

Optical characteristics of cellulose nanofiber film stored for 5 years

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Abstract

Cellulose nanofibers are used for coating in many applications. Its optical properties are an important parameter to maintain high performance. However, cellulose nanofibers degrade over time and the optical properties deteriorated. Currently, the study of degradation of cellulose nanofiber sheets due to aging is still limited especially for non-accelerated aging. In this study, the authors compared the properties of cellulose nanofibers before and after storage at room temperature for five years. Two types of cellulose sheets prepared from TEMPO-oxidized cellulose nanofibers (TOCNF) and aqueous counter collision cellulose nanofiber (ACC-CNF) were used. After five years, the TOCNF sheet showed a significant increase in yellowing index, a decrease in opacity, and relatively stable haze values. On the other hand, the ACC-CNF sheet exhibited only a slight increase in yellowing index, relatively stable opacity, but a decrease in haze values. This result indicates the difference mechanism between TOCNF and ACC-CNF during natural aging process.

Keywords: Aging, Aqueous counter collision CNF, TEMPO-oxidized CNF

Introduction

Recently, people have become more willing to live a sustainable life and the demand for green and sustainable materials has increased among consumers. Cellulose nanofibers are promising natural materials for coating applications. The cellulose nanofiber coating could provide more application for thermal and optical protection, lighting management so that reduced the energy of heater and cooling [1–3] and improving the efficiency of solar cell and organic light-emitting diode (OLED)[4]. As coating materials, the optical performance of cellulose nanofiber is an important parameter. Previous researches showed that cellulose nanofiber (TOCNF) film has 77-90% transparency for visible wavelength of 450–800 nm and low haze values ranging 4-80% [5–7]. These optical properties make TOCNFs attractive candidates for advanced optical and energy-saving applications. However, despite this remarkable potential application, cellulose nanofiber susceptible to degradation.

Cellulose fiber degradation affects the mechanical strength and the optical properties. Hydrogen ions in cellulose can initiate the self-degradation of cellulose, producing shorter polymer chains. Degradation also generates other chromophore molecules that induce yellowing and deteriorating the optical performances [8]. The functional groups of cellulose

played a significant role in aging. Previous study shows that if the carboxylate content in TOCNF was initially low, the carboxylate would not have changed after aging but if the carboxylate content was initially high, the carboxylate content would have increased acceleratively [9]. These findings suggest that the long-term optical stability of TOCNFs is closely related to their chemical structure.

To evaluate cellulose degradation within a practical timeframe, most previous studies have employed accelerated aging methods, particularly exposure to elevated temperatures, artificial sunlight, or UV irradiation [10, 11]. Such studies consistently reported significant discoloration and deterioration of optical properties after accelerated exposure. For example, UV irradiation was shown to increase the yellowness index of cellulose nanofiber films by up to 20 after only 24 h of exposure [11]. Although these accelerated-aging studies provide valuable insight into degradation mechanisms, they may not accurately represent the slow and cumulative changes occurring under normal indoor storage conditions.

Despite the growing interest in cellulose nanofibers for optical applications, studies on their natural aging behavior remain limited. Existing research has mainly focused on changes in mechanical strength, molecular weight, or degree of polymerization during long-term storage, while systematic investigations of appearance changes and optical-property degradation are still scarce. In particular, there is insufficient information regarding how optical performance of difference types of cellulose nanofiber evolves after several years under ambient conditions and how these changes compare with degradation observed under accelerated UV-aging conditions. This lack of knowledge hinders accurate lifetime estimation and reliability assessment for practical optical and coating applications.

Therefore, in this study, we investigate the long-term natural aging behavior of cellulose nanofiber with difference source and production sheets stored at room temperature for five years, with particular emphasis on changes in optical properties and appearance. The results are compared with trends reported in accelerated aging studies to clarify the differences between natural and artificial aging processes. This work provides important insight into the long-term stability of TOCNF-based optical materials and contributes to evaluating their suitability for sustainable optical coating applications.

