Effects of cellulose nanofiber on the thermal, mechanical, and optical properties of triacetate cellulose nanocomposites

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Abstract. In this study, well-dispersed nanocomposite films with triacetate cellulose (TAC) as a matrix and reinforced with lemon peel-cellulose nanofibers (lemon peel-CNF) were developed. The nanofibers in aqueous solution were solvent-exchanged to methanol by a series of centrifuging and re-dispersing steps. Afterward, using the solution casting method, the mixture of recycled TAC (rTAC) film and nanofibers prepared by stirring combined with ball milling technique to achieve full dispersed solution was coated onto glass to obtain a thin film. The dispersion effect of CNF in TAC was observed by transmission electron microscopy. The optical, mechanical, and thermal properties of the nanocomposite films were characterized experimentally. The results showed that with varying CNF content (1–7 wt%), the haze was slightly increased while the transmittance was not affected compared with that of rTAC film (92.7%). The addition of CNF increased the tensile strength by 60%, tensile strain by 150%, and yield strength by 50%. Creep compliance improved for all nanocomposites compared with rTAC film. CNF led to a significant reduction in the thermal expansion properties of rTAC film.

Keywords: nanocomposites, triacetate cellulose (TAC), cellulose nanofiber, mechanical properties

1. Introduction

Nanomaterials have numerous commercial and technological applications in chemical, biomedical, energy, electronics, and space industries. Present-day activity for manufacturing and use of nanomaterials is 49% in the United States, 30% in the European Union, and 21% in other parts of the world [1]. However, future technologies should be more concerned about the environment and harmonize with it, which is related to sustainability in future technologies [2]. Once nanomaterials are released into the environment via manufacturing, usage, or disposal, their transport is a critical factor in assessing their exposure and impact on public health and the ecosystem.

Therefore, understanding the fate of nanomaterials in the environment is critical [3–6]. Green materials can be made from natural products or synthetically produced, and often include recycled products. Green materials are sustainable materials, for example, cellulose, chitosan, starch, collagen, soy protein and casein. These raw materials are abundant and biodegradable and are used to make diverse products such as adhesives and cardboard. Nowadays, green composite materials with natural fibers as reinforcements have become a research hot topic. One important study is the all-cellulose nanocomposite materials, in which the matrix is cellulose that has been dissolved and then precipitated, while

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the reinforcement is undissolved or partially-dissolved cellulose [7–13].

Cellulose materials that can be prepared in nanosize have attracted attention as polymer reinforcement [14–16]. Cellulose nanofillers commonly referred to as nanocrystals, whiskers, nanowhiskers, microfibrillated cellulose, microfibril aggregates, or nanofibers [17–19], can be obtained from various sources such as wood fibers [20], cotton [21], potato tuber cells [22], soybean [23], wheat straw and soy hulls [24], hemp fiber [25], coconut husk fibers [26], pineapple leaf fibers [27], sisal [28], and grass [29, 30]. The use of cellulose nanofibers and their application in nanocomposite materials have gained increasing attention owing to their exceptional mechanical properties, large specific surface area, low coefficient of thermal expansion, high aspect ratio, environmental benefits, and low cost [7, 31]. Among cellulose sources, cellulose nanofibers from plants have recently been used because of their promising mechanical properties [7, 32], especially in maintaining the transparency of nanocomposites with fiber content as high as 70%, a low coefficient of thermal expansion (CTE), and mechanical strength five times that of engineered plastics [32]. While an optically-transparent composite has been obtained using nanofibers of electrospun nylon-4,6 with a fiber content of 3.9%, obtaining high fiber volume composites without losing transparency remains difficult to achieve [33].

TAC films have been used as protective films for the polarizing plate of liquid crystal display (LCD). In general, an LCD monitor needs two polarizers, and each polarizer needs two TAC films to sandwich polyvinyl alcohol (PVA) film. In order to polarize light, the PVA film has to be stretched during manufacture. Thus, TAC film is used as a protective film to prevent the shrinkage of PVA film. With the expected further growth of the LCD market, recycle and reuse of TAC waste films become an important issue [34]. In our previous works, TAC membranes were prepared by electrospinning technique for applications in photocatalytic activity [35] and oil-water separation [36]. Ribeiro *et al.* [37] prepared transparent TAC films in combination with plasticizers for use as photographic film support and as protective films on polarizer plates in LCDs. In view of the increasing environmental temperature and performance requirements of LCDs, the protection of TAC films for PVA needs to be improved. Therefore, it is necessary

to enhance the mechanical properties, dimensional stability, and thermomechanical stability of TAC films. To address these issues, we reinforced TAC films with cellulose nanofibers from plants owing to their excellent mechanical properties and environment-friendliness. However, there are few studies on cellulose nanofiber (CNF)/TAC nanocomposites. Therefore, in this study, we develop a new material using recycled industrial TAC film waste (rTAC) as a matrix and CNF extracted from plant residue (sudachi peel) as reinforcement.

