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Olawale Monsur Sanusi, Abdelkibir Benelfellah, Zoi Terzopoulou, Dimitris N Bikiaris, Nourredine Aït Hocine. Preparation of green montmorillonite/carbon nanotubes hybrid by lyophilization procedure for poly(lactic acid) nanocomposite. 5th International Conference on Materials Engineering and Nano Sciences (ICMENS 2021) to be held in, Mar 2021, Osaka, Japan, Japan. hal-04552017

**HAL Id: hal-04552017**

**<https://hal.science/hal-04552017>**

Submitted on 18 Apr 2024

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# Preparation of green montmorillonite/carbon nanotubes hybrid by lyophilization procedure for poly(lactic acid) nanocomposite

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**Keywords:** Montmorillonite, carbon nanotubes, lyophilization, poly(lactic acid), nanocomposite.

**Abstract.** Montmorillonite (MMT) and multi-walled carbon nanotube (MWCNT) are presently the leading and most effective studied nanofillers reported to impact high properties in various polymeric matrices. Meanwhile, the main challenge in nanocomposite is achieving efficient dispersion of these nanoparticles without agglomeration in the selected matrix. In this study, we investigated the influence of various types of montmorillonite and carbon nanotubes in determining the most stable MMT/MWCNT hybrid formulation, and the optimum mixing ratio of the two fillers was selected to prepare MMT/MWCNT hybrid via lyophilization process. Three kinds of nanoclays (Cloisite MMT Na<sup>+</sup>, MMT 10A and MMT 20A) and two types of MWCNT (pristine MWCNT and functionalized MWCNT "MWCNT-f") have been investigated. The most stable and optimum MMT/MWCNT hybrid was incorporated into poly(lactic acid) (PLA) matrix. The various characterization results revealed the success of the lyophilization procedure, and that the prepared MMT/MWCNT hybrid influenced high properties in the nanocomposites.

## Introduction

Poly(lactic acid) (PLA) is a biodegradable aliphatic polyester, with relatively fair mechanical behavior, thermal properties, fabric ability and biocompatibility. However, some of the PLA properties are not enough for engineering applications [1][2]. Nanofillers roles in the mitigation of the deficiencies of polymers give rise to more innovative academia researches and successive industrial demand for nanocomposites [3]. Montmorillonite (MMT) and multi-walled carbon nanotubes (MWCNT) are the leading and most effective studied nanofillers reported to impact high properties in various polymeric matrices [4][5]. However, efficient and effective dispersion without agglomeration of each of these nanofillers in the selected host polymer remains a challenge [6].

Freeze drying, also referred to as lyophilization, allows ice to transform directly from solid to vapor in the absence of liquid phase (sublimation) and usually used when the drug ingredients lack stability in water [7]. Hence, lyophilization of MMT and MWCNT is supposed to be efficient and simple in preparing MMT/CNT hybrid nanoparticles for superior polymer matrix intercalation. In this study, we investigated the influence of MMT/MWCNT hybrid on the properties of PLA. In order to enhance the interfacial adhesion and dispersibility of the hybrid nanofillers, lyophilisation process was adopted in preparing the MMT/MWCNT hybrid nanoparticles.

## Experimentation

Poly(L-lactic acid) (PLLA) (Ingeo<sup>TM</sup> Biopolymer 3052D), having molecular weight  $M_w = 63.090$  g/mol and intrinsic viscosity  $\eta = 1.055$  dL/g, was used as matrix. Three different Cloisite<sup>®</sup> montmorillonite (MMT) nanoclay types were used: MMT Na<sup>+</sup>, MMT 10A and MMT 20A (Southern Clay Products, Inc. Ganzales, USA). Multi-walled carbon nanotubes (MWCNT) and amine-functionalized MWCNT (MWCNT-f) were used as the second nanofillers (Glonatech SA, Athens, Greece). Reagent-grade dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) (Scharlab S.L. Spain) served as solvent.