Materials and Methods

Two types of cellulose nanofibers were used: TEMPO oxidized cellulose nanofiber (TOCNF, a carboxylate content of 1.3 mmol/g, Nippon Paper Industries Co., Ltd., Japan) and Aqueous Counter collision cellulose nanofiber (ACC-CNF, Chuetsu Pulp & Paper Co., Ltd.,

Japan). 10 grams of CNF suspension (1 wt%) were cast on the petri dish and dried at 65 C for 24 h. After drying, the cellulose nanofiber sheets were stored in plastic bags at room temperature for ~5 years (October 2019-November 2024), Surabaya city, Indonesia. The plastic bag was not sealed, and the samples were maintained to continuously contact the ambient environment. The temperature, humidity, oxygen exposure and light exposure were not controlled to simulate the real condition as close as possible. The zeta potential of TOCNF and ACC-CNF was -69.8 ± 2.85 mV and -33.5 ± 0.53 mV respectively.

Functional groups on the sheet surfaces were characterized by Fourier transform infrared (ATR method, Shimadzu IR Prestige 21, Japan). The thermal properties were characterized by Thermogravimetry Differential Thermal Analysis (TG-DTA, Seiko Instrument, EXSTAR 7300) under Argon gas at a flowrate of 200 mL/min and temperature increasing rate of 10°C/min. The crystallinity of the cellulose nanofiber sheets was measured using X-Ray Diffraction (XRD, Bruker AXS D8 ADVANCE/TSM) from 10 to 40° in 2θ diffraction angle with a wavelength of 1.5418 Å for CuKα for 5861 steps. The crystallinity was calculated based on the equation (1)

$$\%Crystallinity = \frac{Area\ under\ crystalline\ peak}{Area\ under\ all\ peak} \times 100\% \quad (1)$$

The thickness of sheet was measured with a micrometer (TW-21 Tozai Seiki Co., Ltd., Japan). Optical properties of the films were quantified using a UV–Vis–NIR spectrophotometer (Shimadzu UV-3600i Plus, Shimadzu, Japan) equipped with an integrating sphere accessory (Shimadzu MPC-603A). The integrating sphere configuration was used to improve accuracy for semi-transparent films, where forward scattering can bias conventional straight-through transmittance measurements. All optical measurements were conducted in triplicate. For each measurement, the film was mounted flat at the integrating sphere sample port, and baseline correction was performed according to the instrument's standard procedure prior to sample scanning.

Haze (%) was determined at 550 nm using the integrating sphere by separating total transmitted light from the diffusely transmitted component. Haze was calculated as the ratio of diffuse transmittance to total transmittance, expressed as a percentage:

$$Haze(\%) = \left(\frac{T_{diffuse}}{T_{total}} \right) \quad (2)$$

where T_{total} is the total transmittance collected by the sphere and $T_{diffuse}$ is the diffusely transmitted component (i.e., transmitted light excluding the specular contribution). The opacity (thickness-normalized, T_{600}) was calculated from transmittance at 600 nm. These thickness-

normalized indices were used to evaluate visible-range attenuation performance independent of minor variations in film thickness. All optical results are reported as mean $\pm$ standard deviation (SD) from triplicate measurements [12].

The color of the sheets was measured and expressed in CIELAB color parameters with a spectrophotometer for paper (PF 7000, Nippon Denshoku, Japan). The total color difference between the standard white and the sample was calculated by following equation (3)

$$\Delta E = \sqrt{[(L^* - L_{std}^*)^2 + (a^* - a_{std}^*)^2 + (b^* - b_{std}^*)^2]} \quad (3)$$

and between 5 years to 0 years was calculated by following equation (4)

$$\Delta E = \sqrt{[(L_5^* - L_0^*)^2 + (a_5^* - a_0^*)^2 + (b_5^* - b_0^*)^2]} \quad (4)$$

where ΔE , L^* , a^* , b^* are color difference, lightness, red-green values, blue-yellow values, respectively. The *std* and refer to standard white, 0 year and 5 years respectively. The yellowing index was calculated by following equation (5)

$$YI = 142.86b^*/L^* \quad (5)$$

where YI is the yellowing index [13]. The CIELAB color parameters then converted to RGB color parameters using online converter <https://colordesigner.io/> to replicate the color electronically. The zerospan strength (Pulmac, Troubleshooter TSB-1) was used to measure fiber strength.