Sudachi is a variety of citrus fruit whose juice is mostly used in food flavoring. The residue after juice extraction consists of the outermost layer epicarp and middle layer mesocarp, forming what is known as peel, and some remaining empty juice vesicles from the endocarp. A significant portion of the residue is composed of parenchyma tissue. The cells of parenchyma have very thin cell walls with a primary layer, lacking the lignified secondary layers typical of wood fibers [38]. These walls are made up of CNF embedded in matrix substances and can be thought as bag-like cells intended to store juice instead of giving support to plants as in the case of fibers. The strength and stiffness of parenchyma are significantly lower if compared to other plant materials, and consequently, the nanofibers are comparatively easier to extract. For this study, sudachi peel was chosen over wood pulp fiber as the source of CNF.

The purpose of this study is to improve the thermal and mechanical properties of existing TAC films and maintain high transmittance. This high-performance CNF/TAC film can be reapplied to the protective films of a polarizer. The Dichloromethane solvent system and solvent casting method used in the existing TAC production lines were used to prepare CNF/rTAC films to facilitate direct integration with production lines in the future.

2. Experiment

2.1. Materials

TAC is a kind of polymer made from natural cellulose after acetylation. TAC film is produced by combining 85% cellulose triacetate (CTA) with 15% triphenyl phosphate (plasticizer). The TAC films (FNY, Fuji TD, Japan) used in this study have a thickness of 60 μm . Dichloromethane (King Chemical, 95%, TW) and methanol (Jingming Chemical, 99%, TW) were used as solvents.

2.2. Preparation of the cellulose nanofiber

2.2.1. Sudachi residue pulp preparation

Sudachi is a small, round, and green citrus fruit that is a specialty of Tokushima Prefecture in Japan. The raw material for the production of nanofibers consisted of sudachi residue with seeds removed, after juice extraction. A mixture of 1.5 l of distilled water, 10 g of sodium chlorite, and 2 ml of acetic acid was prepared, in which approximately 200 g of sudachi residue was immersed and stirred at 75 °C. The same amount of sodium chlorite and acetic acid were added to the mixture every 1 h of treatment. The total treatment time was 3 h to bleach the material completely. The fibers were then rinsed with running water until the pH became neutral through vacuum filtration. Fibers were dipped in 1.5 l of an aqueous solution containing 6 wt% potassium hydroxide (90 g of KOH in 1.5 l of distilled water) at 80 °C, and stirred for 2 h. After treatment, the fibers were washed with running water until the pH became neutral using vacuum filtration. The pulping treatment was performed with various batches of residue until 50 g (dry weight) of pulp fibers was obtained.

2.2.2. Fibrillation by grinding

An ultrafine friction grinder Supermasscolloider (MKCA6-2, Masuko Sangyo Co., Ltd., Japan) was used. The stator and rotor grindstone aperture were adjusted so that the stones slightly touched each other's surface when dry. A 1.25 wt% fiber in aqueous suspension (50 g of pulp fiber in 4 l of distilled water) was poured into the grinder, and as soon as the grindstone surfaces became wet, the aperture was further closed by 0.2 mm. Approximately 1 l of distilled water was added to the suspension during grinding to prevent drying of the grindstone aperture (heat generation due to friction). The final aqueous suspension after fibrillation was 5 l (1 wt% nanofiber content). Fibrillation was limited to only one pass through the grinder to avoid damaging the nanofibers (reduction in crystallinity and degree of polymerization).

