Heat Treatment's Effect on the Wettability of Cellulose Membranes *via* a Top-Down Approach

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Cellulose is a potential alternative to petroleum-derived polymers, and cellulose membranes are used in many applications such as sensors, flexible materials, and functional membranes. Most bottom-up methods are energy-, chemical-, and time-intensive compared to top-down methods for preparing cellulose membranes. Additionally, most methods to improve the hydrophobicity of cellulose membranes to increase their lifetime are complex and require large amounts of organic solvents. To balance sustainability, degradability, and service life from a whole life cycle perspective, which is the biggest challenge for the industrialization of cellulose membranes, a top-down approach was used here to prepare cellulose membranes using camphor pine, walnut, and loofah materials. The effect of low temperature heat treatment on the prepared membranes' wettability and water stability were investigated. The results showed that the water stability of loofah cellulose membrane was influenced by both surface and internal wettability due to the non-homogeneous structure. The heat treatment temperature of 200 °C for loofah cellulose membrane, 150 °C for camphor pine cellulose membrane, and 225 °C for walnut cellulose membrane was more effective.

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INTRODUCTION

Cellulose is the most abundant renewable biopolymer on Earth and is an essential component of the cell walls of plants and some algae, as well as of biofilms secreted by bacteria (Liu *et al.* 2021). Cellulose is considered an almost inexhaustible source of raw material, especially as one of the most promising substitutes of petroleum-derived synthetic polymers (Zhang *et al.* 2019); however, only 5% is extracted and used for production (Klemm *et al.* 2005; Rana *et al.* 2021). The production and application of cellulose has not yet reached the scale that researchers and entrepreneurs expect it should, despite nearly two centuries of research (Rana *et al.* 2021).

Cellulose is biodegradable and possesses easy processability and biocompatibility. In addition, cellulose enables a variety of functional and transformative applications through its unique multidimensional structure (Li *et al.* 2021a). In particular, with recent advances in materials science and manufacturing methods, cellulose has been applied to

sensors (An *et al.* 2018; Yuk *et al.* 2019), nanogenerators (Cui *et al.* 2017; Luo *et al.* 2019), substrates for flexible electronic devices (Martins *et al.* 2011; Russo *et al.* 2011), and functional membranes (Zhu *et al.* 2017; Fu *et al.* 2018).

A variety of bottom-up approaches are available for the preparation of cellulose membranes. These methods prepare cellulose membranes from nanocellulose (Sharma *et al.* 2019), which has a complex extraction process, by electrostatic spinning or microfluidic control (Nechyporchuk *et al.* 2019; Peng *et al.* 2020), which are often energy, water, and time intensive from a full life-cycle perspective (Li *et al.* 2021b). In contrast, top-down strategies avoid further assembly by removing other components from the raw material (*e.g.*, herbs and wood) and obtain cellulose membranes that maintain the structural properties of the raw material and are simpler and more cost-effective to process.

The most significant challenge for the industrialization of cellulosic functional materials is the balance between sustainability, biodegradability, and durability or dimensional stability (Li *et al.* 2021a). On the one hand, to be truly sustainable, the processing should also be sustainable. On the other hand, the durability of cellulosic materials needs to be balanced with their biodegradability, both of which are influenced by surface wettability. Because the biodegradation process requires the involvement of water, the general strategy to improve the durability of cellulosic materials is to increase hydrophobicity and decrease hygroscopicity, which is to some extent at the expense of biodegradability (Li *et al.* 2021a). Examples include surface coating, sizing, and surface super-hydrophobicity, which inevitably introduce complex processes and large amounts of organic solvents (Gao *et al.* 2018).

Herein, a top-down method was used to prepare cellulose membranes from camphor pine wood, walnut wood, and loofah to represent softwood, hardwood, and herbaceous plants, respectively. The effect of low-temperature heat treatment on the wettability and water stability of the cellulose membranes obtained was investigated to develop a simple, solvent-free approach to balance the degradability and durability.

