

Thermoformed containers based on starch and starch/biochar composites^[4]

Carlos A. Diaz¹, Tyler Evans¹, Rahul Ketan Shah¹, Thomas A. Trabold²

¹ Packaging Science, ² Golisano Institute for Sustainability,
Rochester Institute of Technology, Rochester NY, USA

Abstract: Biodegradable containers support zero-waste initiatives when alternative end-of-life scenarios are available (e.g., composting, biodigestion). Thermoplastic starch (TPS) has emerged as a readily biodegradable and inexpensive biomaterial that can replace traditional plastics in applications such as food serviceware and packaging. This study has two aims. First, demonstrate the thermoformability of starch/polycaprolactone (PCL) as a thermoplastic material with varying starch loadings. Second, incorporate biochar as a sustainable filler that can potentially lower the cost and improve biodegradability. Biochar is a stable form of carbon produced by thermochemical conversion of organic biomass, such as food waste, and its incorporation into consumer products could promote a circular economy. Thermoformed cups were successfully made with starch contents from 40 to 60 wt.%. Increasing the amount of starch increased the viscosity of the material, which in turn affected the compression molding (sheet manufacturing) and thermoforming conditions. PCL content reduced the extent of biodegradation in soil burial experiments, and increased the strength and elongation at break of the material. A blend of 50:50 starch:PCL was selected for incorporating biochar. Thermoformed containers were manufactured with 10, 20 and 30 wt.% biochar. The addition of biochar decreased the elongation at break, but did not significantly affect the modulus of elasticity or tensile strength. Preliminary experiments suggest that adding 10 wt.% biochar increased the biodegradation of the material. The results demonstrate the feasibility of using starch and biochar for the manufacturing of thermoformed containers.

Keywords: starch, biochar, polycaprolactone, bioplastics, biodegradation

*Correspondence to: Carlos A. Diaz, Department of Packaging Science, Rochester Institute of Technology,
29 Lomb Memorial Drive, Rochester NY 14823, USA. E-mail: cdamet@rit.edu



1. Introduction

Zero-waste initiatives call for waste to be either recyclable or compostable. Some municipalities in the US have programs to voluntarily separate organic waste, which is collected and composted. In this scenario, packaging and single-use items that are readily degradable present an opportunity to support and enhance closed loop systems for organic waste.

Thermoplastic starch (TPS) has emerged as a readily biodegradable and inexpensive biomaterial that can replace traditional plastics in applications such as food service and packaging^[1]. Our previous study^[2] investigated the mechanical performance of blends of TPS and polycaprolactone (PCL). A brittle-ductile transition was observed with the addition of PCL, and the degree of anaerobic biodegradation correlated with the amount of TPS. However, the preparation of TPS using water and glycerol showed inconsistencies from batch to batch and it is susceptible to aging^{[2]-[4]}. Therefore, development of TPS-based products would benefit from a manufacturing process that avoids use of water or glycerol.

Here, a direct mixing of starch and PCL is proposed which bypasses some of the drawbacks outlined with TPS and could facilitate scale-up production. Additionally, the manufacturing of composites using biochar is presented as a means to improve biodegradability and valorize a byproduct from conversion of organic waste, thus promoting a circular economy^[5]. Biochar is produced by pyrolysis of organic matter at high temperature

under zero-oxygen conditions^[6]. This technique creates a carbon-rich material with physical properties such as density, surface area and porosity that can be controlled by selecting critical process parameters, including heating rate, maximum temperature (typically in the range of 400 to 800°C) and residence time^[7]. In the process of gasification, some oxygen is introduced to the system (well below the stoichiometric requirement for full combustion), and this may improve biochar quality in some cases, but at the cost of lower yield^[8].

2. Methods

2.1 Materials

Corn starch was obtained from MP Biomedicals LLC. Polycaprolactone (PCL) Capa 6800, was supplied by Perstorp. Biochar was derived from spent coffee grounds obtained from the RIT cafeteria. The material was first dried using an in-house batch dehydrator (Ecovim-250) and then processed in a commercial-scale "Biogenic Refinery" manufactured by Biomass Controls (Putnam, CT, USA) and owned by RIT[9]. To produce biochar, dried coffee grounds were fed through a hopper and auger assembly at an average flow rate of approximately 5 kg/h. The temperature setpoint of 800 °C was maintained within ±25 °C over the course of the approximately 3-hour experiment. After thermochemical conversion, a dual auger system transported the final biochar product to the collection box, where samples were quenched with water spray to cool the material and prevent further reaction with ambient air.

