Electronic supplementary information

New dispersible and low-melting cellulose ester produced with molten adipic acid as a solvent, reagent and catalyst, and its application to improve the mechanical properties of PLA

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1. Reagents

Chloroform (99.5%, Sigma Aldrich, St. Louis, MA, USA), microcrystalline cellulose (MCC, Avicel PH-101, particle size 50 µm, Sigma Aldrich, St. Louis, MA, USA), polylactic acid (PLA, grade PLA2003D, Ingeo Biopolymer, Minneapolis, MN, USA), Adipic acid (AA, 99%, Carl Roth, Karlsruhe, Germany) were used as received, without any further purification.

2. Characterizations and methods

FT-IR spectra through KBr pellets were acquired by a Nicolet Impact 410 FTIR Spectrometer (SpectraLab Scientific Inc., Markham, ON, Canada), in the spectral range 400 - 4000 cm⁻¹ with a resolution of 1 cm⁻¹, with 48 scans per analysis. The substrate was ground with KBr powder (1:100 ratio) and reduced to a pellet with a hydraulic press. Water-soluble by-products (carbohydrates and total organic content) were analyzed by an Evolution 201 Spectrophotometer (ThermoFisher Scientific, Hillsboro, OR, USA), in a range between 200 and 750 nm. The morphology of the composite-PLA films was investigated by a scanning electron microscope (SEM, LEO 420, Leica Microsystems, Cambridge, UK, accelerating voltage of 10 kV) after sputtering with an ultrathin gold layer. The tensile strength and fracture strain of the composite-PLA films were measured on rectangular strips (3 cm in length and 5 mm in width) at a strain rate of 0.1 mm min⁻¹ with a Sauter TVO-S tensile tester equipped with a Sauter FH-1k digital dynamometer and AFH FAST software (Sauter GmbH, Balingen, Germany).

X-Ray diffraction patterns (XRD) were recorded on a Miniflex600 diffractometer (Rigaku, Tokyo, Japan), using a Ni filtered Cu K α wavelength of 1.5418740 Å with a D/teX Ultra2 detector, operating at 40 kV and 15 mA. MCC and CE4, in the form of dry powders, were compacted in the sample holder. PLA and the PLA-3CE composite (300 mg of PLA with no or 3% weight of cellulose ester CE4, entry 3 in Table 3) dissolved in CHCl₃ were poured in the Al holders, the solvent was let to evaporate to dryness, and then the solvent residues were removed in a vacuum oven overnight before the analysis.

¹H MAS NMR measurements were performed with a 2.5 mm double resonance MAS probe. The spectra were acquired through single pulse excitation with a $\pi/2$ pulse of 2.1 µs, spin-rate between 5 and 32 kHz and a delay time of 5 s. ¹³C CP/MAS NMR was recorded at a resonance frequency of 75.468 MHz with a MAS spinning frequency of 5 kHz. A ramped CP MAS sequence was used with a contact time of 3 ms, and ¹H decoupling was performed with a B1 field of 64 kHz. For the acquisition of the ¹³C CP MAS spectrum 9,216 scans were accumulated with a recycle delay of 10 s. Line broadening was 15.

Calorimetric characterization was carried out by a differential scanning calorimeter (DSC200 PC, Netzsch, Selb, Germany). Using a standard procedure, about 10.0 mg of each sample were placed in an aluminum pan and closed tightly with a perforated aluminum lid. Sets of four thermal analyses were performed under a dry nitrogen atmosphere with a flow rate of 20 mL min⁻¹: i) from 20 to 200 °C (heating rate 10 °C min⁻¹); ii) from 200 °C to room temperature (1 °C min⁻¹); iii) from room temperature to 200 °C (heating rate 10 °C min⁻¹); iv) from 200 °C to room temperature (1 °C min⁻¹). The total -COOH content (TCC) of cellulose esters was determined by alkaline hydrolysis and back titration as described elsewhere. ^[75] 0.500 g of cellulose ester were mixed with 40 ml of a 70/30 ethanol/water solution and the suspension was stirred for 30 min. The hydrolysis was carried out at 60° C for 48 h after adding 20.0 ml of NaOH 0.500 M. HCl 0.500 M was used to titrate the unreacted NaOH after the hydrolysis and phenolphthalein was used as the indicator. The equation for calculating the total -COOH content (TCC), in mol/g, is shown below:

$$TCC = \frac{[HCl] \times (V_B - V_S)}{m}$$
(S1)

where [*HCl*] is the exact concentration (mol/l) of the HCl solution; V_B and V_S are the exact volumes (l) of the HCl solution used for titrations of the blank and the sample, respectively; and *m* is the dry weight (g) of the cellulose ester.

