

Supporting Information

Synergistic Reinforcement of a Reversible Diels-Alder Type Network with Nanocellulose

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Experimental Section

Materials. Poly(ethylene-*alt*-maleic anhydride), p(E-*alt*-MA), average M_w 100-500 kg mol⁻¹ (powder), dichlorobenzene (DCB, 99%), furfuryl amine ($\geq 99\%$), heptyl amine (99%), n-hexane (for HPLC, $\geq 95\%$), ethyl acetate (for HPLC, $\geq 99.7\%$) and dimethylsulfoxide-d₆ (99.9 atom% D, contains 0.03 % (v/v) TMS, contains $\leq 0.0250\%$ water as impurities) were all bought from Sigma-Aldrich and used as received. Imide-extended bismaleimide, BMI-1500 was used as bifunctional oligomeric crosslinker, bought from Alfa Aesar™. Microfibrillated cellulose (Exilva Forte, 2.1 wt% solid content in water) was kindly provided by Borregaard AS, Norway.

General synthesis procedure of polymer 2. The product represented in structure 2 (Figure 1) is formed via imide formation between anhydride groups of p(E-*alt*-MA) and primary amines of furfuryl and heptyl. Samples 50f and 10f are obtained by varying the stoichiometry of the reactants (Table 1), the stoichiometry presented below renders 50f as a product. A three necked round bottomed flask of 250 ml was equipped with a reflux condenser, stirring bar and nitrogen inlet, the polymer p(E-*alt*-MA) (20 g, 0.07959 moles) was dissolved in 200 ml of DCB and heated under inert atmosphere up to 130 °C, followed by dropwise addition of primary amines, i.e. a mixture of furfuryl amine (7.04 ml, 0.039795 moles) and heptyl amine (11.8 ml, 0.039795 moles) to the reaction mixture. After 48 h of stirring, the reaction mixture was cooled to room temperature and mixed with ethyl acetate. The organic layer was repeatedly washed with distilled water to remove the unreacted reactants, if any. The organic layer was treated with anhydrous sodium sulphate to trap traces of water, followed by solvent reduction using rotary evaporation. The remaining reaction mixture in ethyl acetate was precipitated in n-hexane, and this process was repeated two times, washed with n-hexane. The precipitate was dried for several hours at 60 °C under reduced pressure. The obtained product, 2: ¹H NMR (d₆-(CH₃)₂S=O) δ_H ppm: 7.95 (traces of ring opened imide structure,

1H, -NH), 7.46 (1H, -CH-O), 6.31 (1H, -CH-), 6.20 (1H, -CH-), 4.49 (2H, -CH₂-N), 3.15 (2H, -CH₂-N), 2.59 (2H, -CH-), 1.81-1.39 (10H, -CH₂), 1.18 (10H, -CH-, -CH₂), 0.80 (3H, -CH₃).

Solvent casting and curing of crosslinked films. The functionalized polymers (50f, 10f) were dissolved in dimethyl formamide (DMF) followed by slow addition of the crosslinker (oligomer BMI1500) dissolved in DMF. The molar stoichiometry was kept at 2:1 furan: maleimide. The reaction mixture was heated at 110 °C for a few minutes until a homogenous solution was observed and subsequently casted onto Teflon coated Petri dishes. The solvent casted films (XL50f, XL10f) were dried in a fume hood for a few days, followed by drying in an oven at 60 °C for several days. For cellulose reinforced CANs, microfibrillated cellulose was solvent exchanged from water to DMF by means of rotary evaporation, yielding dispersions at a consistency of 2 wt%. Films containing 10 wt% MFC were solvent casted using the procedure detailed above, yielding samples XL50f-MFC and XL10f-MFC. All solvent casted films were compression molded at 140 °C for 15 minutes and subsequently cured in an oven at 60 °C for at least 60 h.

Fourier Transform Infrared Spectroscopy (FTIR). Samples for FTIR were cut from films of 15 μm thickness. *In-situ monitoring of associative kinetics.* Evaluation of the kinetics of the DA association reaction was done based on 60 min isotherms collected using a PerkinElmer FTIR spectrophotometer in transmission mode. Prior to measurement, samples were quenched in liquid nitrogen from the dissociated state at 160 °C and immediately sandwiched between KBr pellets and mounted in a Linkam FTIR600 hot stage. Spectra were collected every 60 seconds in the range of 4000 to 400 cm⁻¹ with a spectral resolution of 8 cm⁻¹ and 12 repetitions. *Thermal cycling.* Repeated dissociation/association of the DA network was studied in-situ by thermal cycling, with isotherms at 60 °C for 240 min interspaced with isotherms at 140 °C for 15 min for a total of 5 cycles.