2.2 Sample preparation

Thermoplastic starch was made using an internal shear mixer (CWB Brabender Intelli-torque Plasticorder torque rheometer with a 60cc 3-piece mixing head). TPS starch was blended at 30, 40, 50, and 60 wt. % with PCL in the mixer at 100 °C for 8 minutes and 50 rpm. The equilibrium torque was recorded as an indirect measu-

rement of the viscosity of the melt as shown in Table 1. The samples were compression molded with a heated press (Carver 4391). Thermoforming was performed on a Sencorp Cera TEK 810/1-CE sheet fed laboratory thermoformer using a male mold. Optimum forming conditions were achieved through trial and error by adjusting the heating temperature and dwell time and monitoring the wrapping and webbing in the blisters (see Table 1).

Table 1. Processing conditions for sample preparation

Material Composition PCL:Starch	Mixing	Compression molding			Thermoforming	
	Equilibrium Torque (Nm)	Temperature (°C)	Pressure (tons)	Time (minutes)	Forming Temperature (°C)	Time (minutes)
60:40	12	200	3	7	110	1.5
50:50	13	200	3.5	8	113	1
40:60	17	180	6.5	15	116	1
30:70	21	210	7	15	138	1

Biochar composites were manufactured using the 50:50 PCL:starch blend as the base material, with 10, 20 and 30 wt.% biochar mixed at 85 °C. Thermoforming was performed at 138 °C, a temperature significantly higher than that of the material without biochar. However, going from 10 to 30 wt.% biochar did not affect the thermoforming temperature.

2.3 Mechanical property characterization

Tensile testing of the blend was carried out using an Instron Universal Testing Machine model 5567 at a crosshead speed of 12.5 mm/min. At least five specimens of each sample were tested according to standard ASTM D638. Samples were conditioned at room temperature for at least 24 hours prior to mechanical testing.

2.4 Soil burial test/ Aerobic degradation

Cellulose, PCL60/Starch40 and PCL40/Starch60 samples were cut into 2.54 cm square pieces to obtain a uniform sample size for degradation. 18 samples of each specimen were prepared and weighed to record their initial weight. The samples were buried in the soil at a depth of about 2.5 cm. The test was carried out at room temperature. Water was sprinkled on the soil surface every three days to ensure that the soil remained humid. The samples were measured for the weight loss every 7 days from the day they were initially buried. 3 samples of each specimen were measured by washing them gently with distilled water and drying the samples at 60°C in a vacuum oven, until a constant weight was obtained. Weight loss percentage was calculated based on Equation 1,

$$\text{Weight loss (\%)} = \frac{w_i - w_d}{w_i} \times 100 \quad (1)$$

where w_d is the dry weight of the film after being washed with distilled water and w_i is the initial dry weight of the specimen [10].

3. Results

Table 1 shows the processing conditions for the three stages of sample preparation: mixing, compression molding and thermoforming. As the starch content in the blend increases, the equilibrium torque increases. This indicates that the viscosity of the blend increases due to increase in the starch content. A higher torque requirement for blending with higher starch content also indicates that a higher pressure is required for the conversion process. This can be evidenced in the increase in pressure requirement for the compression molding stage, accompanied with an increase in temperature. Similarly, increase in the starch content increased the forming temperature in the thermoformer (see **Table 1**).

Thermoformed blisters were successfully manufactured with starch contents up to 60 wt.%. Above 60 wt.% starch the material was unsuitable for thermoforming due to decreased pliability and the blend being too fragile (see **Figure 1**).

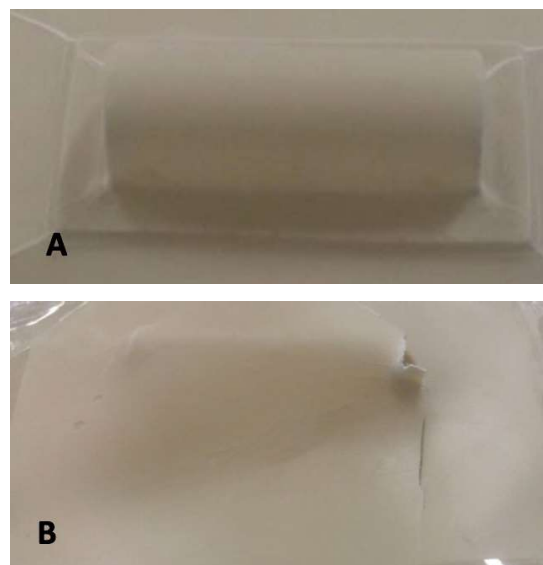


Figure 1. Thermoformed samples containing 60 wt.% starch (A) and 70 wt.% starch (B)