2.3. Preparation of the CNF organogel by a solvent-exchange method

CNF organogel was prepared by aqueous dispersion using a solvent-exchange sol-gel process. Gelation was induced by adding acetone to the CNF dispersion at room temperature. Then, 30 ml of the aqueous cellulose nanofiber dispersion with

1 wt% concentration was placed in a 250 ml beaker. Solvents were used in the process, including acetone and methanol: 60 ml of acetone was gently poured into the beaker, stirred for 2 h, and centrifuged four times at 5000 rpm for 5 min. Because the TAC film was made by solution casting in dichloromethane and methanol, acetone-based nanofiber suspensions were exchanged again to 60 ml methanol by a series of centrifuging and re-dispersing steps. Then, the suspensions were allowed to evaporate by oven drying at 60 °C for 4 h until the CNF organogel was formed.

2.4. Preparation of cellulose nanofiber/triacetate cellulose film

TAC film was dissolved in dichloromethane and methanol to form (~15 wt%) TAC solution. CNF organogel was added to the reaction tank containing TAC solution, stirred, followed by ball milling two times with a ball diameter of 5 mm for 20 min at a rotating speed of 500 rpm to obtain a well-dispersed solution. According to the above steps, by adjusting the amount of CNF organogel added from 1 to 10 wt%, different parameters can be adjusted to change the solid content of CNF/TAC solution. The CNF/TAC solution was coated onto the glass by a solvent coating method. After drying at room temperature, CNF/rTAC films were obtained with a thickness of approximately 50±4 µm.

2.5. Characterization

A universal test machine (QC-508M2, Cometech, Taiwan) was used to perform tensile testing of the samples at room temperature according to ASTM D882. Rectangular specimens with a gauge length of 125 mm, a width of 10 mm, and a thickness of 0.05 mm were prepared for each tensile test; the cross-head speed was 12.5 mm/min. All reported tensile properties are the average values of at least five tests. A dynamic mechanical analyzer (DMA, Q-800, TA Instruments, USA) was used to investigate the relaxation events and the viscoelastic response (creep properties) of the CNF/rTAC films. A rectangular creep specimen with sample size 5.5×30 mm under tension mode was used. The analysis was performed at a preload force of 0.001 N, temperature range from room temperature to 60 °C, a heating rate of 5 °C/min, and recovery time of 30 min. The maximum strain was obtained from the creep area (maximum strain in the creep zone, γ_c) corresponding to the fixed amount of time (time-dependent recoverable strain, $\gamma_r(t)$).

Equation (1) can be used to calculate the equilibrium creep of the Δ sample (equilibrium recoverable compliance (J_{er})) as follows:

$$J_{er} = \frac{\gamma_c - \gamma_r(t)}{\sigma} \quad (1)$$

DMA was also used to measure the CTE of rectangular specimens with a size of 12.5×35.5 mm under three-point bending mode [39]. The analysis was performed at a preload force of 0.001 N, temperature range from room temperature to 160 °C, and heating rate of 5 °C/min to obtain the initial length (l_0), final length (l_1), corresponding initial temperature (T_0), and final temperature (T_1). Equation (2) can be used to calculate the CTEs of the sample α [mm/(mm·°C)] as follows:

$$\alpha = \frac{\Delta l}{\Delta T} = \frac{l_1 - l_0}{l_0(T_1 - T_0)} \quad (2)$$

The morphologies of the samples were analyzed using scanning electron microscopy (SEM, JSM-6390, Japan) at 20 samples were prepared on a glass slide and dried at 50 °C in vacuo. The dispersion of CNF in rTAC was examined through a multimode AFM system (Nanoview 1000, Utek material, Taiwan). The sample was first etched by atmosphere plasma (ATM-1X, AP plasma, Taiwan). A nitrogen gas flow in the working pressure of 0.05 MPa with the output power of 400 W for 120 s was used. AFM images were obtained using the phase mode in a sample box at room temperature to prevent impurities. The AFM system was equipped with a probe scanner and a standard silicon cantilever. The spring constant of the cantilever is 0.2 N/m. Real-time scanning was performed with scan rates of 1.01 Hz, scan angle 0°. The frequency and amplitude is 181.185 kHz and 0.312 V, respectively.

Regular light transmittance (% T) was measured at wavelengths from 200 to 1000 nm using a JASCO (V-670) UV-VIS-NIR spectrometer. The haze values (% H) were measured using TC-HIII DPK Automatic Haze Meter machine. These tests were carried out according to the ASTM D1003 specification, test piece size: 50×50 mm.

3. Results and discussion

3.1. Morphology of the CNF/rTAC nanocomposite film

The SEM images of CNFs extracted from lemon peel are shown in Figure 1a. These samples were

obtained by the solvent-exchange method from nanofibers suspended in acetone, methanol, and ultrasonication treatments. It can be observed that CNFs have an average diameter of 10–20 nm. The SEM image of the lemon peel-CNF showed well-individualized nanofibers.