¹H Nuclear Magnetic Resonance Spectroscopy (¹H NMR). ¹H NMR spectra were recorded on a Varian 400 MHz spectrometer equipped with a Varian OneNMRProbe with a ¹H frequency of 399.95 MHz. Samples were prepared by dissolving 10 mg of monomer or polymer in 0.5 ml deuterated dimethyl sulfoxide (DMSO-d₆). All spectra were referenced against tetramethylsilane (TMS).

Elemental analysis. Elemental analysis was performed using a Elementar Vario MICRO Cube in CHNS mode, with He and O₂ as operating gas. The sample weight was about 2 mg, all samples were run in duplicate.

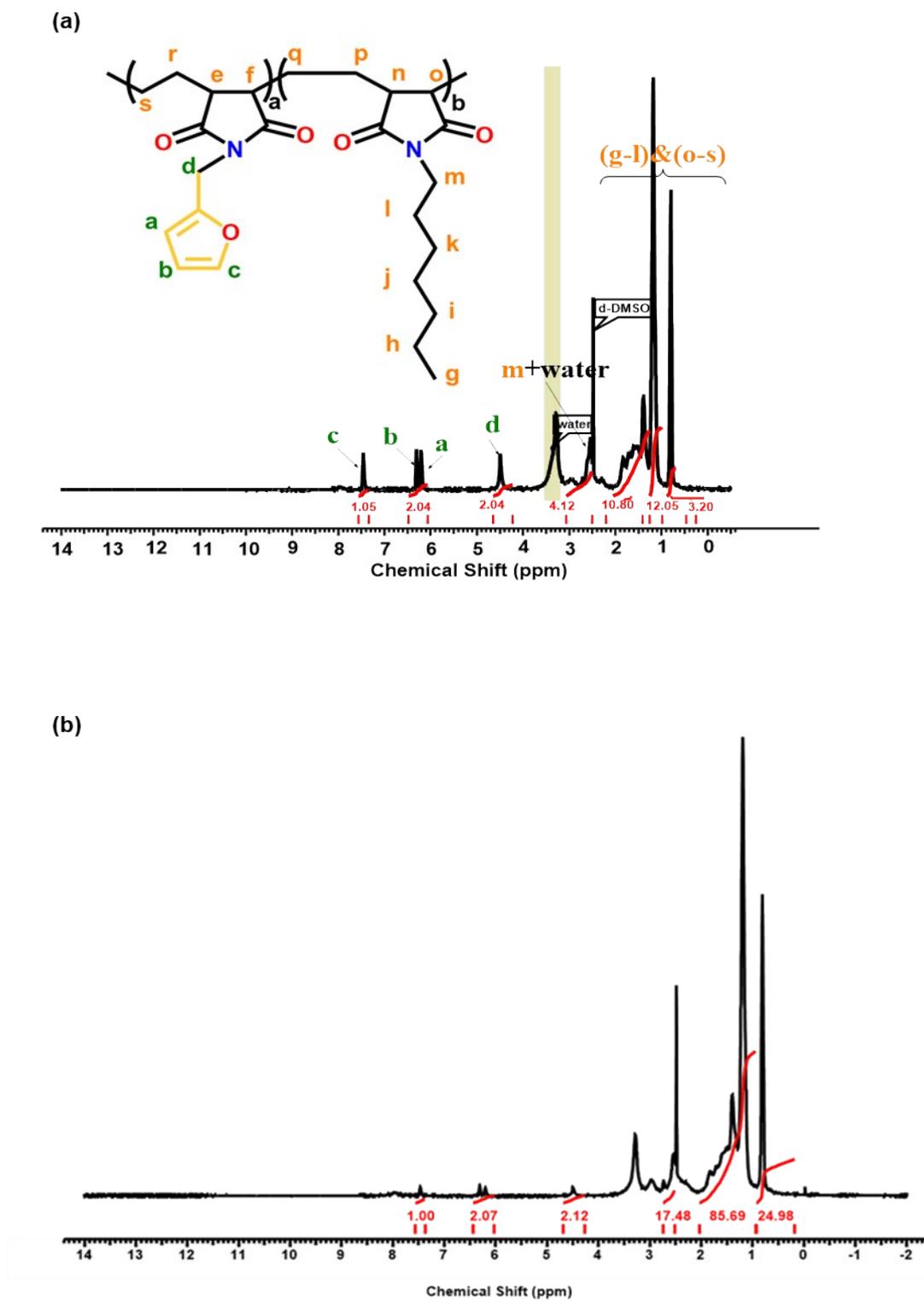
Gel Permeation Chromatography Molecular weight and polydispersity index was obtained from GPC analysis at 70 °C using a PSS SECurity² with a refractive index detector and DMF as eluent. Calibration was made with PS standards.

