UPCYCLING MATTRESS TEXTILE WASTE INTO BIODEGRADABLE 3D-PRINTED CONSUMER PRODUCTS TO REPLACE SINGLE-USE PLASTICS.

Submitted to: Mattress Recycling Council

Submitted by: Dr. Sunidhi Mehta (Principal Investigator)
Assistant Professor
Davis College of Agriculture, Natural Resources and Design
Design and Community Development
West Virginia University
Morgantown, WV 26506

1. Project Overview

More than 50,000 mattresses are discarded in the U.S. alone every day [4], which either end up in landfills or are collected by mattress recycling facilities. Textiles are one of the least recycled components of this waste [1] and it ends up in either landfills or is burned in incinerators as fuel [2]. In the landfill, the decomposition times are remarkably high. It takes weeks to months for natural biodegradable fibers and several hundreds of years for synthetic fibers to decompose [3]. Therefore, it is of utmost importance to find ways to recycle the textile waste generated by discarded mattresses for potential reuse.

In this one-year project, we collected cotton waste from a mattress recycling facility and upcycled it into the fiber-reinforced polymer (FRP) composite for 3D printing of consumer products to replace single-use plastics. The manufacturing of FRP composites has progressed swiftly in recent years because of their high performance compared to pure plastic polymers [4,5]. There is an increasing demand in the market for FRPs due to their high strength-to-weight ratio which results in highly strong yet lightweight material. They have exceptional properties such as high durability, flexural rigidity, stiffness, abrasion, and corrosion resistance. FRPs have a huge potential for applications in industries such as automotive, aerospace, petrochemical, and sporting goods industries [6,7]. The overarching goal of this project was to upcycle cotton fiber waste from discarded mattresses into biodegradable cotton fiber-reinforced PLA polymer composites and study the biodegradability of the composite material.

This report is presented in two sections that correspond with the two main phases of the project. In phase I, our team developed cotton fiber-reinforced PLA composites and 3D printed them into consumer product prototypes. In Phase II of the study, we investigated the soil biodegradability of the PLA/Cotton composites (of varying ratios) in controlled lab experiments to examine the effect of cotton on PLA's biodegradability.

2. Phase I-methods and results

We chose Ingeo™ Biopolymer 3251D for developing the composite compound as it is compostable and processes similarly to polyethylene (PE), though it is relatively brittle in comparison to PE. It is preferable to use PLA that does not crystallize easily. The 100% mote cotton for the composite was provided by the Mattress Recycling Council (MRC) to reinforce the PLA polymer. We started off by sanitizing the cotton fibers (See Fig. 1) by completely soaking them in a sodium hypochlorite solution.

Figure 1. Cotton fibers were procured from used mattresses and provided by MRC for the research activities of the project.

Figure 2 a) and b) cotton-PLA compound internal mixer.

In the next step, we detangled and separated the fibers by hand-carding them. The carded fibers were then mixed with PLA in a lab-scale batch mixer keeping a polymer-to-fiber ratio of 80:20 by weight. For example, our first sample consisted of 2.5 gm of cotton and 10 gm of PLA (3251D). Mixing was done at 180ºC at a rotor speed of 80 rpm for 5 minutes. The mixed material was spooned out at the end of a 5-minute mixing cycle and allowed to cool at room temperature. Figure 2 (a and b) shows the output resulting from the mixer.

In order to find optimum mixing conditions, we blended PLA and cotton fibers under different thermal (180-200 ºC) and mechanical conditions (80-200 rpm for 5-10 minutes) and found that the PLA and cotton blended at 180 ºC at 80 rpm for 5 minutes had the most favorable characteristics needed for the purpose of the study. To further study the interfacial bonding of fiber with the polymer and their dispersion behavior in the polymer compound, we conducted a scanning electron microscopy (SEM) analysis of the compound sample. Figure 3 (a-c) showcases the SEM micrographs of the PLA-cotton compound prepared with the above-mentioned mixing conditions. It shows a fairly good dispersion of cotton fibers in the PLA polymer matrix as well as decent polymer adhesion to the cotton fiber as shown in Fig. 3 (a-c).

