

Self-standing films of octadecylaminated-TEMPO-oxidized cellulose nanofibrils with antifingerprint properties

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ARTICLE INFO

Keywords:

Self-standing oil-repellent film
Hydrophobic nanocellulose
Octadecylamine
Contact angle
Antifingerprint property

ABSTRACT

Self-standing films of cellulose nanofibril derivatives were prepared via oxidation by the 2,2,6,6-tetramethyl-1-piperidinyloxy radical and amidation with octadecylamine (ODA). The transparency and rigidity of the films decreased and their flexibility increased as the amide/carboxyl ratio increased. The introduction of the ODA also resulted in rising contact angles of water (from 43.5° to 117°) and oleic acid (from 22.5° to 57.1°). Furthermore, the films exhibited unique oil repellency: a drop of hexadecane slipped without tailing on the surface modified by ODA. This phenomenon was observed after moderate modification (water contact angle: 95–114°) and was absent for the films with the lowest and highest extents of modification. Then, the antifingerprint property of the films was examined by means of the powder test, and a reduction in fingerprints on the films was demonstrated. These results suggest the usefulness of developing transparent, self-standing oil-repellent films without per-fluorinated compounds for antifingerprint and other antifouling applications.

1. Introduction

The development of portable electronics such as smartphones has driven the demand for functional films to protect the devices. The films should first prevent the adhesion of water and oil, which could damage device, and second, prevent fingerprints, which decrease visibility of the smartphone screen. Conventionally, fluorinated compounds have been used for these purposes. However, these compounds are persistent and could be unreasonable for commercialization. Therefore, the development of alternative materials is required to reduce the environmental and trade loads. Recently, many works have reported the preparation of films with antifingerprint properties by controlling the hydrophobic and oleophobic components without persistent organic compounds. Typically, biodegradable polymers such as poly(vinyl alcohol) (Nakashima et al., 2017), polycaprolactone (Kim, Park, & Hammond, 2008), poly(lactic acid) (Suyatma, Copinet, Tighzert, & Coma, 2004), poly(lactic acid-co-glycolic acid) and polyhydroxybutyrate (Kaplan et al., 2014) have been reported for this purpose. However, these materials have

technical/economic issues that must be solved and optical/mechanical properties that must be improved. To fulfill the demands in advanced applications, further improvements are required for these materials.

Cellulose is the most abundant renewable and biodegradable polymer on earth (10^{11} – 10^{12} tons produced annually) (Hoeng, Denneulin, & Bras, 2016). Its derivatives are attractive because of their low cost, easy syntheses, and sufficient mechanical properties. Traditionally, cellulose esters have been used for optical applications such as movie films, and regenerated cellulose is also used in fabrics and wrapping materials. However, films of regenerated cellulose, such as cellophane, take cellulose II structure (Miyamoto et al., 2009) and require additional processes of orientational control to improve mechanical properties. Without the processes, the regenerated cellulose is of low crystallinity and mechanically weaker than natural cellulose with high crystallinity in the natural form (cellulose I) (Moon, Martini, Nairn, Simonsen, & Youngblood, 2011). On the other hand, the natural celluloses are obtainable as coarse fibers (e.g., cellulose pulp and cotton fiber) and limited in their application by their opacity. To improve both of the

Abbreviations: DIC, Differential interference contrast; EDC, N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride; FTIR, Fourier transform infrared; NHS, N-hydroxysuccinimide; OCA, oleic acid contact angle; ODA, octadecylamine; TEMPO, 2,2,6,6-tetramethyl-1-piperidinyloxy radical; TGA, thermogravimetric analysis; TOCNF, TEMPO-oxidized nanocellulose nanofibril; UV-vis-NIR, ultraviolet-visible-near-infrared; WCA, water contact angle.

