Evaluation of 3D Printable Sustainable Composites

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Abstract

Polylactic acid (PLA) is rapidly becoming the mainstay material for use in desktop grade 3D printers based on FDM technology in part due to the environmental sustainability of this polymer. While biodegradability is an advantage; as compared to other materials used by FDM-type platforms, there is a lack of desirable physical attributes. The work presented here evaluates the altering of the physical properties of PLA through the addition of sustainable additives. Here, the physical properties of PLA were modified while, at the same time the two desirable aspects of 3D printer compatibility and biodegradability were retained. Rheological analysis of the material systems was performed by dynamic mechanical analysis and failure analysis of 3D printed tensile specimens was carried out through the use of scanning electron microscopy. Finally, biodegradability of the novel PLA-based material systems was assessed based on in-soil exposure testing.

Key Words: 3D Printing; Materials Characterization; Polymer Matrix Composites

Introduction

Desktop-grade additive manufacturing (AM) platforms based on Fused Deposition Modeling (FDM) technology have become a mainstay among home users, educators, and entrepreneurs. Predominantly relying on acrylonitrile butadiene styrene (ABS) or polylactic acid (PLA) as feedstock, there has been a recent trend of PLA-specific platforms such as the fifth generation MakerBot Replicator and the Printrbot Simple 3D printer. The reason for this shift in material type to PLA is debatable and could be related to perceived health detriments due to the use of ABS in 3D printing applications [1] or the environmentally friendly nature of PLA due to its biodegradability [2, 3].

PLA is a biopolymer derived from renewable resources such as corn and sugarcane and while there are examples of other polymers; namely polyethylene, which have been synthesized from the same sustainable resources, the biodegradable aspect of PLA sets it apart from other engineering plastics. The need for biodegradable polymers stems from the environmental impact of the use of polymeric waste most exemplified by the great garbage patches found in both the Atlantic and Pacific oceans [4-6].

Though PLA does have the unique aspect of being a biodegradable biopolymer; other than 3D printing, the main use of this material is food packaging and disposable utensils. To find a broader range of applicability, the physical attributes of PLA must be altered. As demonstrated by Roberson *et. al*, [7] expanding the applicability of FDM-type 3D printing also lies in the altering of the material properties of feedstock constituents. Therefore, the broadening of the physical capabilities of PLA will contribute to expanding the applicability of polymer extrusion 3D printing technologies.

Several instances of the development of 3D-printer compatible polymer matrix composites (PMC)s with specific end use applications can be found in literature. For example, Shemelya *et al*. [8] demonstrated a tunable polycarbonate matrix tungsten composite for 3D-printable radiation shielding while Masood and Song [9] demonstrated the capability to alter the heat transfer kinetics of nylon by compounding either copper or iron particles where the end goal was the creation of 3D-printable injection mold tooling.

The work presented in this paper demonstrates the altering of the physical properties of PLA while maintaining 3D printer compatibility and biodegradability. Polymer matrix composites were created from a PLA base resin where the filler materials were sustainable substances. Here, we combined PLA with NaCl, jute plant fiber and organo nanoclay pigments. Sodium chloride was chosen due to its abundance, while jute plant fiber was chosen due to examples in literature if the use of this constituent in plant fiber reinforced PMCs [10-13]. Palygorskite-based (palygorskite is an organo nanoclay) pigments, originally developed by the Mayan Culture of Mesoamerica were chosen for this study based on work demonstrating an improvement to the mechanical properties of high density polyethylene (HDPE) [14].

Experimental Procedure

For this work, Ingeo PLA, Grade 4043D (NatureWorks, LLC, Minnetonka, MN, USA) was extruded into a polymeric monofilament through the use of a twin screw extruder/compounder (Dr. Collin Model ZK 25T, Dr. Collin, Ebersberg, Germany) equipped with intermeshing co-rotating screws. Baseline PLA and composite PLA-based filaments were extruded to a target diameter of 1.75mm, one of the two standard diameters common among material extrusion 3D printers (the other being 3mm). In the case of composites, a masterbatch of concentrated material was first created by manually kneading PLA pellets with filler materials through the use of a Carver hot press (Carver, Inc., Wabash, IN, USA). The masterbatch was then granulated with a Brabender GranuGrinder (C.W. Brabender South Hackensack, NJ, USA) and subsequently combined with virgin PLA material in the extruder system.