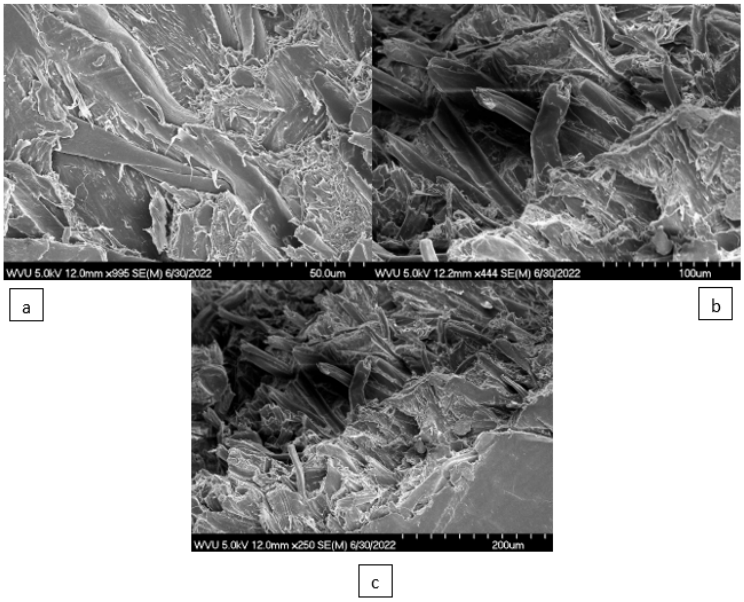

Figure 3. SEM micrographs of the compressed PLA-Cotton compound processed at 180 ºC for 5 minutes- 50 µm (a),100 µm (b) and 200µm (c) respectively.

1.2.1 Extruder and winder used to make strands for 3D Printing.

In the next step, we developed a 3D printing filament with the help of a filament extruder (Figure 4) designed in our lab specifically for this project. Figure 4 on the right shows the overall extruder setup and Figure 5 below depicts the 3D printed hopper used for extrusion of the 3D printing filament. This device melts the compounded polymer, pressurizes it, and extrudes it through a nozzle. The machine has multiple heating and cooling settings, speed, sensors, etc. to ensure that the filament comes out correctly. Material is fed through a hopper (see Fig. 5) that acts as a funnel.

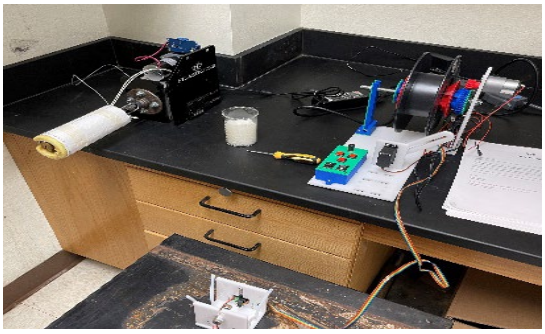

Figure 4. Extruder and winder with important parts.

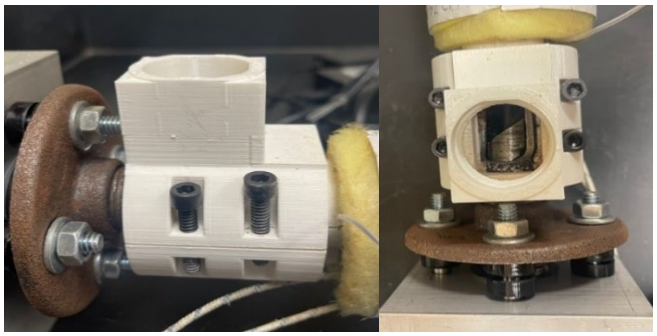

Figure 5. The 3D printed hopper designed for filament extrusion.

The extruded materials in the form of filaments are shown in Figure 6 (a). As can be seen in figure 6, there are clear differences between the different filaments. From left to right, neat PLA filament and PLA/cotton filaments compounded at different ratios of PLA and cotton. Lastly, figure 6 (b and c) shows a 3D print of a dental floss pick and a coat button respectively.

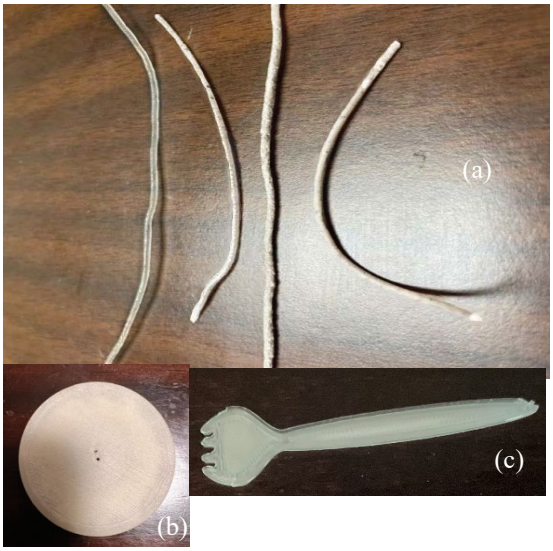

Figure 6. (a) Composite and neat PLA filament samples. (b) 3D printed coat button (c) 3D printed spork