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<https://doi.org/10.1016/j.carbpol.2020.117536>

Received 31 August 2020; Received in revised form 2 December 2020; Accepted 15 December 2020

Available online 1 January 2021

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optical and mechanical properties, modifications of natural cellulose to improve transparency with maintaining its high crystallinity have been desired. Nanocellulose can solve this issue, and the decomposition of cellulose has been examined through both mechanical and chemical approaches. While conventional acidic and enzymatic hydrolyses result in rather short cellulose crystals (< 500 nm in length) (Phanthong et al., 2018), long nanofibers were recently developed. One preparation method is the oxidation of cellulose pulp with 2,2,6,6-tetramethyl-1-piperidinyloxy radical (TEMPO). After oxidation, the pulp is mechanically disintegrated into a nanofibril, which is called a TEMPO-oxidized nanofibril (TOCNF). In this process, the oxidation is confined to the side groups of the crystal domains in the material because of the large steric hindrance of TEMPO, and the crystallinity of the cellulose is maintained. Therefore, the diameter of the nanofibers can be as small as the crystal domain in the natural cellulose resource (i.e., 3–4 nm) (Ujihara, Hsu, Liou, & Imae, 2018). Because of this fineness and high crystallinity, the films prepared from TOCNFs are transparent and mechanically strong.

Although TOCNF films are expected to be useful as antifingerprint films, it is still hydrophilic/oleophilic and has a high water retention value (Saito, Kimura, Nishiyama, & Isogai, 2007) and small contact angle. To control the hydrophobicity of TOCNFs, further chemical modifications are required. Such modification of TOCNFs can be achieved via the functionalization of the carboxyl groups introduced by oxidation. Typically, alkyl chains can be attached on the nanofiber by esterification and amidation reactions. (Johnson, Zink-Sharp, & Glasser, 2011) reported a hydrophobized TOCNF film prepared via amidation with octadecylamine (ODA) and showed that its water contact angle increased from 36 to 108°. However, hydrophobized TOCNF films have been studied mainly in terms of improved hydrophobicity for selective oil absorption from aqueous suspensions, but its oleophobicity for antifouling property has never been reported. Recently, a unique hydrophobic and oleophobic glass surface has been reported (Urata, Masheder, Cheng, & Hozumi, 2012). Alkyl chains introduced on the surface at a proper distance increased the oil repellency. This oil repellency was attributed to the conformational change of the alkyl chains, and the importance of the gaps between the alkyl chains was explained. Therefore, we hypothesized that the modification of TOCNFs with a proper ODA content could also achieve oil repellency on the surface without perfluorinated compounds. In this work, the hydrophobicity and oleophobicity of ODA-modified TOCNFs are reported. Since the films of ODA-modified TOCNFs are available as self-standing films, their appearance and mechanical strength are also evaluated. From the viewpoint of applications, the antifingerprint property is also examined. The goal of this work is to verify the relation of the modification content by ODA and the film properties mentioned above including oil repellency and antifingerprint property, as reports of oil-repellent film without fluorinated compounds remains underdeveloped. These results are useful for developing coating films that prevent the adhesion of both water and oil by means of eco-friendly materials.

2. Experimental section

2.1. Materials

Never-dried pulp (bleached eucalyptus kraft pulp, cellulose 95–98 wt%, hemicellulose 2–5 wt%, and lignin < 0.5 wt%) was acquired from the Chung Hwa Pulp Corporation, Taiwan. Sodium bromide (NaBr), TEMPO, sodium hydroxide standard solution (NaOH, 1.0 M), and hydrogen chloride standard solution (HCl 1.0 M) were purchased from Acros Organics, USA. A solution of sodium hypochlorite (NaOCl) (reagent grade, 12 % available chlorine) was purchased from Shimadzu Pure Chemicals, Japan. Sodium borohydride (NaBH_4) was purchased from Wako Pure Chemical Industries, Japan. ODA was obtained from Alfa Aesar, USA. N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC), N-hydroxysuccinimide (NHS), potassium bromide

(KBr) and hexadecane were obtained from Acros Organics, USA. The hexadecane was colored by 100 ppm Sudan III for high visibility. Sudan III and oleic acid were purchased from Sigma-Aldrich, USA. Throughout the experiments, ultrapure water (Yamato, Japan) with a resistivity of 18.2 M Ω cm was used.

