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Supplementary Information

Synthesis and mechanical performance of thermoformable cellulose fatty acid esters using natural soap

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EXPERIMENTAL SECTION

Materials. Natural solid soap, composed of fatty acids (or their sodium salts) and glycerol, was kindly provided by Shabondama Soap Co., Ltd. (Fukuoka, Japan). Microcrystalline cellulose (MCC) with a particle size of 20 µm was purchased from Sigma-Aldrich and was dried overnight under vacuum conditions at 60 ºC before use. *p*-Toluenesulfonyl chloride (*p*-TsCl, >99.0%), sodium oleate (>97.0%), and sodium stearate (>97.0 %) were supplied by Tokyo Chemical Industry Co., Ltd. (TCI, Tokyo, Japan). Pyridine and other solvents were obtained from FUJIFILM Wako Pure Chemical Corporation (Osaka, Japan). All reagents were used without further purification.

Synthesis of cellulose esters via heterogeneous esterification. A mixture of MCC (0.4 g, 2.5 mmol), the natural soap (1.6, 2.4, 3.2, or 4 g), and 12 mL of pyridine were stirred at 60 ºC for 1 h. *p*-TsCl (2.82 g, 15.0 mmol) was added to the dispersion and the reaction was conducted at 60 ºC for 4 h. After cooling to room temperature, the resulting solution was poured into excess methanol. The precipitate was filtered, washed thoroughly with methanol, dissolved in chloroform, and then purified through reprecipitation in methanol. The reprecipitated compound was filter and further washed with methanol followed by deionized water. Finally cellulose ester was obtained in powder form after drying overnight in a vacuum oven at 60 ºC. MCC-C18:1, MCC-C18, and MCC-C18:1 were synthesized using sodium oleate (2.26 g, 7.5 mmol), sodium stearate (2.27 g, 7.5 mmol), and a mixture containing 3.75 mmol of each, respectively.

Characterization. Fourier transformation infrared (FT-IR) spectroscopy were performed on a FT-IR spectrometer (Nicolet iS5, Thermo Fsiher Scientific K.K., Japan). 3 mg of dried sample was grinded with 300 mg of potassium bromide (KBr) and the mixture was pressed into a pellet. Absorbance spectra were collected with 16 scans in a wavenumber range of 400-4000 cm^{-1}. Proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy for chloroform-soluble fraction of cellulose esters were carried out using NMR spectrometer (JNM-ECZ500R, JEOL Ltd., Japan). Deuterated chloroform ($CDCl_3$) was used as solvent and chemical shifts are expressed with respect to the resonance of tetramethyl silane ($\delta = 0$ ppm). Each cellulose ester sample was stirred with chloroform (10 mg/mL), filtrated, and then the solution was concentrated using an evaporator followed by precipitation in methanol. The obtained soluble fraction was used for NMR measurement after drying. The degree of substitution (DS) was calculated from integrals of peaks as stated in the following equation:

$$DS = \frac{I_{0.7-0.9ppm}/3}{(I_{0.7-0.9ppm}/3) + (I_{3.6-5.0ppm}/7)} \times 3$$

where $I_{0.7-0.9ppm}$ is the integration of peak for the –CH_3 group and $I_{3.6-5.0ppm}$ is the integration of ^{1}H-NMR peak for the AGU of cellulose. The crystal structure was characterized by X-ray diffraction (XRD; MiniFlex, Rigaku Co., Japan) at 40 kV and 15 mA in reflection mode with Cu Kα radiation (λ = 0.154 nm). The diffraction patterns were acquired with a 2θ range from 1 to 70° at a scanning speed of 10 °/min and a step size of 0.02. Thermogravimetric analysis (TGA) was performed using EXSTAR TG/DTA 7200 (SII Nanotechnology Inc., Japan) with scan range from 30 to 600 °C at a heating rate of 10 °C/min under nitrogen flow rate of 100 ml/min. Differential scanning calorimetry (DSC; EXSTAR DSC 6220, SII Nanotechnology Inc., Japan) was carried out to investigate the thermal phase transition. The samples were first heated from 30 to 150 °C at heating rate of 10 °C/min, and held for 1 min. After quenching to -100 °C and holding for 1 min, the second heating was conducted from -100 to 200 °C at a scanning rate of 5 °C/min to determine the glass-transition temperature (T_g) and melting temperature (T_m). Morphology observations of MCC and cellulose esters were carried out using a JCM-6000 SEM (JEOL, Tokyo, Japan). Each sample was coated with Pt using vacuum sputter coater before observation. The surface wettability of cellulose ester films was analyzed by using a contact angle meter (DMs-401, Kyowa Interface Co., Ltd., Japan) with analysis software FAMAS. 1 μm of water droplet was placed on the surface of films and photographs were captured after 0.1 sec for analysis. The mechanical properties of cellulose esters were evaluated by tensile tests with a tensile-compressive tester (IMC-18E0, Imoto Machinery Co., Ltd., Japan) at a tensile speed of 1 mm/min. The as-prepared cellulose ester films were cut into a dumbbell shape standardized as JIS-K6251-7 sizes (length 35 mm, width 6 mm, gauge length 12 mm, inner width 2 mm) using a dumbbell cutter (Dumbbell Co., Ltd., Japan).