Results and Discussion

Figure 1 shows the FTIR spectra of cellulose nanofiber. A broad peak at around 3000 cm^{-1} to 3700 cm^{-1} corresponds to stretching of water molecules and hydroxyl groups of cellulose[14]. All ACC-CNF shows a peak at 2900 cm^{-1} corresponding to $-\text{CH}_2$ [15], meanwhile TOCNF shows a broad $-\text{CH}_2$ peak. This is due to the shift of C6 from $-\text{CH}_2\text{-OH}$ to $-\text{COOH}$. TOCNF has a peak at 1588 cm^{-1} corresponding to $-\text{COO}-$ of its carboxylate group. After 5 years storage, the ACC-CNF (ACC-CNF 5Y) slightly shows a $-\text{COO}-$ peak indicating that the oxidation of hydroxyl groups. The peak at 1650 cm^{-1} corresponds to adsorbed water [15–17]. The peak at 1443 cm^{-1} corresponds to the C-H symmetric bending vibration. Those at 1035 and 1080 cm^{-1} correspond to C-O-C and C-O stretching of C1 and C5 [18] and peak at 1175 cm^{-1} correspond to C–O–C asymmetric stretching vibration at β -glucosidic linkage (C1 and C4) [15]. The peak at 896 cm^{-1} corresponds to C-C of glucopyranose ring [14, 19]. After 5 years passed, ACC-CNF shows a sharper peak at 1000-1200 cm^{-1} . However, the TOCNF had

almost no tendency of a functional group change. The peak at 1190–1139 cm^{-1} is affected by water adsorption[15]. Therefore, during storage, ACC-CNF might have absorbed water vapor from the atmosphere and stored the water molecules as primary water. Accelerated aging showed high concentrations of single ketone oxidation on C2 meanwhile naturally aging showed high concentrations of aldehyde on C6 [20]. Open air thermal treatment which the sample has a direct contact to open air and humidity but minimum contact to the generated gases during degradation produced higher CCO and CHO. Closed air thermal treatment which the sample has limited contact to open air but direct contact to controlled humidity and generated gases produced higher ketone on C2 [20]. Dry thermal accelerated aging promotes the desorption of water content which the intensity of -OH group becomes less intense[21]. The difference between accelerated aging methods signifies the importance of natural aging study.

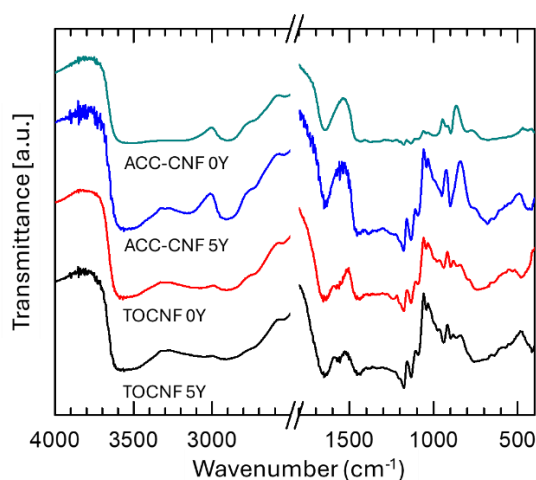


Figure 1. FTIR spectra of cellulose nanofiber sheets before and after aging.