2.2. Measurements

The infrared absorption spectra were obtained by means of an FTIR spectrometer (Thermo Nicolet, Nexus 6700, USA) with an attenuated total reflection mode. Dried samples were put and compressed on a ZnSe prism. The measurements were carried out in the wavenumber range of 4000–650 cm^{-1} with 256 scans of single-reflection. For further analyses of chemical components, the X-ray photoelectron spectroscopy (XPS, VG Scientific, ESCALAB 250, England) was conducted. The sample film was attached on a stage with carbon-coated conductive double-faced adhesive tape (Ted Pella, Inc., USA). The thermal properties were investigated via thermogravimetric analysis (TGA, Perkin Elmer, UK). The samples were loaded into alumina pans at a weight of 4–10 mg. TGA was performed under air flow in the range of 30 °C–1000 °C with a heating rate of 10 °C/min. The morphologies were observed by the differential interference contrast (DIC) method at $\times 20$ magnification with a uEye Cockpit analyzer equipped with an optical microscope (Nikon Eclipse TE2000-U, Japan). The cross-sectional observation was performed by the freeze-fracture method using a field emission scanning electron microscopy (FE-SEM, JEOL JSM-6500 F, Japan). The film was put on a carbon tape before observation. The fiber diameter was analyzed with AFM (ParkScientific Instruments, NX 10, USA). Dispersion of sample was spread on a glass slide surface with a spin-coater, and then measured with tapping mode. The light transmittance was measured in the wavelength range of 400–800 nm with an ultraviolet (UV)-visible-near-infrared (NIR) absorption spectrophotometer (JASCO, V-670, Japan). Contact angles were calculated by the 2 θ method from photographs obtained using a digital microscope (Upmost, UPG650, Taiwan). A drop of water or oleic acid (~ 10 μL) was placed on the sample film at 25 °C for the measurement. The oil repellency was measured as the oil-slipping performance by putting a drop of hexadecane (~ 50 μL) on the surface of the sample film, which was set at a tilt angle of 10° (Urata et al., 2012b). The antifingerprint properties were verified by using a human fingerprint on the sample film. Human fingerprints were left on the films by pressing a finger onto films formed on a glass plate. Then, the fingerprint was covered by abundant ZnO powder in a cosmetic compound, and the excess powder was removed by a brush. The powder bound to the fingerprint was recorded with a photograph to visualize the fingerprint. The scratch resistance of the films was measured by the pencil hardness method on a QHQ-A pencil hardness apparatus (Tianjin Instrument Co., China) with a weight of 500 N using pencils of different hardness grades at a fixed angle of 45° for the films coated on glass slides at relative humidity of 50 % at room temperature. The mechanical properties of tensile strength, yield strain, and Young's modulus were investigated using a universal testing machine (Orientec., model STA-1150, Japan) at room temperature with a speed of 25 mm/min for sample films with a rectangular area of 8 $\times$ 20 mm^2 and a cross-sectional thickness of 15–25 μm . To discuss about effects of humidity, the measurements were performed at two different conditions: dry and wet conditions. The dry condition was the relative humidity of 50 %, and wet condition was prepared by immersing the film in water for 1 min and removed excess water from the film surface. The scratch resistance of the films couldn't be measured at the wet condition because the wet films were easily broken.

2.3. Preparation of TOCNFs

The TEMPO oxidation of never-dried pulp was carried out as previously reported (Kebede, Imae, Wu, & Cheng, 2017). A slurry of never-dried pulp (9.5 wt% dry weight: 2.0 g) was dispersed in 200 mL of

water, and after stirring for 2 h, 0.2 g of NaBr, 32 mg of TEMPO and 5.2 mL of NaOCl were added to the pulp mixture at room temperature. The reaction dispersion was adjusted to pH 10 by HCl. Subsequently, NaOH was constantly dropped into the dispersion to maintain the pH at 10. After the consumption of NaOH was stopped, the reaction product was filtered. The filter cake was repeatedly washed by centrifugation with water until the supernatant was neutral. Then, the obtained oxidized pulp was dispersed in an aqueous solution, 0.2 g of NaBH₄ was added, and the solution was stirred for 8 h. The final product was washed by filtration with sufficient water to remove the byproducts from NaBH₄. The carboxyl content of the obtained TEMPO-oxidized pulp was determined to be 1.08 ± 0.02 mmol/g by measuring the conductivity (Liljenzin, 2017; Sun, Gu, Ma, & Liang, 2005) and then the degree of oxidation was calculated to be $\sim 18\%$ of the glucose units in the cellulose. The TEMPO-oxidized pulp was suspended at a concentration of 0.3 wt% dry weight in 15 mL of water. The suspension was cooled on an ice bath and treated by ultrasonication for 20 min at 50 W with a half-inch probe (Qsonica sonicator, USA). The resulting TOCNF suspension was kept in a refrigerator at 4 °C until used.