Thermogravimetric Analysis (TGA). Thermal stability of the synthesized polymers was evaluated using thermogravimetric analysis (TGA). TGA was carried out under nitrogen using a Mettler Toledo TGA/DSC 3+. Samples were heated from 25 to 400 °C at a heating rate of 10 °C/min.

Differential Scanning Calorimetry (DSC). Measurements were carried out under nitrogen using a Mettler Toledo DSC2 calorimeter equipped with a HSS7 sensor and a TC-125MT intercooler. The glass transition temperature of the synthesized polymers and networks, as well as other thermal transitions, were determined from using standard heating/cooling scans between -25 and 180 °C at a scan rate of 40 °C min⁻¹. The sample weight was 3-4 mg for all measurements.

Density Measurements. Determination of the density of CANs was done using a Mettler Toledo analytical balance equipped with the Density determination kit.

Dynamic Mechanical Analysis (DMA) Samples for DMA and creep were cut from films of 500 μm thickness into strips, 6*20 mm. Samples were either associated for at least 60 h at 60 $^{\circ}\text{C}$ or dissociated for 15 min at 140 $^{\circ}\text{C}$ prior to analysis. *DMTA*. DMA thermograms were recorded between 30 to 180 $^{\circ}\text{C}$ at a heating rate of 3 $^{\circ}\text{C min}^{-1}$, a frequency of 1 Hz and 0.05% strain using a TA Q800 DMA instrument in tension-film mode. Prior to temperature sweeps, strain sweeps were carried out to ensure that the applied strain was within the linear viscoelastic region. *Creep*. Creep measurements were performed at 80 and 140 $^{\circ}\text{C}$, using a constant stress of 50 kPa and 180 min test time. *Thermal cycling*. Repeated dissociation/association of the DA network was studied by following the storage modulus during thermal cycling, with isotherms at 60 $^{\circ}\text{C}$ for 240 min interspaced with isotherms at 140 $^{\circ}\text{C}$ for 15 min for a total of 5 cycles.



