SYNTHESIS OF A BIODERIVED BIOPLASTICIZER FOR BIOPOLYMERS

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OVERVIEW

ABSTRACT

Novel plasticizers from sustainable resources provide an opportunity to meet market needs for materials with increased biobased and biodegradability content, while mitigating environmental and human health concerns. This study involved the synthesis of a bioplasticizer and melt viscosity enhancer that enabled biopolymers to be functional in standard processes such as injection molding and film extrusion. Its influence as a plasticizer on the thermal and mechanical properties of polylactic acid (PLA) was investigated. The results were compared with properties of PLA blends containing commercially available plasticizers. It was found that the bioplasticizer promoted toughness and flexibility without sacrificing modulus while minimizing glass transition temperature reduction. The bioplasticizer also enabled high concentrations of inorganic fillers to be compounded into PLA, which resulted in the production of a composite "book cover".

OBJECTIVE

To develop a compatible biodegradable plasticizer for biopolymers made from renewable resources.

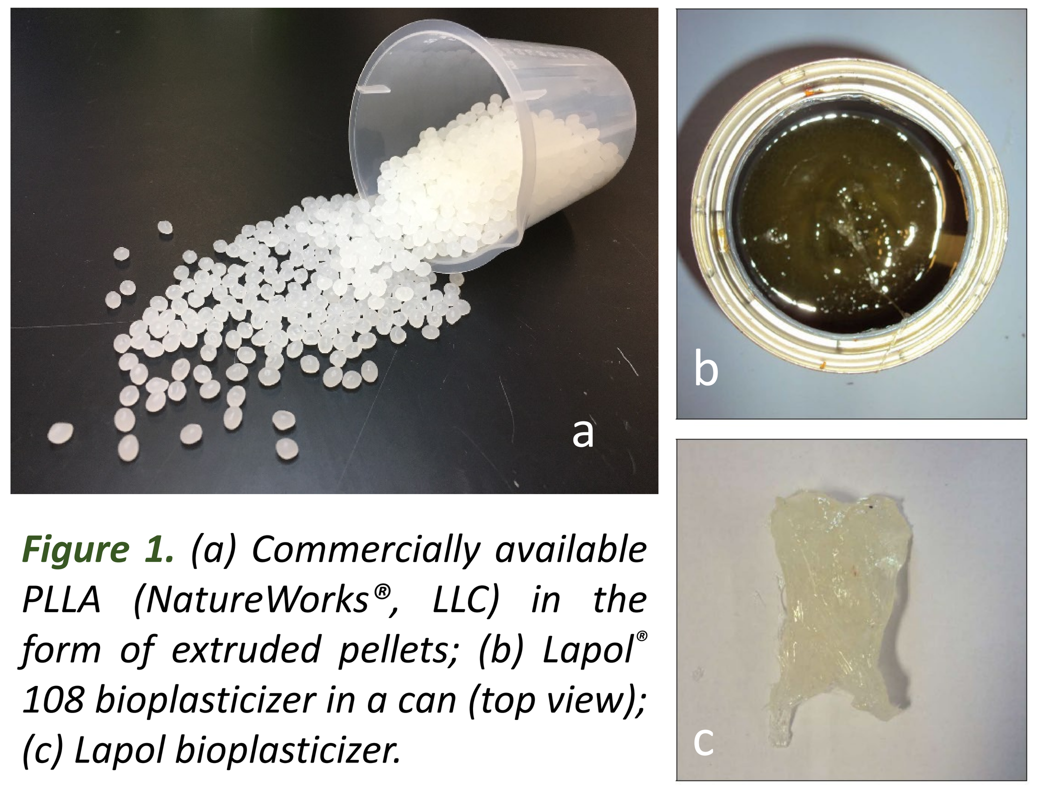


Figure 1. (a) Commercially available PLLA (NatureWorks®, LLC) in the form of extruded pellets; (b) Lapol® 108 bioplasticizer in a can (top view); (c) Lapol bioplasticizer.

RESEARCH PLAN

1. Synthesis and characterization of bioplasticizer.
2. Compounding commercial PLA with bioplasticizer and testing composite mechanical properties.
3. Incorporation of bioplasticizer into industrial applications.

EXPERIMENTAL

SYNTHESIS OF MULTIBRANCHED BIOPLASTICIZER

A multibranched bioplasticizer was synthesized via a one-pot two-step synthesis, as outlined in Figure 2 (see below).