Figure 2 shows the effect of PCL:starch proportions on the mechanical properties. Pure PCL has the highest average tensile strength at 55 MPa. The plot displays a U-shape where the strength decreases and then increases at higher starch concentrations (i.e., 70 wt.%). This behavior could indicate an incompatibility of the PCL and starch since the strength of some blends is lower than that of pure PCL and sample with 70 wt.% starch [11]. Similarly, PCL has the highest percentage of elongation at break, which was expected due to its rubbery nature [12]. As the starch content increases, the elongation decreases. Increasing the starch content from 60 to 70 wt.% causes a sharp drop in the elongation from 740% to 26%.

The modulus of elasticity is highest at 70 wt.% starch. The stiffness drops significantly from 70 to 60 wt.% starch. Further decrease in the amount of starch showed a nearly linear increase in modulus of elasticity from 60 to 40 wt.% from 43 to 224 MPa, just above the modulus of elasticity of neat PCL (156 MPa).

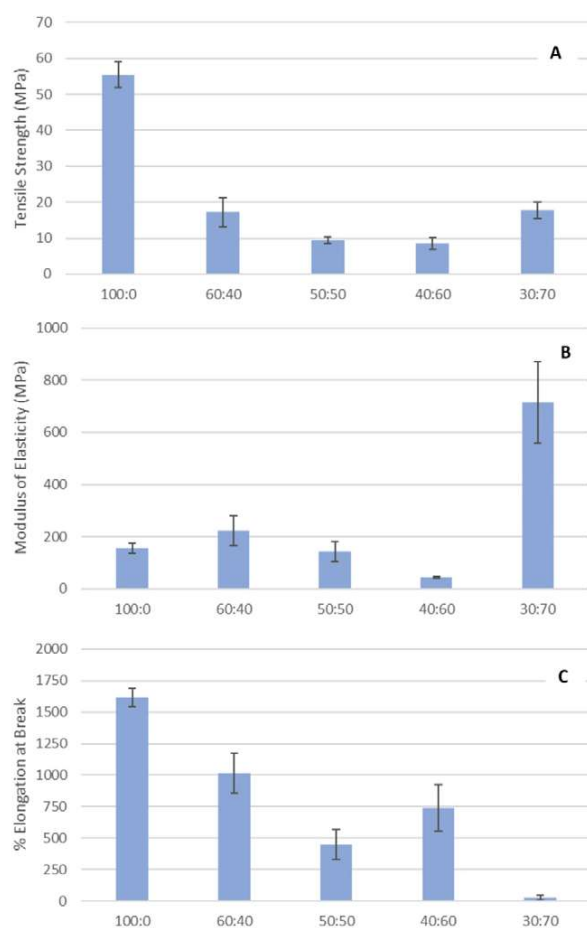


Figure 2. Effect of blend ratio of PCL:Starch on (A) tensile strength, (B) modulus of elasticity and (C) percentage of elongation at break

All the mechanical properties drastically changed going from 60 to 70 wt.% starch, suggesting a major change in the structure of the blend where PCL is not the majority component and the properties of starch dictate the properties of the blend. This lack of elongation and high stiffness supports the inability to thermoform the 70 wt.% starch blend.

Figure 3 shows the effect of adding biochar to the TPS containing 50:50 PCL:starch. Adding biochar increased the modulus of elasticity and slightly reduced the tensile strength. Similar results have been observed when reinforcing bioplastics with natural fibers [13]. Varying the biochar content from 10 to 30 wt.% did not have a significant effect on the tensile stress and modulus of elasticity of the material (Figures 3A and B). Conversely, the elongation at break was drastically reduced with the inclusion of biochar. Increasing the amount of biochar from 10 to 30 wt.% further reduced the elongation at break making the composites significantly more brittle.