The crystal structure and crystallinity of cellulose nanofiber sheet was subjected to XRD as shown in Figure 2. Cellulose I has 2θ peaks at 14.5° , 16.5° , and 22.5° corresponding to the $(1\ \bar{1}\ 0)$, $(1\ 1\ 0)$, and $(2\ 0\ 0)$ planes, respectively [22]. The peak of TOCNF and ACC-CNF at 14.5° and 16.5° are overlapping due to the peak broadening of small crystal of cellulose nanofiber [23, 24]. No change of crystal structure of TOCNF and ACC-CNF after 5 years however, the crystallinity increases after 5 years from 23.13% to 25.09% for TOCNF and from 20.75% to 23.39% for ACC-CNF because during degradation, the amorphous phase is more easily degraded. Accelerated aging of cellulose by dry heat treatment of cellulose from cotton, paper and viscous shown a little effect to the degree of crystallinity due to the aging did not proceed enough[25]. Furthermore, accelerated aging by dry heat treatment of cellulose from historical paper showed an increase in crystallinity due to the degradation of amorphous part

of cellulose. However, further aging make the crystalline area degraded thus decreasing the crystallinity[21].

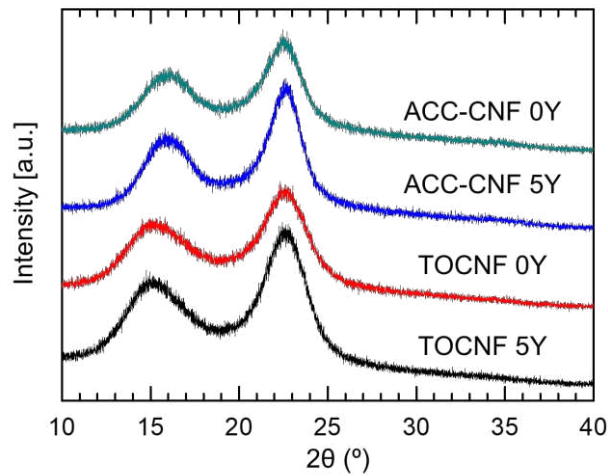


Figure 2. XRD spectra of cellulose nanofiber sheets before and after aging

Previous research showed that the degradation of cellulose, chromophores formation, crystallinity of cellulose nanofiber, and roughness and fiber size affect the light transmission and higher fiber diameter tends to create a hazy appearance because of light scattering [26, 27]. It was reported that ACC-CNF has a higher roughness because of higher fiber diameter [28].

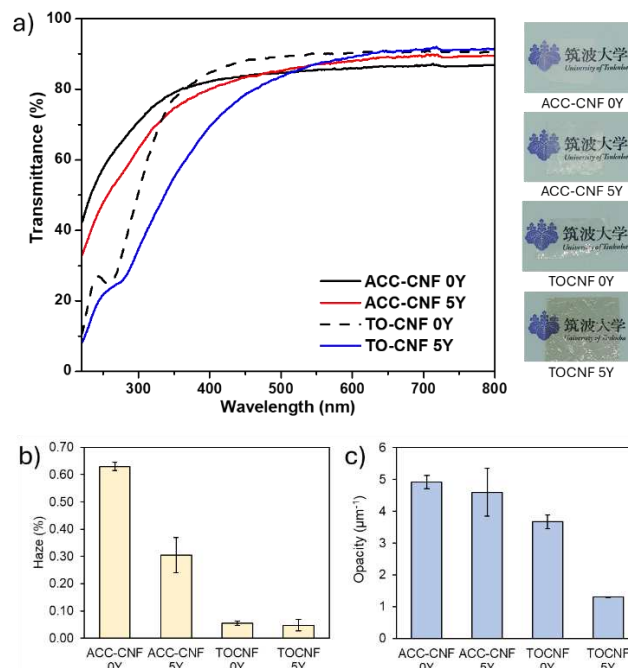


Figure 3. UV-Vis spectra (a), Haze (%) (b), and Opacity (T_{600}) (c) of sheets.