STEP 1

Glycerin, di(ethylene glycol), & maleic anhydride were charged into a four-neck 5 L reaction vessel equipped with an overhead stirrer, a condenser and collection flask, and a nitrogen purge. The reaction was slowly heated to under a nitrogen blanket. After the maleic anhydride briquettes melted and dissolved in glycerine and di(ethylene glycol) solution, stannous octoate was added. The reaction was heated to 150 °C and left to react until the acid number dropped to a range between 80 and 90.

STEP 2

Then, an 88% L-lactic acid solution was then added to the reaction vessel. The reaction was allowed to continue at 150 °C until the acid number decreased again to the range between 70 and 80. The reaction temperature was increase to 200 °C and maintained at that temperature until the acid number dropped further to about 20 to 40 and a viscosity measurement of 250 Poise (at 50 rpm and 100 °C, Spindle 6 Brookfield viscometer) was obtained. The product was then poured out and analyzed.

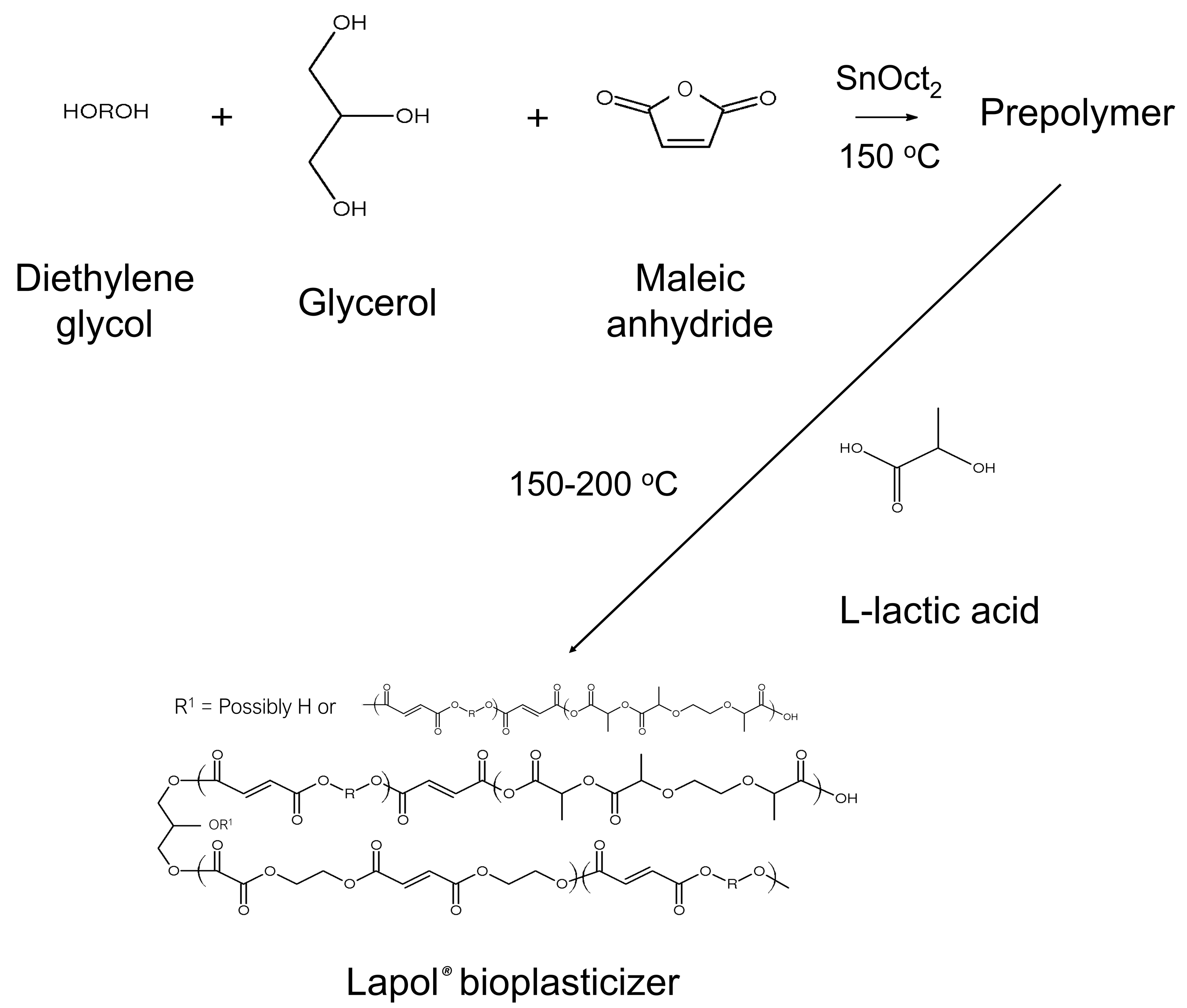


Figure 2. Synthetic scheme for the production of the Lapol® bioplasticizer.

