



Enhancing the Thermal and Mechanical Properties of Organic-Inorganic Hybrid Nanocomposite Films Based on Poly Lactic Acid/OMMT Nano Clay

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Abstract: Organic (PLA) inorganic (OMMT nano clay) hybrid nanocomposite films were fabricated using poly lactic acid (PLA) with various weight percentages (1-3wt%) of organically modified montmorillonite (OMMT) nano clay by means of one step solvent casting method. The thermal, mechanical and water absorption properties were determined as per standard testing methods to determine the optimum percentage of OMMT nano clay within the nanocomposite was investigated. The surface morphology of the organic-inorganic hybrid nanocomposite films was analyzed through XRD, SEM, and TEM surface analytical techniques. The incorporation of OMMT clay in to PLA matrix is found to have enhanced the thermo-mechanical properties. The water absorption and solubility test results also support the data from thermo-mechanical tests. The 2 wt % OMMT clay loaded PLA films showed the best results among all. The obtained results showed that the thermal, mechanical and water absorption properties could be increased significantly with the optimum incorporation of OMMT nano clay in a PLA matrix, in comparison with the neat PLA.

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1. INTRODUCTION

Since the last few years, bioplastics that play an important role in the industrial economies have been regularly used as matrix materials worldwide, [1,2]. Especially for food packaging, an essential part of the economic sector, which deals with high amounts of plastic materials. In general, food packaging materials that are in use are made from petroleum-based raw polymers such as polyethylene (PE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET) and polyvinyl alcohol (PVA) etc., These are the polymers readily available at low cost, possess adequate mechanical and good barrier properties [3-5]. However, petroleum-based polymers have a negative impact as waste plastics in the global environment due to the increasing growth of pollution, wide spreading usage of plastics in our day-to-day life and also more challenging to remove plastic waste in the environment [6-8]. In order to reduce the dependency on petroleum-based polymers, decrease the accumulation of endless plastic waste and simultaneously to control the emission of CO₂ in the global environment [9-11], research now is focused on green-bio polymer like poly (lactic acid) PLA, which will have direct

impact on environment and high profit margin for corporate sector. PLA is one of the supreme outstanding materials to substitute petroleum-based raw materials, which can reduce the carbon footprint and waste hazard to the global environment. The nomenclature of the PLA is an alphabetic thermoplastic polymer, derived from agricultural sugar feedstocks like corn, sugar beet, and other agricultural products etc., [12,13]. PLA being remarkable finds application in various areas such as drug delivery, bio-medical, food packaging, agriculture, cutleries, etc., Furthermore, PLA is brittle in nature, with low mechanical, thermal properties and imparts uncontrollable degradation pattern, which restrict its utility for food packaging materials. In order to overcome the above said properties of PLA and to make it suitable for food packaging applications, different strategies such as blending of PLA with flexible biodegradable polymers like polycaprolactone (PCL), poly (butylene succinate) (PBS), poly (butylene adipate-co-terephthalate) (PBAT) etc., were reported in the literature [14,15]. Nonetheless, the addition of toughening polymer into the PLA matrix consequently decreases the tensile strength and modulus properties of PLA, [16]. The bitter truth is none of these methods seem to have improved the toughness of PLA without the loss of rigidity [17]. Quite recently PLA has been modified with nanoparticles to have good toughness and strength balanced by proper dispersion phase morphology and interfacial

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properties between the components [18, 19]. Furthermore, the introduction of nanofillers such as clay minerals, carbon nanotubes, and graphene etc., into the PLA matrix, can enhance its properties in terms of mechanical, thermal, gas barrier, optical and antimicrobial properties [20, 21]. The rationale of this present work is to modify PLA by reinforcing it with organically modified MMT (OMMT) nano clay, thereby making organic- inorganic hybrid PLA-OMMT nanocomposite films with properties that are ideally suited for food packaging application. Thus PLA films incorporated with OMMT clay will have better properties when compared with the neat PLA film. PLA flexible films are developed in the present work using solvent casting method. The mechanical, thermal and water absorption properties are studied using tensile test and thermo-gravimetric analysis, thereby determining the optimum percentage of OMMT clay to be loaded in PLA matrix. The surface morphology of the organic-inorganic hybrid nanocomposite films was investigated by means of SEM and TEM analysis. The scope of this work is to extend the level and usage of PLA in packaging and other outdoor applications.

EXPERIMENTAL SECTION

Materials Required

PLA, Ingeo™ Biopolymer 3052D was bought from Natur Tec India Pvt. Ltd., MMT clay was bought from Sigma Aldrich. Zinc Stearate (with ZnO 12.5 – 14 %) and silver nitrate were bought from Alfa Aesar. Tetrahydrofuran (THF), benzene, dimethyl sulfoxide (DMSO), acetone, ethyl acetate, chloroform, diethyl ether and petroleum ether were obtained from SD fine chemical company, India.