EXPERIMENTAL

Materials

Sodium hypochlorite was supplied by Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China). Camphor pine wood, walnut wood rotary cut wood films (thickness of 0.15 mm), and loofah were obtained from a local store. Rotational cutting exposes vessels and pits located extensively throughout the cell wall, creating different types of pores on the films that facilitate fluid transport (Li *et al.* 2018). The camphor pine wood and walnut wood samples were cut to a size of 10 mm × 50 mm × 0.15 mm (tangential × longitudinal × radial).

Preparation of Samples

Peeled loofah was cut into segments and boiled in water for 1.0 h to remove water-soluble organic matter and air from the fibers. The camphor pine wood, walnut wood samples, and loofah segments were then delignified using 5 wt% NaClO solution at 25 °C for 4 h. The delignified samples were then dried at room temperature for 12 h to obtain cellulose membranes from camphor pine and walnut wood samples.

Cellulose membranes from loofah were prepared in a similar way as in previous work (Xing *et al.* 2022). About 0.5 g of the irregular inner part of the delignified loofah

segments was pulped and dried to form a cellulose membrane with a length of 70 mm and a width of 50 mm, and the regular outer ring was unfolded to form a structural cellulose membrane that maintains the original loofah. After spraying a small amount of water on the surface of both membranes, they were stacked like a sandwich and hot-pressed (AP2047, Fujian Auplex Appliance Co., Ltd. Fujian, China, 60 °C, 15 MPa) to form a morphologically composite cellulose membrane.

The samples were placed in a muffle furnace and heated from room temperature to 150, 175, 200, 225, and 250 °C for 1.0 h at a heating rate of 10 °C/min, after which they were naturally cooled.

Characterization

Water droplets (5 μL) were added to the surface of samples, and after the drops were relatively stable (3-5 s), static contact angle detection was performed using a contact angle goniometer (JC2000D, Shanghai Zhongchen Power Technology Co., Ltd., Shanghai, China). Tensile strength tests were conducted using an electronic tensile testing machine (WH-5000, Ningbo Weiheng Testing Instrument Co., Ltd., Ningbo, China) equipped with a 5 kN/100 N load cell.

RESULTS AND DISCUSSION

The cellulose films of camphor pine and walnut wood prepared by the top-down strategy retained the original structure of the wood, faded the wood color, and changed the color to light yellow or white (shown in Figs. 1A and 1B). In contrast, the loofah cellulose films prepared under the same conditions were too porous, so microporous films were formed by partial pulping and then laminated with macroporous films (shown in Fig. 1C) and then hot-pressed to form cellulose films with a sandwich structure (shown in Fig. 1C), as mentioned in Preparation of Samples.
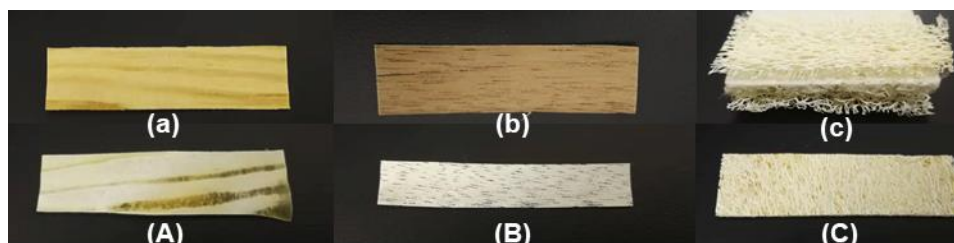
Fig. 1. Cellulose films prepared by a top-down strategy: Camphor pine cellulose films before (a) and after (A) delignification; walnut cellulose films before (b) and after (B) delignification; loofah cellulose films before (c) and after (C) hot pressed

