312 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

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

316

periods.





Fig. 4. Sedimentation of different ratios of (a) Mt Na<sup>+</sup>/MWCNT; (b) Mt Na<sup>+</sup>/MWCNT-f; (c)
Mt 10A/MWCNT; (d) Mt 10A/MWCNT-f; (e) Mt 20A/MWCNT; (f) Mt 20A/MWCNT-f at
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 conformity with the results found in sedimentation experiment, and agrees with the 330 331 bibliography (Chu et al., 2012). Single Mt 20A solution recorded -4 mV. In combination with any of the MWCNTs, absolute  $\zeta$ -potential values of Mt 20A/MWCNT hybrid nanofillers 332 333 were ~14 mV, suggesting high tendency of aggregation, as observed in the sedimentation 334 results.

335 Meanwhile, the ζ-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 functionalization (Guadagno et al., 2011; Vennerberg et al., 2014; Alshammari and 342 343 Wilkinson, 2016).





346

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

### 347 3.3. Structural characterization of the Mt/MWCNT hybrid

348 The prepared Mt/MWCNT hybrid was characterized by XRD and FTIR, which are 349 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 350 351 hybridization with MWCNT. The shift in the diffraction peak position is caused by the 352 increase in the basal spacing in the clavs from 1.918 nm in Mt 10A to 2.006 nm in hyb. This 353 suggests intercalation of MWCNT in the clay platelets, which could prevent the reaggregation of MWCNT, as the nanoclays do prevent the formation of van da Waal forces 354 355 between the nanotubes (Zhuang et al., 2015; Qin et al., 2018). The diffraction peak of 356 MWCNT at 26 ° 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 357 the same angle. Similarly, the diffraction peaks of Mt at 20° and 35° correspond to 358

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, suggesting improved exfoliation of Mt 10 platelets (Manikandan et al., 2012; Raji et al., 361 362 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 intercalated structure. Furthermore, two new characteristic peaks at 45.4° and 31.6° are 364 identified. The peak at  $45.4^{\circ}$  corresponds to the (100) reflection of graphite, along with the 365 366 (002) plane at 26°, which is believed to arise from high quality multi-walled MWCNTs (Zhu et al., 2004; Wu et al., 2019). The peak at 31.6° is likely to be impurity of iron catalyst on 367 368 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).



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

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



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 reagglomeration of MWCNT particles due to van da Waal attraction forces in the PLA matrix. 404 405 This PLA-hyb interaction is assumed to translate into improved properties in the ternary bulk 406 nanocomposites. After annealing, the three peaks (17.87°, 20.25° and 23.44°) emerge on the 407 diffractogram of PLA (Fig. 8c) and correspond to the orthorhombic crystalline  $\alpha$ -PLA form (Jia et al., 2019). They are all retained in the diffractograms of the nanocomposites, which 408 409 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 °C for 1 h.

Fig. 9 (a-f) represent the TEM images of PLA0.5hyb (a and b), PLA1.0hyb (c and d) and PLA2.0hyb (e and f). These images reveal that MWCNT and Mt particles are homogenously dispersed in all the samples, which corroborate the XRD analyzes, and agree with the findings of Bai et al. (2020) and Ma et al. (2007). This result suggests that the hybridization 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 dispersed MWCNT. Fig. 9 (b, d and f) highlights single carbon nanotubes in connection with 421 422 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 nanofillers. Finally, from the TEM results presented above, one may conclude that the 424 425 lyophilization treatment and the nanocomposites preparation process have positive effect on 426 the distribution of the hybrid nanoparticles in PLA matrix.





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

In the FTIR spectrum of neat PLA (Fig. 10), the peaks at 3657 and 3507 cm<sup>-1</sup> correspond 430 431 to -OH stretching vibrations (Arjmandi et al., 2014; Shabanian et al., 2016). Both peaks at 2994 and 2943 cm<sup>-1</sup> are attributed to the aliphatic asymmetric stretching vibration of the –CH 432 moiety (Arjmandi et al., 2015a; Shabanian et al., 2016). The carbonyl (C=O) group stretching 433 vibration appears at 1757 cm<sup>-1</sup> as a sharp peak (Fu et al., 2018; Huang et al., 2020). The 434 characteristics bands at 1454 and 1047 cm<sup>-1</sup> are the bending groups of -CH<sub>3</sub> and -OH, 435 436 respectively, while 1361 cm<sup>-1</sup> represents the bending vibrations of –CH<sub>2</sub> (Choksi and Desai, 2017; Fu et al., 2018). The band at 1097 cm<sup>-1</sup> corresponds to the C-O stretching vibration 437 (Arjmandi et al., 2015a; Hu et al., 2017). The C-C stretching vibrations are reflected at 954 438 439 and 865 cm<sup>-1</sup> (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 cm<sup>-1</sup> that represent the stretching vibrations of Al-O and bending vibrations of Si-O from the nanohybrid (Zhang et al., 2003; Arjmandi et al., 2014; 443 444 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).