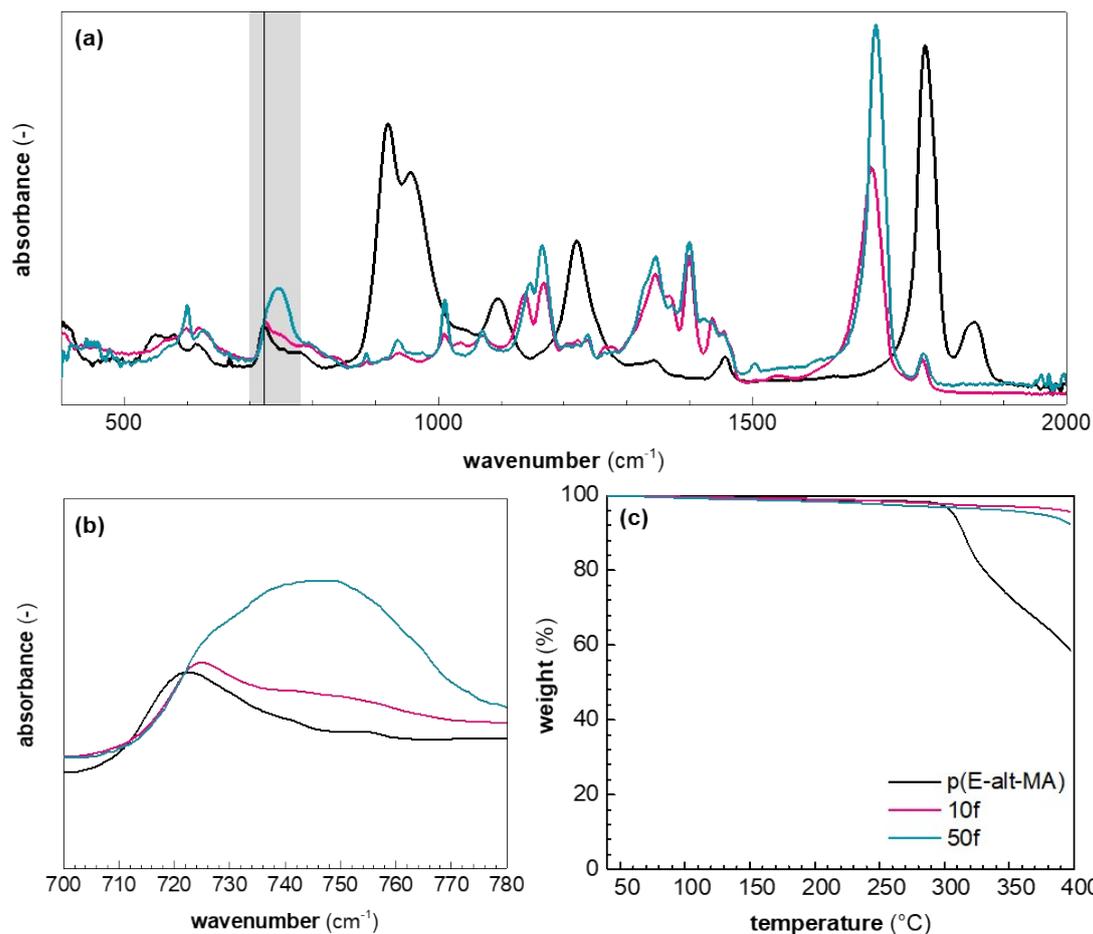


Figure S2. p(E-*alt*-MA) (black) along with 10f (pink) and 50f (blue) characterized by (a) FTIR, highlighting the furan peak area around 754 cm⁻¹, (b) zoom in of the same area as in (a) and (c) TGA.

$$\text{furan content (\%)} = \frac{\text{area}_{\text{furan modified p(E-alt-MA)}} - \text{area}_{\text{p(E-alt-MA)}}}{\text{area}_{\text{p(E-alt-MA)}}} \quad \text{Eq. S1}$$

The furan content of the modified polymers was calculated according to Eq. S1, from the peak area of the CH out of plane deformation of furan at 754 cm⁻¹, after normalization to the C-H methyl rock at 722 cm⁻¹.

Table S1. Elemental analysis of samples, together with theoretical predictions.

		N%	C%	H%
10f	<i>experimental</i>	(6.23 ± 0.12)	(67.58 ± 0.03)	(9.17 ± 0.17)
	<i>theoretical</i>	6.32	69.37	9.07
50f	<i>experimental</i>	(6.30 ± 0.04)	(65.15 ± 0.21)	(7.39 ± 0.02)
	<i>theoretical</i>	6.55	67.15	7.44
p(E-alt-MA)	<i>experimental</i>	(0.00 ± 0)	(56.18 ± 0.04)	(4.89 ± 0.03)
	<i>theoretical</i>	0	57.14	4.80