The effect of temperature on cellulose membranes from various cellulose sources prepared by top-down methods was generally similar, while exhibiting subtle differences (Fig. 2). Overall, the color of the cellulose membranes gradually changed from pale yellow to black with increasing temperature, but there were differences in the pace of the transformation. The cellulose membrane made of camphor pine changed most rapidly, while the membrane made of loofah changed most sluggishly. Specifically, the color of the camphor pine cellulose membrane after heat treatment at 150 °C was similar to that of the walnut cellulose membrane after heat treatment at 175 °C and the loofah cellulose

membrane after heat treatment at 200 °C. When the heat treatment temperature was 250 °C, all three cellulose membranes showed a certain degree of wrinkling, while becoming fragile and showing burn marks at individual locations, so the subsequent experiments excluded the samples heat treated at 250 °C and focused on the characteristics of the 150 °C and 225 °C treated samples.
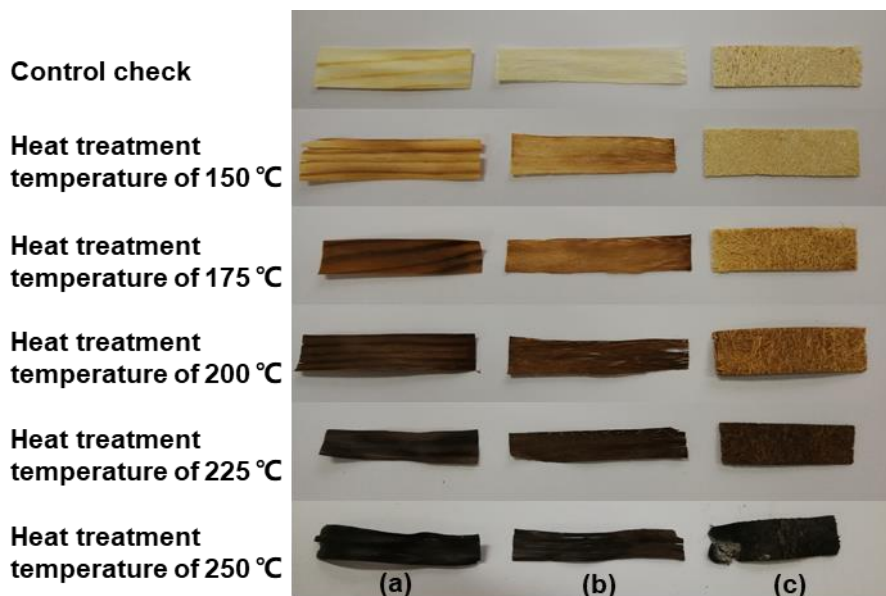
Fig. 2. Effect of heat treatment on the appearance of cellulose membrane of (a) camphor pine wood, (b) walnut wood, and (c) loofah

The hydrophilic property of cellulose made the cellulose membranes unstable when they were placed in an aqueous environment. Changing the surface wettability of cellulose membranes can affect their water stability. The samples heat-treated at different temperatures were placed in an aqueous environment for water stability testing (shown in Fig. 3). The control group without heat treatment rapidly took up water after its placement, and obvious changes could already be seen around 1.0 min. The cellulose membrane of camphor pine and walnut became transparent in the course of water absorption, while the cellulose membrane of loofah treated by hot pressing swelled and deformed, and it completely lost dimensional stability. After 12 h of impregnation in water, the cellulose membrane of camphor pine and walnut fractured and lost dimensional stability.