Synthesis of Na-MMT Clay

Crude (MMT) clay was dispersed into the stoichiometric amount of NaCl solution. Stirring was continued for 24 hr at

70°C. After that the solution mixture was centrifuged at high speed till an opaque whitish layer accumulates obtained at the bottom of the centrifuge tubes beneath a translucent gel. The resultant gel was removed and isolated. The whitish layer was washed with distilled water several times until no chlorine was detected in the centrifuged. The purified clay was further dried at 70°C and stored in a desiccator. [22]

Synthesis of Organically Modified Montmorillonite (OMMT) Nano Clay

Na-MMT clay was dispersed into distilled water and mixed for 24 hr and then 200 ml of diethyl ether solution and 5.6 g of zinc stearate was slowly poured into the clay dispersion. The resulting system contained a clear upper organic layer and a turbid bottom mineral phase. After a 12 hr of moderate mixing, the mineral phase became transparent and the organic phase became turbid. Special care was taken to avoid diethyl ether evaporation. At this point, the system was warmed up to evaporate the diethyl ether, using a roto-evaporator. After solvent evaporation, the organic phase became a sticky solid precipitate. The precipitated organoclay was filtered and dispersed in hot water (80°C) for 4 hr. Washing was repeated three times, until no chloride traces were detected with silver nitrate after the third washing. The resulting organoclay paste was manually mixed with 40 ml of petroleum ether using a spatula. After free petroleum ether evaporation, the organoclay was dried at 80°C, grounded using a pestle mortar and stored [23].

Optimization of Film Formation

The film formation was done using different solvents before optimizing the film formation. The films formed using different solvents have different textures, opacity, and strength. Observation and inference made during the optimization of the film are illustrated in Figure 1. The film formed using chloroform was found to have the characteristics of flexibility,



Figure 1: Optimization of film formation.

translucent to transparent and also tough. With these observations, chloroform was chosen as an ideal solvent for the preparation of PLA films.

Preparation of Organic-Inorganic Hybrid Nanocomposite (PLA-OMMT) Films

Organic-inorganic hybrid nanocomposite films were prepared by solvent casting method as follows: 2.0 g of neat PLA was mixed in 100ml of chloroform solvent and the mixture was continuously stirred for 2hr using a magnetic stirred at room temperature until a transparent solution was obtained. The obtained product of PLA solution was mixed with different weight percentage of OMMT nano clay (1, 2 and 3wt %) (Table 1), and was kept in an ultra-sonication of 70 mins until a homogeneous solution was obtained. The resultant product was poured into Petri dishes to get thin films which were further dried under ambient condition to slowly evaporate the solvent for 24 h [24]. The final organic-inorganic hybrid (PLA-OMMT) nanocomposite films obtained were further dried in an oven under vacuum at 40°C for 24hr (Figure 2).

Table 1: Nomenclature of the Organic-Inorganic Hybrid Nanocomposite Films

Systems	PLA/wt% of OMMT nano clay	Solvent
a	100/0	Chloroform
b	100/1%	Chloroform
c	100/2%	Chloroform
d	100/3%	Chloroform

CHARACTERIZATION

Mechanical Analysis

The tensile properties of the solution casting organic-inorganic hybrid nanocomposite films were determined as per ASTM method using an Instron Mechanical Tester (Model 5564) at a crosshead speed of 5 mm/min at room temperature. The specimens were prepared by cutting strips 20 mm wide by 110 mm.

Thermal Gravimetric Analysis (TGA)

Thermo-gravimetric analysis of organic-inorganic hybrid nanocomposite films was carried out using TGA-Thermal Analyst NETZSCH STA 409 PC (TA instruments, USA) at a

heating rate of 10°C/min from 0°C to 800°C under a continuous flow of N₂ atmosphere to determine thermal degradation temperature, percentage weight loss and char yield formation. About 5mg of samples were taken for each analysis.

X-Ray Diffraction (XRD)

XRD patterns were recorded for Na-MMT clay, OMMT clay, neat PLA and PLA/OMMT nano clay films having varied percentages at room temperature by monitoring the diffraction angle 2θ from 10° to 70° as a standard and 0.5° to 10° as a low angle on a Rich Seifert (Model 3000) X-ray powder diffractometer. The diffractometer was equipped with a Copper target (λ 1.5405 Å) radiation using Guinier type camera used as focusing geometry and a solid state detector. The curved nickel crystal was used as the monochromator. The step width (scanning speed) used was 2θ= 0.04 deg/min.

Scanning Electron Microscopy (SEM)

A JEOL JSM-6360 scanning electron microscope was used for the sample analysis and the fractured samples were prepared by coating gold on the surface of the samples and analyzed further.