Table S1 Preparation of cellulose esters

Cellulose ester	MCC	Fatty acid salts	*p*-TsCl	Yiel

	(g, mmol)	C18:1Na (g, mmol)	C18Na (g, mmol)	Natural soap (g)	(g, mmol)	d (g)
MCC-MFA_10	0.4, 2.5	-	-	4	2.82, 15.0	0.95
MCC-MFA_8	0.4, 2.5	-	-	3.2	2.82, 15.0	1.27
MCC-MFA_6	0.4, 2.5	-	-	2.4	2.82, 15.0	1.45
MCC-MFA_4	0.4, 2.5	-	-	1.6	2.82, 15.0	1.16
MCC-C18:1/C18	0.4, 2.5	1.13, 3.75	1.14, 3.75	-	2.82, 15.0	1.68
MCC-C18	0.4, 2.5	-	2.27, 7.5	-	2.82, 15.0	1.73
MCC-C18:1	0.4, 2.5	2.26, 7.5	-	-	2.82, 15.0	1.66

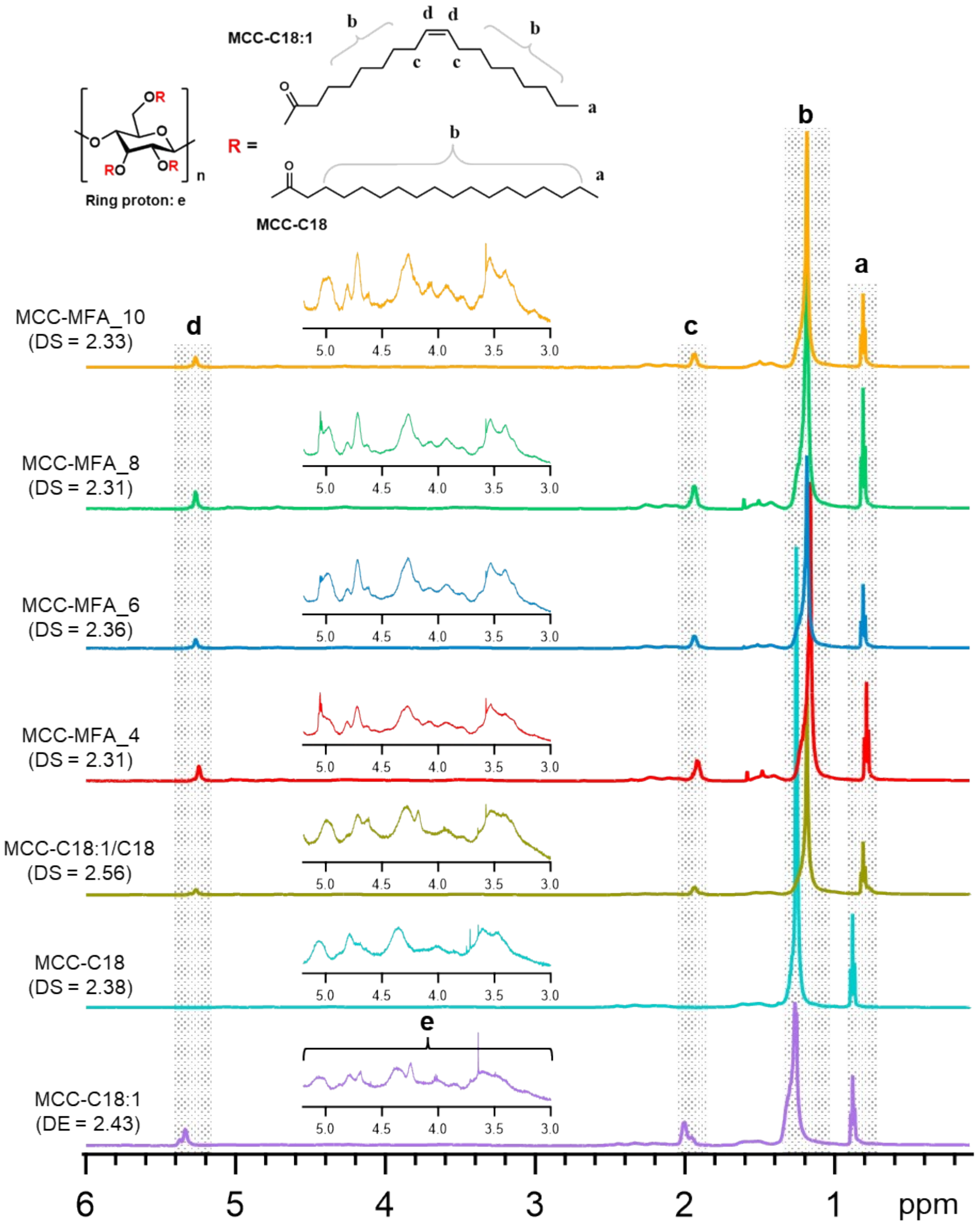

Fig. S1 ^{1}H-NMR spectra for chloroform-soluble fraction of cellulose esters.

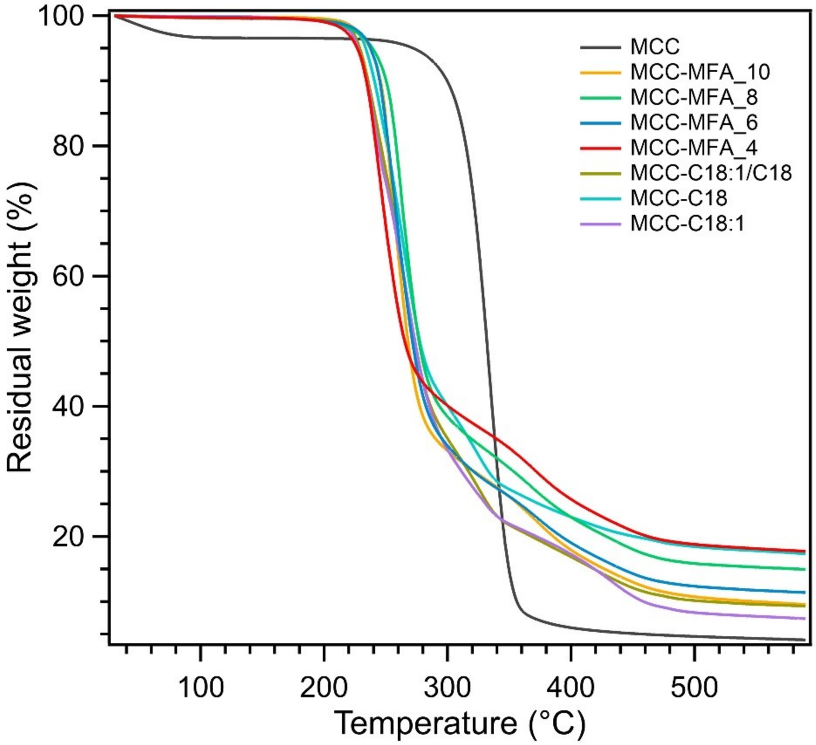

Fig. S2 TGA curves of cellulose esters.