Phase II- methods and materials

In phase II we conducted 4 experiments, each experiment lasted between 60-90 days. In the first experiment, we standardized the minimum amount of control (100% cotton and 100% MCE) reference material needed to measure the traces of evolved CO_2. Therefore, we used 10 milligrams of each 100% cotton and 100% MCE as control samples of the biodegradation study. The results of our second and third sets of experiments helped us develop a repeatable experimental protocol for this study, which is discussed below.

3.1 Composite Sample Preparation

As discussed in phase I, we developed PLA/Cotton compounds of varying ratios. In total, we developed 6 FRP compounds of varying concentrations of cotton (0% /5% /10% /15% /20% and 25% cotton) and PLA to run our phase II biodegradation experiments. The PLA/cotton compound at different ratios was converted into sheets of approximately 0.5 mm in thickness by pressing at

190 °C for 3 min under 5 MPa followed by cooling at room temperature for 5 min. Thereafter, the compression molded samples were cut into 10 mm × 10 mm size and weighed.

3.2. Biodegradation tests

A biodegradation test was conducted with a laboratory-scale Li-Cor gas analyzer on standard test methods designed for biodegradable plastics (GB/T19277–2003/ISO 14855-1:2005) (determination of the ultimate aerobic biodegradability of plastic materials under controlled composting conditions—method by analysis of evolved CO_2). Most of the carbon in the metabolized substrates generates energy through chemical transformation to CO_2 in aerobic environments [9]. Therefore, measurements of the generation of CO_2 are considered the most appropriate measure of biodegradation in most circumstances. The standard specifies a procedure to determine the ultimate aerobic biodegradability by measuring the amount of evolved CO_2 and the percentage of the biodegradation degree of the test materials under controlled composting conditions. The composting inoculum was prepared from store-bought organic compost, which was sieved to sizes under 5 mm. Thereafter, the fine fraction was used as inoculums.

3.3. Preparation of sample jars

Each of the composite samples was tested in triplicates (6 conc. X 3= 18 samples in one batch of samples) along with one (in triplicate) set of 0.1 g of the reference material (i.e., microcrystalline cellulose (MCE), which was suggested by the standard) and 0.1 g of 100% cotton control sample in triplicates. The test samples (i.e., each composite film $1cm^2$ were weighted and labeled before degradation. Our trials indicated that 80 g of inoculum and 325 g of dry sea sand provide good homogeneous conditions and an improved aerobic environment inside the inoculum. Therefore, we prepared a bulk amount of inoculum and divided it evenly into incubation jars. Thereafter, the composite samples were placed in an incubation jars and placed in a preheated lab oven at 50 ± 2 °C through an experiment time of 60 days.

3.4 Data collection

Aeration was initiated using water-saturated CO2-free air twice a day at an interval of 12 hours. At this time, we also collected the data from each sample to study the amount of CO_2 produced in each jar. We continued our experiment for 60 days until we observed a plateau in the evolved CO_2 among all samples. We also collected specimens for the surface morphology analysis for all six concentrations of PLA/Cotton after 15, 30, 45, and 60 days of incubation time.

3. Results and discussion

4.1. Observational data

Polymer degradation is associated with changes in its characteristics, such as color, surface morphology, and mechanical properties. In this project, we studied the biodegradation of PLA/cotton composites in multiple ways. The neat PLA specimens which were initially transparent slowly started to turn opaque as the water permeation and microorganism incubation progressed. We also observed similar trends of change in the surface appearance of all specimens as indicated in figure 7. We observed the highest loss of strength in the neat PLA specimen across all the samples. As depicted in Figure 7, we couldn't collect all three specimens of neat PLA fully

intact from the inoculum as it fell apart into pieces during the process of collecting. The samples with the highest (25%) percentage of cotton were found to be the strongest across all the samples.