2.4. Modification of TOCNFs with octadecylamine and film formation

A TOCNF suspension was mixed with EDC, and after 30 min, NHS equimolar to EDC was added to the suspension. The reaction suspension was intermittently shaken for 1 h at room temperature, and a powder of ODA equimolar to EDC and NHS was added to the suspension. The reaction mixture was sonicated for 2 h in a sonication bath and subsequently stirred vigorously for 2 h. Suspensions of the ODA-TOCNF products were washed by centrifugation with HCl (0.1 M) and ethanol,

poured (15 mL) into polystyrene petri dishes or spread (3 mL) onto glass plates, and dried at 40 °C for 24 h. The films prepared with amine/carboxyl unit mol ratios (x) of 0.5, 1, 1.5, 2, 2.5, and 3 were prepared and named x-ODA-TOCNF, respectively. Similar films were also prepared from the TOCNF and named 0-ODA-TOCNF.

3. Results and discussion

3.1. Characterization of ODA-TOCNF films

The reaction scheme and molecular structures of TOCNF and ODA-TOCNF were shown in Fig. 1A. The chemical structures of TOCNF films, and ODA-TOCNF films were analyzed by FTIR absorption spectroscopy (Fig. 1). For comparison, the spectra were normalized against the absorption band at 1161 cm^{-1} (corresponding to C—OC— stretching). The broad band in the range of $3600\text{--}3100\text{ cm}^{-1}$ was due to O—H stretching (Kondo, 1997), and it was not significantly changed in the TOCNF and ODA-TOCNF spectra. The band at 1645 cm^{-1} was assigned to OH— bending of cellulose, and it was overlapped by adsorbed water band and the other bands. The absorption band at 1720 cm^{-1} in the TOCNF spectrum was assigned to COOH group formed by selective oxidation at the C6 position. After ODA grafting, absorption bands appeared at 1645 and 1547 cm^{-1} , which were attributed to amide I and amide II, respectively. The sharp absorption bands at 2918 and 2850 cm^{-1} corresponded to the CH— stretching modes of CH₂ in ODA, which overlapped with the band attributed to the C—H stretching mode in the glucose unit (broad band at $2990\text{--}2820\text{ cm}^{-1}$). Thus, the amidation reaction between TOCNFs and ODA was confirmed (Araki, Wada, & Kuga, 2001). In this work, the amount of ODA used in the reaction was