The stability and zeta potential ( $\zeta$ -potential) of different types of MMT (MMT Na<sup>+</sup>, MMT 10A, MMT 20A) and MWCNT (MWCNT, MWCNT-f) as well as different MWCNT/MMT mass ratios were examined to choose the optimum composition of the hybrid MWCNT/MMT nanofillers. First, an MMT aqueous dispersion was prepared by stirring and ultrasonication (UP100H Ultrasonic Processor Hielscher Ultrasound Technology, Germany) for 10 min. Afterwards, appropriate quantity of MWCNT was added in the MMT dispersion, stirred and ultrasonicated until there were no visible aggregates. The final concentration of the dispersions was 1 mg/mL and the MMT/MWCNT mass ratios tested were 1:1, 2:1 and 4:1. The colloidal stability of the prepared MMT/MWCNT dispersions was tested 1 h after preparation by measuring the  $\zeta$ -potential with a Dynamic Light Scattering (DLS) apparatus, Zetasizer 5000, Malvern Instruments, UK.

The most stable MMT/MWCNT dispersion was lyophilized with a Scanvac Coolsafe freeze dryer (Germany), equipped with vacuum pump (2.3/2.8 m<sup>3</sup>/h,  $4 \cdot 10^{-4}$  mbar). The freeze-dried nanofillers, that is MMT/MWCNT hybrid produced by this lyophilization process, is referred to as hybrid and abbreviated as "hyb" in the rest of the paper.

Each of the nanofillers and the lyophilized MMT/MWCNT hybrid were characterized by sedimentation; Dynamic light scattering (DLS); X-ray diffractometer (XRD), and Fourier-transform infrared spectroscopy (FTIR). The XRD test was done with Rigaku MiniFlex II DESKTOP X-ray Diffractometer (Rigaku RU-H3R rotating copper anode X-ray generator) with wavelength 0.154 nm and peaks generated between 2 - 50° Bragg's angle. 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.

A two-step solution mixing and melt mixing method was adopted for the preparation of PLA nanocomposites. The first step was preparation of a masterbatch film through solution mixing. The hybrid nanoparticles were dispersed by ultrasonication in dichloromethane. Afterwards, PLA was dissolved in the dispersion under continuous magnetic stirring until most of the solvent evaporated. The resulting slurry was dried under vacuum at 50 °C to obtain the masterbatch film. Next, the dried masterbatch film and the remaining PLA were fed into a Haake-Buchler Reomixer (model 600) of 69 cm<sup>3</sup> volumetric capacity, with twin-roller blades, at 180 °C and a speed 30 rpm for 5 min to prepare the nanocomposites (Table 1). Thereafter, the obtained nanocomposites were characterized via XRD and FTIR.

Table 1. Composition of PLA nanocomposites.

	PLA (%wt)	hyb (%wt)
PLA	100	0
PLA0.5hyb	99.5	0.5
PLA1.0hyb	99	1
PLA2.0hyb	98	2

## Results and Discussion

Fig. 1 represents the  $\zeta$ -potential of various combinations of MMTs and MWCNTs in aqueous solution. Particles with more than +30 mV or lower than -30 mV is considered as stable particles [8]. When MWCNT was added to MMT solution, the  $\zeta$ -potential values increased irrespective of the clay-type or MWCNT-type. Considerably, MMT-10A in combination with either of the MWCNT at ratio 2:1 (MMT:MWCNT) showed the peak values (>45 mV) which implies good stability

formulation. Thus, for economic and environmental benefits, pristine MWCNT was selected over functionalized (MWCNT-f) for preparing MMT/MWCNT hybrid by freeze-drying.