Test specimens were fabricated according the Type V dimensions as described in the ASTM D638-10 standard by printing test specimens with a MakerBot Replicator 2X (MakerBot Industries, Brooklyn, NY, USA) or a Rostock Max Delta 3D printer (SeeMe CNC, Goshen, IN, USA) where the latter unit was modified with an E3D V6 hotend (E3D-Online Limited, Chalgrove Oxfordshire , UK). Tensile testing was carried out with an Instron® 5866 (Instron, Norwood, MA) tensile testing machine equipped with a 10kN load cell. Dynamic mechanical analysis (DMA) was also performed on all material systems with a TA Q800 (TA Instruments, New Castle, DE, USA).

Four individual filler materials were combined with PLA in the formation of sustainable 3D printable polymer matrix composites: 1) Sodium chloride (NaCl) (Sigma); 2) jute plant fiber sourced from rope purchased from Home Depot; 3) MayaCrom® Blue; and 4) MayaCrom® yellow (both from Mayan Pigments. Inc., El Paso, TX, USA). The filler materials evaluated in this study were chosen based on the perceived environmental sustainability. All additives were blended at a 5% (by weight) ratio to PLA.

Fracture surface analysis was carried out through the use of a tabletop scanning electron microscope (SEM) operating with an acceleration voltage of 15kV and equipped with a backscatter electron (BSE) detector (Hitachi, Model TM-1000,Hitachi High-Technologies Europe GmbH, Germany). To reduce charge effects within the SEM, all samples were sputter coated with a gold palladium target for 30s with a Gatan Model 682 Precision Etching Coating System (Gatan, Inc., Pleasanton, CA, USA) prior to microscopic analysis.

Results

Tensile test results (Fig. 1) revealed that the addition of jute plant fiber and MayaCrom® Blue led to tensile test specimens with lower ultimate tensile strength values lower than those printed from PLA alone. This decrease in strength may be due to the degradation of the organic components of each additive as noted in Torrado et al. [15] However, the addition of jute plant fiber increased the % elongation specimens were able to endure during the tensile test process. The addition of NaCl did not greatly affect the mechanical properties.

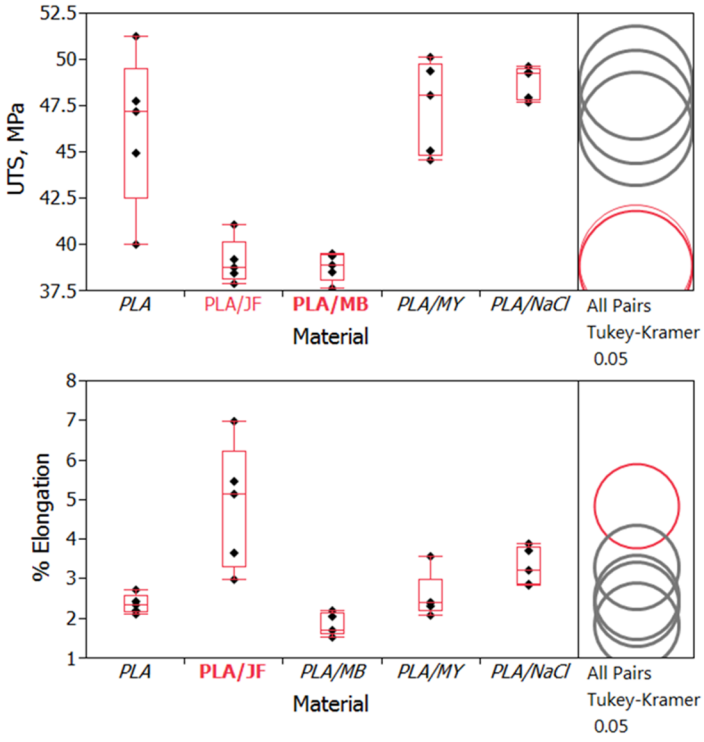

Fig. 1. Tensile test results of materials tested here.

