

Fully Recyclable Bio-Based Thermoplastic Materials from Liquefied Wood

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A novel, low-cost, and fully recyclable thermoplastic material is produced from liquefied lignocellulosic biomass and natural fibers. The matrix, which is the heavy fraction of the liquefaction product, is characterized in terms of molecular weight distribution, density, viscosity, softening point and tensile strength. It is possible to increase the mechanical strength of the matrix by a factor of up to 100 by reinforcing it with flax fibers. Specifically, the tensile strength increased from 0.4 MPa for the non-reinforced matrix, to 55 MPa for the matrix/flax composite with a fiber content of 20 wt%. These values are comparable to conventional thermoplastics, such as poly(methyl methacrylate), polyvinyl chloride, or polystyrene.

Transforming today's petrochemical industry into a sustainable and circular industry will require intensive recycling of waste plastic and a switch to renewable carbon and energy sources. Biomass is the most promising option for renewable carbon feedstock,^[1-3] as it has already captured CO₂ and accomplished a large part of the reduction duty towards today's polymers.^[4,5]

Lignocellulose is a very promising feedstock as it is widely available, can be grown in a sustainable manner, and is cheap.^[3,5-8] However, the lignocellulose structure is rather complex (composed of various carbohydrate and lignin polymers), and significantly resistant to enzymatic and chemical degradation,^[2,8,9] which complicates further processing. Therefore, bio-based plastics are typically produced through a complex and expensive manufacturing chain that comprises the following steps:^[3,4,10-13] 1) Biomass fractionation to extract the sugars; 2) complex chemical and/or biotechnological conversion steps to convert them into valuable intermediates; 3) expensive recovery and purification steps to bring the intermediates to specification; 4) a polymerization step to produce the desired polymer. These production processes lead to expensive materi-

als that require high-performance applications to justify the considerable production cost. Consequently, research is still needed for converting lignocellulosic biomass into added-value chemicals with high yields and low cost.^[10]

Herein, we propose an alternative and low-cost approach to a lignocellulosic thermoplastic, namely a single-step conversion of lignocellulose to a solid thermoplastic followed by reinforcement with cellulosic fibers to produce a low-cost thermoplastic composite. The thermoplastic matrix consists of the high molecular weight fraction of a liquefaction bio-oil that solidifies upon cooling to room temperature. Bio-oil can be produced by either pyrolysis or liquefaction.^[3,14-17] However, liquefaction is preferred here because of the higher liquid yield ($\approx 90\%$), the lower oxygen content, and the higher homogeneity of the bio-oil.^[17-20] The material obtained after liquefaction and subsequent distillation was characterized in terms of physicochemical and mechanical properties and then reinforced with natural fibers. In contrast to conventional composites, this biocomposite can be fully recycled by liquefying the spent material, matrix, and fibers, back into bio-oil.^[21]

First, liquefaction of pinewood was performed in six consecutive refill runs using guaiacol as starting solvent (as described in the Supporting Information and reported elsewhere^[19]). This approach led to an increase in the molecular weight of the bio-oil from $M_w \approx 2000$ to $M_w \approx 8000$ Da with a polydispersity index reaching 2.7 (Table 1). A wide distribution of the molecular weight was observed for all samples (see the Supporting Information; Figure S1).

Atmospheric and vacuum distillation of the final bio-oil delivered a thermoplastic matrix with an overall yield of 60 wt% (mass of matrix over mass of lignocellulosic feed). The solvent content decreased from 30 wt% prior to distillation to 0.8 wt% after distillation. The final matrix had a M_w of around 6000 Da and a density of 1.43 g cm^{-3} (± 0.06). Compared to convention-

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Table 1. Average molecular weight and polydispersity index (PDI) of the bio-oil (after each liquefaction run) and the matrix (after solvent distillation). The solvent fraction is not considered for the calculations.

Sample	M_n	M_w	PDI
Oil_Run 1	962	1923	2.00
Oil_Run 2	1227	2539	2.07
Oil_Run 3	1332	2841	2.13
Oil_Run 4	1570	3565	2.27
Oil_Run 5	2188	5541	2.53
Oil_Run 6	2870	7797	2.72
Matrix	2467	5840	2.37

al thermoplastics, the matrix has a low M_w and high density (Figure 1). However, these properties fall in the same range as the lignin used for the Arboform composite ($\approx 1.3 \text{ g cm}^{-3}$), produced by Tecnar GmbH.^[22,23] The matrix has an elemental composition of 76.3% C, 5.7% H, 0.1% N, and 17.9% O (by difference). Based on previous analyses, the matrix is expected to consist mainly of aromatic/phenolic component groups.^[20] The matrix has hydrophobic character, confirmed by the contact angle of a drop of water on its surface (Figure S3).