Transmission Electron Microscopy (TEM)

A JEOL JEM-3010 analytical transmission electron microscope, operating at 300 kV with a measured point-to-point resolution of 0.23nm, was used to characterize the phase morphology of the organic-inorganic hybrid nanocomposite films. TEM samples were prepared by dissolving polymers in DMF mounted on a carbon-coated Cu TEM grids and dried 24h at room temperature (RT) to form a film in <100 nm size.

Water Absorption Test

The water absorption measurements of organic-inorganic hybrid nanocomposite films were carried out according to ASTM D570-81 for 24h at 25°C and the percentage of water absorbed by the specimens was calculated using the following equation (1).

$$\% \text{ water absorption} = (W_2 - W_1) \times 100 / W_1 \quad (1)$$

Where, W₁ is the initial weight of the sample and

W₂ is the weight of the sample after immersion in water for 24 h at 25 °C.

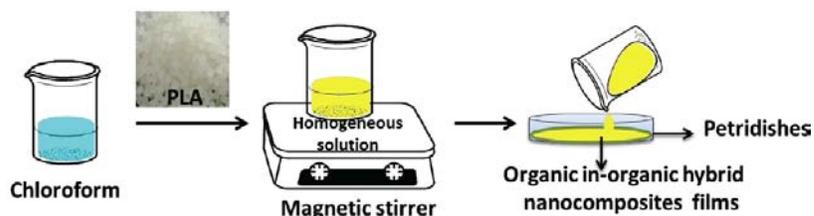


Figure 2: Schematic diagram of sample preparation.

RESULTS AND DISCUSSION

Mechanical Analysis

Figure 3 shows the mechanical properties of organic-inorganic hybrid nanocomposite films with different OMMT nano clay contents obtained from the tensile test. The tensile stress of the organic-inorganic hybrid nanocomposite films increased remarkably with the addition of OMMT nano clay content and possesses a maximum value up to 2 wt% of OMMT nano clay are illustrated in Figure 3 and Table 2 respectively. It can be clearly seen from Figure 3 and Table 2 that the tensile strength values of systems 'b' and 'c' increased to 5.4 Mpa and 6.3 Mpa respectively with increasing OMMT nano clay content, which was found to be higher than that of the neat PLA film (4.7 Mpa). This might be due to the uniform distribution (Figure 6a) and interaction of OMMT nanoclay [25, 26] within the PLA matrix. However, system 'd' having 3wt% of OMMT clay showed a slight decreased value of tensile strength compared to other systems 'a' and 'b' are shown in Figure 3. This could be due to the improper dispersion (Figure 6b) of higher weight percentage loaded OMMT nano clay of 3wt%, which led to agglomeration and subsequently cracks were initiated, and the cracks tend to propagate inside the agglomerated PLA matrix [27]. It was interesting to notice that the elongation at break has also increased with an increase in the OMMT nano clay up to 2wt% corresponds to the maximum value at 37.17%, whereas the elongation at break for neat PLA film was found to be 1.32% and 4.50% for system 'd' respectively (Table 2). Thus, it can be concluded from the above observations that an optimum introduction of OMMT nano clay in the PLA matrix could enhance both strengthening and toughening of the PLA due to the homogeneous dispersion (Figure 6a) of OMMT nano clay within the PLA. A similar trend was observed by Bouakaz *et al.* [28].

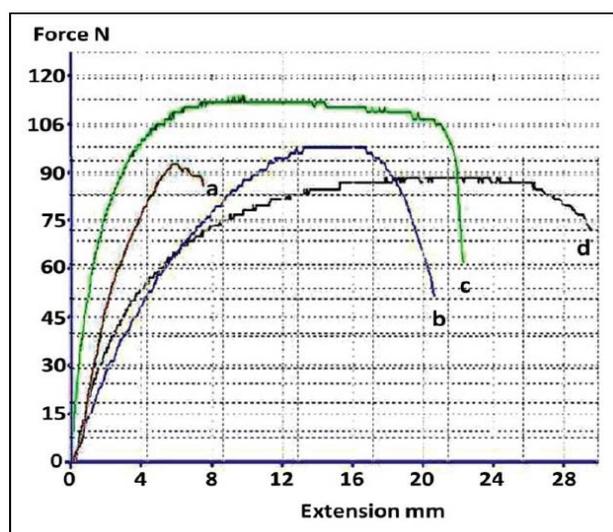


Figure 3: Tensile Tests of systems (a) neat PLA film (b) PLA/1wt% of OMMT nano clay film (c) PLA/2wt% of OMMT nano clay film and (d) PLA/3wt% of OMMT nano clay film.

