Supplementary Information

Structure and Properties of All-Cellulose Composites Prepared by Controlling the Dissolution Temperature of NaOH/Urea Solvent

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Figure S1 shows the effects of dissolution time on the mechanical properties of ACCs-10. It is obvious that the mechanical properties of ACCs-10 obtained after one minute of dissolution are inferior to those of the ACCs-10 obtained after five minutes of dissolution. As the dissolution time exceeds five minutes, the mechanical properties of the ACCs-10 begin to decrease because more cellulose is dissolved. After ten minutes, the cellulose reaches the maximum solubility. As the dissolution time increases, the mechanical properties of the ACCs no longer decline. Therefore, 5 min is set as the optimal dissolution time for the preparation of ACCs-10. To guarantee single variable, the dissolution time for the other ACCs are all set to 5 min.



Figure S1. The effects of dissolution time on mechanical properties of ACCs-10.

Figure S2 shows the XRD profiles of ACCs-10 and the corresponding peak deconvolution process. The degree of crystallinity is determined by resolving the diffraction profile into cellulose I, cellulose II and amorphous diffraction peaks, which are fitted by Gaussian curves. Specifically, the (0 -1 0), (1 1 0) and (2 0 0) peaks of cellulose I are set at $2\theta = 14.8^{\circ}$, 16.5° and 22.8°, respectively¹, the (0 -1 0), (1 1 0), (0 2 0) peaks of cellulose II are set at $2\theta = 12.1^{\circ}$, 19.8° and 21.8°, respectively,^{2,3} white the central position of the amorphous peak is set at 18.6°, according to Segal et al.⁴



Figure S2. XRD profiles of ACCs-10 and the corresponding peak deconvolution process to estimate the crystallinity. The measured pattern (black line), simulated pattern (red line) and simulated curves for cellulose I (orange line), cellulose II (green line) and amorphous cellulose (blue line) are shown.

Raw materials	Methods	Solvents	Reinforcements	Tensile	References
				strength (MPa)	
Cotton linter pulps	One-step	NaOH/urea/H ₂ O	Self-reinforcing	108.1	This work
Softwood sulphite					
dissolving and abaca	One-step	NaOH/urea/H ₂ O	Self-reinforcing	48	5
pulp					
Cotton linter pulps	One-step	NaOH/urea/H ₂ O	Self-reinforcing	135	6
Bleached spruce	One-step	NaOH/urea/H ₂ O	Self-reinforcing	24	7
Eucalyptus	One-step	NaOH/urea/H ₂ O	Self-reinforcing	24.6	7
Bleached pine	One-step	NaOH/urea/H ₂ O	Self-reinforcing	39.4	7
Unbleached pine	One-step	NaOH/urea/H ₂ O	Self-reinforcing	20.3	7
Filter paper	One-step	NaOH/urea/H ₂ O	Self-reinforcing	53	8
Softwood sulphite	One-step	NaOH/urea/H ₂ O	Self-reinforcing	52.4	9
dissolving wood pulp					
Rayon textile	One-step	NaOH/urea/H ₂ O	Self-reinforcing	114.1	10
Cotton fabric	One-step	Ionic liquid	Self-reinforcing	22	11
Lyocell fabric	One-step	Ionic liquid	Self-reinforcing	102.6	12
rayon fiber textile	One-step	Ionic liquid	Self-reinforcing	77.7	13
Filter paper	One-step	LiCl/DMAc	Self-reinforcing	211.8	14
Filter paper	One-step	PEG/NaOH	Self-reinforcing	74.7	15
Cotton linter pulps	Two-step	NaOH/urea/H ₂ O	Cellulose	167	16
			nanofibrils		
Cotton linter pulps	Two-step	NaOH/urea/H ₂ O	Cellulose	124	1
			nanowhiskers		
Cotton linter pulps	Two-step	NaOH/urea/H ₂ O	Ramie fibers	124.3	17
Alfa pulp	Two-step	NaOH/H ₂ O	Alfa fibers	16	18
Filter paper	Two-step	Ionic liquid	Rice husk	89.0	19
Cellulose diacetate	Two-step	Acetone	Nanofibrillated	102.3	20
			cellulose		
Unbleached hardwood	Two-step	Water	Nanofibrillated	53.2	21
craft pulp			cellulose		

Table S1. Comparison of tensile strength of the ACCs prepared by different methods