Table 1. Characteristics of Lapol® bioplasticizer.

CHARACTERISTICS	LAPOL® BIOPLASTICIZER
Lactyl units (wt. %)	40-50
Acid number	20-40
Viscosity (Poise, @ 100 °C, 50 rpm)	255
M_w (Daltons)	50k-90k
Polydispersity	4-5
Total solids (%)	99.7
Moisture content (%)	0.3

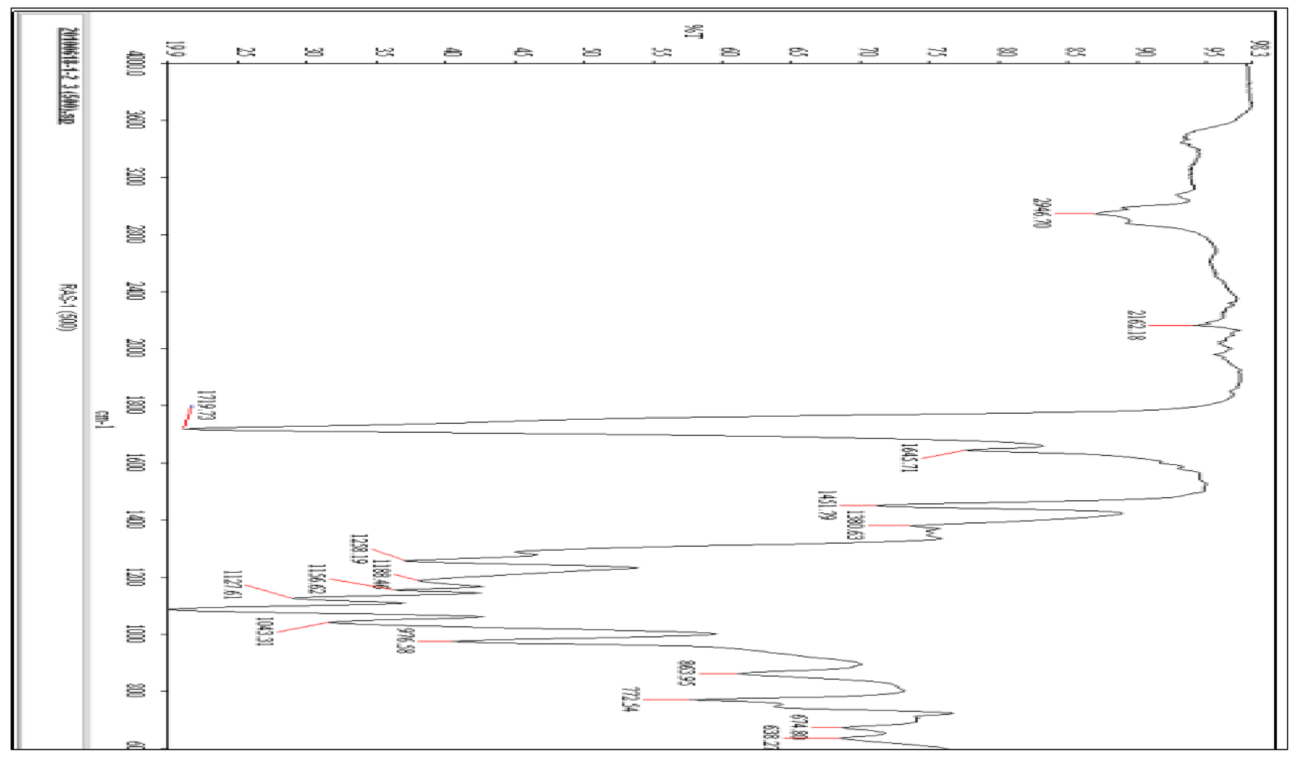


Figure 3. AT-IR spectrum of Lapol® bioplasticizer.