The optical behaviour of ACC-CNF and TOCNF films after long-term natural aging was evaluated using integrating-sphere UV–Vis measurements to ensure accurate quantification of total transmittance and scattering effects in thin films. As shown in Figure 3a, all samples exhibited the expected wavelength-dependent transmittance, with strong attenuation in the UV region (200–340 nm) and high transmission in the visible range (340–800 nm). The TOCNF had a linier transmittance of 89% and slightly decreased to 87% after 5 years at 550 nm. Meanwhile, ACC-CNF transmittance is same around 86% at 550 nm before and after 5 years. Quantitative analysis of haze at 550 nm (Figure 3b) and thickness-normalized opacity (T_{600}) (Figure 3c) reveal different aging result. ACC-CNF initially exhibited the highest haze (0.63 ± 0.01 %), which decreased substantially after five years (0.30 ± 0.06 %), accompanied by a modest reduction in T_{600} from 4.9 ± 0.2 to 4.6 ± 0.8 . This combination indicates that natural aging in ACC-CNF primarily reduces light scattering rather than strongly altering visible-range absorption. In contrast, TOCNF films showed consistently low haze values (<0.1 %) at both aging states (from 0.06 ± 0.01 to 0.05 ± 0.02) yet displayed a pronounced decrease in T_{600} from 3.67 ± 0.22 to 1.30 ± 0.01 after aging, indicating a significant improvement in visible transparency per unit thickness. The decoupling of haze and T_{600} in TOCNF suggests that reduced overall optical attenuation, rather than changes in scattering, governs the improved visual clarity of aged TOCNF films.

Several studies on transparent cellulose nanofiber have reported high transmittance at 600 nm, reaching up to 93.62% for TOCNF [29]. For carboxymethyl cellulose, UV–visible analysis also showed high transmittance of 94.1% at 600 nm [30]. The haze of cellulose nanofiber was reported to be 4.1% with a transmittance of 90.1% [31]. Transparent cellulose paper with carboxylate groups synthesized from carboxymethyl cellulose showed a transmittance of 90% and a haze of 70% at 600 nm, with minimal decreases in transmittance and haze after UV aging for 100 h in the UV region [32]. Another transparent carboxymethyl cellulose paper showed no significant decrease in transmittance and haze at 550 nm after UV exposure for 192 h, but only a minimal decrease in transmittance after heat exposure at 180 °C for 30 min [33]. This suggests that the aging process depend on aging conditions and chemical of cellulose, amplifying the importance of selection of aging method to mimic the natural aging conditions.

Further analysis regarding the color of cellulose nanofiber sheet was conducted. The yellowing index calculated from equation (4) is shown in Figure 4a. The L^* , a^* , b^* values were converted to RGB value then plotted to replicate the visual color as shown in Figure 4b and Table 1. TOCNF 5Y shows relatively more yellow than TOCNF 0Y, ACC-CNF 0Y and ACC-CNF 5Y. The acidic properties of TOCNF derived from its carboxyl groups presumably

accelerated its degradation and generated chromophore compounds than ACC-CNF, causing more color change (Figure 4c)[34]. Although the carboxylate content of TOCNF is relatively low (16 mmol/kg), the color difference is as relatively high as 11.22 than previously reported which was only 8.43[9]. Compared to standard white, the ACC-CNF 0Y showed the lowest difference (Figure 4d). This suggests that although the ACC-CNF 0Y is relatively opaque, its relatively white color makes the ACC-CNF 0Y have the lowest color difference value. Accelerated aging of filter paper showed that a^* is not significantly change while L^* and b^* is significantly changed[35]. Heat or light accelerated aging of cellulose from filter paper increased a^* and b^* values and decreased L^* values. Light accelerated aging significantly increased in a^* value up to eight times than heat accelerated aging that increased up to three times[36]. However, heat accelerated aging showed greater effect in overall color change. Color change of cotton cellulose increased to 0.8 after 6 days of UV treatment but increased to 21.5 after 5 days of heat treatment at 150 °C[37].