References

- Qi, H.; Cai, J.; Zhang, L.; Kuga, S. Properties of Films Composed of Cellulose Nanowhiskers and a Cellulose Matrix Regenerated from Alkali/Urea Solution. *Biomacromolecules* 2009, *10* (6), 1597–1602.
- Gong, J.; Li, J.; Xu, J.; Xiang, Z.; Mo, L. Research on Cellulose Nanocrystals Produced from Cellulose Sources with Various Polymorphs. *RSC Adv.* 2017, 7 (53), 33486–33493.
- (3) Ling, Z.; Chen, S.; Zhang, X.; Takabe, K.; Xu, F. Unraveling Variations of Crystalline Cellulose Induced by Ionic Liquid and Their Effects on Enzymatic Hydrolysis. *Sci. Rep.* 2017, 7 (1), 10230.
- Segal, L.; Creely, J. J.; Martin, A. E.; Conrad, C. M. An Empirical Method for Estimating the Degree of Crystallinity of Native Cellulose Using the X-Ray Diffractometer. *Text. Res. J.* 1959, *29* (10), 786–794.
- (5) Hildebrandt, N. C.; Piltonen, P.; Valkama, J. P.; Illikainen, M. The Effect of Calendering on the Mechanical Properties of Paper-Based, Self-Reinforcing Composites. *Cellulose* 2018, 25 (7), 4001–4010.
- (6) Cheng, G.; Zhu, P.; Li, J.; Cheng, F.; Lin, Y.; Zhou, M. All-Cellulose Films with Excellent Strength and Toughness via a Facile Approach of Dissolution-Regeneration. J. Appl. Polym. Sci. 2019, 136 (2), 46925.
- (7) Hildebrandt, N. C.; Piltonen, P.; Valkama, J. P.; Illikainen, M. Self-Reinforcing Composites from Commercial Chemical Pulps via Partial Dissolution with NaOH/Urea. *Ind. Crops Prod.* 2017, *109*, 79–84.

- (8) Duchemin, B.; Le Corre, D.; Leray, N.; Dufresne, A.; Staiger, M. P. All-Cellulose Composites Based on Microfibrillated Cellulose and Filter Paper via a NaOH-Urea Solvent System. *Cellulose* 2016, 23 (1), 593–609.
- (9) Piltonen, P.; Hildebrandt, N. C.; Westerlind, B.; Valkama, J. P.; Tervahartiala,
 T.; Illikainen, M. Green and Efficient Method for Preparing All-Cellulose
 Composites with NaOH/Urea Solvent. *Compos. Sci. Technol.* 2016, *135*, 153–158.
- (10) Dormanns, J. W.; Schuermann, J.; Müssig, J.; Duchemin, B. J. C.; Staiger, M.
 P. Solvent Infusion Processing of All-Cellulose Composite Laminates Using an Aqueous NaOH/Urea Solvent System. *Compos. Part A Appl. Sci. Manuf.* 2016, *82*, 130–140.
- (11) Shibata, M.; Teramoto, N.; Nakamura, T.; Saitoh, Y. All-Cellulose and All-Wood Composites by Partial Dissolution of Cotton Fabric and Wood in Ionic Liquid. *Carbohydr. Polym.* **2013**, *98* (2), 1532–1539.
- (12) Adak, B.; Mukhopadhyay, S. A Comparative Study on Lyocell-Fabric Based
 All-Cellulose Composite Laminates Produced by Different Processes.
 Cellulose 2017, 24 (2), 835–849.
- (13) Mat Salleh, M.; Magniez, K.; Pang, S.; Dormanns, J. W.; Staiger, M. P. Parametric Optimization of the Processing of All-Cellulose Composite Laminae. *Adv. Manuf. Polym. Compos. Sci.* 2017, 3 (2), 73–79.
- (14) Nishino, T.; Arimoto, N. All-Cellulose Composite Prepared by Selective Dissolving of Fiber Surface. *Biomacromolecules* 2007, 8 (9), 2712–2716.