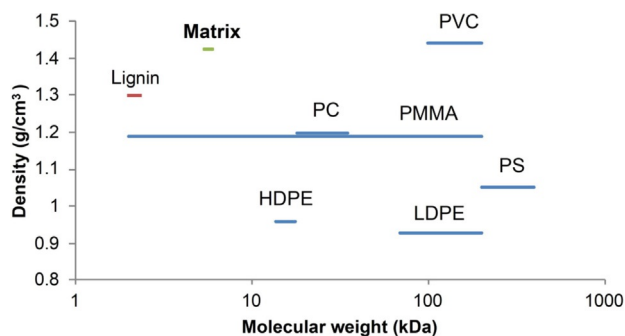


Figure 1. Density and molecular weight (M_w) of vacuum residue compared with lignin and conventional thermoplastics.^[24–32] PVC: polyvinyl chloride; PC: polycarbonate; PMMA: poly(methyl methacrylate); PS: polystyrene; HDPE: high-density polyethylene; LDPE: low-density polyethylene.

Differential scanning calorimetry of the thermoplastic matrix showed one endothermic peak at 60–65 °C, which corresponds to the glass transition temperature, but no clear peak that would indicate the melting temperature (Figure S4), suggesting that the matrix is an amorphous polymer. A softening point at a temperature of around 130 °C was determined by visual inspection of the grains that were spread in the cup after heating to various end temperatures. This is comparable to other conventional thermoplastics, in which T_m values range from 105 °C [poly(methyl methacrylate)] to 265 °C (polycarbonate).^[23–25] Moreover, Arboform also has a melting temperature within that range ($T_m = 150$ °C). Rheology measurements (Figure S5) show a matrix viscosity that varied between 30 000 Pas at 120 °C to below 100 Pas above 160 °C. This is a very low viscosity, since the melting viscosity of polymers is usually between 100 and 10 000 Pas, depending on the molecular weight of the material.^[33]

Dog-bone samples prepared by compression molding at 170 °C broke at low tensile force and displayed little to no plastic deformation during the tensile tests (Figure S6). The tensile strength of the matrix material was ≈ 0.4 MPa, which is very low in comparison with 10–100 MPa measured for conventional thermoplastics.^[24]

In an attempt to improve the tensile strength of the material, we prepared new dog-bone samples that were reinforced with 3, 8.5, and 20 wt% of infinite flax fibers and were pressed at temperatures between 150 and 240 °C (see Table S1 for detailed process conditions). The variation in compression temperature aimed at exploring the importance of viscosity and eventual fiber degradation on the fiber–matrix dispersion and

adhesion. Interestingly, fibers deposited on the cold matrix sank into the matrix upon heating (Figure 2a,b), whereas they did not sink into water, which is a liquid with lower density and viscosity than the melted matrix (Figure 2c,d). Accordingly, the fibers are not sinking by gravity but are pulled into the melted (hydrophobic) matrix by chemical affinity.

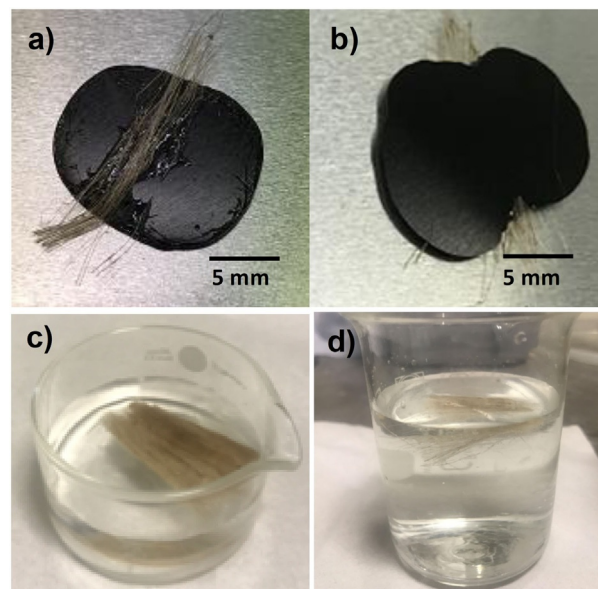


Figure 2. a, b) Matrix/fiber addition after 30 min in the oven at 180 °C. c, d) Flax fibers floating in water.