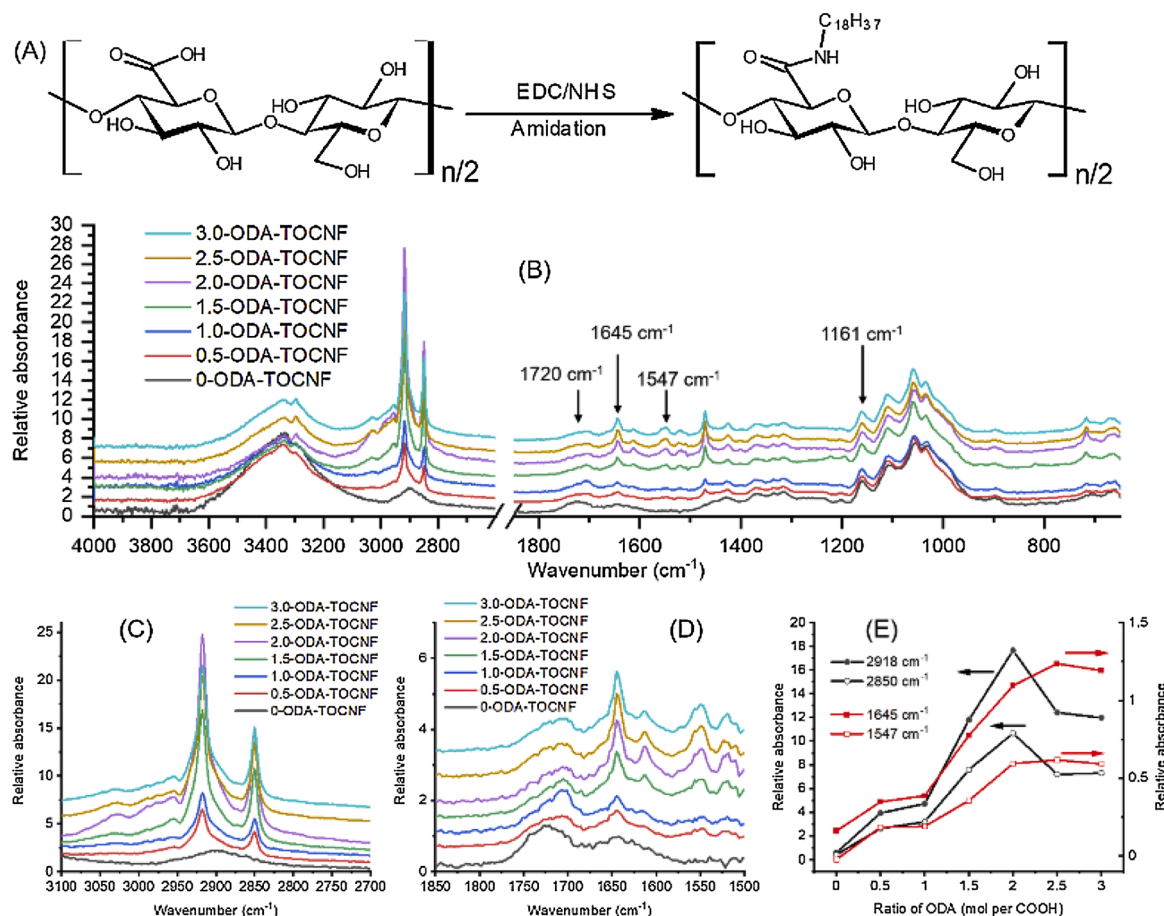


Fig. 1. (A) Preparation of TEMPO-oxide nanocellulose fibers with octadecylamine; (B–D) FTIR absorption spectra of x-ODA-TOCNF normalized against absorbance at 1161 cm^{-1} ; and (E) relative absorbance at 2918 , 2850 , 1645 , and 1547 cm^{-1} .

varied from 0.5 to 3 mol/unit mol of carboxyl groups in TOCNFs. The band intensity of bands attributed to alkyl chains (C–H stretching) and amide groups did not significantly increase at ODA/carboxyl ratios higher than 2.0 (Fig. 1C-E). It should be noted that the COOH groups remained even at the highest ODA/carboxyl ratio, although the absolute values were not analyzed because of broadening and shifting (Fig. 1D). This saturation of the band intensity suggests that the amidation reaction with ODA was mostly saturated remaining carboxyl groups at an ODA/carboxyl ratio of 2 mol/unit mol.

To analyze the components in the film, the 2.5 ODA-TOCNF was analyzed with XPS (Fig. 2). Deconvolution of each peak showed that the binding energy of C1s was attributed to three components except a C=C bond from the adhesive tape (284.3 eV); they were C–C (alkyl, 285.0 eV), C–OH/C(O)N– (hydroxyl and amine/amide, 285.6 eV), and C–OC– (ether, 286.5 eV) bonds, as expected from the chemical structure of ODA and TOCNF. The binding energy of O1s was also assigned as C–OH/COC (533.5 eV) and CO= (531.3 eV), respectively. For N1s, the binding energy was attributed to two structures, $\text{N}^+\text{H}_3\text{C}$ (401.8 eV) and $\text{N}-\text{C}(\text{O})$ (400.6 eV). While the $\text{N}-\text{C}(\text{O})$ confirmed the amide structure as shown in the FTIR absorption spectra (Fig. 1), the $\text{N}^+\text{H}_3\text{C}$ indicated the ODA remained even after washing with HCl. The remaining ODA was estimated as almost the comparable amount with amide (area ratio = 106:108 for $\text{N}^+\text{H}_3\text{C}/\text{N}-\text{C}(\text{O})$). This result lets us to estimate the adsorption of ODA on hydroxyl or free carboxyl group of TOCNF by the hydrogen bonding and the stabilization by the hydrophobic interaction between ODA besides amide bonding formation.