452

451

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 glass transition temperature  $(T_g)$ , cold crystallization temperature  $(T_{cc})$  and melting 456 457 temperature  $(T_m)$ , crystallization enthalpy  $(\Delta H_{cc})$ , melting enthalpy  $(\Delta H_m)$  and crystallinity  $(X_c)$  were obtained and summarized in Table 3. For neat PLA,  $T_g$  was identified at 63.6 °C. 458 459 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 literature (Choksi and Desai, 2017; Terzopoulou et al., 2019a; Pires et al., 2020). The  $T_g$  of 461 the nanocomposites are approximately unchanged, while  $T_m$  of these nanocomposites slightly 462 463 increased compared to the neat PLA. Chattopadhyay et al. (2009) reported similar little

change in  $T_g$  and related it to the possibility of more prominent filler-filler interaction than 464 the polymer-filler interaction. The bimodal  $T_g$  peaks recorded on PLA2.0hyb can be related 465 466 to several factors such as crystal structures, processing conditions (Pires et al., 2020). The observed minor changes in  $T_m$  may be traced to perturbation of the PLA stereoregularity that 467 468 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 increase of the crystallization temperature for all the nanocomposites supports that there is a 474 475 strong interaction between the PLA matrix and the incorporated lyophilized nanohybrid (Sibeko, 2012). Furthermore, the obvious increase in the nanocomposites  $T_{cc}$  compared to 476 477 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 (PLA0.5hyb; 0.5 % wt Mt/MWCNT) shows the most significant  $T_{cc}$  and  $T_m$  increase. Except 479 480 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 crystal structure (Shayan et al., 2019). In other words, the initial  $X_c$  depression may be due to 483 484 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). Meanwhile, the subsequent crystallinity improvement can be due to uniform dispersion 486 revealed by the TEM images, and increased active nucleation sites generated by the 487 Mt/MWCNT hybrid (Chu et al., 2012). Mt (Jia et al., 2019) and MWCNT (Vukić et al., 488

489 2019) are revealed sometimes to be a nucleating agent, so their incorporation as components 490 of Mt/MWCNT is suspected to play a synergistic role of improving  $X_c$  in PLA. Hence, it can 491 be inferred that the lyophilized Mt/MWCNT hybrid increased the amount of crystallinity in 492 the matrix, and thus reinforced the matrix.

#### 493 **Table 3**

494 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 <sub>c</sub>
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





498 *3.6. Thermal stability* 

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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 PLA degradation, due to reduced  $T_{d,10\%}$  at lower temperature, forms thermally insulating 509 510 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 homogenously distributed in PLA and could lead to the formation of 3D network of the 517 518 Mt/MWCNT hybrid in the matrix.

Influence of heating rate is another vital factor that affects thermal degradation process, for instance, the conversion and thermal distribution (Lv et al., 2019). In Fig. 13, the mass loss thermograms of the neat PLA and PLA1.0hyb are shown, for four different heating rates of 5, 10, 15 and 20 °C/min. It is clear that the mass loss curves of the samples degradation properties similarly shift towards higher temperature regions with the heating rate increment. This can be due to the heat flow rate variations inside the studied samples (Lv et al., 2019); and thermal lag (i.e. temperature gradient) across the materials sections as a result of the different heating rates (Mishra and Mohanty, 2018). At lower heating rate, temperature profile in the sample cross-section is presumed to be linear because the inner and outer cores of the material achieve the same temperature at a given time as there exists enough time for heating; while higher heating rate generates reduced heat distribution and poorer heat transfer efficiency (Niu et al., 2017; Lv et al., 2019).

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532

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

### **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



Fig. 13. Mass loss curves of (a) PLA; (b) PLA1.0hyb for four different heating rates of 5, 10,
15 and 20 °C/min. The arrow indicates the increase of heating rate.

#### 540 3.7. Mechanical properties

537

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).

The tensile strength increased from 35.5 MPa for PLA to 43.8 MPa for nanocomposite reinforced with 0.5 wt% of Mt/MWCNT, and the values slightly reduced at higher concentrations. The results are in consonant with literature (Zhou et al., 2018; Arjmandi et al., 2015a). It also signified that the Mt/MWCNT particles reduced the mobility of PLA 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.





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 improved nanoclay exfoliation and dispersed MWCNT, while the lyophilization approach 571 572 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 mixing) were fully characterized by XRD, FTIR, TEM, DSC, TGA and mechanical 575 576 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.

589 Acknowledgements

590 Petroleum Technology Development Fund (PTDF) is acknowledged for the doctoral591 scholarship grant (Grant Number: 18GFC/PHD/065).

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Aqueous solution

Magnetic stirring

Sonication

Freezing Freeze-drying



Characterization



PLA/Mt/CNT nanocomposite

Melt-mixing PLA + Masterbatch

Masterbatch preparation

PLA

Mt/CNT hybrid Dichloromethane