The AFM images in Figure 1b–1e show the dispersion of CNF different content (1–7 wt%). The phase AFM image allows the unambiguous resolution of the different material phases. The morphologies of the CNF with typical diameters between 20 and 60 nm. These results show that well-dispersed CNF/rTAC films were successfully obtained by stirring and ball milling. The substrate and reinforcing material were completely covered with high compatibility, and no voids were generated between the interfaces.

3.2. Optical properties of the CNF/rTAC nanocomposite film

One of the advantages of TAC film is its outstanding optical transmittance. The impact of the addition of CNF to TAC film on optical properties is shown in Figure 2. The nanocomposites with lemon peel-CNF are still quite transparent when CNF increased from 0 to 7 wt%, with a transparency of more than 90%, while the haze slightly increased (0.2 to 0.6%). However, when CNF content reached 10 wt%, the haze increased by 1.6% while transparency decreased to 86.3% (Table 1). The reason is that the CNF started to aggregate and made the translucent films. This indicates that the presence of lemon peel-CNF (1–7 wt%) did not significantly reduce the high transparency of rTAC film. These results are attributed to the good dispersion of lemon peel-CNF in the TAC solution. Because the transmittance decreased significantly at 10 wt%, the other properties of nanocomposites were measured with CNF content ranging from 1 to 7 wt%.

3.3. Thermal properties of the CNF/rTAC nanocomposite film

Another important property of the nanocomposite film is its significantly low thermal expansion, which can improve dimensional stability. Figure 3 shows the clear tendency of increasing dimensional change values for all samples as temperature increased from 40 to 120 °C. Generally, the dimensional change curves of nanocomposite films decrease after adding CNF. The CTE of the rTAC film was measured to be $(4.00 \cdot 10^{-5}) \text{ K}^{-1}$ (Table 1). It was observed that the

CTE values of rTAC was significantly decreased by adding CNF. Comparison with the CTE of CNF/rTAC film at 7 wt% ($1.48 \cdot 10^{-5}$) K⁻¹ showed that the

cellulose nanofiber network acted as a reinforcement agent and reduced the thermal expansion of rTAC film by up to 2.5 times its original value. It is

Figure 1. SEM image of CNF (a) and AFM images of its CNF/rTAC nanocomposites 1% (b), 3% (c), 5% (d), 7% (e).

Figure 2. Light transmittance of rTAC and its CNF/rTAC nanocomposites.

Figure 3. CTE results of rTAC film and its CNF/rTAC nanocomposites.

Table 1. Transparency, haze and CTE results of rTAC and its CNF/rTAC nanocomposites.

CNF contents [wt%]	Transmittance [%]	Haze [%]	CTE [1/K]
0	92.7	0.2	$(4.0 \pm 1.5) \cdot 10^{-5}$
1	92.3	0.5	$(3.4 \pm 1.6) \cdot 10^{-5}$
3	91.6	0.6	$(2.3 \pm 1.9) \cdot 10^{-5}$
5	91.7	0.5	$(1.7 \pm 1.2) \cdot 10^{-5}$
7	91.2	0.5	$(1.5 \pm 1.8) \cdot 10^{-5}$
10	86.3	1.6	NA

believed that the induced thermal stresses are small enough to be almost completely constrained by the rigid cellulose nanofiber networks [40]. Furthermore, the expansion includes the volume increase of the actual atom and free volume. The strong interaction between CNF and TAC molecules may increase the constraint force to the TAC molecular structure, thus reducing the free volume increase.

3.4. Mechanical properties of the CNF/rTAC nanocomposite film

In this experiment, the effect of different CNF content (1–7 wt%) on the tensile properties of nanocomposite films was investigated. Figure 4 shows the stress-strain curves of the nanocomposites prepared in this study. When the amount of CNF added increased to 5 wt%, the mechanical tensile properties of the film were apparent as a whole. The test results are shown in Table 2. The tensile strain of unreinforced rTAC film was 1.83%; however, when 1 wt% CNF was added, its strain increased to 2.81%. When the amount of added CNF reached 5 wt%, the tensile strength increased by 60%; the yield strength increase by 50%; and tensile modulus increased slightly by 10%. These can be explained by the optical and TEM results for good dispersion. When the amount of added CNF reached 7 wt%, the tensile strength and tensile strain began to decrease. This can be attributed to the CNF started to aggregate. This experiment proves that lemon peel-CNF can effectively improve the mechanical properties of rTAC film; it made the rTAC film tougher and stronger (Figure 4).