The water stability of the cellulose membranes increased considerably with the temperature of the heat treatment, and after 12 h of impregnation in water, the heat-treated camphor pine cellulose membrane maintained its dimensional stability. The heat-treated walnut cellulose membrane maintained its basic form except for the sample at 175 °C, while the loofah cellulose membranes maintained their basic form only when the heat treatment temperature was higher than 200 °C. The water stability of the samples was measured by measuring (three times at different positions of the film) the thickness of the samples before impregnation and after drying. As shown in Fig. 4a, the rate of thickness change showed that the loofah cellulose films tended to swell, while the camphor and walnut cellulose films tended to shrink, and the thickness change of the former was about five times that of the latter.
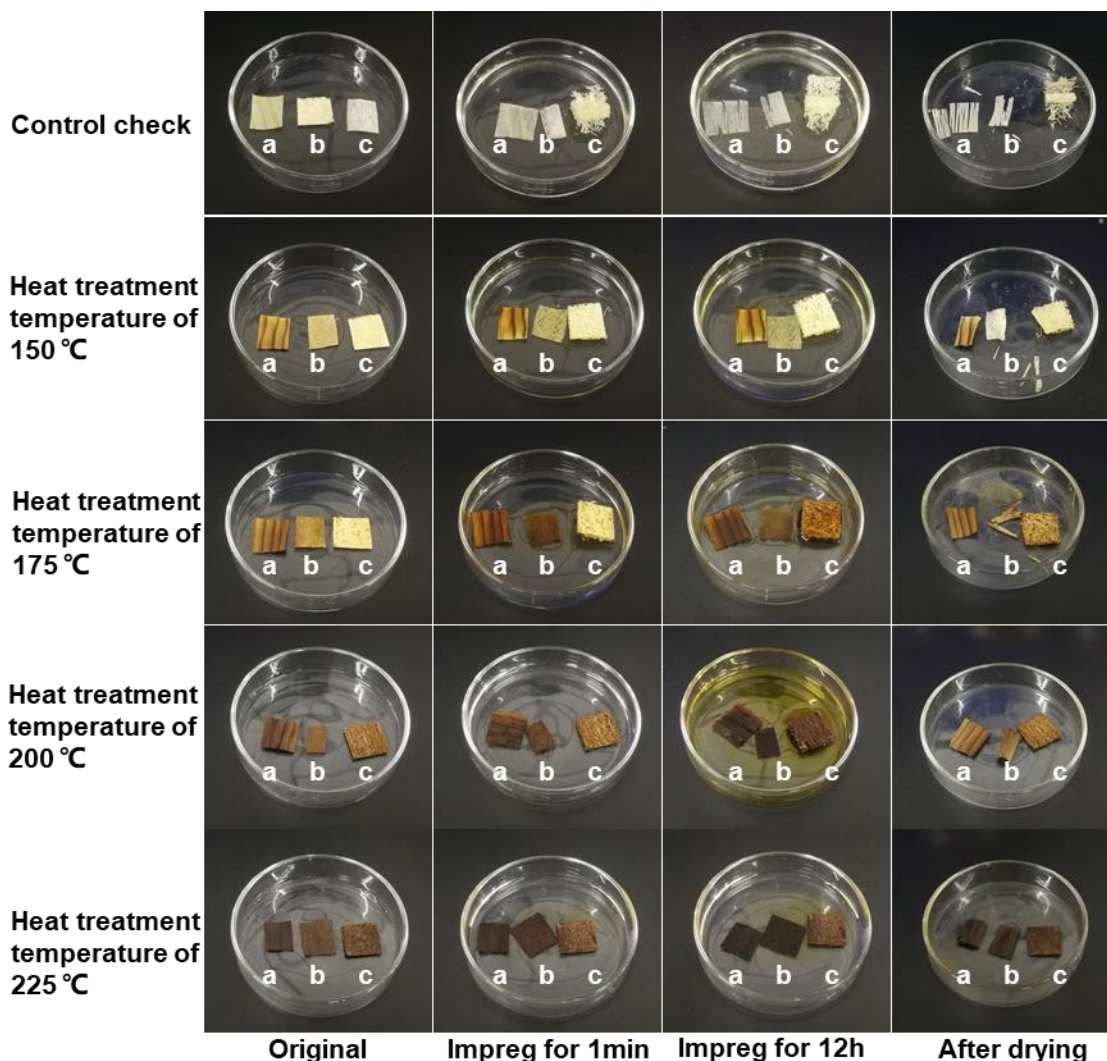
Fig. 3. Water stability test of camphor pine cellulose membrane (a), walnut cellulose membrane (b), and loofah cellulose membrane (c)

The tendency of loofah cellulose films to absorb water to recover their original shape after the hot-pressing process disappeared after the heat treatment temperature was higher than 200 °C, and the water stability of loofah cellulose films increased accordingly. Camphor cellulose film was better at low heat treatment temperature, while walnut film was better at heat treatment temperature higher than 200 °C.