Subjecting the material types evaluated here to DMA testing revealed differences in the thermomechanical behavior of the composite materials as compared to the baseline PLA resin. The addition of both NaCl and jute plant fiber to PLA reduced slightly the onset of glassy behavior as determined by the storage modulus curve, however the temperature at which the maximum tan δ occurred was increased, which effectively broadened the thermal window of elastic behavior as compared to baseline PLA (Table 1.) where the addition of jute increased this window by ~8.4°C. In the case of NaCl, though the temperature at which the maximum tan δ occurred was increased, the actual value of this parameter was virtually the same as PLA (1.8) meaning the elasticity was not altered. The addition of both types of MayaCrom®

pigments as well as jute plant fiber decreased the maximum tan δ indicating and increase in the elasticity of these composites as compared to the PLA base resin.

Table 1. DMA Data for the materials tested here.

Material	Storage modulus at 40 °C, MPa	Complex viscosity at 80 °C, MPa·sec	Max tan delta
PLA	2683	8.76	1.8
PLA/ MayaCrom® Blue	2162	1.052	1.166
PLA/ MayaCrom® Yellow	2146	3.58	0.8233
PLA/NaCl	2302	0.4133	1.797
PLA/Jute	2113	2.307	0.8206

Fractography (Fig. 2) of tensile test specimens printed from the composites tested here allowed for observations related to the robustness of the filler/matrix interface as wells the effect of additives to the crack surface morphology to be made. Baseline PLA tensile specimens possessed a fracture surface morphology indicative of a brittle failure mode which correlates will with the low % elongation at break values observed for the material. Fracture surface analysis revealed NaCl to adhere well to the PLA matrix. Crack propagation is evident on the surfaces (highlighted in Fig 3) of the individual particles. There is also no evidence of particle pull out nor were there any gaps between the particles and the matrix. By contrast the fracture surface of the PLA/jute plant fiber composite possessed features indicating a poor interface between the fibers and the matrix (indicated by white arrows in Fig. 1b). The addition of MayaCrom® pigments had the effect of inducing voids within the PLA matrix which accounts for the decrease in tensile strength as compared to baseline samples.

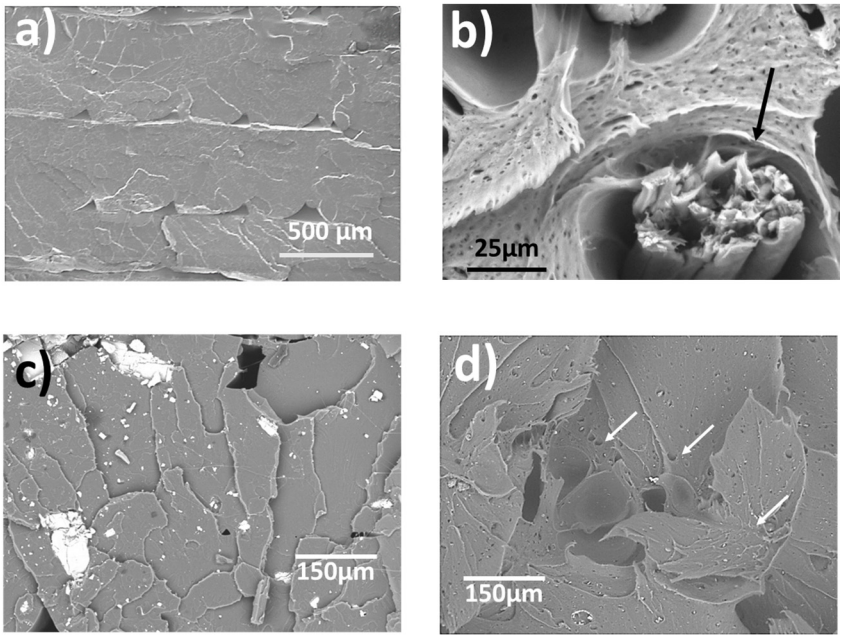

Fig. 2. SEM Micrographs of materials tested in this study: a) PLA; b) PLA/jute plant fiber; c) PLA NaCl; and d) PLA/MayaCrom® Blue.