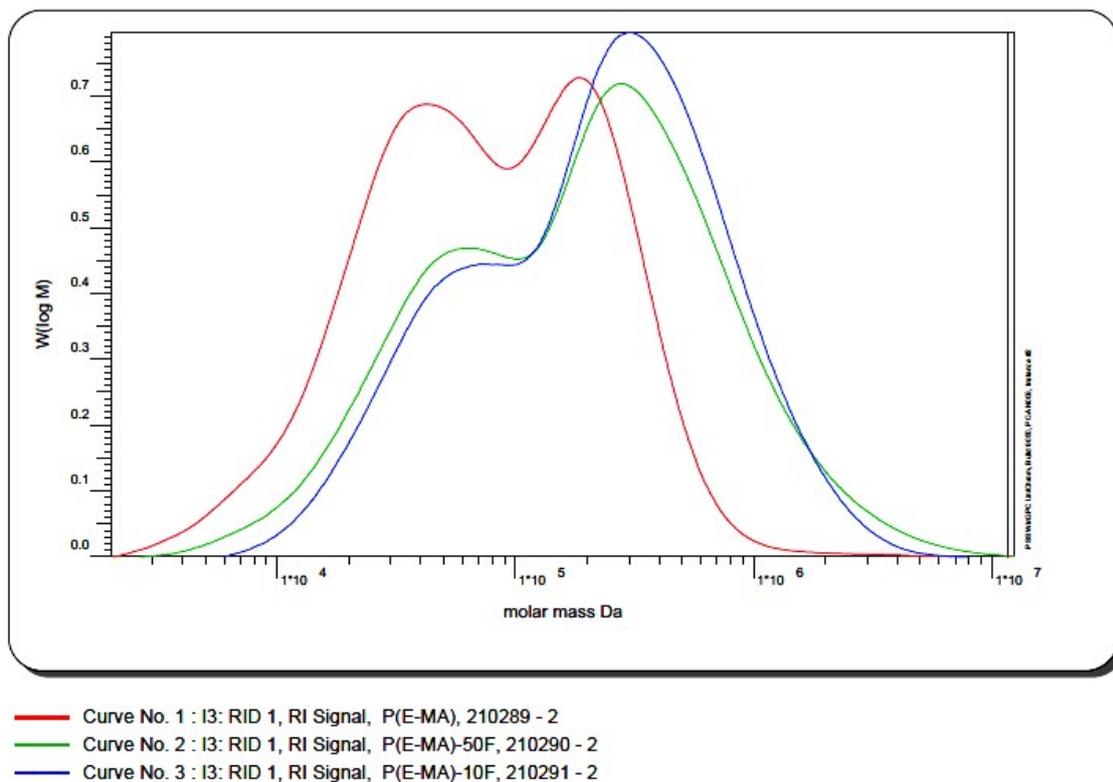


Figure S3. Chromatogram of p(E-*alt*-MA) (red trace) along with 50f (green trace) and 10f (blue trace).

Table S2. Solubility chart in organic solvents.

	Water	Methanol	DCM	EA	CHCl₃	DMF	Toluene	Acetone
p(E- <i>alt</i> -MA)	--	--	--	--	--	++	--	++
50f	--	++	++	+	p.S	+++	--	++
10	--	-	+	-	+	+++	+	++

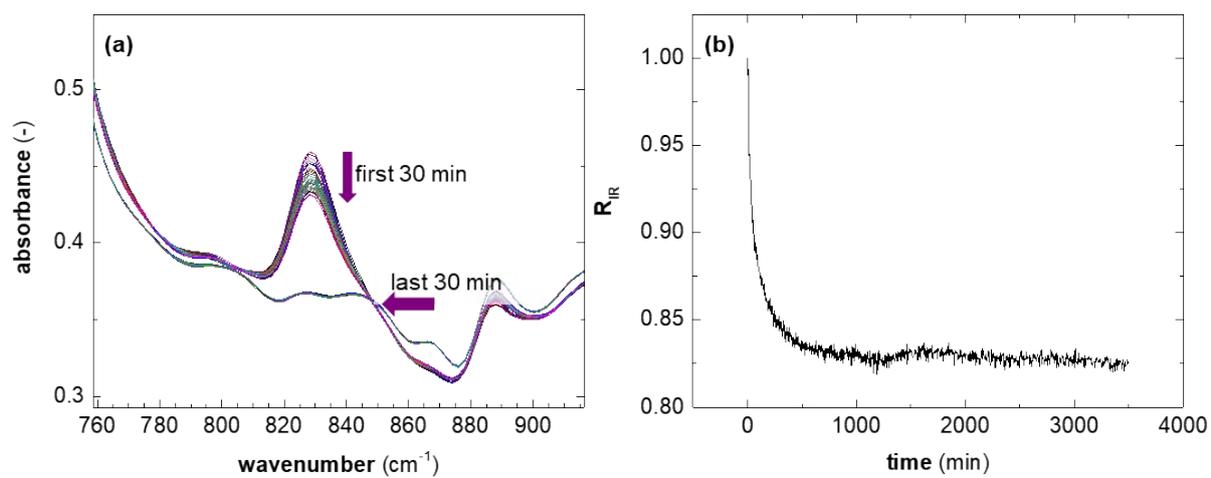


Fig S4. Analysis based on a 60 h, 60 °C isotherm of XL50f (sample was dissociated at 160 °C and quenched in liquid N₂ prior to analysis) **(a)** FTIR absorption spectra focusing on the first and last 30 min of the isotherm **(b)** normalized intensity of the 828 cm⁻¹ maleimide absorption peak as a function of time.