4.2. Surface Morphology

The surface morphology analysis of the specimens is presented in Figure 8. showing the periodic biodegradation of the composite specimens over a period of 60 days. As seen in the day 0

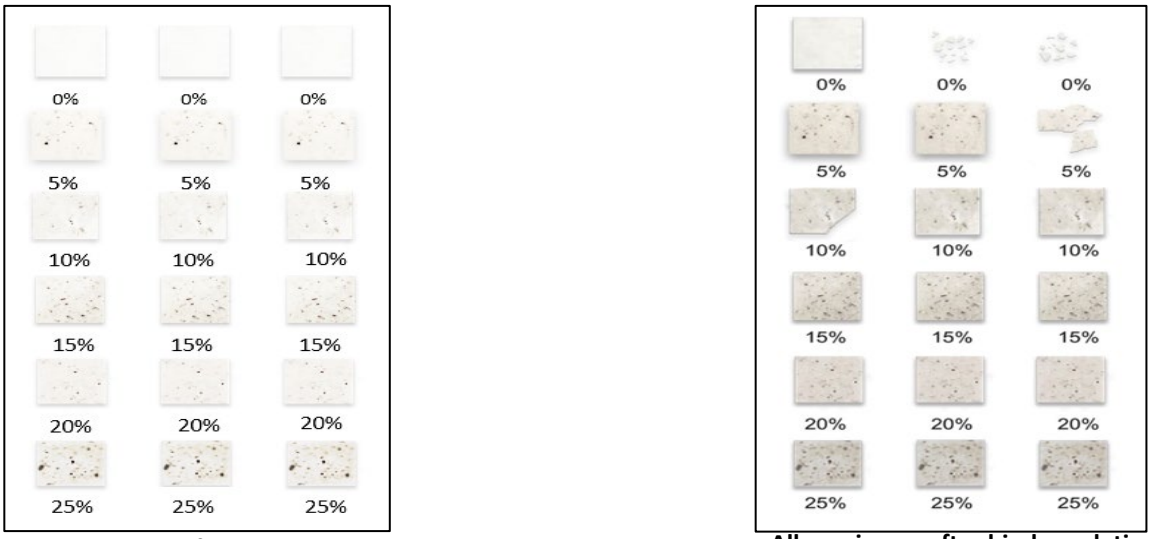

Figure 7. PLA/cotton composite specimens (in triplicates) before and after 60-day biodegradation.