Table S2. Thermal properties of cellulose esters

Cellulose ester	$T_{d\text{-}5\%}$ (ºC)	T_g (ºC)	T_m (ºC)
MCC	294	-	-
MCC-MFA_10	237	-46.7, -15.5, 65.3	-
MCC-MFA_8	239	-16.3, 61.2	-
MCC-MFA_6	237	-11.4, 65.9	-
MCC-MFA_4	227	-44.2, -16.1, 66.9	-
MCC-C18:1/C18	229	-58.5	-8.7
MCC-C18	234	-40.2	30.2
MCC-C18:1	227	-20.3	-

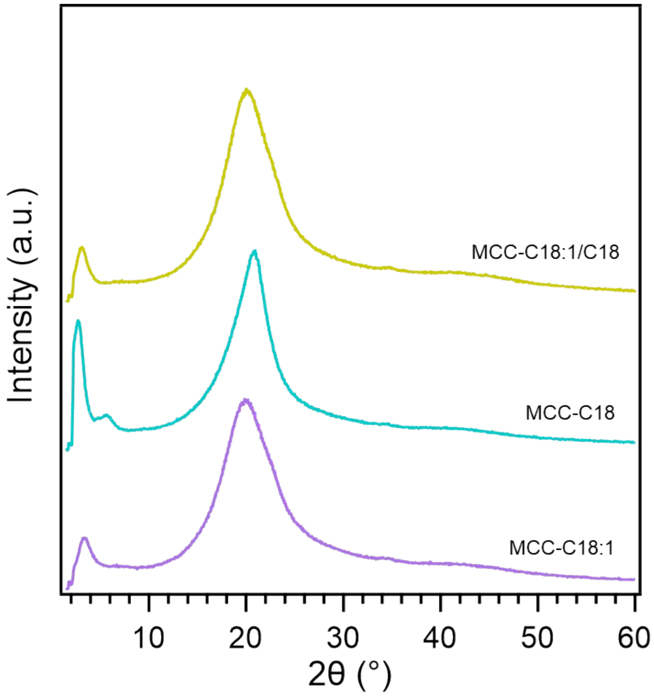

Fig. S3 XRD spectra of MCC-C18:1, MCC-C18, and MCC-C18:1/C18.

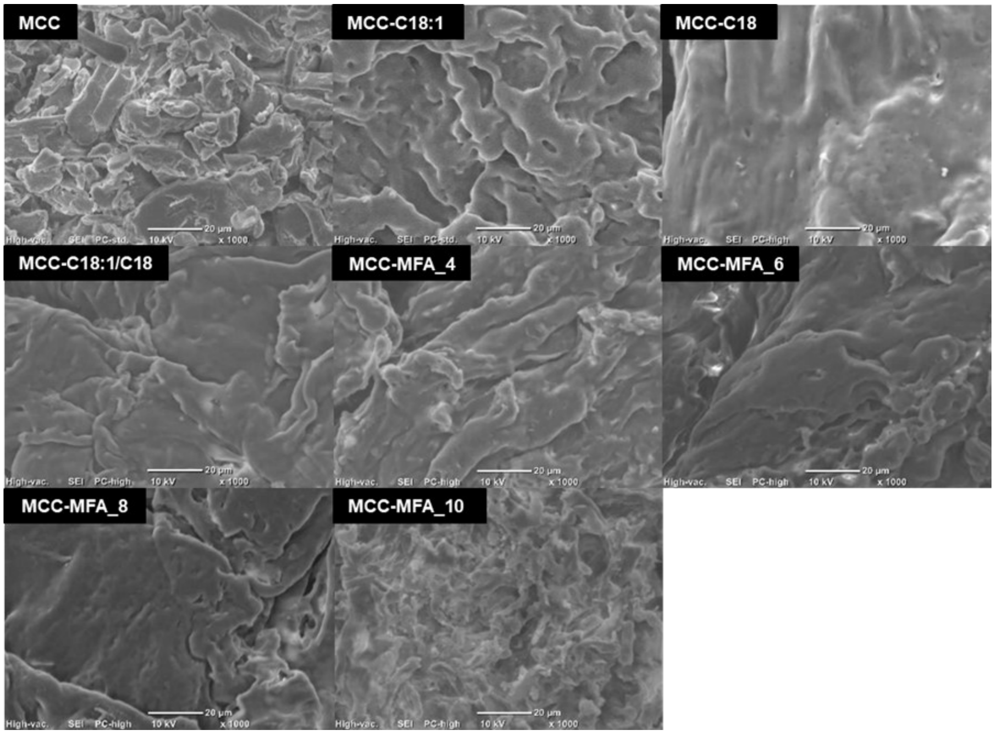

Fig. S4 SEM images of MCC and cellulose esters.