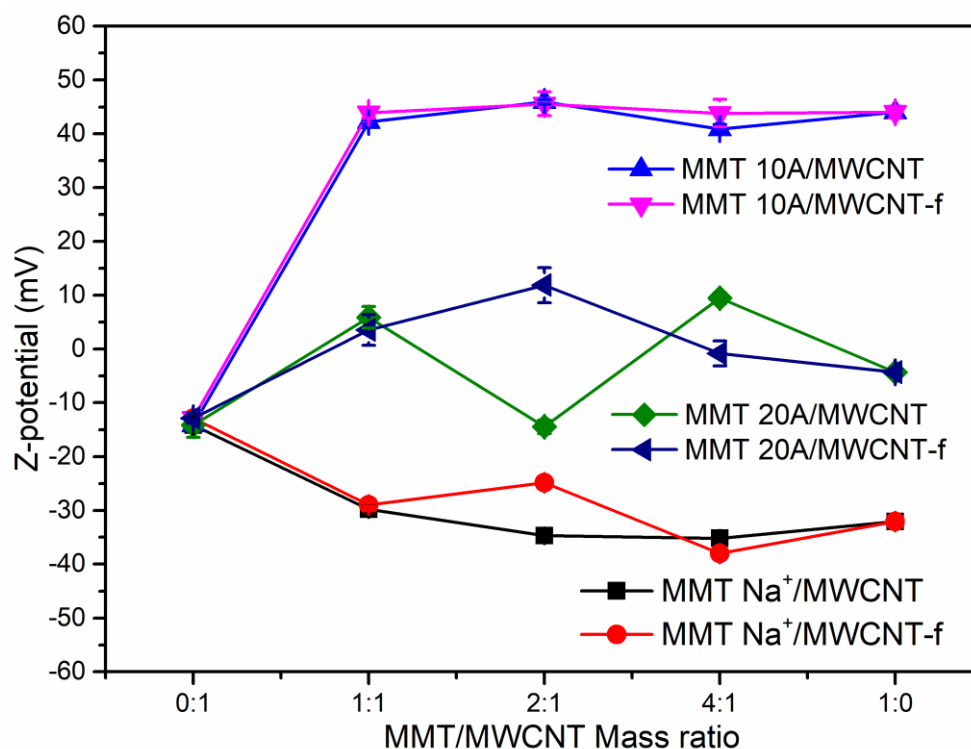


Figure 1.  $\zeta$ -potential of various combinations of MMT/MWCNT.

Fig. 2 shows the FTIR spectra of the MMT 10A, MWCNT and lyophilized MMT/MWCNT hybrid. For MMT 10A, the absorption band at  $3631\text{ cm}^{-1}$  represents the -OH stretching of Si-OH and Al-OH. The band at  $1046\text{ cm}^{-1}$  is ascribed to Si-O-Si stretching vibration of MMT. The two peaks at  $516$  and  $462\text{ cm}^{-1}$  correspond to stretching vibration of the Al-O and bending vibration of Si-O in MMT, respectively [9]. The strong bands of MWCNT at  $3465\text{ cm}^{-1}$  indicates isolated surface stretching vibrations of -OH group and/or carboxyl group, while  $1636\text{ cm}^{-1}$  is assigned to aromatic ring stretching, of the backbone of MWCNT, that indicates the presence of graphitic structure [4].

The hybrid filler (hyb) shows all the peaks of MMT 10A at the same wavenumbers, but the main peaks of MWCNT are absent. As explained from XRD result, MWCNT intercalated between the clay platelets, which probably prevents its detection by FTIR. It can also be related to the higher amount of MMT 10A (MMT:MWCNT = 2:1) in the hybrid formulation.