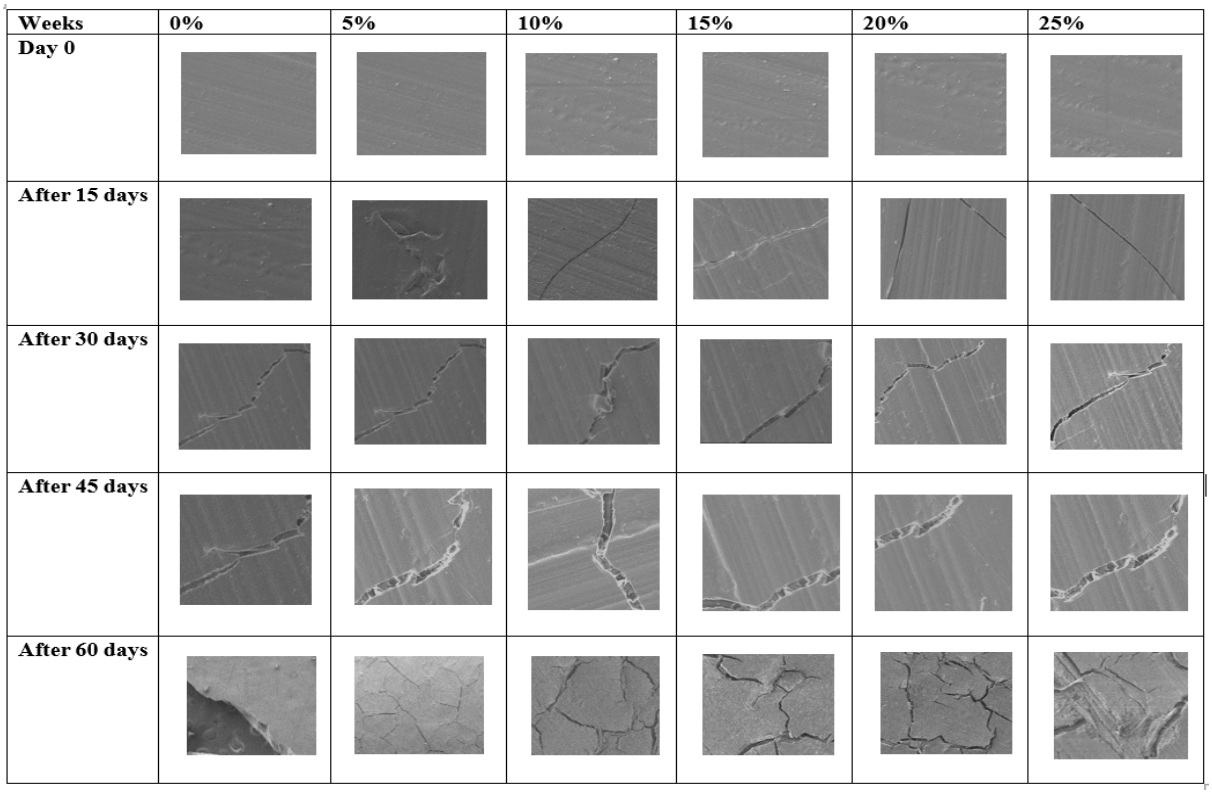

Figure 8. SEM micrographs of the biodegraded PLA/Cotton (0-25% cotton) composite samples over a period of 60 days.

micrographs, all the specimens had a fairly smooth surface free of any cracks, voids, or other signs of biodegradation. However, the biodegradation effect can be clearly seen in the SEM micrographs captured at 15, 30, 45, and 60 days of incubation time. The biodeterioration signs such as cracks, voids, and increased surface roughness of the specimens indicate biodegradation over time and can be clearly seen across all samples except day 0 samples. This could be attributed to the hydrolysis of PLA and the microbial decaying process. With increasing incubation time, the cracks and voids became substantially deep and large (Fig. 8), thereby suggesting mass loss and surface erosion as the incubation time progressed. The bulk erosion phenomenon for all test materials was similar to the hydrolytic degradation process of the PLA and PLA/Cotton composites.

Similarly, figure 9 shows the CO_2 evolution as a function of incubation time for neat PLA and PLA/Cotton composites, which suggests the biodegradation of all samples. We took the first observation of CO_2 data after 12 hours of setting up the experiment and collected CO_2 data every

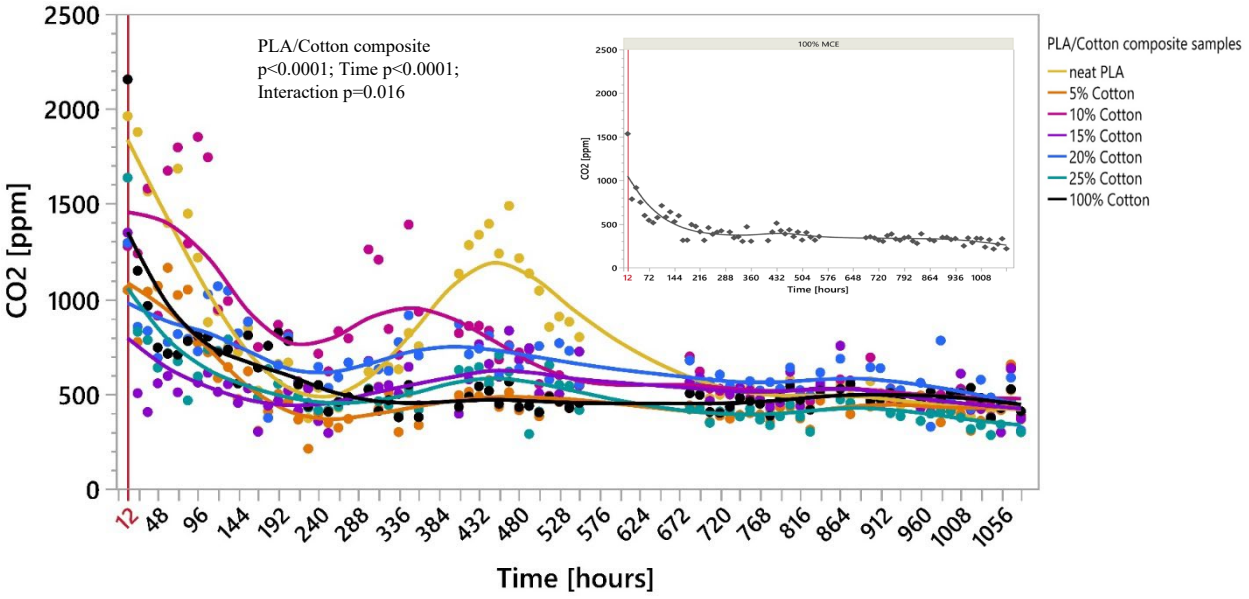

Figure 9. The CO_2 evolution data as a function of incubation time (45 days shown) for neat PLA and PLA/Cotton composites. The inserted graph is the CO_2 evolution as a function of time for the reference material- microcrystalline cellulose (MCE).