Heat treatment changed the wettability of the cellulose membrane surface, and the cellulose membrane gradually changed from hydrophilic to hydrophobic with increasing heat treatment temperature (shown in Fig. 4b). The water stability on the surface of the walnut cellulose membrane was best at the heat treatment temperature of 225 °C, with the highest water contact angle. It was lowest at 175 °C, which was consistent with the maximum thickness change and breakage of the samples after 12 h of impregnation at this heat treatment temperature. Contrastingly, the camphor pine cellulose membrane had the highest surface contact angle and the best water stability at 150 °C. The loofah cellulose membranes showed similar trends in surface water contact angle to that of camphor pine, but exhibited different patterns of thickness variation and water stability. To investigate the reason for this, the pattern of surface contact angle variation with heat treatment

temperature of the internal plasma membrane of loofah was added. Figure 3b shows that the contact angle of loofah cellulose plasma membrane surface increased with heat treatment temperature and was higher than 90° at heat treatment temperature above 200 °C. Balancing the surface and internal wettability of the loofah cellulose membrane, 200 °C is a better heat treatment temperature, which was consistent with the better water stability of the loofah cellulose membrane after the heat treatment temperature higher than 200 °C.
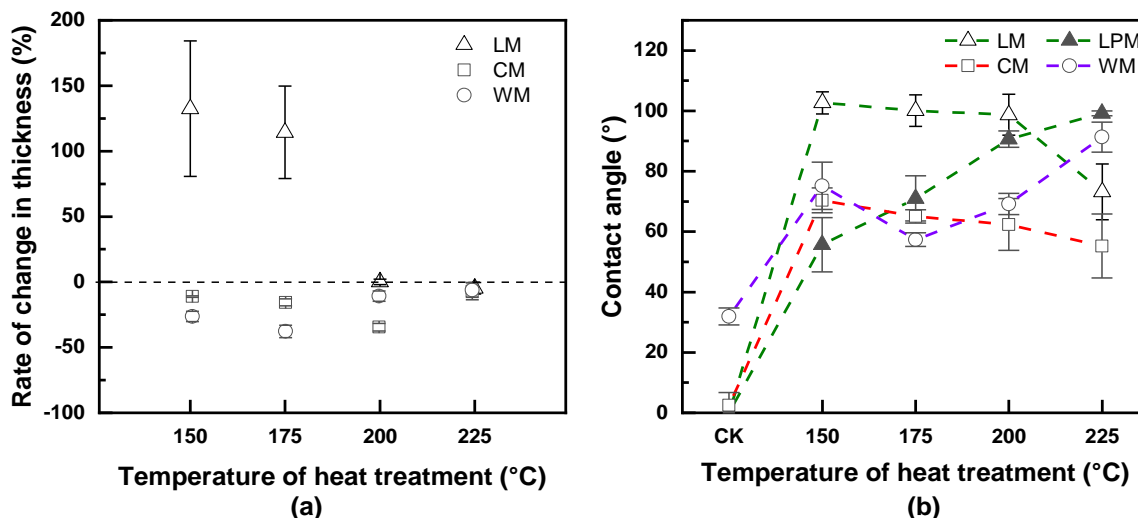
Fig. 4. Rate of change in thickness (a) and contact angle (b) with heat treatment temperature of loofah cellulose membrane (LM), loofah fiber pulp membrane (LPM), camphor pine cellulose membrane (CM), and walnut cellulose membrane (WM)

In the heat treatment range of 150 to 250 °C, fats and waxes moved to the surface first and were no longer detected on the surface when the temperature was greater than 180 °C; resin acids disappeared when the temperature was greater than 200 °C (Nuopponen *et al*. 2003). However, none of the hydrophobicity of the samples at 225 °C in the experiment was lost, so the migration of hydrophobic substances such as fats and waxes was not a major factor in the increase of hydrophobicity caused by heat treatment. In contrast, the degradation of hemicellulose starts below 180 °C, where the deacetylation reaction occurs first, producing formic acid and acetic acid, among others (Sundqvist *et al*. 2006). Due to the presence of acid, the degradation products of carbohydrates may produce lignin-like substances (Zaman *et al*. 2000). When the temperature exceeds 200 °C, inter- and intra-molecular dehydration reactions start to occur in the amorphous region of cellulose (Scheirs *et al*. 2001). The hydroxyl groups in the cellulose molecular chain are reduced. Thus, the decomposition of residual hemicellulose and the reduction of hydroxyl groups on the cellulose molecular chains are the main factors for the increase of hydrophobicity due to heat treatment.