Of the additives tested here, NaCl produced results worthy of deeper investigation. While the addition of jute plant fiber increased the glass transition window, the poor adhesion to the matrix at room temperature was a detractor to the overall performance of this composite. Since NaCl exhibited characteristics indicating a robust bond with the PLA matrix, another experiment was carried out where jute plant fiber was first functionalized in an aqueous NaCl solution prior to compounding. The result was a decrease in % elongation while the UTS remained the same (Fig. 4). Further analysis of the fracture surface via SEM (Fig. 5) revealed the presence of polymer fibrils joining the matrix to the jute fiber which formed during the tensile testing process. The presence of these fibrils indicated a robust bond had formed between the matrix and the fiber as the formation of fibrils is cause by the elongating of polymer chains under tension. The decrease in % elongation in conjunction with yield strength values similar to those of the non-functionalized samples indicates an increase in stiffness caused by an increase in the bond strength between the fiber and the matrix.

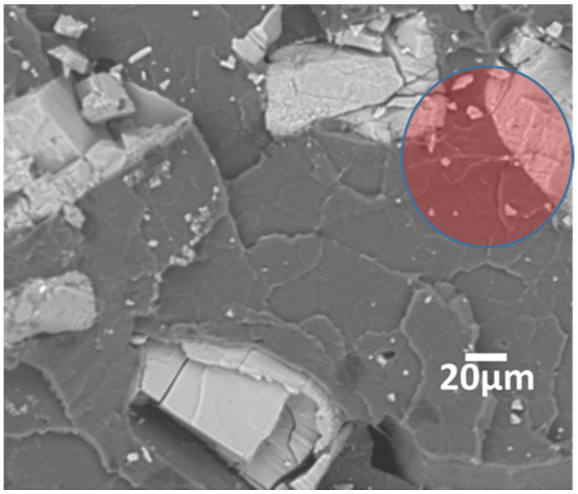

Fig. 3 NaCl adhered well to the matrix and exhibited a robust interface and shared crack propagation features with the matrix.

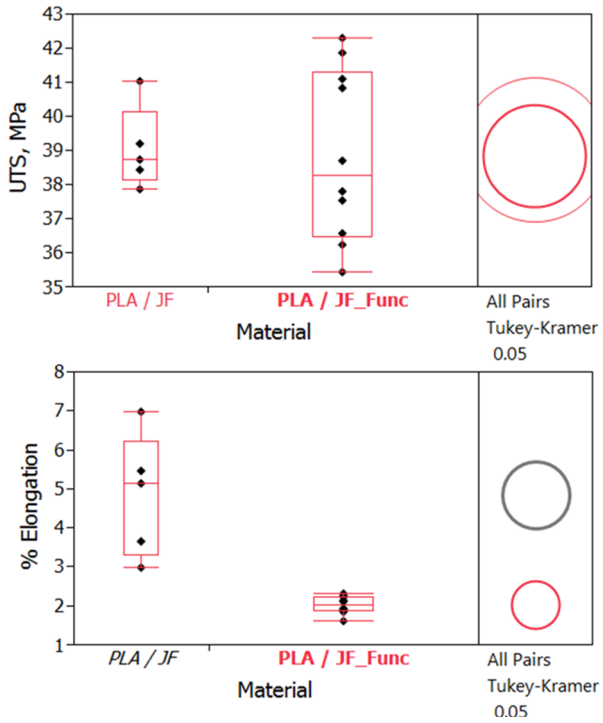

Fig. 4 The effect of NaCl functionalization of jute plant fiber on the mechanical properties of PLA/jute fiber composites.