- (15) Han, D.; Yan, L. Preparation of All-Cellulose Composite by Selective Dissolving of Cellulose Surface in PEG/NaOH Aqueous Solution. *Carbohydr. Polym.* 2010, 79 (3), 614–619.
- (16) Yang, Q.; Saito, T.; Berglund, L. A.; Isogai, A. Cellulose Nanofibrils Improve the Properties of All-Cellulose Composites by the Nano-Reinforcement Mechanism and Nanofibril-Induced Crystallization. *Nanoscale* 2015, 7 (42), 17957–17963.
- (17) Yang, Q.; Lue, A.; Zhang, L. Reinforcement of Ramie Fibers on Regenerated Cellulose Films. *Compos. Sci. Technol.* **2010**, *70* (16), 2319–2324.
- (18) Labidi, K.; Korhonen, O.; Zrida, M.; Hamzaoui, A. H.; Budtova, T. All-Cellulose Composites from Alfa and Wood Fibers. *Ind. Crops Prod.* 2019, 127, 135–141.
- (19) Zhao, Q.; Yam, R. C. M.; Zhang, B.; Yang, Y.; Cheng, X.; Li, R. K. Y. Novel All-Cellulose Ecocomposites Prepared in Ionic Liquids. *Cellulose* 2009, *16* (2), 217–226.
- Wang, W.; Liang, T.; Bai, H.; Dong, W.; Liu, X. All Cellulose Composites Based on Cellulose Diacetate and Nanofibrillated Cellulose Prepared by Alkali Treatment. *Carbohydr. Polym.* 2018, 179, 297–304.
- (21) Alcalá, M.; González, I.; Boufi, S.; Vilaseca, F.; Mutjé, P. All-Cellulose Composites from Unbleached Hardwood Kraft Pulp Reinforced with Nanofibrillated Cellulose. *Cellulose* 2013, 20 (6), 2909–2921.

- (9) Dormanns, J. W.; Schuermann, J.; Müssig, J.; Duchemin, B. J. C.; Staiger, M.
 P. Solvent Infusion Processing of All-Cellulose Composite Laminates Using an Aqueous NaOH/Urea Solvent System. *Compos. Part A Appl. Sci. Manuf.* 2016, *82*, 130–140.
- (10) Shibata, M.; Teramoto, N.; Nakamura, T.; Saitoh, Y. All-Cellulose and All-Wood Composites by Partial Dissolution of Cotton Fabric and Wood in Ionic Liquid. *Carbohydr. Polym.* **2013**, *98* (2), 1532–1539.
- (11) Adak, B.; Mukhopadhyay, S. A Comparative Study on Lyocell-Fabric Based
 All-Cellulose Composite Laminates Produced by Different Processes.
 Cellulose 2017, 24 (2), 835–849.
- Mat Salleh, M.; Magniez, K.; Pang, S.; Dormanns, J. W.; Staiger, M. P.
 Parametric Optimization of the Processing of All-Cellulose Composite
 Laminae. Adv. Manuf. Polym. Compos. Sci. 2017, 3 (2), 73–79.
- (13) Nishino, T.; Arimoto, N. All-Cellulose Composite Prepared by Selective Dissolving of Fiber Surface. *Biomacromolecules* 2007, 8 (9), 2712–2716.
- (14) Han, D.; Yan, L. Preparation of All-Cellulose Composite by Selective Dissolving of Cellulose Surface in PEG/NaOH Aqueous Solution. *Carbohydr. Polym.* 2010, 79 (3), 614–619.
- (15) Yang, Q.; Saito, T.; Berglund, L. A.; Isogai, A. Cellulose Nanofibrils Improve the Properties of All-Cellulose Composites by the Nano-Reinforcement Mechanism and Nanofibril-Induced Crystallization. *Nanoscale* 2015, 7 (42),

17957–17963.

- (16) Labidi, K.; Korhonen, O.; Zrida, M.; Hamzaoui, A. H.; Budtova, T. All-Cellulose Composites from Alfa and Wood Fibers. *Ind. Crops Prod.* 2019, *127*, 135–141.
- (17) Zhao, Q.; Yam, R. C. M.; Zhang, B.; Yang, Y.; Cheng, X.; Li, R. K. Y. Novel All-Cellulose Ecocomposites Prepared in Ionic Liquids. *Cellulose* 2009, *16* (2), 217–226.
- Wang, W.; Liang, T.; Bai, H.; Dong, W.; Liu, X. All Cellulose Composites
 Based on Cellulose Diacetate and Nanofibrillated Cellulose Prepared by Alkali
 Treatment. *Carbohydr. Polym.* 2018, 179, 297–304.
- (19) Alcalá, M.; González, I.; Boufi, S.; Vilaseca, F.; Mutjé, P. All-Cellulose Composites from Unbleached Hardwood Kraft Pulp Reinforced with Nanofibrillated Cellulose. *Cellulose* 2013, 20 (6), 2909–2921.