CONCLUSIONS

1. The loofah cellulose films tended to swell, while the camphor and walnut cellulose films tended to shrink upon placement in water, and the thickness change of the former was approximately five times that of the latter.

2. Due to the non-homogeneous structure of the loofah cellulose membrane, its water stability is influenced by both surface and internal wettability, and 200 °C is an effective heat treatment temperature for this film.

3. The wettability of camphor pine and walnut cellulose membrane surfaces echoes water stability, and the heat treatment temperature of 150 °C for cellulose membrane of camphor pine and the temperature of 225 °C for cellulose membrane of walnut was more effective.

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REFERENCES CITED

An, B. W., Heo, S., Ji, S., Bien, F., and Park, J.-U. (2018). "Transparent and flexible fingerprint sensor array with multiplexed detection of tactile pressure and skin temperature," *Nature Communications* 9(1), Article Number 2458. DOI: 10.1038/s41467-018-04906-1

Cui, P., Parida, K., Lin, M.-F., Xiong, J., Cai, G., and Lee, P. S. (2017). "Transparent, flexible cellulose nanofibril–phosphorene hybrid paper as triboelectric nanogenerator," *Advanced Materials Interfaces* 4(22), article ID 1700651. DOI: 10.1002/admi.201700651

Fu, Q., Ansari, F., Zhou, Q., and Berglund, L. A. (2018). "Wood nanotechnology for strong, mesoporous, and hydrophobic biocomposites for selective separation of oil/water mixtures," *ACS Nano* 12(3), 2222-2230. DOI: 10.1021/acsnano.8b00005

Gao, S., Dong, X., Huang, J., Li, S., Li, Y., Chen, Z., and Lai, Y. (2018). "Rational construction of highly transparent superhydrophobic coatings based on a non-particle, fluorine-free and water-rich system for versatile oil-water separation," *Chemical Engineering Journal* 333, 621-629. DOI: 10.1016/j.cej.2017.10.006

Klemm, D., Heublein, B., Fink, H.-P., and Bohn, A. (2005). "Cellulose: Fascinating biopolymer and sustainable raw material," *Angewandte Chemie International Edition* 44(22), 3358-3393. DOI: 10.1002/anie.200460587

Li, T., Liu, H., Zhao, X., Chen, G., Dai, J., Pastel, G., Jia, C., Chen, C., Hitz, E., Siddhartha, D., Yang, R., and Hu, L. (2018). "Scalable and highly efficient mesoporous wood-based solar steam generation device: Localized heat, rapid water transport," *Advanced Functional Materials* 28(16), article ID 1707134. DOI: 10.1002/adfm.201707134

Li, T., Chen, C., Brozena, A. H., Zhu, J. Y., Xu, L., Driemeier, C., Dai, J., Rojas, O. J., Isogai, A., Wågberg, L., *et al.* (2021a). "Developing fibrillated cellulose as a sustainable technological material," *Nature* 590(7844), 47-56. DOI: 10.1038/s41586-020-03167-7

Li, Z., Chen, C., Xie, H., Yao, Y., Zhang, X., Brozena, A., Li, J., Ding, Y., Zhao, X., Hong, M., *et al.* (2021b). "Sustainable high-strength macrofibres extracted from natural bamboo," *Nature Sustainability* 5, 235-244. DOI: 10.1038/s41893-021-00831-2

Liu, K., Du, H., Zheng, T., Liu, H., Zhang, M., Zhang, R., Li, H., Xie, H., Zhang, X., Ma, M., *et al.* (2021). "Recent advances in cellulose and its derivatives for oilfield applications," *Carbohydrate Polymers* 259, article ID 117740. DOI: 10.1016/j.carbpol.2021.117740

Luo, J., Wang, Z., Xu, L., Wang, A. C., Han, K., Jiang, T., Lai, Q., Bai, Y., Tang, W., Fan, F. R., *et al.* (2019). "Flexible and durable wood-based triboelectric nanogenerators for self-powered sensing in athletic big data analytics," *Nature Communications* 10(1), article no. 5147. DOI: 10.1038/s41467-019-13166-6