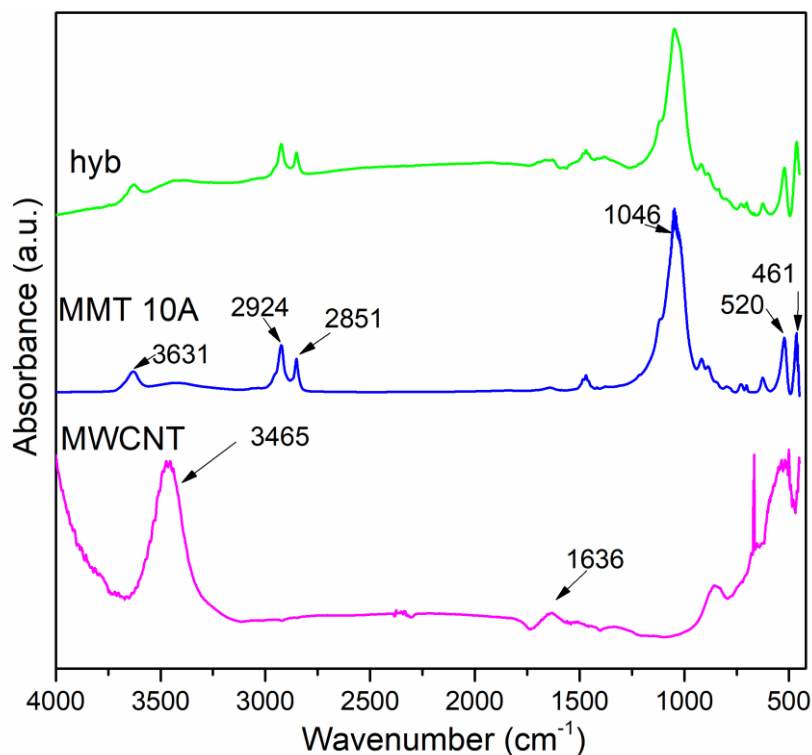


Figure 2. FTIR of MMT 10A, MWCNT and hyb.

Fig. 3 displays the small-angle X-ray diffraction (SAXD) (a) and wide-angle X-ray diffraction (WAXD) (b) of the MMT 10A, MWCNT and lyophilized MMT/MWCNT hybrid. The diffraction peak of MMT becomes broader and shifts from  $2\theta = 4.6^\circ$  (MMT 10A;  $d_{100} = 1.918$  nm) to  $4.4^\circ$  (hyb;  $d_{100} = 2.006$  nm) after its hybridization with MWCNT. The shift to lower angle is caused by the increase in the basal spacing of the MMT platelets from 1.918 nm in MMT 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 Waal forces between the nanotubes [10]. The diffraction peak of MWCNT at  $26^\circ$  corresponds to the (002) plane of graphitized carbon nanotubes, and it is repeated in the MMT/MWCNT hybrid at the same angle. Similarly, the diffraction peaks of MMT at  $20^\circ$  and  $35^\circ$ , correspond to montmorillonite (110) and (105) planes [11], are also present in the prepared hybrid but with lower intensities, suggesting improved exfoliation of MMT 10 platelets. Hence, the SAXD and WAXD studies on MMT/MWCNT hybrid shows that adequate interactions occurred between MWCNT and MMT nanoparticles that resulted in an intercalated structure. Thus, the lyophilization procedure can be said to be successful.

Fig. 4 shows the FTIR spectra of PLA and PLA/hyb nanocomposites. The spectra indicate that all the characteristics peaks of PLA are duplicated in all the PLA/hyb nanocomposites. Besides, the spectra of the nanocomposites show two new weak peaks at  $516$  and  $462$   $\text{cm}^{-1}$  that represent the stretching vibrations of Al-O and bending vibrations of Si-O from the hybrid particles [12]. From Figure 5a, the SAXD showed that the prepared MMT/MWCNT hybrid diffraction peak at  $2\theta = 4.4^\circ$  disappeared in all the samples, suggesting full exfoliation of the MMT/MWCNT particles. Further study of the samples by WAXD showed high level of MWCNT dispersion in the matrix as both hyb constituents' peaks were not reflected in the PLA structure (Figure 5b). Thus, MMT can be said to prevent re-agglomeration of the MWCNT particles in the PLA matrix.