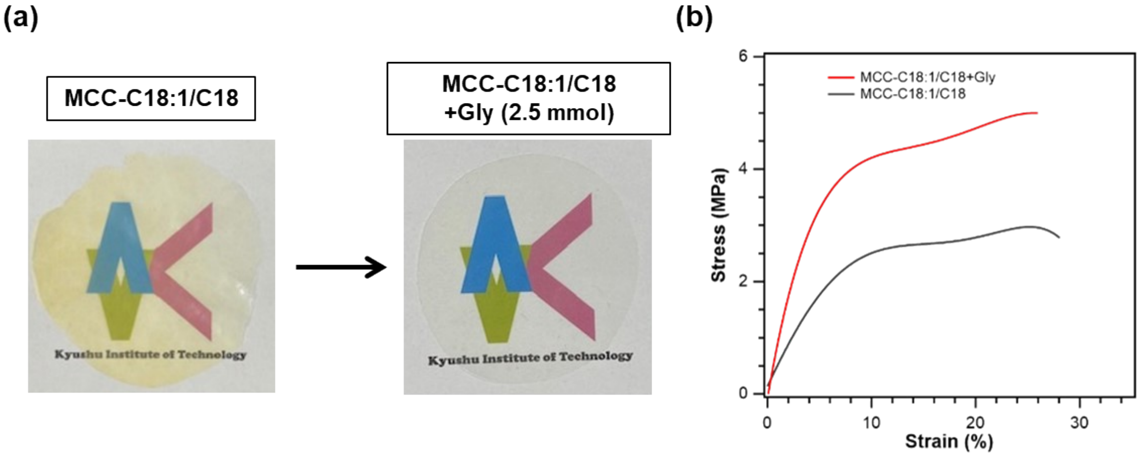

Fig. S5 (a) Representative images and (b) stress-strain curves of cellulose ester films prepared from MCC-C18:1/C18 with and without adding glycerol.

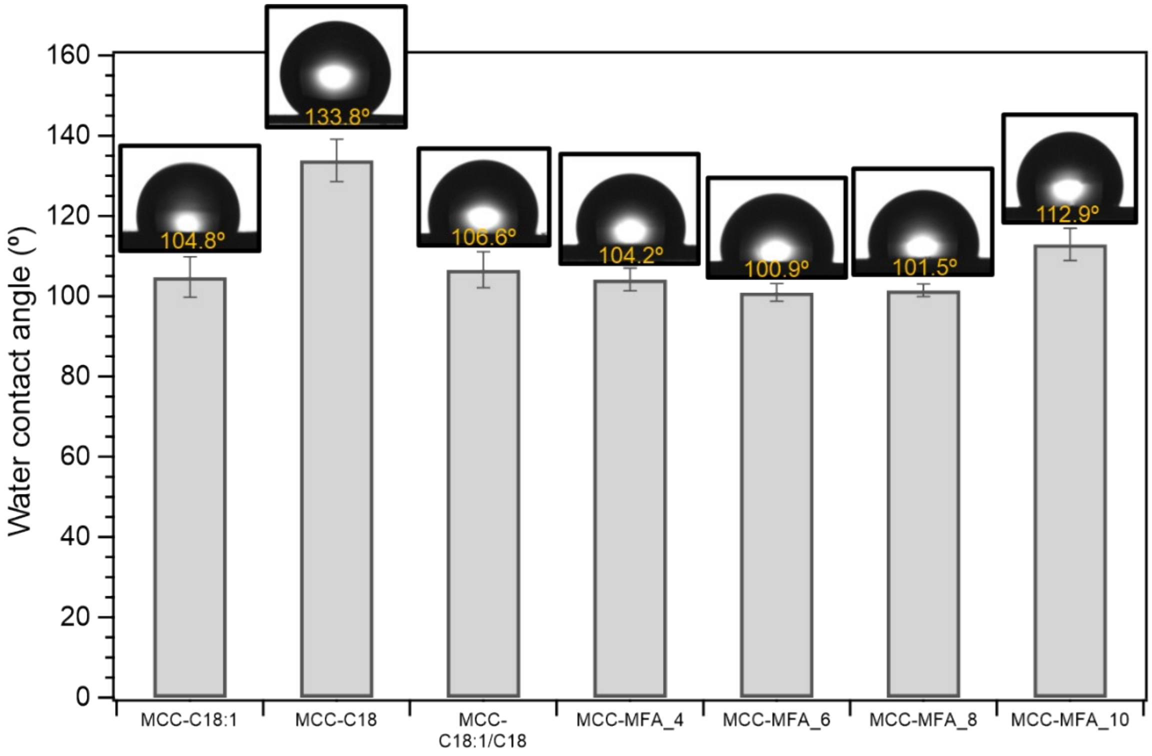

Fig. S6 Water contact angles of cellulose ester films.