The thermal behaviors of pulp, 0-ODA-TOCNF, 2.5-ODA-TOCNF, and ODA were investigated by TGA in an air atmosphere (Fig. 3A and B). All compounds lost weight (less than 10 wt%) at temperatures up to 150 °C due to the removal of adsorbed small molecules. The pulp exhibited two-step decomposition at 350 and 850 °C. The weight loss at 220–315 °C was not observed in TGA of pulp, indicating the nondetectable inclusion of hemicellulose in the pulp (Yang, Yan, Chen, Lee, & Zheng, 2007). The thermal decomposition of 0-ODA-TOCNFs consisted of five steps. The first step was a series of weight losses between 230 and 320 °C, the second was a gradual degradation in the range of 350–500 °C, and the third was a weight loss above 700 °C after a minor loss at approximately 600 °C. After the ODA modification, the thermogram of the 2.5-ODA-TOCNF film indicated five main decomposition steps. In the first step, the weight loss between 150 and 200 °C could be due to the degradation of ODA in the film, since ODA decomposed at 190 °C. The subsequent weight loss observed above 250 °C may be mainly due to TOCNF decomposition. Above 320 °C, cellulose pyrolysis started with influence of ODA modification. A gradual weight loss around 400 °C could be attributed to the same processes to the process in 0-ODA-TOCNF. A decomposition appeared as the fifth step above 800 °C. This process could be the carbonization of the ODA-TOCNF. Thus, both results of the FTIR absorption spectra and the TGA analyses confirmed the successful synthesis of ODA-TOCNF.

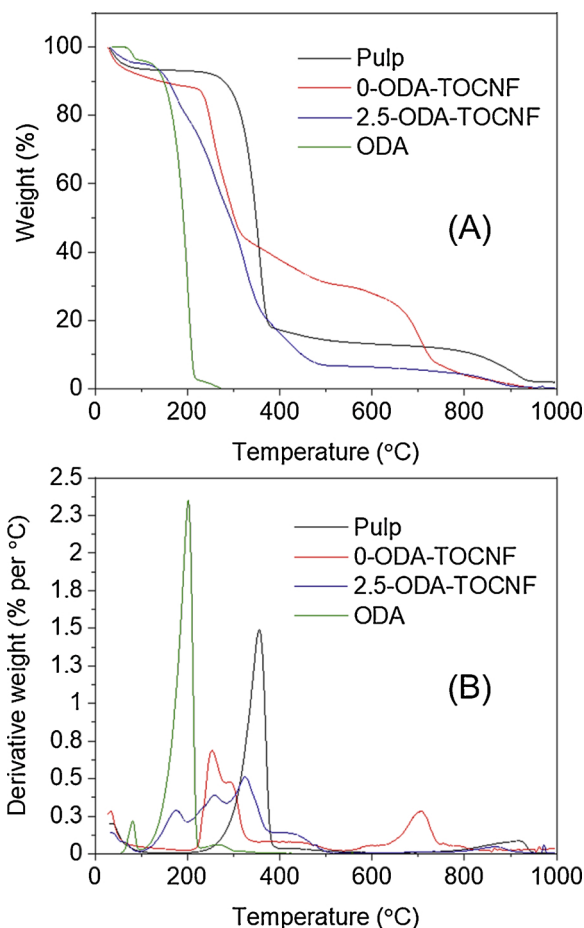


Fig. 3. (A) TGA thermograms and (B) derivatives of the weight loss curves of pulp, TOCNF, 2.5-ODA-TOCNF, and ODA.

Both TOCNF and ODA-TOCNF films could be dried to form self-standing films, but their macroscopic appearances changed with the extent of ODA modification (Fig. 4A). At low ODA/carboxyl ratio (x -ODA-TOCNF, $x \leq 1.5$), the films became opaque as this ratio increased. The films with higher ODA/carboxyl ratios showed white spots in the films and decreased transparency. The haze and spots were attributed to aggregates of nanofibers formed in the aqueous dispersions because the hydrophobicity of the TOCNF film increased upon ODA modification.