Table 2. Tensile properties of rTAC and its CNF/rTAC nanocomposites.

CNF contents [wt%]	Strain [%]	Strength [MPa]	Modulus [GPa]	Yield strength [MPa]
0	1.8 ± 0.2	44.1 ± 4.3	2.9 ± 0.3	40.2 ± 3.5
1	2.8 ± 0.7	42.2 ± 12.0	3.0 ± 0.3	46.9 ± 13.0
3	3.3 ± 1.0	49.9 ± 10.0	3.1 ± 0.3	47.5 ± 9.3
5	4.6 ± 0.9	61.8 ± 5.8	3.2 ± 0.3	51.8 ± 4.4
7	4.4 ± 1.4	58.1 ± 7.3	3.1 ± 0.4	50.0 ± 7.0

Figure 4. Stress-Strain curves of rTAC and its CNF/rTAC nanocomposites.

The critical addition amount of CNFs was 7 wt%. If more than 7 wt% was added, the CNF started to aggregate, which led to a decrease in tensile properties. Furthermore, the results demonstrated that brittle resin material became ductile by reinforcement with cellulose nanofiber networks, which reveals how the nanofiber network suppressed crack propagation in the matrix resin.

3.5. Dynamic thermal mechanical properties of the CNF/rTAC nanocomposite film

The temperature dependence of storage modulus (E'), loss modulus (E'') and loss tangent ($\tan \delta$) of CNF/rTAC films are shown in Figure 5. The E' increased with the increase of CNF content and reached a maximum at 5 wt%, and then its E' value decreased slightly at 7 wt%. This result is consistent with the aforementioned tensile properties. It is worth noting that E' drops sharply around 103 °C. This transition temperature can be assigned as the β -relaxation and attribute it to the local side-chain movement of the TAC molecules (short-range movement of polymer chains). The $\tan \delta$ peak as shown in Figure 5b, related to the glass transition of the matrix. The T_g shifted to higher temperatures with increasing CNF content from 175.4 °C (0 wt%) to 181.4 °C (7 wt%).

Other important properties of nanocomposite films include dynamic thermomechanical properties (creep behavior), which control dimensional stability, especially in applications where the material has to support loads for long periods of time. Figure 6 shows the strain curve of the rTAC film and its nanocomposite films as a function of time. The creep strain of rTAC film decreased with the addition of reinforcement materials. As shown in Table 3, the maximum strain value of rTAC film in the creep region is

Table 3. Creep properties of rTAC and its CNF/rTAC nanocomposites.

CNF contents [wt%]	Maximum strain value, γ_c [%]	Recoverable strain, γ_r [%]	Equilibrium recoverable compliance, Jer [m^2/N]
0	12.49	8.58	$9.78 \cdot 10^{-9}$
1	10.85	7.30	$8.88 \cdot 10^{-9}$
3	8.47	5.31	$7.90 \cdot 10^{-9}$
5	6.97	4.32	$6.38 \cdot 10^{-9}$
7	8.32	5.04	$8.20 \cdot 10^{-9}$

12.49%, the maximum strain value of the films after reinforcement by 1 wt% CNF was 10.85%. When the amount of CNF reached 5 wt%, the balance creep (Jer) values of the lemon peel-CNF reinforced films was $6.38 \cdot 10^{-9}$, compared with that of rTAC at $9.78 \cdot 10^{-9}$. Since rTAC film is a low crystalline polymer, the motion unit can freely slide in the active space. When the rTAC film was subjected to stress at 60 °C, the mobility of the molecular chain increased, which increased the distance between the component chains and the relaxation process; hence,

Figure 6. Creep behavior of rTAC and its CNF/rTAC nanocomposites.

Figure 5. DMA results of rTAC and its CNF/rTAC nanocomposites, (a) storage modulus, (b) $\tan \delta$.

the creep compliance is significantly higher. Conversely, adding CNF into the TAC solution resulted in lower equilibrium creep compliance, and the stress causes less distortion. This is because the presence of nanofibers limited the free-slip deformation of TAC molecular chains. Both intermolecular and molecular chains were entangled to increase the frictional resistance of molecular chain motion. Based on this good interface, the stress of the film can be completely transferred to the reinforcement materials to limit creep behavior.