Table S3. Mechanical properties of hot-pressed cellulose ester films

Cellulose ester	Tensile strength (MPa)	Elongation (%)	Young's modulus (GPa)	Toughness (J/m^3)
MCC-MFA_10	6.06 ± 0.35	15.69 ± 1.86	1.24 ± 0.08	0.71 ± 0.13
MCC-MFA_8	5.43 ± 0.31	33.19 ± 6.25	0.53 ± 0.16	1.22 ± 0.29
MCC-MFA_6	5.19 ± 0.09	34.65 ± 4.36	0.49 ± 0.12	1.26 ± 0.13
MCC-MFA_4	5.63 ± 0.52	30.56 ± 3.67	0.88 ± 0.09	1.33 ± 0.19
MCC-C18:1/C18	3.26 ± 0.21	36.69 ± 11.67	0.21 ± 0.09	0.82 ± 0.27
MCC-C18	10.23 ± 0.91	8.69 ± 0.72	2.18 ± 0.21	0.63 ± 0.05
MCC-C18:1	3.41 ± 0.43	14.96 ± 0.77	0.31 ± 0.11	0.29 ± 0.04

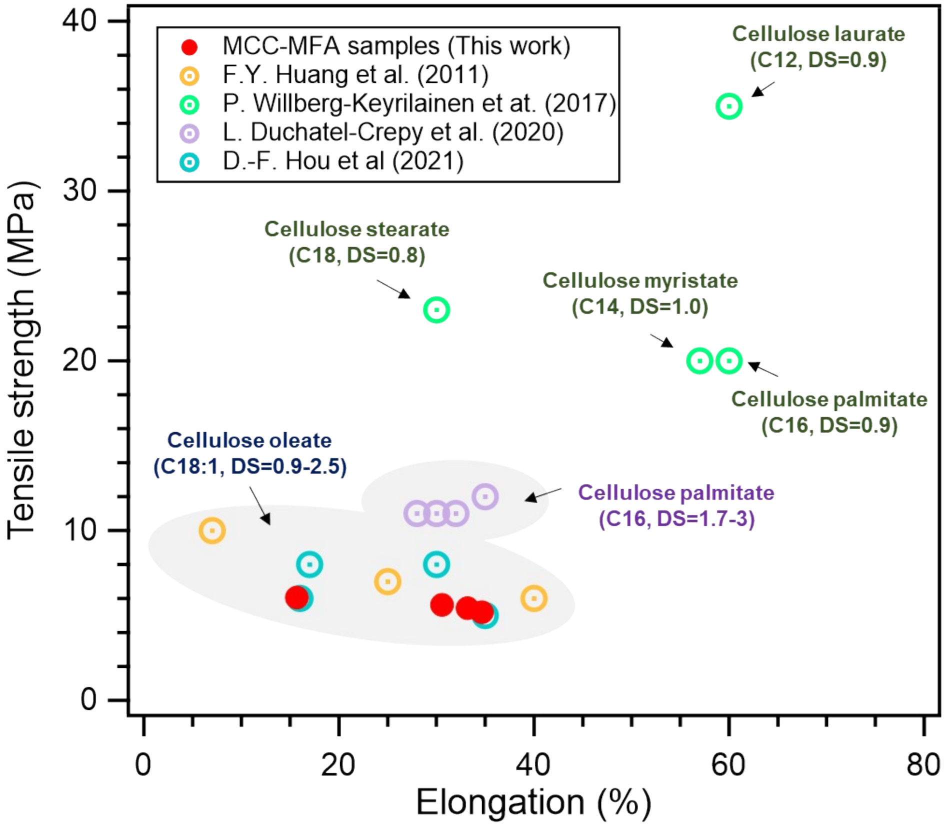

Fig. S7 Comparison of mechanical properties of MCC-MFA samples and various long-chain cellulose esters (data from [1-4]).

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