To evaluate the aggregation of nanocelluloses which caused the changes in macroscopic appearances, TOCNF and ODA-TOCNF films were viewed with the aid of an optical microscope (Fig. 4B). The TOCNF film was highly transparent, since small fibrils dispersed homogeneously in water and dried without aggregation. However, the transparency of

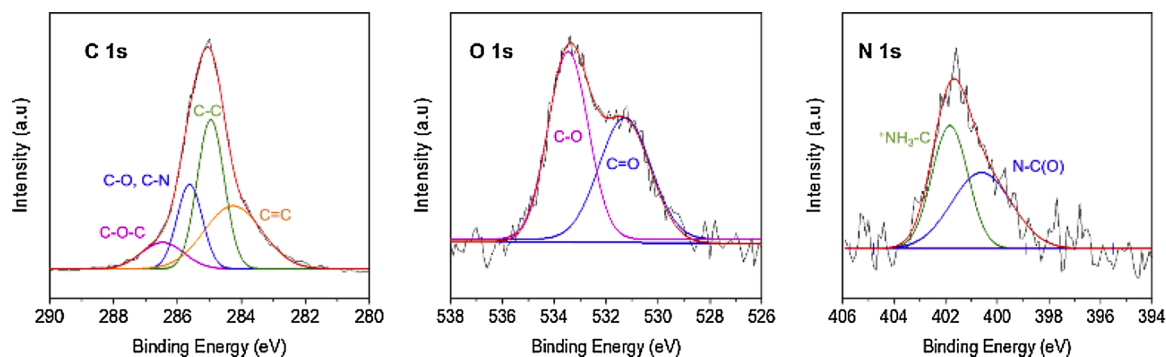


Fig. 2. XPS spectra of 2.5 ODA-TOCNF for C1s, N1s, and O1s.