4. Conclusions

The lemon peel-CNF in aqueous solution was solvent-exchanged successfully to methanol by a series of centrifuging and re-dispersing steps. The successful fabrication of TAC films reinforced with CNF with excellent transparency was achieved by stirring combined with a ball milling technique to obtain a fully-dispersed solution. Compared with rTAC film, the nanocomposites reinforced with CNFs had significantly improved mechanical and thermal properties and maintained their optical properties. CNFs from lemon peel exhibit very promising characteristics as reinforcement material for optically-functional composites. Moreover, the nanofiber network led to remarkable reinforcement of the resin substrate, producing composites with significantly higher mechanical strength and lower thermal expansion coefficients. Therefore, the optimal CNF content is 5 wt% to obtain nanocomposites with excellent thermal and mechanical properties.

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References

- [1] Aitken R. J., Chaudhry M. Q., Boxall A. B. A., Hull M.: Manufacture and use of nanomaterials: Current status in the UK and global trends. *Occupational Medicine*, **56**, 300–306 (2006).
<https://doi.org/10.1093/occmed/kql051>
- [2] Kim J-H., Shim B. S., Kim H. S., Lee Y-J., Min S-K., Jang D., Abas Z., Kim J.: Review of nanocellulose for sustainable future materials. *International Journal of Precision Engineering and Manufacturing-Green Technology*, **2**, 197–213 (2015).
<https://doi.org/10.1007/s40684-015-0024-9>
- [3] Biswas P., Wu C-Y.: Nanoparticles and the environment. *Journal of the Air and Waste Management Association*, **55**, 708–746 (2005).
<https://doi.org/10.1080/10473289.2005.10464656>
- [4] Colvin V. L.: The potential environmental impact of engineered nanomaterials. *Nature Biotechnology*, **21**, 1166–1170 (2003).
<https://doi.org/10.1038/nbt875>
- [5] U.S. Environmental Protection Agency: Nanotechnology white paper. Washington, 1–137 (2007).
https://www.epa.gov/sites/production/files/2015-01/documents/nanotechnology_whitepaper.pdf
- [6] Wiesner M. R., Lowry G. V., Alvarez P., Dionysiou D., Biswas P.: Assessing the risks of manufactured nanomaterials. *Environmental Science and Technology*, **40**, 4336–4345 (2006).
<https://doi.org/10.1021/es062726m>
- [7] Nishino T., Matsuda I., Hirao K.: All-cellulose composite. *Macromolecules*, **37**, 7683–7687 (2004).
<https://doi.org/10.1021/ma049300h>
- [8] Gindl W., Keckes J.: All-cellulose nanocomposite. *Polymer*, **46**, 10221–10225 (2005).
<https://doi.org/10.1016/j.polymer.2005.08.040>
- [9] Gindl W., Martinschitz K. J., Boesecke P., Keckes J.: Structural changes during tensile testing of an all-cellulose composite by in situ synchrotron X-ray diffraction. *Composites Science and Technology*, **66**, 2639–2647 (2006).
<https://doi.org/10.1016/j.compscitech.2006.03.020>
- [10] Gindl W., Schöberl T., Keckes J.: Structure and properties of a pulp fibre-reinforced composite with regenerated cellulose matrix. *Applied Physics A*, **83**, 19–22 (2006).
<https://doi.org/10.1007/s00339-005-3451-6>
- [11] Nishino T., Arimoto N.: All-cellulose composite prepared by selective dissolving of fiber surface. *Biomacromolecules*, **8**, 2712–2716 (2007).
<https://doi.org/10.1021/bm0703416>
- [12] Duchemin J-C. B., Newman R. H., Staiger M. P.: Phase transformations in microcrystalline cellulose due to partial dissolution. *Cellulose*, **14**, 311–320 (2007).
<https://doi.org/10.1007/s10570-007-9121-4>
- [13] Soykeabkaew N., Arimoto N., Nishino T., Peijs T.: All-cellulose composites by surface selective dissolution of aligned ligno-cellulosic fibres. *Composites Science and Technology*, **68**, 2201–2207 (2008).
<https://doi.org/10.1016/j.compscitech.2008.03.023>
- [14] Dweib M. A., Hu B., O'Donnell A., Shenton H. W., Wool R. P.: All natural composite sandwich beams for structural applications. *Composite Structures*, **63**, 147–157 (2004).
[https://doi.org/10.1016/S0263-8223\(03\)00143-0](https://doi.org/10.1016/S0263-8223(03)00143-0)
- [15] Bhatnagar A., Sain M.: Processing of cellulose nanofiber-reinforced composites. *Journal of Reinforced Plastics and Composites*, **24**, 1259–1268 (2005).
<https://doi.org/10.1177/0731684405049864>