Martins, R., Ferreira, I., and Fortunato, E. (2011). "Electronics with and on paper," *Physica Status Solidi (RRL) – Rapid Research Letters* 5(9), 332-335. DOI: 10.1002/pssr.201105247

Nechyporchuk, O., Håkansson, K. M. O., Gowda.V, K., Lundell, F., Hagström, B., and Köhnke, T. (2019). "Continuous assembly of cellulose nanofibrils and nanocrystals into strong macrofibers through microfluidic spinning," *Advanced Materials Technologies* 4(2), article ID 1800557. DOI: 10.1002/admt.201800557

Nuopponen, M., Vuorinen, T., Jämsä, S., and Viitaniemi, P. (2003). "The effects of a heat treatment on the behaviour of extractives in softwood studied by FTIR spectroscopic methods," *Wood Science and Technology* 37(2), 109-115. DOI: 10.1007/s00226-003-0178-4

Peng, Q., Cheng, J., Lu, S., and Li, Y. (2020). "Electrospun hyperbranched polylactic acid–modified cellulose nanocrystals/polylactic acid for shape memory membranes with high mechanical properties," *Polymers for Advanced Technologies* 31(1), 15-24. DOI: 10.1002/pat.4743

Rana, A. K., Frollini, E., and Thakur, V. K. (2021). "Cellulose nanocrystals: Pretreatments, preparation strategies, and surface functionalization," *International Journal of Biological Macromolecules* 182, 1554-1581. DOI: 10.1016/j.ijbiomac.2021.05.119

Russo, A., Ahn, B. Y., Adams, J. J., Duoss, E. B., Bernhard, J. T., and Lewis, J. A. (2011). "Pen-on-paper flexible electronics," *Advanced Materials* 23(30), 3426-3430. DOI: 10.1002/adma.201101328

Scheirs, J., Camino, G., and Tumiatti, W. (2001). "Overview of water evolution during the thermal degradation of cellulose," *European Polymer Journal* 37(5), 933-942. DOI: 10.1016/S0014-3057(00)00211-1

Sharma, A., Thakur, M., Bhattacharya, M., Mandal, T., and Goswami, S. (2019). "Commercial application of cellulose nano-composites – A review," *Biotechnology Reports* 21, e00316. DOI: 10.1016/j.btre.2019.e00316

Sundqvist, B., Karlsson, O., and Westermark, U. (2006). "Determination of formic-acid and acetic acid concentrations formed during hydrothermal treatment of birch wood and its relation to colour, strength and hardness," *Wood Science and Technology* 40(7), 549. DOI: 10.1007/s00226-006-0071-z

Xing, T., Dong, C., Wang, X., Hu, X., Liu, C., and Lv, H. (2022). "Biodegradable, superhydrophobic walnut wood membrane for the separation of oil/water mixtures," *Frontiers of Chemical Science and Engineering* 16(9), 1377-1386. DOI: 10.1007/s11705-022-2157-z

Yuk, H., Lu, B., and Zhao, X. (2019). "Hydrogel bioelectronics," *Chemical Society Reviews* 48(6), 1642-1667. DOI: 10.1039/C8CS00595H

Zaman, A., Alén, R., and Kotilainen, R. (2000). "Thermal behavior of Scots pine (*Pinus sylvestris*) and silver birch (*Betula pendula*) at 200-230°," *Wood and Fiber Science* 32(2), 138-143.

Zhang, X.-F., Ma, X., Hou, T., Guo, K., Yin, J., Wang, Z., Shu, L., He, M., and Yao, J. (2019). "Inorganic salts induce thermally reversible and anti-freezing cellulose hydrogels," *Angewandte Chemie International Edition* 58(22), 7366-7370. DOI: 10.1002/anie.201902578

Zhu, M., Li, Y., Chen, G., Jiang, F., Yang, Z., Luo, X., Wang, Y., Lacey, S. D., Dai, J., Wang, C., *et al.* (2017). "Tree-inspired design for high-efficiency water extraction," *Advanced Materials* 29(44), article 1704107. DOI: 10.1002/adma.201704107