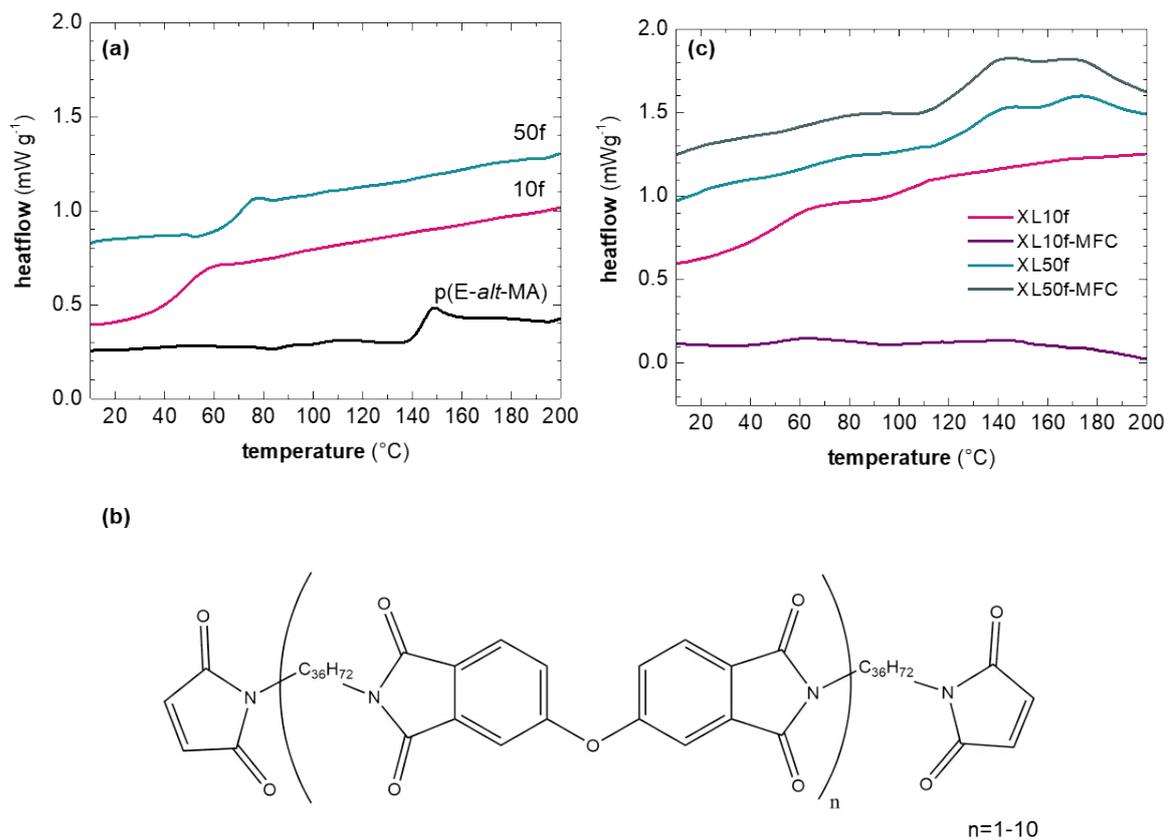


Figure S5. (a) DSC first heating thermograms of p(E-alt-MA) along with 10f and 50f **(b)** molecular structure of BMI 1500 **(c)** DSC first heating thermograms of XL10f, XL10f-MFC, XL50f and XL50f-MFC after curing at 60 °C for 60 h.

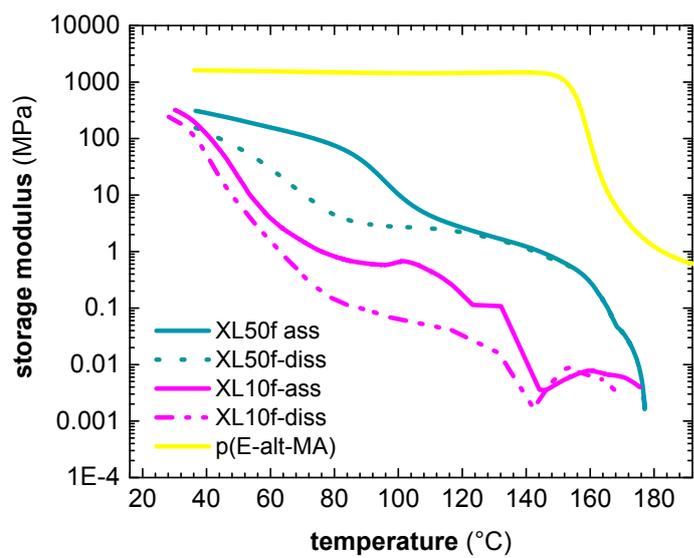


Figure S6. DMA temperature ramps of p(E-*alt*-MA), XL10f and XL50f in the dissociated and associated state.