Table 2: Data Resulted from Mechanical Properties of Organic-Inorganic Hybrid Nanocomposite Films

Systems	PLA/wt% of OMMT nano clay	Tensile Stress (Mpa)	Elongation at break (%)
a	100/0	4.7±1	1.32
b	100/1%	5.4±7	3.43
c	100/2%	6.3±1	37.17
d	100/3%	5.2±8	4.50

Thermo-gravimetric Analysis (TGA)

TGA analysis was carried out in order to investigate the effect of OMMT nano clay on the thermal stability of organic-inorganic hybrid nanocomposite films are presented in Table 3 and Figure 4 respectively. It can be seen that the initial degradation temperatures (IDT) along with char residue for systems 'b' and 'c' were increased to 334°C to 341°C with the increasing loading of OMMT nano clay, when compared with the neat PLA film whose IDT value was 329°C. Generally the introduction of inorganic components (OMMT nano clay) into organic (PLA) materials can significantly improve their thermal stabilities. Higher thermal stability of organic-inorganic hybrid (PLA-OMMT) nanocomposite films may be attributed to presence and interaction of inorganic nano particles with the organic polymer matrix. It was interesting note that the systems 'b' and 'c' imparted better thermal stability when compared with all systems of the present study. This increase in thermal stability observed in the case of system 'b' and 'c' could be attributed to the uniform distribution of OMMT nano clay within the PLA matrix [29, 30]. These results were in good agreement with tensile strength (Figure 3), SEM and TEM results (Figure 6). A similar observation was reported by Ogata *et al.* [31]. However, under higher loading of 3wt% (system 'd') of OMMT nano clay loaded PLA nanocomposite film showed a slightly decreased thermal stability compared to the systems 'b' and 'c'. The inferior thermal stability imparted by system 'c' could be attributed to the high content of inorganic particles (OMMT nano clay) that formed agglomeration within the PLA films [32]. From the above observations, we conclude that an optimum wt% loading of OMMT nano clay in PLA can enhance both IDT and char residue.

Table 3: Data on Thermal Properties of Organic-Inorganic Hybrid Nanocomposite Films

Systems	PLA/wt% of OMMT nano clay	Initial decomposition Temperature (°C)	Char yield (%)
a	100/0	329	1.14
b	100/1%	334	4.4
c	100/2%	341	7.2
d	100/3%	336	12.5

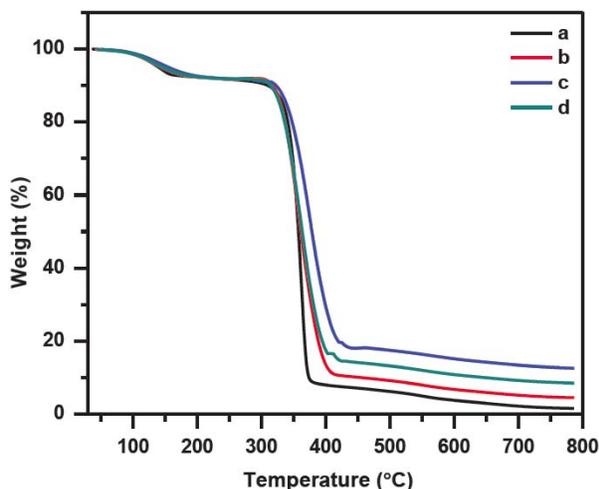


Figure 4: TGA of systems (a) neat PLA film (a) neat PLA film (b) PLA/1wt% of OMMT nano clay film (c) PLA/2wt% of OMMT nano clay film and (d) PLA/3wt% of OMMT nano clay film.

XRD Analysis

X-Ray Diffraction (XRD) analysis was carried out for the neat PLA films and different weight percentage OMMT nano clay loaded PLA nanocomposite films. The results are illustrated in Figure 5. The XRD patterns obtained for organic in-organic hybrid nanocomposite films (systems 'b', 'c' and 'd') were found to exhibit a mixed intercalated and exfoliated behavior with different interlayer spacing morphology. It was observed that upon increasing OMMT nano clay concentration within the PLA films, the 2θ value shifted towards the lower angle indicating that the OMMT nano clay platelets were not fully exfoliated but intercalated towards greater extent. Similar observations were made by Najafi *et al.* 2015 [33].

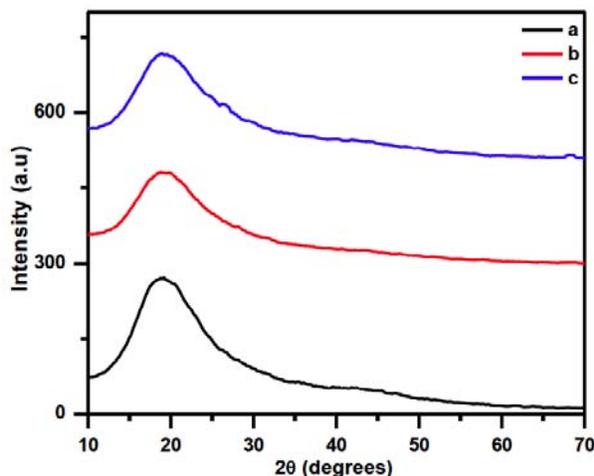


Figure 5: XRD of systems (a) neat PLA film (b) PLA/1wt% of OMMT nano clay film (c) PLA/2wt% of OMMT nano clay film.

