

Polymer and Colloid Highlights

Division of Polymers, Colloids and Interfaces

A Division of the Swiss Chemical Society

From Non-edible Biomass to Performance Thermo-plastics with Sustainable End-of-life

Lorenz P. Manker and Jeremy S. Luterbacher*

*Correspondence: Prof. J. S. Luterbacher

E-mail: jeremy.luterbacher@epfl.ch

Laboratory of Sustainable and Catalytic Processing (LPDC), Institute of Chemical Sciences and Engineering (ISIC), School of Basic Sciences (SB), EPFL, Lausanne.

Keywords: Bioplastic · Chemical Recycling · Degradable · Lignocellulose · Sustainable

In order for renewable and sustainable plastics to comprise more than the current ~1% of the global plastics market, they need to either be produced at very low cost (competitive with fossil-based materials), or they need to be performance-advantaged^[1] to make the extra cost worthwhile. Currently, the majority of bioplastics are produced from purified sugars derived from edible starches, which are relatively expensive feedstocks for production of high-volume, commodity plastics. Lignocellulosic biomass on the other hand is a far cheaper, more abundant, and sustainable feedstock but comes at the large tradeoff of increased process complexity due to its heterogeneous and recalcitrant nature. Therefore, lignocellulosic plastics can likely only be realized if we can design strategic (bio) chemical processes to handle this complexity and convert solid, non-edible biomass into plastic precursors with high yield and efficiency at scale. Implementation would be further eased if the resulting materials are performance plastics.

In our recent work,^[2] we developed a rigid, tricyclic diester directly from the hemicellulosic fraction of non-edible biomass in high yield, while also valorizing the remaining fractions of the biomass (the cellulose and lignin) (Fig. 1). We were able to incorporate ~25 % of the mass of raw corn cobs into this diester precursor. This was enabled by strategic trapping of the cyclic sugar structure of xylose within the plastic precursor, which led to its remarkably simple production from biomass with high atomic efficiency (97%). By techno-economic analysis, we projected the cost of the monomer to be cheaper than polymerization grade lactic acid and almost cost-competitive with purified terephthalic acid, even when produced from purified xylose. Production of the diester from lignocellulose would likely further reduce selling price, but selling prices have not yet been estimated. Notably, the resulting diester has a fused, tricyclic, asymmetric, non-planar, and highly-polar structure that leads to attractive material properties.

When polymerized with 1,4-butanediol, 1,5-pentanediol, and 1,6-hexanediol by melt condensation, high-molecular weight ($M_n = 30\text{--}45$ kDa) amorphous polyesters with good dispersities (2.0–2.5) were achieved. The resulting materials demonstrated high glass transitions (72–100 °C), tough mechanical properties (ultimate tensile strengths of 63–77 MPa, tensile moduli of 2000–2,500 MPa and elongations at break of 50–80%), good gas barriers (oxygen transmission rates (100 μm)

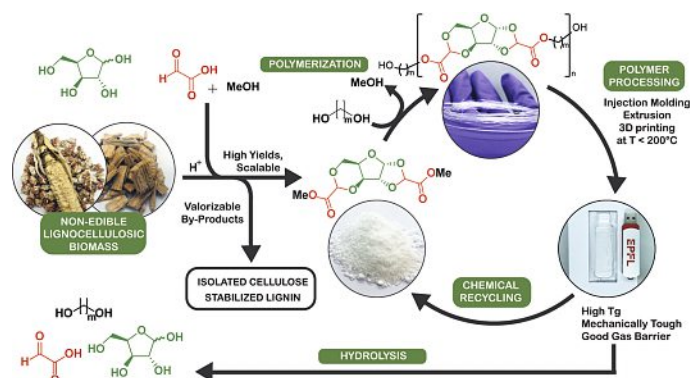


Fig. 1. Overall life-cycle of PAX polyesters. This figure was reproduced from the original publication in *Nature Chemistry*.^[2]

of 11–24 $\text{cc m}^{-2} \text{day}^{-1} \text{bar}^{-1}$ and water vapour transmission rates (100 μm) of 25–36 $\text{g m}^{-2} \text{day}^{-1}$) and were processable by twin-screw extrusion, injection-moulding, thermoforming and 3D printing at temperatures between 160–200 °C.

Notably, these materials were highly susceptible to ester hydrolysis. This enabled high-yield chemical recycling from mixed-plastic waste streams by methanolysis with very mild reaction conditions (64 °C, 1 atm, 25 mM H_2SO_4). Their structure also enabled the degradation of these plastics (0.5 mm thick films) in room-temperature water in relatively short time-frames (on the order of ~6 months to years). The thermomechanical properties of these films remained intact for at least 80 days before they began to solubilize. This hydrolysis rate could be tuned by varying the stereochemistry of the diester monomer, by varying the diol comonomer used, and potentially by additive engineering.^[3]

Here we have found a material that combines both performance properties and a (tunable) degradable nature and that can be produced at low projected costs from highly abundant, non-edible biomass with highly valorizable co-products. The main drawback is that the production relies on an external reagent, glyoxylic acid, that is currently produced from fossil-fuels. However, its production from CO_2 is already being demonstrated at pilot scale.^[4] If this green reagent can be produced cheaply, this material could be entirely produced from non-edible biomass and carbon dioxide, with potential routes for a sustainable end-of-life by chemical recycling or hydrolysis.

Received: August 24, 2022

- [1] R. M. Cywar, N. A. Rorrer, C. B. Hoyt, G. T. Beckham, E. Y.-X. Chen, *Nat. Rev. Mater.* **2022**, *7*, 83, <https://doi.org/10.1038/s41578-021-00363-3>
- [2] P. Manker, G. R. Dick, A. Demongeot, M. A. Hedou, C. Rayroud, T. Rambert, M. J. Jones, I. Sulaeva, M. Vieli, Y. Leterrier, A. Potthast, F. Maréchal, V. Michaud, H.-A. Klok, J. S. Luterbacher, *Nat. Chem.* **2022**, *14*, 979, <https://doi.org/10.1038/s41578-022-00974-5>.
- [3] P. Stloukal, G. Jandikova, M. Koutny, V. Sedlařík, *Polym. Test.* **2016**, *54*, 19, <https://doi.org/10.1016/j.polymertesting.2016.06.007>
- [4] E. Schuler, M. Demetriou, N. R. Shiju, G.-J. M. Gruter, *ChemSusChem* **2021**, *14*, 3636, <https://doi.org/10.1002/cssc.202101272>

If you are interested in submitting a new highlight, please contact:

Prof. Dr. Christoph Weder, Adolphe Merkle Institute, University of Fribourg

E-mail: christoph.weder@unifr.ch, Tel.: +41 26 300 94 65