- [16] Yano H., Nakahara S.: Bio-composites produced from plant microfibril bundles with a nanometer unit web-like network. *Journal of Materials Science*, **39**, 1635–1638 (2004).
<https://doi.org/10.1023/B:JMSC.0000016162.43897.0a>
- [17] Azizi Samir M. A. S., Alloin F., Dufresne A.: Review of recent research into cellulosic whiskers, their properties and their application in nanocomposite field. *Biomacromolecules*, **6**, 612–626 (2005).
<https://doi.org/10.1021/bm0493685>
- [18] Eichhorn S. J., Dufresne A., Aranguren M., Marcovich N. E., Capadona J. R., Rowan S. J., Weder C., Thielemans W., Roman M., Renneckar S., Gindl W., Veigel S., Keckes J., Yano H., Abe K., Nogi M., Nakagaito A. N., Mangalam A., Simonsen J., Benight A. S., Bismarck A., Berglund L. A., Peijs T.: Current international research into cellulose nanofibres and nanocomposites. *Journal of Materials Science*, **45**, 1–33 (2010).
<https://doi.org/10.1007/s10853-009-3874-0>
- [19] Marins J. A., Soares B. G., Dahmouche K., Ribeiro S. J., Barud H., Bonemer D.: Structure and properties of conducting bacterial cellulose-polyaniline nanocomposites. *Cellulose*, **18**, 1285–1294 (2011).
<https://doi.org/10.1007/s10570-011-9565-4>
- [20] Abe K., Iwamoto S., Yano H.: Obtaining cellulose nanofibers with a uniform width of 15 nm from wood. *Biomacromolecules*, **8**, 3276–3278 (2007).
<https://doi.org/10.1021/bm700624p>
- [21] de Moraes Teixeira E., Corrêa A. C., Manzoli A., de Lima Leite F., de Oliveira C. R., Mattoso L. H. C.: Cellulose nanofibers from white and naturally colored cotton fibers. *Cellulose*, **17**, 595–606 (2010).
<https://doi.org/10.1007/s10570-010-9403-0>
- [22] Dufresne A., Dupeyre D., Vignon M. R.: Cellulose microfibrils from potato tuber cells: Processing and characterization of starch–cellulose microfibril composites. *Journal of Applied Polymer Science*, **76**, 2080–2092 (2000).
[https://doi.org/10.1002/\(SICI\)1097-4628\(20000628\)76:14<2080::AID-APP12>3.0.CO;2-U](https://doi.org/10.1002/(SICI)1097-4628(20000628)76:14<2080::AID-APP12>3.0.CO;2-U)
- [23] Wang B., Sain M.: Dispersion of soybean stock-based nanofiber in a plastic matrix. *Polymer International*, **56**, 538–546 (2007).
<https://doi.org/10.1002/pi.2167>
- [24] Alemdar A., Sain M.: Isolation and characterization of nanofibers from agricultural residues – Wheat straw and soy hulls. *Bioresource Technology*, **99**, 1664–1671 (2008).
<https://doi.org/10.1016/j.biortech.2007.04.029>
- [25] Wang B., Sain M., Oksman K.: Study of structural morphology of hemp fiber from the micro to the nanoscale. *Applied Composite Materials*, **14**, 89–103 (2007).
<https://doi.org/10.1007/s10443-006-9032-9>
- [26] Rosa M. F., Medeiros E. S., Malmonge J. A., Gregorski K. S., Wood D. F., Mattoso L. H. C., Glenn G., Orts W. J., Imam S. H.: Cellulose nanowhiskers from coconut husk fibers: Effect of preparation conditions on their thermal and morphological behavior. *Carbohydrate Polymers*, **81**, 83–92 (2010).
<https://doi.org/10.1016/j.carbpol.2010.01.059>
- [27] Cherian B. M., Leão A. L., de Souza S. F., Costa L. M. M., de Olyveira G. M., Kottaisamy M., Nagarajan E., Thomas S.: Cellulose nanocomposites with nanofibres isolated from pineapple leaf fibers for medical applications. *Carbohydrate Polymers*, **86**, 1790–1798 (2011).