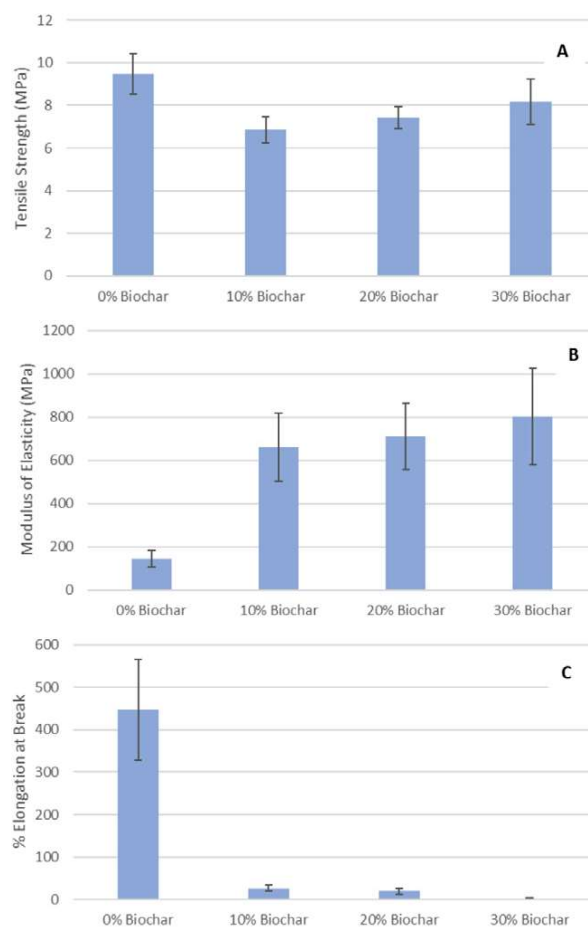


Figure 3. Effect of biochar content in 50:50 PCL:starch blend on (A) tensile strength, (B) modulus of elasticity and (C) percentage of elongation at break

To demonstrate the thermoforming ability of the composite with biochar, a male mold of a coffee lid was manufactured to demonstrate a potential application for this biodegradable composite material. All the composites with biochar allowed the sheet to be thermoformed into coffee lids with loadings up to 30 wt.%. Figure 4 shows a coffee lid containing 10 wt.% biochar. Increasing the biochar load did not affect the thermoforming ability, however the surface was rougher with less resolution of the details of the mold. The results demonstrate the potential to use biochar as a filler material in thermoform containers and packaging. Additionally, this is an example of a product for the coffee shops made from their own waste (i.e., spent coffee grounds). Biochar thus may offer an op-

portunity for a close-loop economy while displacing plastic or creating fully biodegradable solutions.



Figure 4. Thermoformed coffee lid made with 10 wt.% biochar from spent coffee grounds

Ongoing research is looking at structure-property relationships to better understand the changes observed here. Additionally, the rheology of the material should be further studied to expand the findings of this research to other conversion processes such as injection molding and blown film extrusion.

Finally, Figure 5 shows the biodegradation of two samples containing 40 and 60 wt.% starch. Higher starch content resulted in a higher level of degradation. These results agree with previous studies [2]. Preliminary experiments suggest that the addition of biochar enhances the biodegradation, but further experimentation is ongoing.

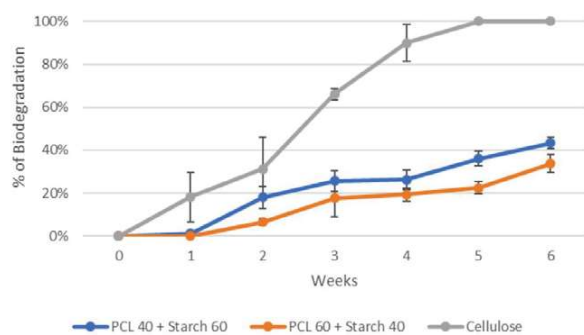


Figure 5. Cumulative biodegradation of selected samples and a positive (cellulose) control

4. Conclusion

This study demonstrates the thermoforming of fully biodegradable thermoplastic starch without the use of water or glycerol but instead a rubbery biopolymer (i.e., PCL). The ratio of PCL and starch affected the processing conditions as well as the mechanical properties. Thermoformed blisters were successfully made with starch contents from 30 to 60 wt.%. Increasing the starch content beyond that point drastically changed the properties and rendered the material unsuited for thermoforming. Biochar composites were made using the 50:50 PCL:starch material. Prototype thermoformed coffee lids were made with contents up to 30 wt.% biochar. Manufacturing of composites using biochar demonstrates

the possibility to manufacture fully biodegradable items and the valorization of a byproduct from the pyrolysis of organic waste, thus promoting a circular economy model for future sustainable packaging products.

5 References

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