BIODEGRADABILITY

AEROBIC COMPOSTING CONDITION

Lapol® 108 bioplasticizer resin was tested on biodegradability under dry, aerobic conditions in a controlled composting test for 45 days according to ISO 14855. From the results (Figure 4), it was be concluded that the resin fulfilled the requirements of ASTM D6400 and EN 13432 standards within a period of 45 days and can be called biodegradable under controlled composting conditions.

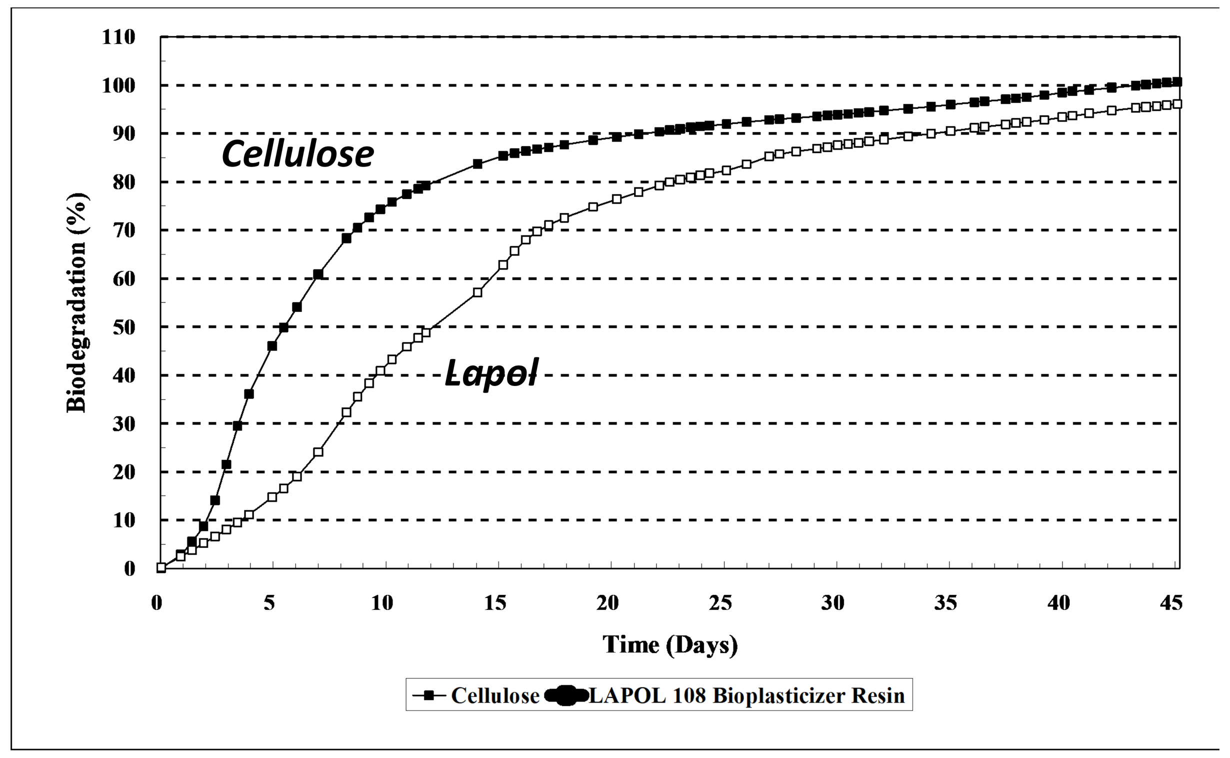


Figure 4. Evolution of the biodegradation % of the cellulose reference and Lapol® bioplasticizer.

COMPOSITE FORMATION

Lapol bioplasticizer was melt blended with commercial PLA. For comparison, Ecoflex®(petroleum-based plasticizer from BASF) was also prepared. Blends were molded into tensile bars, which were tested according to ASTM D638.