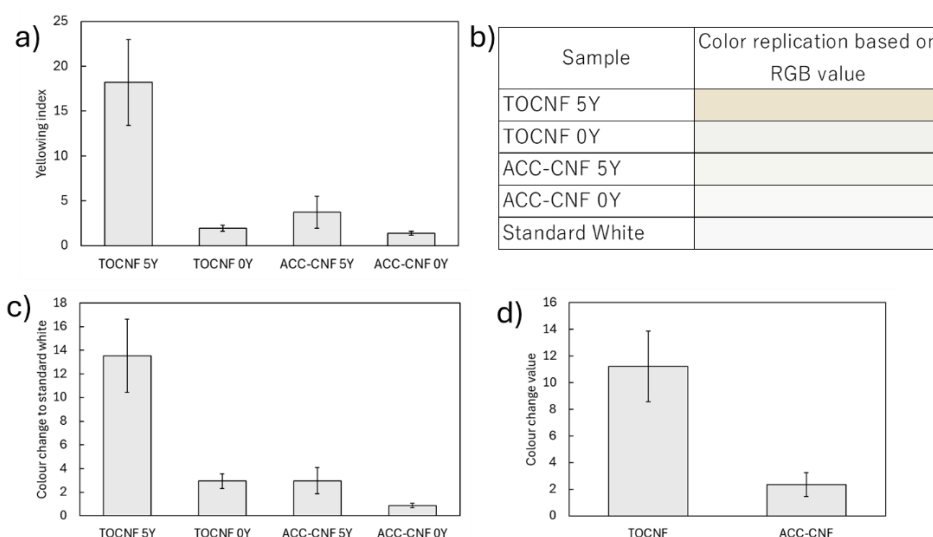


Figure 4. Yellowing index (a). The color replication is based on RGB value (b). Color changing value between 0 and 5 years (c) and color difference between sample and standard white (d).

The yellowing observed in TOCNF after five years of storage is consistent with previously reported accelerated aging studies of cellulose materials under UV irradiation. UV exposure is known to induce photo-oxidation reactions in cellulose, generating carbonyl and conjugated chromophore groups that absorb visible light and lead to yellow discoloration. For example, Zhao et al. [11] reported that continuous UV irradiation significantly increased the yellowness index of cellulose-based films within 24 h of exposure. Similar trends were also

observed in cellulose paper where photo-aging increased b^* values while decreasing L^* values due to the formation of chromophore oxidation products. The yellowing index carboxymethyl cellulose paper using UV light exposure for 192 h increase only 1 degree but increase to 5 degree after exposure to 180 °C for 30 min[33]. A similar report for cotton cellulose showed that heat treatment at 150 °C caused a different effect in the yellowing index. 6 days of UV exposure decreased the yellowing index from 4.10 to 2.64 due to a bleaching effect, whereas 5 days of heat treatment increased it from 4.10 to 41.45.[37].

Compared with these accelerated aging results, the color change observed in the present study occurred over a much longer time scale under natural storage conditions. This suggests that although the degradation mechanisms (oxidation and chromophore formation) may be similar, the kinetics of degradation are significantly slower in natural aging. Therefore, the five-year storage experiment provides valuable insights into the long-term optical stability of cellulose nanofiber films under realistic environmental conditions. The cellulose degree of polymerization (DP) measurement is essential analysis to compare the polymer degradation. However, due to the material and time scale experimental limitations, we are unable to perform the DP measurement.