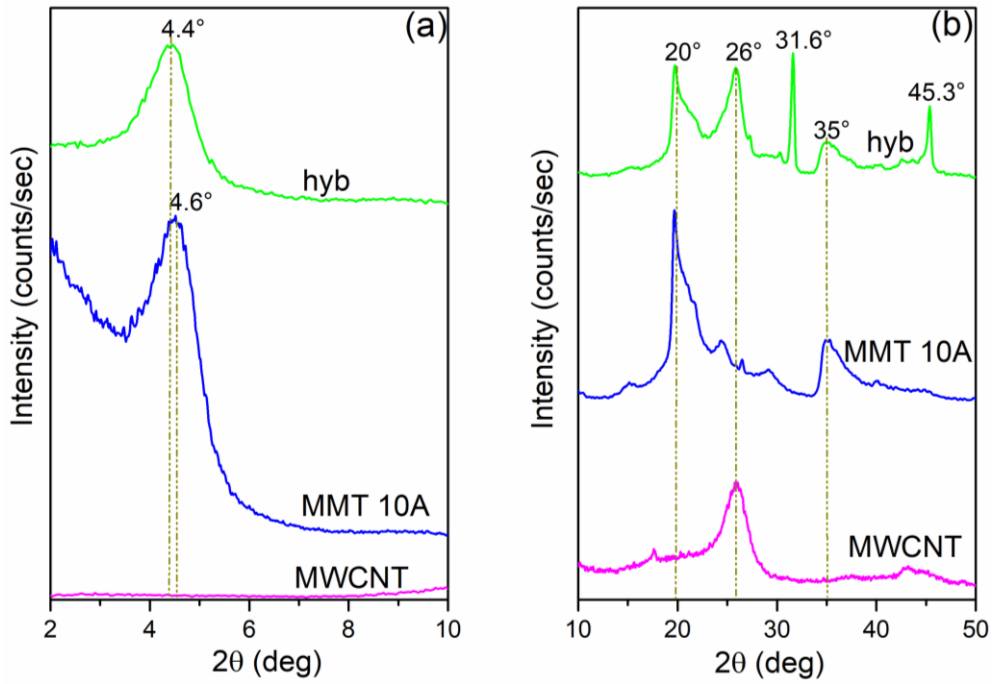


Figure 3. (a) SAXD; (b) WAXD of MMT 10A, MWCNT and hyb.

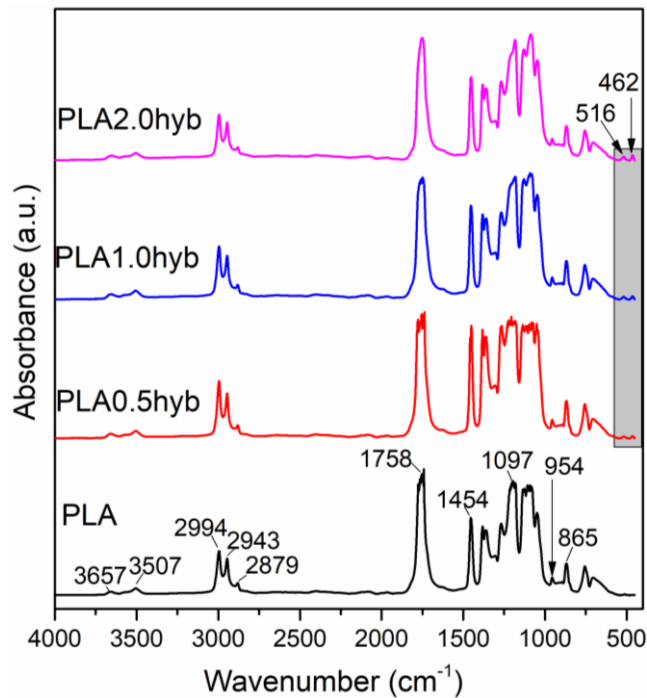


Figure 4. FTIR of PLA and its nanocomposites.

## Conclusion

A green and ease method of MMT/MWCNT hybrid synthesis was achieved through lyophilisation of MMT and MWCNT nanoparticles. Various combinations of different types of MMT and MWCNT were studied to identify the most stable MMT/MWCNT formulation, and the optimum MMT-MWCNT concentration ratio determined to be 2:1. Through the XRD and FTIR characterizations, the hybrid was successfully prepared with improved MMT exfoliation and

dispersed MWCNT. Thereafter, the synthesized MMT/MWCNT hybrid particles was incorporated in poly(lactic acid) to study its influence on the matrix structural properties. The physicochemical studies showed structural interaction between the MMT/MWCNT hybrid and polymer without altering the PLA structure. This indicates the suitability of the lyophilized MMT/MWCNT hybrid as nanoparticles for reinforcing polymer matrices.

## Acknowledgement

Petroleum Technology Development Fund is acknowledged for the PhD grant (18GFC/PHD/065).

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