SEM and TEM Analysis

The tensile fractured surface morphology of organic-inorganic hybrid nanocomposite films (systems 'b', 'c' and 'd') is

presented in Figure 6. From the Figure, we can clearly see the fractured surface morphology of system 'b' (2 wt%) depicts uniformly dispersed OMMT nano clay in the PLA (Figure 6a). This uniform dispersion of OMMT nano clay within PLA may be the reason for the effective chemical interaction between PLA and OMMT nano clay [34, 35]. Because of which an enhancement in tensile strength and thermal stability of system 'b' was noticed. However, the higher loading of 3wt% OMMT nano clay with PLA (system 'd') offered improper dispersion (Figure 6b) that led to decreased mechanical and thermal properties [36, 37].

Water Absorption Test

The rate of water absorption of the neat PLA film and organic-inorganic hybrid nanocomposite films (systems 'b', 'c' and 'd') are presented in Table 4 and Figure 7 respectively. It can be seen that the water absorption properties decreased with increased percentage of OMMT nano clay. For example, the lower water uptake values observed for the systems 'b' (3.6) 'c' (2.8) and 'd' (1.8) when compared to neat PLA film system 'a' whose water absorption value was found to be the maximum (4.3) among all other systems (Table 4). This may be due to the presence of inorganic groups of OMMT that acted as barrier, thereby providing protected pathways to the entry of water molecules thus leading to a reduced hydrophilicity in systems 'b', 'c' and 'd' respectively [38].

CONCLUSION

Organic-inorganic hybrid nanocomposite films were prepared by one-step solvent casting method. The thermal, mechanical and water absorption properties of nanocomposite films were determined as per standard testing methods in comparison with the neat PLA film to determine the optimum percentage loading of OMMT nano clay within the PLA-OMMT nanocomposite composition. The surface morphology of the organic-inorganic hybrid nanocomposite films was analyzed through XRD, SEM, and TEM surface analytical techniques. The obtained results showed that the thermal, mechanical and water absorption properties could be increased significantly with the optimum incorporation of OMMT nano clay in a PLA matrix, in comparison with the neat PLA. The optimized OMMT-PLA nanocomposite film (system 'c' of 2wt% of OMMT nano clay loaded PLA film) imparted superior mechanical, thermal and water resistant behaviour when compared to the 3wt% OMMT loaded PLA film (system 'd'). The surface morphology of organic-inorganic hybrid nanocomposite films (b, c, and d) from SEM was found to exhibit surface roughness and the surface roughness increases up to 3wt% of OMMT nano clay concentration, which in turn increases torturous path to crack propagation. Based on the data obtained from the above study, we conclude that the 2wt% OMMT nano clay loaded PLA nanocomposite films could be tried as a possible replacement for conventional and commercial packaging materials that are currently being used.

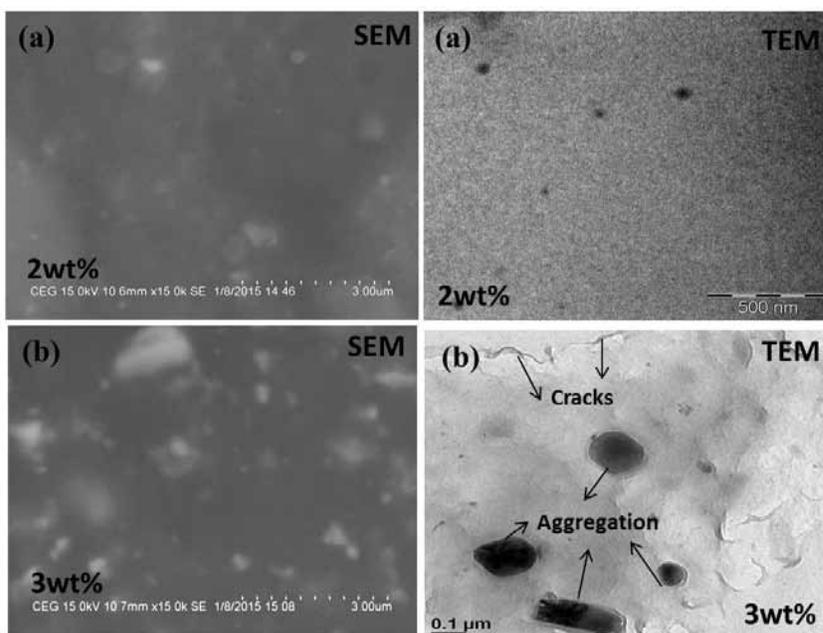


Figure 6: SEM and TEM photographs of systems (a) PLA/2wt% of OMMT nano clay film and (b) PLA/3wt% of OMMT nano clay film.