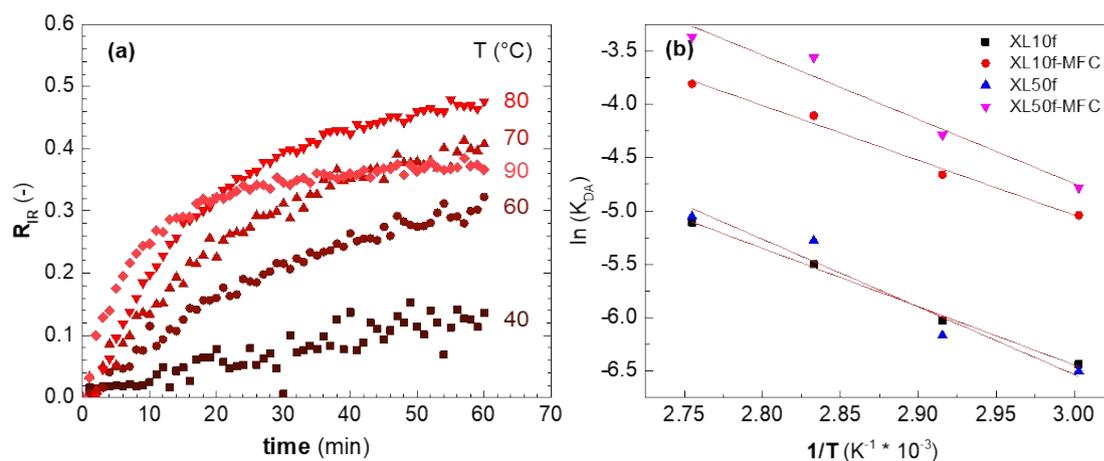


Figure S7. (a) Relative intensity of imide peak (R_{IR}) during the forward DA reaction in XL50f at temperatures from 40-90 °C (b) Arrhenius plots of the of the natural logarithm of k_{DA} versus reciprocal temperature based on pseudo-first order kinetics.

Table S3. Activation energy (E_a) and pre-exponential factor (A) calculated from pseudo first and second order kinetics using the linearized version of the Arrhenius equation.

Sample	E_a (kJ mol ⁻¹)		A (s ⁻¹)		R^2	
	1 st order	2 nd order	1 st order	2 nd order	1 st order	2 nd order
XL50f	44.3	42.7	11.1	10.4	0.999	0.989
XL50f-MFC	49.0	50.0	12.9	13.3	0.967	0.965
XL10f	50.3	45.4	11.1	9.9	0.995	0.996
XL10f-MFC	52.2	52.7	12.32	12.5	0.946	0.949

Density determination of CANs. The densities of XL50f and XL10f at 20 °C were determined based on the Buoyancy Method using a Mettler Toledo analytical balance equipped with the Density determination kit. Densities at 20 °C were measured as 1.09 and 1.20 g cm⁻³ for samples XL50f and XL10f, respectively. The densities of samples at 80 °C, the temperature of creep, cannot be measured using the Buoyancy Method due to excessive evaporation of water at this temperature. Instead samples were heated to 80 °C in an oven and subsequently immersed in water at 80 °C, in which both samples sank. The density of water at 80 °C is 0.972 g cm⁻³,¹ hence the densities of samples are confirmed to be above this value. For calculation of the density of crosslinks the sample densities at 20 °C were used, which, most probably, are a slight overestimation of the densities of samples at 80 °C. The results of the calculation of M_w between crosslinks were hence reported with merely one significant digit as the density measurements are attached with a high uncertainty.

Table S4. Densities of CANs at 20 and 80 °C.

Sample	ρ (g cm ⁻³) at 20.22 °C	ρ (g cm ⁻³) at 80 °C
XL10f	1.2	$0.972 \leq \rho \leq 1.20$
XL50f	1.09	$0.972 \leq \rho \leq 1.09$

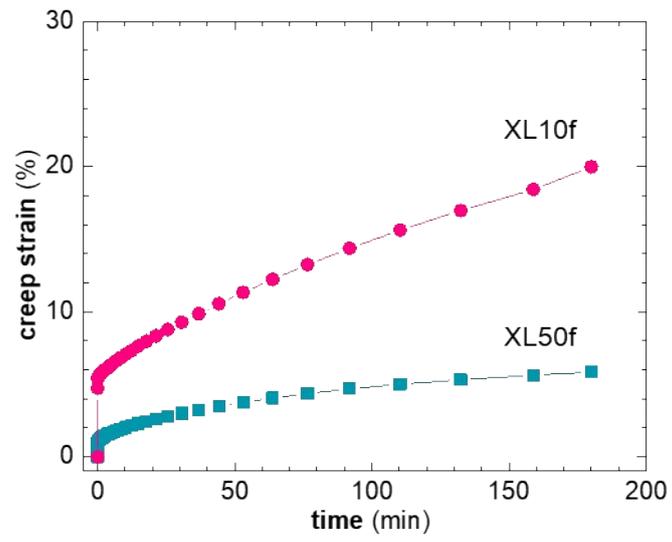


Figure S8. Creep strain as function of time for samples XL10f and XL50f.