Reinforcement with flax fibers increased the tensile strength 100-fold, with values reaching 55 MPa with 20 wt % fiber loading (Figure 3). The corresponding strain–stress curves are shown Figure S7. We may speculate on the possibility to reach strengths of around 100 MPa for fiber loadings of approximately 40 wt%, as applied for Arboform, a fiber-reinforced lignin composite.^[23] Such high loadings require a different procedure to prepare the fiber–matrix composite and are subject of

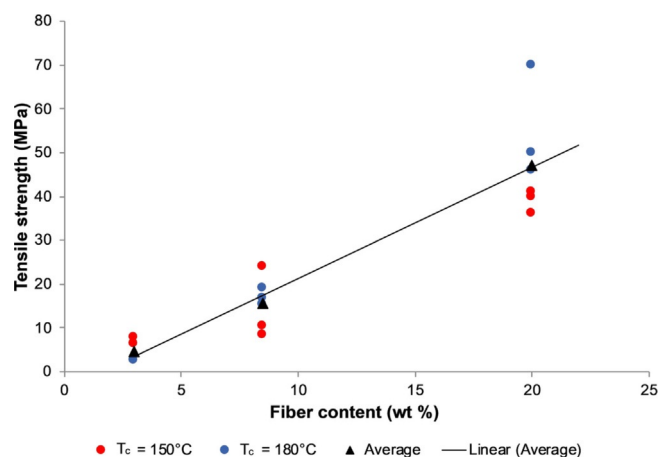


Figure 3. Effect of fiber content on the tensile strength of the composites. Experiments were run in triplicate at two temperatures and the resulting average is given.

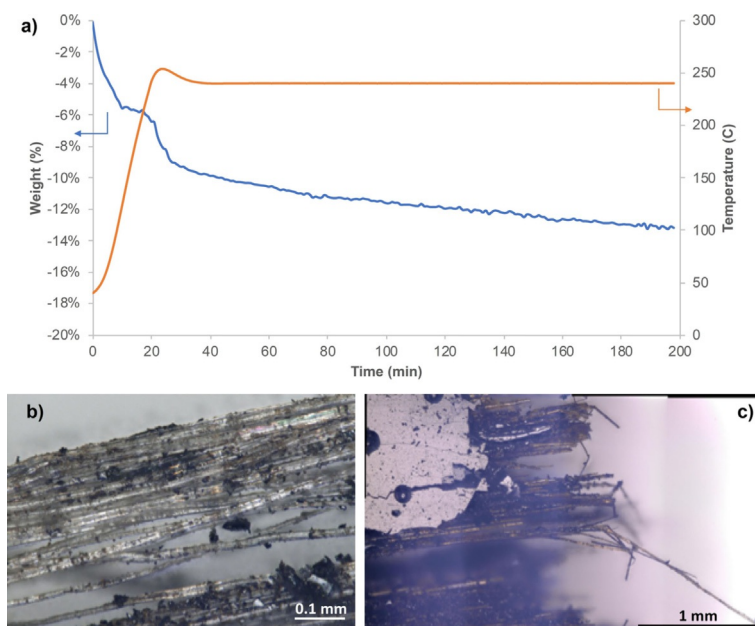


Figure 4. a) Thermogravimetric analysis of the fibers in nitrogen (heating rate $10^{\circ}\text{Cmin}^{-1}$ up to 240°C , and kept at that temperature for 3 h. The TGA was run for 3 h to mimic the slow cooling of the samples in the press. b, c) Microscopy images of the fibers in the composites produced at 180°C (b) and 220°C (c).

present research. Figure 3 also shows a significant spread in mechanical strength data, mostly at higher fiber contents. This spread may be due to the heterogeneity of the fiber distribution that has likely resulted from the manual distribution of layers of fibers and matrix in the mold (Figures S8 and S9).