Table 1. CIELAB color parameter to RGB color parameter

Sample	L	a*	b*	R	G	B
TOCNF 5Y	90.31	-0.52	11.47	236	227	205
TOCNF 0Y	95.03	-0.34	1.29	241	241	238
ACC-CNF 5Y	96.04	-0.51	2.50	245	244	239
ACC-CNF 0Y	97.79	-0.40	0.94	249	249	247
Standard White	97.71	-0.14	0.13	248	248	248

During aging, the cellulosic polymers are shortened. Smaller degrees of polymerization tend to degrade further or burn at lower temperatures. The parameter used to determine the thermal stability is temperature onset which is the meeting point of horizontally flat region after dehydration and a vertical region after the first pyrolysis state [38]. Figure 5 shows the TG-DTA result of TOCNF and ACC-CNF sheets. The TOCNF shows lower thermal stability than ACC-CNF. The onset temperature for TOCNF and ACC-CNF are 222 °C and 307 °C respectively. After natural degradation for five years, the onset temperature for TOCNF and ACC-CNF are 216 °C and 305 °C, respectively. As TOCNF has higher surface charge than ACC-CNF, the thermal stability also decreases [38, 39]. The previous report showed that accelerated aging by heat and UV exposure lowered the onset temperature due to a reduced degree of polymerization. For cotton cellulose, the onset temperature decreased from 334 °C to 326 °C after 6 day of light exposure and 5 days of heat treatment [37]. Accelerated aging of

palm leaf manuscripts under high humidity (70–90%) showed faster decomposition and pyrolysis than under low humidity (10–50%). Meanwhile lignin degradation decomposes in higher and broader range of temperature because of its more stable aromatic ring[40].

The TOCNF has a char residue of 29% and decreases to 23.5% after 5 years. The char residue for TOCNF 0Y is relatively high compared to other TOCNF results such as 16.5%[41]. The TOCNF with carboxylate groups has a higher char content than ACC-CNF without carboxylate groups [16]. A lot of sodium in COONa of TOCNF remain after burning. A sample of 1.68 mmol/g of COONa remains in the form of ash as high as 40% at 400 °C [42, 43]. ACC-CNF contains a char residue of 17% and can increase up to 19%.