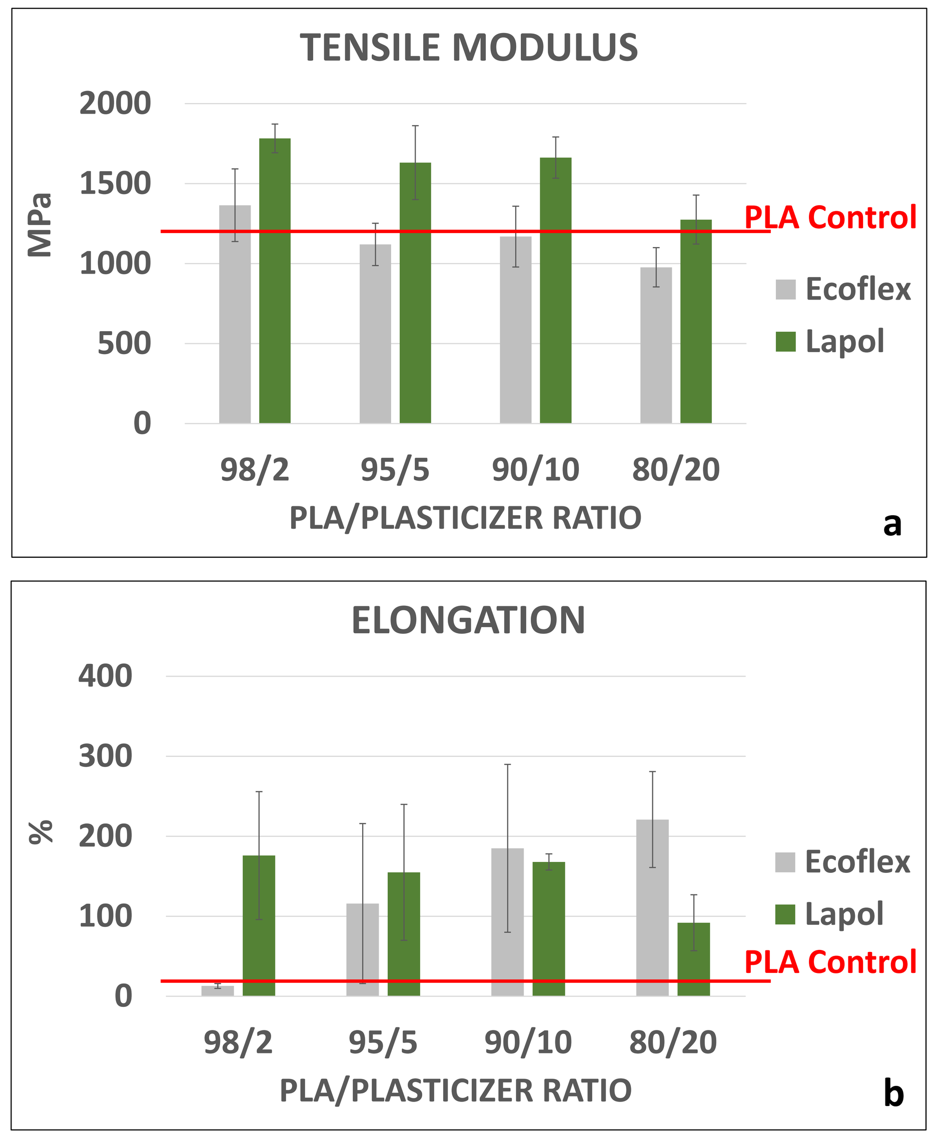


Figure 5. Tensile properties of Ecoflex® & Lapol® composites and PLA control (red line): tensile modulus (a) and elongation (b).

REFERENCES & ACKNOWLEDGEMENTS

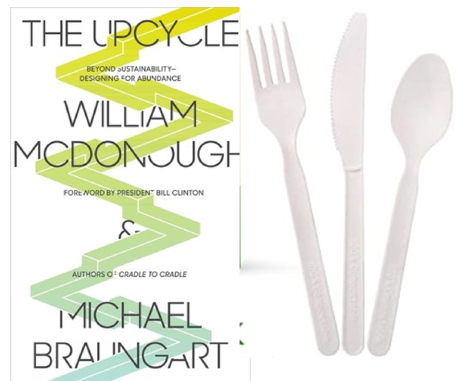
The authors would like to thank Randy Smith from Lapol, LLC for his support of this project.

U.S. Patent 9139689.

CONCLUSION

- Lapol® bioplasticizer combines lactic acid and low Tg polyester to create a PLA miscible internal plasticizer
- Low doses of Lapol® bioplasticizer improves flexibility of PLA with limited effects on its modulus.
- 90% degradation in 20 days.
- Commercial products were produced using Lapol® bioplasticizer including a book cover, cutlery, and food packaging.

INDUSTRIAL APPLICATION



Lapol® bioplasticizer has been incorporated into a number of commercial products such as cutlery and food packaging, most notably as part of a formulation for a book cover (image on the left).

USDA

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Enabling Bioplastics