These results also reveal no significant effect of the compression temperature on the material strength for 150 and 180°C . However, higher compression temperatures (220 and 240°C) led to a loss of tensile strength ($<7\text{ MPa}$), probably owing to the degradation of the flax fibers, as confirmed by thermogravimetric analysis (TGA) of the fibers performed in nitrogen (Figure 4a) and their color change observed by microscopy (Figure 4b,c). The conditions of the TGA (see caption of Figure 4a) were chosen to mimic the heating/cooling time in the press and revealed 6–7% weight loss at $>200^{\circ}\text{C}$, which can be assigned to fiber degradation. The weight loss below 100°C is most likely due to water evaporation. A single attempt to blend the matrix with 10 wt% of short bagasse fibers also improved the material strength by a factor of 5 to 2.3 MPa. Although weaker, short fiber composites would offer the advantage of being fully moldable. More research would be needed to explore this alternative.

In order to test our hypothesis on the recyclability of the fiber-reinforced material, we performed a new liquefaction experiment by using the 20% flax fiber composite as feedstock and guaiacol as solvent. The operating conditions were similar to the previous liquefaction experiments (see the Supporting Information). A new oil was obtained out of this feedstock, with a similar molecular weight (MW) distribution to the previous liquefaction runs (see recycling experiment, Figure S1), confirming the validity of the recyclability concept.

Furthermore, different types of biomass were subjected to liquefaction to test their suitability for this overall process. The

oils produced from eucalyptus, beech, bagasse, hemp, and oak bark had similar MW distributions to that produced from pine (Figure S2), making them in principle also appropriate for the process. Further investigation may be required to analyze potential differences in the mechanical properties of their respective matrices.

The woody biocomposites discussed herein offer several attractive features in terms of sustainability. Firstly, they are based on lignocellulose, which can potentially be produced with a minimum environmental footprint.^[8] For example, this is the case when the lignocellulose is produced as a residue of agriculture or forestry, produced on degraded land and/or with marginal input from fertilizers, pesticides, and irrigation water. Beyond being bio-based, these composites are fully recyclable; a feature that is unusual for composites that need proper separation of fibers and matrix prior to being recycled.^[34] Indeed, the spent wood composites can be recycled to a liquefaction plant that will melt the matrix and liquefy the fibers into more matrix (Figure 5). The recycled matrix can then be blended with fresh fibers to produce new composite. It should be noted that liquefaction even allows removal of eventual solid contaminants such as stones, screws, and nails, by simply filtering the liquefaction oil prior to recovering the solvent and precipitating the tarry material.

Finally, the woody biocomposites have the potential to be truly low-cost materials. They are based on cheap lignocellulosic biomass that is generally valued at $\$50\text{--}100\text{ t}^{-1}$. The process also has a reasonably high mass efficiency. We demonstrated here a carbon yield of approximately 40 wt% and are confident to be able to increase this quite significantly through process fine-tuning. The process uses no catalyst and no chemicals. The liquefaction solvent consists of the light fraction of the bio-oil that is recycled to the liquefaction reactor after frac-

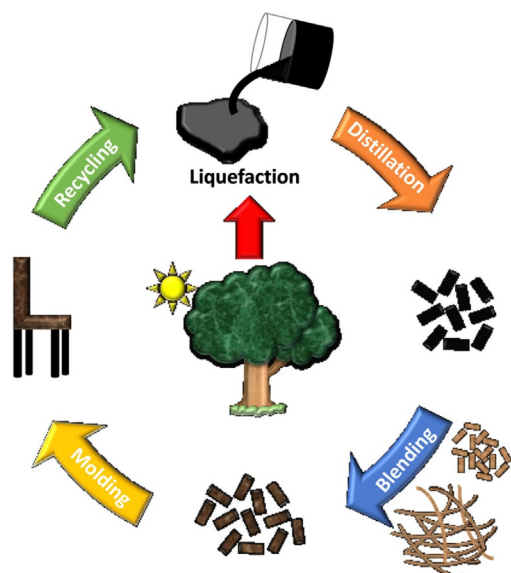


Figure 5. Proposed scheme for the fully recyclable woody material production and processing.

tionation.^[35] Fractionation can be either by vacuum distillation, as applied here, or liquid/liquid (L/L) extraction as proposed elsewhere.^[35,36] Finally, the liquefaction process is very simple and would therefore require modest investment. Preliminary economic analysis estimated a CapEx intensity of about \$500 per annual ton and overall production cost of the full liquid product of about \$380 t⁻¹ at 800 kt a⁻¹ biomass intake.^[35] Since the investment cost has a modest contribution to the overall cost, downscaling the process to 80 kt a⁻¹ would result in an only modest increase in overall production cost, possibly to \$450–500 t⁻¹.