Calculation of the theoretical percolation threshold for MFC. The percolation threshold, V_c of rod-like nanoparticles is linked to the aspect ratio via²

$$V_c = \frac{0.7}{L/d} \quad \text{Eq. S2}$$

where L and d are the length and diameter of the nanoparticle. The diameter of the MFC used has been reported as 60 ± 40 nm in an earlier publication by our research group.³ The length of microfibrils are typically described as several micrometers,⁴ based on the length of a cellulose fibril aggregate. The long, entangled strands of MFC makes determination of fibril length from microscopic methods almost impossible. We hence assume a fibril length of 2000 nm. Equation S1 suggests that the here used MFC, which has an aspect ratio of $L/d = 33$, can percolate above a fraction of 2.1 vol%. Conversion from vol% to wt% is done using Eq. S3

$$wt\%_{CNC} = \frac{vol\%_{CNC} * \rho_{CNC}}{vol\%_{CNC} * \rho_{CNC} + vol\%_{XL50f} * \rho_{XL50f}} \quad \text{Eq. S3}$$

with $\rho_{CNC} = 1.5 \text{ g cm}^{-3}$ and $\rho_{XL50f} = 1.14 \text{ g cm}^{-3}$, rendering a value of to 2.7 wt%.

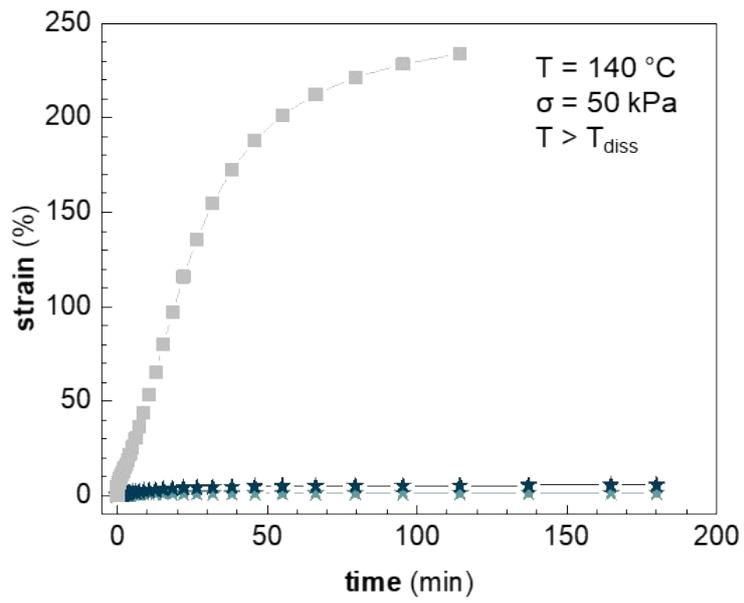


Figure S9. Creep strain as function of time for XL50f in the dissociated state (grey squares), as well as samples reinforced with MFC, 10 wt% (dark blue stars) or 5 wt% (light green stars).

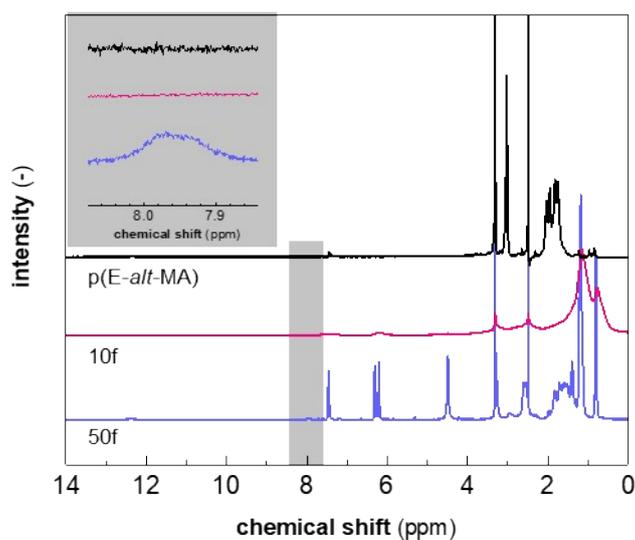


Figure S10. ^1H NMR spectra of p(E-*alt*-MA) along with 10f and 50f highlighting the region around 7.95 ppm, which reveals a signal assigned to the ring opened imide structure.

1. Jones, F. E.; Harris, G. L., ITS-90 Density of water formulation for volumetric standards calibration. *J. Res. Natl. Inst. Stand. Technol.* **1992**, *97*, 335-340.
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4. Klemm, D.; Kramer, F.; Moritz, S.; Lindström, T.; Ankerfors, M.; Gray, D.; Dorris, A., Nanocelluloses: A new family of nature-based materials. *Angew. Chem. Int. Ed.* **2011**, *50*, 5438-5466.