<https://doi.org/10.1016/j.carbpol.2011.07.009>
- [28] Morán J. I., Alvarez V. A., Cyran V. P., Vázquez A.: Extraction of cellulose and preparation of nanocellulose from sisal fibers. *Cellulose*, **15**, 149–159 (2008).
<https://doi.org/10.1007/s10570-007-9145-9>
- [29] Nakagaito A. N., Ikenaga K., Takagi H.: Cellulose nanofiber extraction from grass by a modified kitchen blender. *Modern Physics Letters B*, **29**, 1540039/1–1540039/5 (2015).
<https://doi.org/10.1142/S0217984915400394>
- [30] Amiralian N., Annamalai P. K., Memmott P., Taran E., Schmidt S., Martin D. J.: Easily deconstructed, high aspect ratio cellulose nanofibres from *Triodia pungens*: An abundant grass of Australia's arid zone. *RSC Advances*, **5**, 32124–32132 (2015).
<https://doi.org/10.1039/C5RA02936H>
- [31] Orts W. J., Shey J., Imam S. H., Glenn G. M., Guttman M. E., Revol J.-F.: Application of cellulose microfibrils in polymer nanocomposites. *Journal of Polymers and the Environment*, **13**, 301–306 (2005).
<https://doi.org/10.1007/s10924-005-5514-3>
- [32] Yano H., Sugiyama J., Nakagaito A. N., Nogi M., Matsuura T., Hikita M., Handa K.: Optically transparent composites reinforced with networks of bacterial nanofibers. *Advanced Materials*, **17**, 153–155 (2005).
<https://doi.org/10.1002/adma.200400597>
- [33] Bergshoeff M. M., Vancso G. J.: Transparent nanocomposites with ultrathin, electrospun nylon-4,6 fiber reinforcement. *Advanced Materials*, **11**, 1362–1365 (1999).
[https://doi.org/10.1002/\(SICI\)1521-4095\(199911\)11:16<1362::AID-ADMA1362>3.0.CO;2-X](https://doi.org/10.1002/(SICI)1521-4095(199911)11:16<1362::AID-ADMA1362>3.0.CO;2-X)
- [34] Sata H., Murayama M., Shimamoto S.: 5.4 properties and applications of cellulose triacetate film. *Macromolecular Symposia*, **208**, 323–333 (2004).
<https://doi.org/10.1002/masy.200450413>
- [35] Wu C., Huang C., Yang X.: Fabrication and photocatalytic activity of porous recycled cellulose triacetate nanofibrous membranes embedded with TiO₂. in 'Proceeding of CAMX 2016 Conference, Anaheim, USA' 479–488 (2016).
- [36] Naseem S., Wu C.-M., Xu T.-Z., Lai C.-C., Rwei S.-P.: Oil-water separation of electrospun cellulose triacetate nanofiber membranes modified by electrophoretically deposited TiO₂/graphene oxide. *Polymers*, **10**, 746/1–746/14 (2018).
<https://doi.org/10.3390/polym10070746>

- [37] Ribeiro S. D., Filho R., Meneguim A. B., Prezotti F. G., Boni F. I., Cury B. S. F., Gremião M. P. D.: Cellulose triacetate films obtained from sugarcane bagasse: Evaluation as coating and mucoadhesive material for drug delivery systems. *Carbohydrate Polymers*, **152**, 764–774 (2016).
<https://doi.org/10.1016/j.carbpol.2016.07.069>
- [38] Gibson L. J.: The hierarchical structure and mechanics of plant materials. *Journal of the Royal Society Interface*, **9**, 2749–2766 (2012)
<https://doi.org/10.1098/rsif.2012.0341>
- [39] Deng S., Hou M., Liu X., Qi B., Ye L.: Determination of CTEs of cured epoxy and polyester (PET) stitching threads. *Journal of Composite Materials*, **45**, 2071–2081 (2011)
<https://doi.org/10.1177/0021998311401058>
- [40] Nogi M., Yano H.: Transparent nanocomposites based on cellulose produced by bacteria offer potential innovation in the electronics device industry. *Advanced Materials*, **20**, 1849–1852 (2008).
<https://doi.org/10.1002/adma.200702559>