In summary, woody composites made from liquefaction residue and infinite flax fibers show a tensile strength that can be tuned between that of polyolefins (at low fiber content) and that of polystyrene or PVC (at high fiber content; Figure 6). Beyond being bio-based, these materials are fully recyclable and cheap to make. These promising results set the basis for future studies on novel bio-based materials.

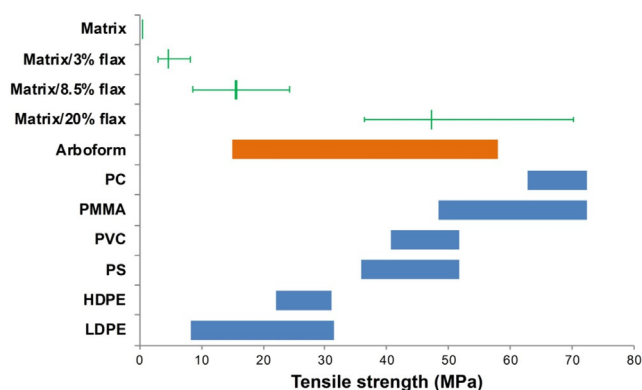


Figure 6. Comparison of the flax fibers/bio-based matrix with conventional thermoplastics and Arboform.

Experimental Section

The woody matrix was produced by liquefaction of pine (6 × 0.3 kg) in guaiacol (2.2 kg) as starting solvent and model component for recycled light bio-oil.^[35] Consecutive refills of wood were applied to build up the concentration of the bio-oil in the solvent.^[19] The matrix was then isolated by vacuum distillation of the solvent.^[36] The amount of matrix recovered after distillation corresponds to a yield of 43 wt% (based on wood intake). However, the amount of heavy product that was removed between each sample is estimated to amount to 17 wt% of the wood intake, which brings the overall yield to 60 wt%.

Composites were produced by depositing a layer of ground woody matrix in a dog-bone mold, manually depositing the flax fibers along the whole length of the mold, depositing a second layer of ground matrix and flax fibers and a last layer of matrix (Figure S9). The composite test pieces were then produced in a table press at different compression temperatures. For the preparation of the composite material with short bagasse fibers, the fibers were blended with the woody matrix in a twin-screw mixer. Tensile tests and microscopy images were performed on the produced pieces. A more detailed description of the production and characterization of the matrix and the composites is provided in the Supporting Information.

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Conflict of interest

The authors declare no conflict of interest.

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- [1] A. Corma, S. Iborra, A. Velty, *Chem. Rev.* **2007**, *107*, 2411–2502.
- [2] C. H. Zhou, J. N. Beltramini, Y. X. Fan, G. Q. Lu, *Chem. Soc. Rev.* **2008**, *37*, 527–549.
- [3] J. Lange, S. G. Solutions, *Biofuels Bioprod. Biorefin.* **2007**, *1*, 39–48.
- [4] A. J. Ragauskas, C. K. Williams, B. H. Davison, G. Britovsek, J. Cairney, C. A. Eckert, W. J. Frederick, J. P. Hallett, D. J. Leak, C. L. Liotta, J. R. Mielenz, R. Murphy, R. Templer, T. Tschaplinski, *Science* **2006**, *311*, 484–489.
- [5] C. H. Zhou, X. Xia, C. X. Lin, D. S. Tong, J. Beltramini, *Chem. Soc. Rev.* **2011**, *40*, 5588–5617.
- [6] C. Somerville, H. Youngs, C. Taylor, S. C. Davis, S. P. Long, *Science* **2010**, *329*, 790–792.
- [7] E. Taarning, C. M. Osmundsen, X. Yang, B. Voss, S. I. Andersen, C. H. Christensen, *Energy Environ. Sci.* **2011**, *4*, 793–804.
- [8] J. P. Lange, I. Lewandowski, P. M. Ayoub in *Sustainable Development in the Process Industries: Cases and Impact* (Eds.: J. Harmsen, J. B. Powell), Wiley, New York, **2010**, pp. 171–208.
- [9] A. Barakat, H. de Vries, X. Rouau, *Bioresour. Technol.* **2013**, *134*, 362–373.
- [10] D. M. Alonso, S. G. Wettstein, J. A. Dumesic, *Green Chem.* **2013**, *15*, 584–595.
- [11] F. H. Isikgor, C. R. Becer, *Polym. Chem.* **2015**, *6*, 4497–4559.
- [12] M. Stöcker, *Angew. Chem. Int. Ed.* **2008**, *47*, 9200–9211; *Angew. Chem.* **2008**, *120*, 9340–9351.
- [13] A. K. Mohanty, M. Misra, L. T. Drzal, *J. Polym. Environ.* **2002**, *10*, 19–26.
- [14] L. Zhang, C. C. Xu, P. Champagne, *Energy Convers. Manage.* **2010**, *51*, 969–982.
- [15] J. M. Bouvier, M. Gelus, S. Maugendre, *Appl. Energy* **1988**, *30*, 85–98.