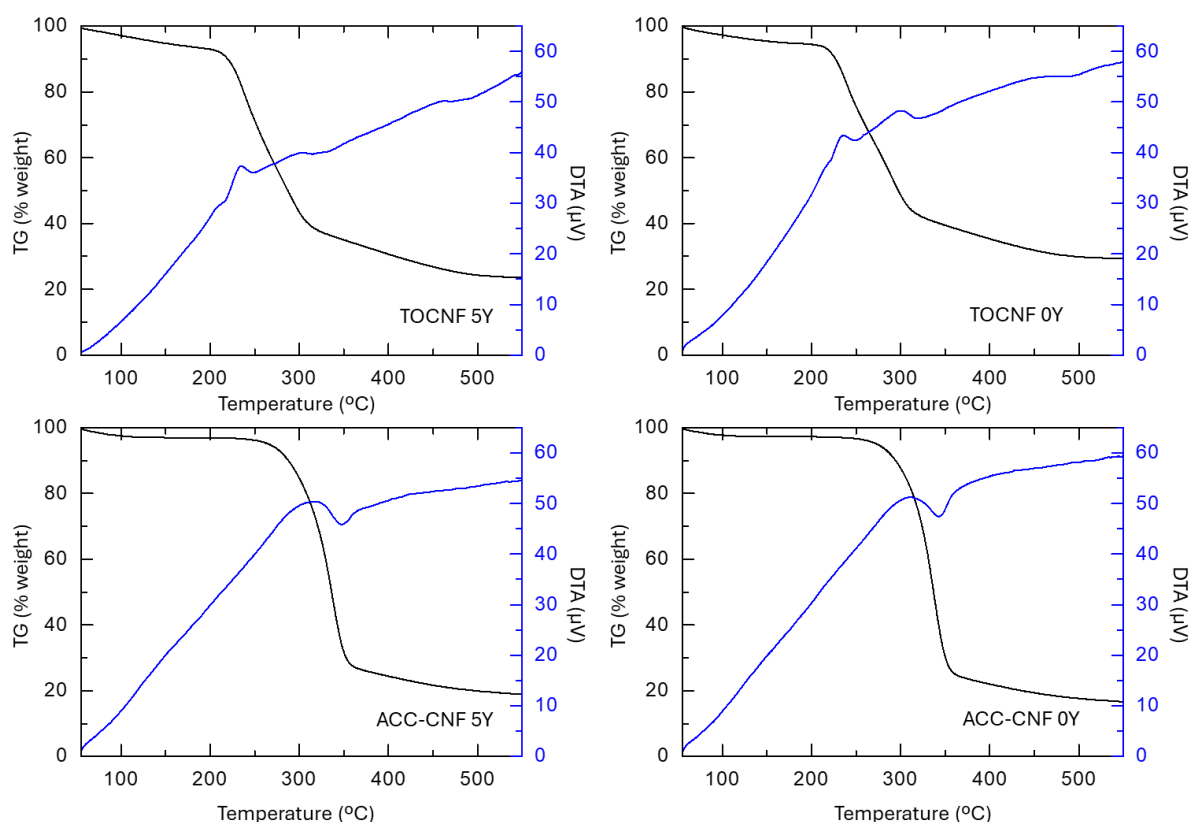


Figure 5. TG-DTA analysis of cellulose nanofiber sheets before and after aging

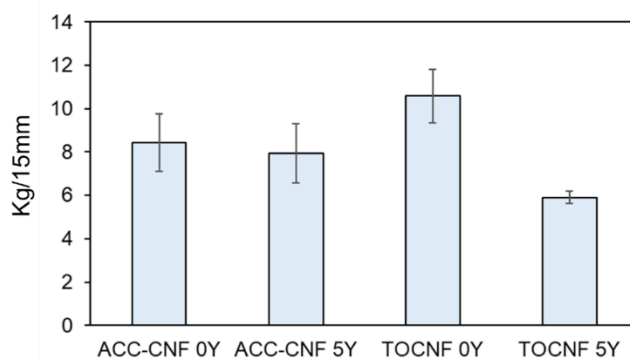


Figure 6 Zerospan test of CNF sheet

The mechanical strength of individual fiber of ACC-CNF and TOCNF was measured by Zerospan test as shown in Figure 6. Zerospan of ACC-CNF slightly lower after aging but did not significantly change after aging. However, zerospan of TOCNF drastically decreased after aging, indicating that TOCNF degraded more rapidly compared to the ACC-CNF. The degradation rate is affected by the acidity of cellulose and degraded cellulose will lose its mechanical strength [8]. TOCNF contain carboxylate group and relatively higher negative zeta potential, therefore, degrade more easily than ACC-CNF. Heat accelerated aging of filter paper showed negative logarithmic trend and decrease from 17 kg/15mm to 11.5 kg/15mm only within 100h of treatment but required more than 800h to achieve 5 kg/15mm[44].

Conclusions

The type of cellulose nanofiber influences the naturally aging results. After aging for five years, ACC-CNF became less hazy but no difference in opacity, but the TOCNF was no difference in haziness, but decreased in opacity. The crystallinity of ACC-CNF and TOCNF increase after 5 years of natural aging. Thermal stability of TOCNF decreased although that of ACC-CNF was kept relatively high.

CRedit authorship contribution statement

Conceptualization: AH, AZ, AAG; methodology: AH, AZ, RMMNF, AAG; validation: AZ, RMMNF, AAG; formal analysis: AH, AAG; investigation: AH, AZ, RMMNF, AAG; resources: AH, AAG, TE; data curation, AH; writing—original draft preparation: AH; writing—review and editing: AH, AAG, AZ; visualization, AH, AAG; supervision: AH, TE; funding acquisition: AH, AAG. All authors have read and agreed to the published version of the manuscript.

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