The content of free -COOH groups (*FCC*, mol/g) of the cellulose esters was determined by conductometric titration as previously described. ^[76,77] 100.0 mg of each cellulose ester was mixed with 100 ml of water and 10 ml of NaCl 0.01 M. Then, 0.100 M HCl was added to the mixture to set the pH value in the range of 2.5-3.0. The suspension was then stirred for 1 h and titrated with NaOH 0.0100 M. The calculation of the content of free -COOH groups is based on the equation below:

$$FCC = \frac{[NaOH] \times V_{NaOH}}{m}$$
(S2)

where [NaOH] is the molar concentration of the NaOH solution (mol/l), V_{NaOH} is the volume (l) of the NaOH solution used for titration before the conductivity increased from the plateau of the titration curve, and *m* is the dry weight (g) of the cellulose ester.

The DS of cellulose esters was calculated from the results of titrations using the following formula:

$$DS = \frac{162.14 \times [HCl] \times (V_B - V_S) \times (1 - FC)}{m - [HCl] \times (V_B - V_S) \times (1 - FC) \times [146.14 - 18.015 \times (2 - 2FC)]}$$
(S3)

where FC is the ratio of free -COOH content to total -COOH content (FCC/TCC). 146.14 g/mol is the molecular weight of adipic acid, with the correction for the molecules of water (2-2FC) lost during the esterification.

3. ¹H MAS NMR spectrum of cellulose adipate



Fig. S1. ¹H MAS NMR spectrum of esterified cellulose (CE4) at 32 kHz MAS rate.

4. UV-Vis spectrum of cellulose adipate by-products

After the synthesis of CE4, the obtained product was crushed and washed with 1 ml of distilled water in order to extract sugars, furanic compounds and other water soluble substances. The solution was filtered with a sintered glass funnel (porosity 160-250 μ) and mixed with 3 ml of concentrated sulfuric acid. Finally, a UV-Vis spectrum was recorded (Fig. S2). The signal around 315 nm, indicating the presence of carbohydrates and total carbon ^[78], is extremely weak, and it is not distinguishable from the same signal obtained from a blank test. In addition, no detectable traces of carbohydrates, carbohydrate derivatives or organic molecules.



Fig. S2. UV-Vis spectrum of the hydrolyzed hydrophilic washings of the crude CE4 product.



5. DSC thermograms

Fig. S3. DSC profile of microcrystalline cellulose (MCC), first heating run (10 C min⁻¹).



Fig. S4. DSC profile of microcrystalline cellulose (MCC), second heating run (10 C min⁻¹).



Fig. S5. DSC profile of cellulose adipate CE-4, first heating run (10 °C min⁻¹).



Fig. S6. DSC profile of cellulose adipate CE-4, first cooling run (1 °C min⁻¹).



Fig. S7. DSC profile of cellulose adipate CE-4, second heating run (10 °C min⁻¹).



Fig. S8. DSC profile of cellulose adipate CE-4, second cooling run (1 °C min⁻¹).



Fig. S9. DSC profile of polylactic acid (PLA), first heating run (10 °C min⁻¹).



Fig. S10. DSC profile of polylactic acid (PLA), second heating run (10 °C min⁻¹).



Fig. S11. DSC profile of the composite PLA-3CE, made of polylactic acid and 3% cellulose adipate CE4, first heating run (10 °C min⁻¹).



Fig. S12. DSC profile of the composite PLA-3CE, made of polylactic acid and 3% cellulose adipate CE4, second heating run (10 °C min⁻¹).

6. SEM images of MCC and CE



Fig. S13. SEM images of MCC and CE4.





7. Images of the PLA-composite films



Fig. S14. Digital images of the polylactic acid composites PLA-xCE, made of polylactic acid and x wt% cellulose adipate CE4.

8. Stress vs strain curves of PLA and PLA-3CE



Figure S15. Stress vs strain curves of PLA and PLA-CE films.

9. References

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