- [16] E.-B. M. Hassan, N. Shukry, *Ind. Crops Prod.* **2008**, *27*, 33–38.
- [17] J. P. Lange, *ChemSusChem* **2018**, *11*, 997–1014.
- [18] S. Kumar, A. Segins, J. P. Lange, G. Van Rossum, S. R. A. Kersten, *ACS Sustainable Chem. Eng.* **2016**, *4*, 3087–3094.
- [19] G. Van Rossum, W. Zhao, M. C. Barnes, J. P. Lange, S. R. A. Kersten, *ChemSusChem* **2014**, *7*, 253–259.
- [20] M. C. Barnés, J. P. Lange, G. Van Rossum, S. R. A. Kersten, *J. Anal. Appl. Pyrolysis* **2015**, *113*, 444–453.
- [21] J.-P. Lange, *Thermoplastic Composite*, WO 2018/073132 A1, **2018**.
- [22] “TECNARO—The Biopolymer Company,” can be found under <http://tecnaro.de/en/home.html>, n.d.
- [23] H. Nagele, J. Pfitzer, L. Ziegler, E. R. Inone-Kauffmann, W. Eckl, N. Eisenreich in *Bio-Based Plastics: Materials and Applications* (Ed.: S. Kabasci), Wiley, Chichester, **2014**, pp. 89–115.
- [24] W. D. Callister, Jr., *Materials Science and Engineering: An Introduction*, Wiley, Chichester, **2000**.
- [25] C. D. Tran, J. Chen, J. K. Keum, A. K. Naskar, *Adv. Funct. Mater.* **2016**, *26*, 2677–2685.
- [26] I. Fischer, W. F. Schmitt, H.-C. Porth, M. W. Allsopp, G. Vianello, *Poly(Vinyl Chloride)*, in *Ullmann’s Encyclopedia of Industrial Chemistry*, Wiley, Hoboken **2014**.
- [27] G. Abts, T. Eckel, R. Wehrmann, *Polycarbonates*, in *Ullmann’s Encyclopedia of Industrial Chemistry*, Wiley, Chichester, **2014**.
- [28] D. J. Brunelle, *Polycarbonates*, in *Kirk–Othmer Encyclopedia of Chemical Technology*, Wiley, Hoboken, **2014**.
- [29] D. Jeremic, *Polyethylene*, in *Ullmann’s Encyclopedia of Industrial Chemistry*, Wiley, Hoboken, **2014**.
- [30] N. Maraschin, *Polyethylene, Low-density*, in *Kirk–Othmer Encyclopedia of Chemical Technology*, Wiley, Hoboken, **2005**.
- [31] R. V. Slone, *Methacrylic Ester Polymers*, in *Encyclopedia of Polymer Science and Technology*, Wiley, Hoboken, **2002**.
- [32] M. Chanda, S. K. Roy, *Industrial Polymers, Specialty Polymers, and Their Applications*, CRC Press, Boca Raton, **2008**.
- [33] A. Rudin, P. Choi, *The Elements of Polymer Science and Engineering*, Academic Press, Cambridge, **2013**.
- [34] J. V. Sunny in *Recycling of Polymers: Methods, Characterization and Applications*, Wiley-VCH, Weinheim, **2016**, pp. 209–222.
- [35] S. Kumar, J. P. Lange, G. Van Rossum, S. R. A. Kersten, *Biomass Bioenergy* **2015**, *83*, 96–104.
- [36] S. Kumar, J. P. Lange, G. V. Rossum, S. R. A. Kersten, *ACS Sustainable Chem. Eng.* **2015**, *3*, 2271–2280.

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