Further analysis of the addition of NaCl to PLA on 3D printed tensile specimens entailed examining the effect of NaCl on the mechanical property sensitivity to raster orientation of 3D printed tensile test specimens. Here two raster patterns were used to print the tensile test specimens: 1) a crosshatched raster pattern where layers alternated by 90°; and 2) a transversal raster pattern where the print layers were perpendicular to the length of the tensile specimen. In the case of the transversal specimen, there was no perimeter shell and it is noted that Torrado [16] noted this print raster pattern to be equivalent in terms of UTS with tensile test specimens printed in the ZXY print orientation. Comparing the sensitivity to raster pattern between PLA and the PLA/NaCl composite revealed the addition of NaCl to reduce the difference in UTS between the

transversal and crosshatched raster pattern (Fig. 6.). More notable is that this decrease in mechanical property anisotropy did not come at the expense of overall yield strength as has been the case in work related to decreasing the anisotropy of ABS-based ternary polymeric blends as explored in Torrado *et al.* [17].

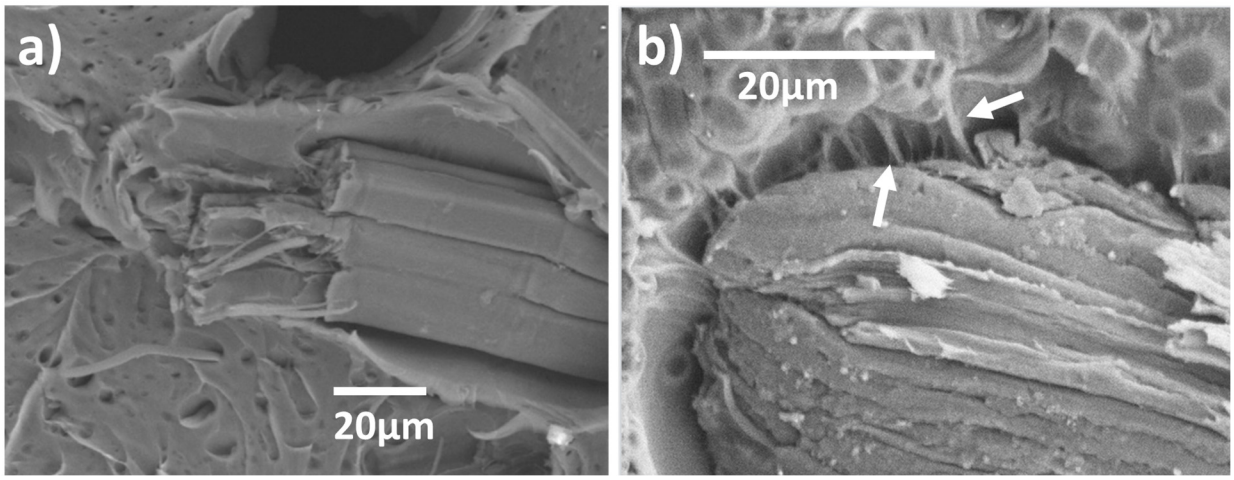

Fig. 5. a) non functionalized jute fiber and b) NaCl functionalized jute fiber. Note the presence of fibrils for the functionalized plant fibers.

Biodegradability

An attempt to assess the biodegradability of the PLA based composites evaluated in this study. Samples were buried for two and twelve weeks in topsoil which was moistened with food grade vinegar. The effect of exposure to the soil environment was assessed by tensile testing of the exposed samples as well as the monitoring of weight change before and after exposure. No observable difference to weight was observed for any of the samples buried in the soil environment for two weeks. However, after 12 weeks, PLA specimens exhibited an increase in weight, while (1.95± 0.02 g increasing to 2.03 ± 0.01 g) the PLA/NaCl composite exhibited a decrease in weight (2.49 ± 0.03 g decreasing to 2.24 ± 0.12 g). In terms of tensile strength, both PLA and the PLA/jute fiber composite exhibited an increase in tensile strength compared to non-exposed control samples while the PLA/NaCl composite exhibited a decrease in tensile strength as compared to non-exposed samples (Fig. 7.) Further exploration is needed to understand if the decrease in tensile strength and tensile strength is due to biodegradation or the effect of moisture. NaCl is water soluble and the decrease in weight and tensile strength could be due to dissolution of this substance within the PLA matrix. The increase in tensile strength and weight for PLA as