Table 4: Data on Water Absorption of Organic-Inorganic Hybrid Nanocomposite Films

Systems	PLA/wt% of OMMT nano clay	Water absorption
a	100/0	4.3
b	100/1%	3.6
c	100/2%	2.8
d	100/3%	1.8

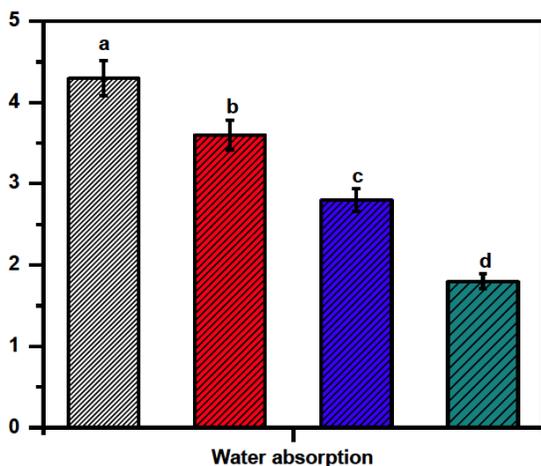


Figure 7: Water absorption of systems (a) neat PLA film (b) PLA/1wt% of OMMT nano clay film (c) PLA/2wt% of OMMT nano clay film and (d) PLA/3wt% of OMMT nano clay film.

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REFERENCES

- [1] Carol TM, Pellegrino J, Paster MD. Opportunities in the industrial biobased products. *Applied Biochemistry and Biotechnology* 2004; 113: 871-885. <https://doi.org/10.1385/ABAB:115:1-3:0871>
- [2] Molinaro S, Romero MC, Boaro M, Sensidoni A, Lagazio C, Morrise M, Kerry J. Effect of nanoclay-type and PLA optical purity on the characteristics of PLA-based. *Journal of Food Engineering* 2013; 117: 113-123. <https://doi.org/10.1016/j.jfoodeng.2013.01.021>
- [3] Badia JD, Strömberg E, Ribes-Greus A, Karlsson S. Assessing the MALDI-TOF MS sample preparation procedure to analyze the influence of thermo-oxidative ageing and thermo-mechanical degradation on poly(lactide). *Eur Polym J* 2011; 47(7): 1416-1428. <https://doi.org/10.1016/j.eurpolymj.2011.05.001>
- [4] Bouwmeester H, Hollman PC, Peters RJ. Potential Health Impact of Environmentally Released Micro- and Nanoplastics in the Human Food Production Chain: Experiences from Nanotoxicology. *Environmental Science Technology* 2015; 49: 8932-8947. <https://doi.org/10.1021/acs.est.5b01090>
- [5] Koelmans AA, Bakir A, Burton GA, Janssen CR. Microplastic as a Vector for Chemicals in the Aquatic Environment: Critical Review and Model-Supported Reinterpretation of Empirical Studies. *Environmental Science Technology* 2016; 50: 3315-3326. <https://doi.org/10.1021/acs.est.5b06069>
- [6] Araújo A, Botelho G, Oliveira M, Machado AV. Influence of clay organic modifier on the thermal-stability of PLA based nanocomposite. *Applied Clay Science* 2014; 88-89: 144-150. <https://doi.org/10.1016/j.clay.2013.12.005>
- [7] Niu X, Liu Y, Song Y, Han J, Pan H. Rosin modified cellulose nanofiber as a reinforcing and co-antimicrobial agents in poly(lactic acid) /chitosan composite film for food packaging. *Carbohydrate Polymers* 2018; 183(1): 102-109. <https://doi.org/10.1016/j.carbpol.2017.11.079>
- [8] Bouakaz BS, Habi A, Grohens Y, Pillin I. Organomontmorillonite/graphene-PLA/PCL nanofilled blends: New strategy to enhance the functional properties of PLA/PCL blend. *Applied Clay Science* 2017; 139: 81-91. <https://doi.org/10.1016/j.clay.2017.01.014>
- [9] Nampoothiri KM, Nair NR, John RP. An overview of the recent developments in poly(lactide) (PLA) research. *Bioresource Technol* 2010; 101(22): 8493-501. <https://doi.org/10.1016/j.biortech.2010.05.092>
- [10] Mikos AG, Thorsen AJ, Czerwonka LA, Bao Y, Langer R, Winslow DN, et al. Preparation and characterization of poly(L-Lactic Acid) foams. *Polymer* 1994; 35(5): 1068-77. [https://doi.org/10.1016/0032-3861\(94\)90953-9](https://doi.org/10.1016/0032-3861(94)90953-9)