12 hours, thereafter till 60 days. However, in this figure, we show data from only the first 45 days because a plateau phase was observed after 720 hours/30 days across all samples including neat PLA. Similar behavior was observed for the PLA/Cotton composite samples except for the 100% cotton samples that experienced a plateau after 360 hours/15 days. Interestingly, a steep decline in CO_2 evolution was first observed which is then followed by a steep to mild (varied across all samples) linear increase in CO_2 and thereafter another drop followed by an ultimate plateau phase after ~30 days of incubation time for all samples. The steepness of the increase/decrease should be indicative of increased/decreased degradation respectively.

To further assess how our composite samples degraded compared to neat PLA (Fig. 10), we calculated the decay rate of our samples by using equation: $C\_t=C\_0*e-kt$ by fitting $C/C0=-kt$. Where C is the CO_2 concentration in ppm, t is time and k is the first (or pseudo-first) order rate

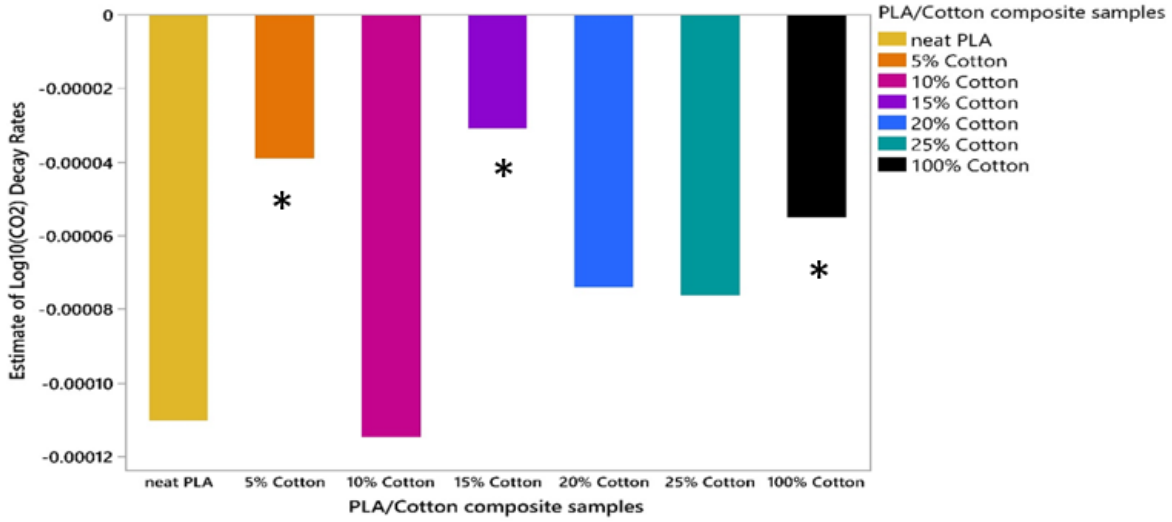

Figure 10. The mean decay rates of all samples compared to the neat PLA. *denotes significantly different decay rate compared to the neat PLA.

constant. Specifically, mean decay rate of every group was compared to the neat PLA sample. The decaying rates of 5%, 15%, and 100% cotton samples were significantly different from the neat or 100% PLA samples; while the decay behaviors of 10%, 20%, and 25% cotton samples were statistically similar to the neat PLA samples. We anticipate that this divergence in the data could be due to the irregular dispersion of cotton fibers in the compounded PLA matrix since the only variable among the incubation jars was the PLA/Cotton samples' varying ratio of cotton in PLA matrix. All the other conditions were the same across all the incubation jars. For example, the PLA/cotton composite sheets may have an uneven dispersion of the cotton fibers due to which some of our samples may have higher/lower percentages of cotton in a given surface area of the PLA/Cotton composite sheets. In future work, we propose to study the dispersion rate of fiber in the PLA matrix to examine the proportion of fiber in a given surface area of the composite mixture prior to a biodegradation study. It is important that the fibers are dispersed evenly in the polymer matrix otherwise the disproportionate amount of mixed fibers can skew the biodegradation rates of the composite samples. We also propose to increase the number of replicates per sample for the biodegradation study as opposed to the current standard triplicate sampling approach to better understand the biodegradation behaviors of the individual samples in our future work.

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