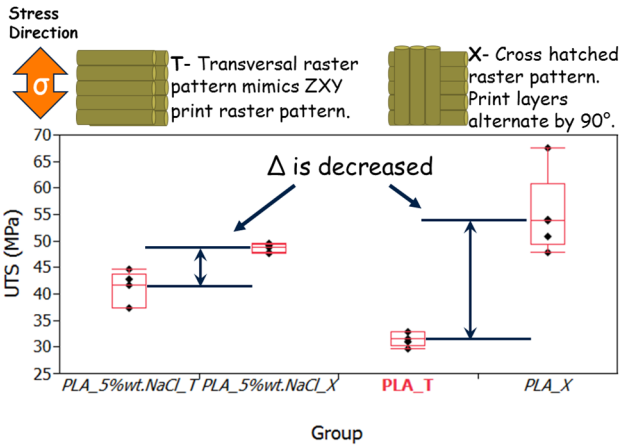

Fig. 6 The addition of NaCl to PLA decreases mechanical property sensitivity to print raster orientation.

well as the increase in tensile strength for the PLA/jute plant fiber composite is also a finding that merits further study. Future work will include subjecting samples to biodegradability testing following ASTM D6954, a standard for assessing the biodegradability of polymers.

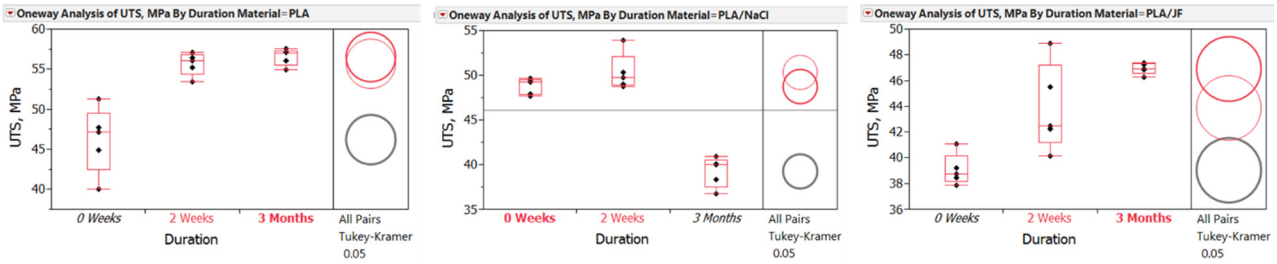

Figure 7. The effect of moist soil exposure to PLA, PLA/jute fiber composite and PLA/NaCl composites.

Conclusions

Tailoring the physical properties of the biopolymer, PLA is possible through the addition of sustainable additives. Here, when melt compounding was used to combine PLA with jute plant fiber, organo nanoclay pigments, and NaCl a discernable difference in physical properties was observed as compared to PLA alone. Explored in greatest detail was the effect of the addition of NaCl to PLA. Fractography of tensile test fracture surfaces revealed NaCl to adhere well to the PLA matrix as there was no evidence of particle pull out. The robustness of the bond between NaCl and PLA was also displayed by evidence of crack front propagation shared between the NaCl particle and the surrounding matrix. Further exploration of the benefit of combining PLA with NaCl was observed through the functionalization of jute plant fiber with aqueous NaCl. The use of palygorskite-based organonanoclay pigments also shows potential in playing a role in future PLA based 3D printable material systems. Several aspects of this work bear the need for future study such as the increase in strength observed after exposing PLA and PLA/jute plant fiber composites to a moist soil environment for durations of two and twelve weeks.

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