- [11] Zhao H, Cui Z, Wang X, Turng L-S, Peng X. Processing and characterization of solid and microcellular poly(lactic acid)/polyhydroxybutyrate-valerate (PLA/PHBV) blends and PLA/PHBV/Clay nanocomposite. *Composites: Part B* 2013; 51: 79-91. <https://doi.org/10.1016/j.compositesb.2013.02.034>
- [12] Lim LT, Auras R, Rubino M. Processing technologies for poly(lactic acid). *Prog Polym Sci* 2008; 33: 820-852. <https://doi.org/10.1016/j.progpolymsci.2008.05.004>
- [13] De Silva RT, Pasbakhsh P, Mae LS, Kit AY. ZnO deposited/encapsulated halloysite-poly (lactic acid) (PLA) nanocomposite for high performance packaging films with improved mechanical and antimicrobial properties. *Applied Clay Science* 2015; 111: 10-20. <https://doi.org/10.1016/j.clay.2015.03.024>
- [14] Urquijo J, Guerrica-Echevarra I G, Eguiazabal JI. Melt processed PLA/PCL blends: Effect of processing method on phase structure, morphology, and mechanical properties. *J Appl Polym Sci* 2015; 132: 42641. <https://doi.org/10.1002/app.42641>
- [15] Zhang N, Zeng C, Wang L, Ren J. Preparation and properties of biodegradable poly(lactic acid)/poly(butylene adipate-co-terephthalate) blend with epoxyfunctional styrene acrylic copolymer as reactive agent. *J Polym Environ* 2012; 21: 286-292. <https://doi.org/10.1007/s10924-012-0448-z>
- [16] Zhou Y, Lei L, Yang B, Li J, Ren J. Preparation of PLA-based nanocomposite modified by nanoattapulgit with good toughness-strength balance. *Polymer Testing* 2017; 60: 78-83. <https://doi.org/10.1016/j.polymertesting.2017.03.007>
- [17] Duraibabu D, Madhumitha V, Alagar M, Kumar SA, Abhinandan S. Development and Characterization of a Novel Skeletal Modified Tetraglycidyl Epoxy Toughened DGEBA Epoxy Matrices. *Polymer Science Ser A* 2014; 56: 480-487. <https://doi.org/10.1134/S0965545X1404004X>
- [18] Gu JRSY, Dong B. Melt rheology of polylactide/montmorillonite nanocomposite. *J Polym Sci B-Polym Phys* 2007; 45: 3189-3196. <https://doi.org/10.1002/polb.21317>
- [19] Yu F, Huang HX. Simultaneously toughening and reinforcing poly(lactic acid)/thermoplastic polyurethane blend via enhancing interfacial adhesion by hydrophobic silica nanoparticles. *Polym Test* 2015; 45: 107-113. <https://doi.org/10.1016/j.polymertesting.2015.06.001>
- [20] Rhim J-W, Hong S-I, Ha C-S. Tensile, water vapor barrier and antimicrobial properties of PLA/nanoclay composite films. *LWT-Food Sci Technol* 2009; 42(2): 612-7. <https://doi.org/10.1016/j.lwt.2008.02.015>
- [21] Aghjeh MR, Kazerouni Y, Otadi M, Khonakdar HA, Jafari SH, Ebadi-Dehaghani H, Mousavi SH. A combined experimental and theoretical approach to quantitative assessment of microstructure in PLA/PP/Organo-Clay nanocomposite; wide-angle x-ray scattering and rheological analysis. *Composites Part B* 2018; 137: 235-246. <https://doi.org/10.1016/j.compositesb.2017.10.036>
- [22] Dhanapal D, Selvarasu V, Muthu Karuppan A, Srinivasan AK. Synthesis and Characterization of New Ether Linked Tetraglycidyl Epoxy Silicate Nanocomposite, Silicon, 2014. <https://doi.org/10.1007/s12633-014-9183-5>
- [23] Duraibabu D, Rajagopal D, Kumar SA. A first MMT reinforced nanocomposite functionalized with ether linkage derived from tetraglycidyl/diglycidyl epoxy building block. *Progress in Organic Coatings* 2017; 104: 135-140. <https://doi.org/10.1016/j.porgcoat.2016.12.014>
- [24] Narayanan M, Loganathan S, Valapa RB, Thomas S, Varghese TO. UV protective poly(lactic acid)/rosin films for sustainable packaging. *International Journal of Biological Macromolecules* 2017; 99: 37-45. <https://doi.org/10.1016/j.ijbiomac.2017.01.152>
- [25] Krishnaiah P, Ratnam CT, Manickam S. Development of silane grafted halloysite nanotube reinforced polylactide nanocomposite for the enhancement of mechanical, thermal and dynamic-mechanical properties. *Applied Clay Science* 2017; 135: 583-595. <https://doi.org/10.1016/j.clay.2016.10.046>
- [26] Arjmandi R, Hassana A, Mohamad Haafizb MK, Zakaria Z. Partial replacement effect of montmorillonite with cellulose nanowhiskers on polylactic acid nanocomposite. *International Journal of Biological Macromolecules* 2015; 81: 91-99. <https://doi.org/10.1016/j.ijbiomac.2015.07.062>
- [27] Wang L, Qiu J, Sakai E, Wei X. The relationship between microstructure and mechanical properties of carbon nanotubes/polylactic acid nanocomposite prepared by twin-screw extrusion. *Composites: Part A* 2016; 89: 18-25. <https://doi.org/10.1016/j.compositesa.2015.12.016>
- [28] Bouakaz BS, Habi A, Grohens Y, Pillin I. Organomontmorillonite/graphene-PLA/PCL nanofilled blends: New strategy to enhance the functional properties of PLA/PCL blend. *Applied Clay Science* 2017; 139: 81-91. <https://doi.org/10.1016/j.clay.2017.01.014>
- [29] Arjmandi R, Hassana A, Haafizb MKM, Zakaria Z, Md. Islam S. Effect of hydrolysed cellulose nanowhiskers on properties of montmorillonite/polylactic acid nanocomposite. *International Journal of Biological Macromolecules* 2016; 82: 998-1010. <https://doi.org/10.1016/j.ijbiomac.2015.11.028>
- [30] Arjmandi R, Hassan A, Haafiz MKM, Zakaria Z. Partial replacement effect of montmorillonite with cellulose nanowhiskers on polylactic acid nanocomposite. *Int J Biol Macromol* 2015; 81: 91-99. <https://doi.org/10.1016/j.ijbiomac.2015.07.062>
- [31] Ogata N, Jimenez G, Kawai H, Ogihara T, J of Polym Science: Part B: Polymer Physics 1997; 35: 389-396. [https://doi.org/10.1002/\(SICI\)1099-0488\(19970130\)35:2<389::AID-POLB14>3.0.CO;2-E](https://doi.org/10.1002/(SICI)1099-0488(19970130)35:2<389::AID-POLB14>3.0.CO;2-E)
- [32] Ebadi-Dehaghani H, Barikani M, Khonakdar HA, Jafari SH, Wagenknecht U, Heinrich G. On O₂ gas permeability of PP/PLA/clay nanocomposite: A molecular dynamic simulation approach. *Polymer Testing* 2015; 45: 139-151. <https://doi.org/10.1016/j.polymertesting.2015.05.010>
- [33] Najafi N, Heuzey M-C, Carreau PJ, Theriault D, Park CB. Mechanical and morphological properties of injection molded linear and branched-poly(lactide) (PLA) nanocomposite foams. *European Polymer Journal* 2015; 73: 455-465. <https://doi.org/10.1016/j.eurpolymj.2015.11.003>
- [34] Zhou Y, Lei L, Yang B, Li J, Ren J. Preparation of PLA-based nanocomposite modified by nanoattapulgit with good toughness-strength balance. *Polymer Testing* 2017; 60: 78-83. <https://doi.org/10.1016/j.polymertesting.2017.03.007>
- [35] Scaffaro R, Botta L, Maio A, Gallo G. PLA graphene nanoplatelets nanocomposite: Physical properties and release kinetics of an antimicrobial agent. *Composites Part B* 2017; 109: 138-146. <https://doi.org/10.1016/j.compositesb.2016.10.058>
- [36] Araújo A, Botelho G, Oliveira M, Machado AV. Influence of clay organic modifier on the thermal-stability of PLA based nanocomposite. *Applied Clay Science* 2014; 88-89: 144-150. <https://doi.org/10.1016/j.clay.2013.12.005>
- [37] Pinto VC, Ramos T, Alves ASF, Xavier J, Tavares PJ, Moreira, R.M. Guedes PMGP. Dispersion and failure analysis of PLA, PLA/GNP and PLA/CNT-COOH biodegradable nanocomposite by SEM and DIC inspection. *Engineering Failure Analysis* 2017; 71: 63-71. <https://doi.org/10.1016/j.engfailanal.2016.06.009>
- [38] Ayana B, Suin S, Khatua BB. Highly exfoliated eco-friendly thermoplastic starch (TPS)/poly (lactic acid)(PLA)/clay nanocomposite using unmodified nanoclay. *Carbohydrate Polymers* 2014; 110: 430-439. <https://doi.org/10.1016/j.carbpol.2014.04.024>