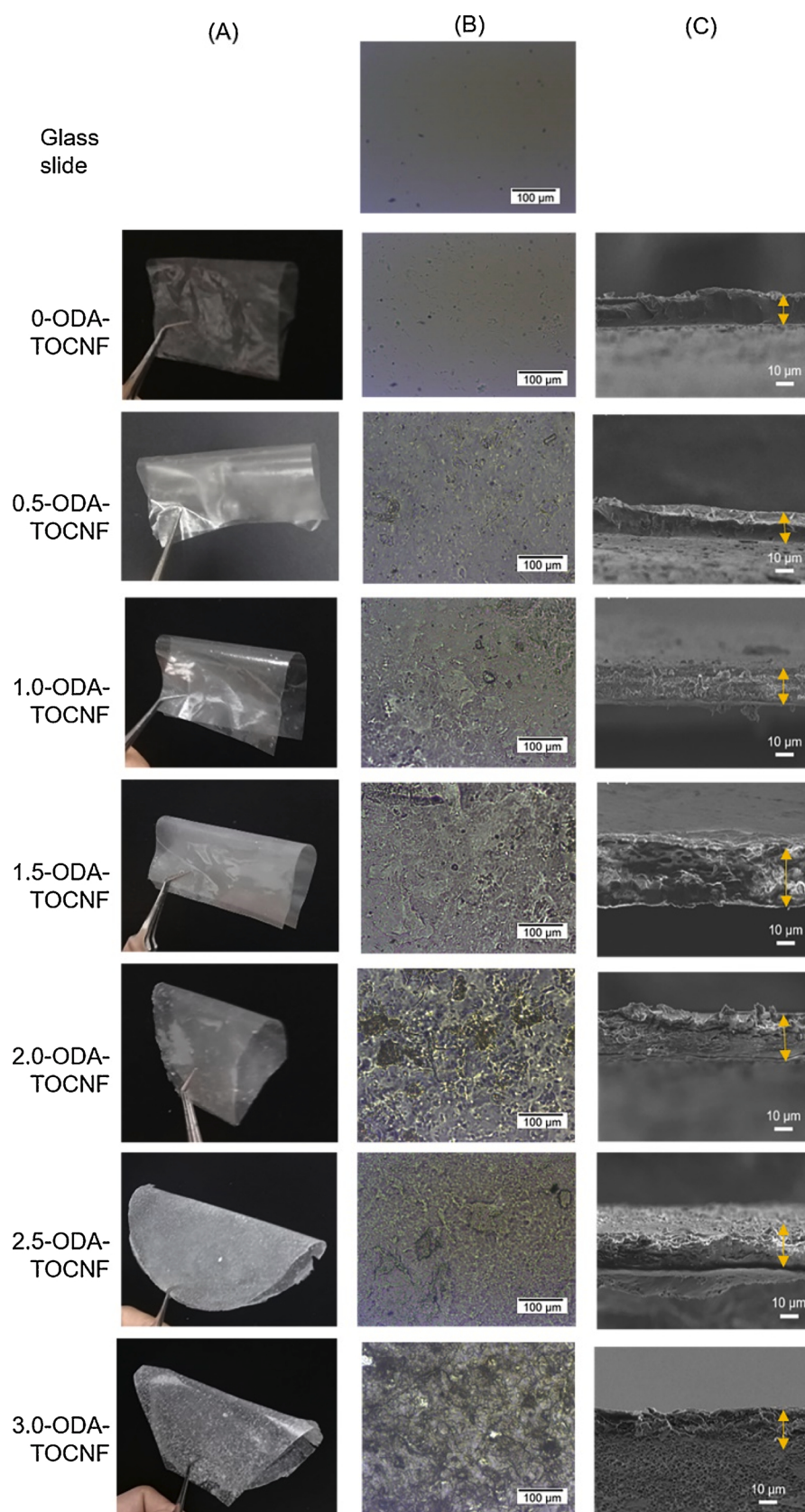


Fig. 4. (A) Visual observation, (B) DIC images and (C) cross-sectional SEM images of x-ODA-TOCNF self-standing films. Yellow arrows indicate thickness directions at edges of the films.

ODA-TOCNF films decreased as the amount of ODA increased because the ODA moiety undergoes aggregation as a result of the hydrophobic interaction between alkyl chains. At low ODA/carboxyl ratios (x-ODA-TOCNF, $x \leq 1.5$), the dispersed fibrous structures became more pronounced, and high ratios resulted in node formation by aggregates of ODA, which was associated with spot formation at high ODA/carboxyl ratios (x-ODA-TOCNF, $x \geq 2.0$).

The film structures were further characterized by the cross-sectional observation using SEM (Fig. 4C). The TOCNF film exhibited a dense structure, and the higher ratio of ODA resulted in the coarse structures in the film, as expected from the optical microscopic images. The coarse networks were distributed in whole film, and specific segregation was not found. The horizontal orientation of coarse networks, which could be formed during the drying process, was weakly observed in the films with high ODA/carboxyl ratios (x-ODA-TOCNF, $x \geq 2.0$).

To analyze the fiber diameter, the dispersions of TOCNF and 2.5-ODA-TOCNF were respectively observed by AFM method (Fig. 5). The dried TOCNF exhibited the height of nanofibrils around 3 nm, which agreed with a literature value (Ujihara et al., 2018). On the other hand, the height of nanofibrils in 2.5 ODA-TOCNF was mainly 5–15 nm, which suggests that the fibrillation state of ODA-TOCNF was not kept. The TOCNF would be hydrophobized by the ODA introduced onto the nanofibrils, and the hydrophobic interaction could promote formation of bundles/knots. This hydrophobic interaction could also provide hydrophobic domains to encapsulate free ODA molecules in the ODA-TOCNF even after washing process, as suggested from the XPS and TGA results (Fig. 2 and 3). Although the size of bundled nanofibrils in the ODA-TOCNF remained nanometer-scale, their stiffness and hydrophobic interaction could facilitate the flocculation to decrease the transparency of films (Fig. 5).

The transparency of the films was also evaluated by UV–vis–NIR absorption spectroscopy (Fig. 6). The transmittance of the TOCNF film was higher than 80 % in the range of 350–800 nm, which is consistent with previous reports (Fujisawa, Okita, Fukuzumi, Saito, & Isogai, 2011; Yang, 2011). As the amount of ODA increased, the transparency at 600 nm decreased from 73 to 32 %. When the films are used in optical applications, the transparency should be increased by improving the dispersibility of nanofibers in an appropriate medium.

The mechanical properties of the self-standing x-ODA-TOCNF films were evaluated. The scratch resistance properties, namely, the pencil

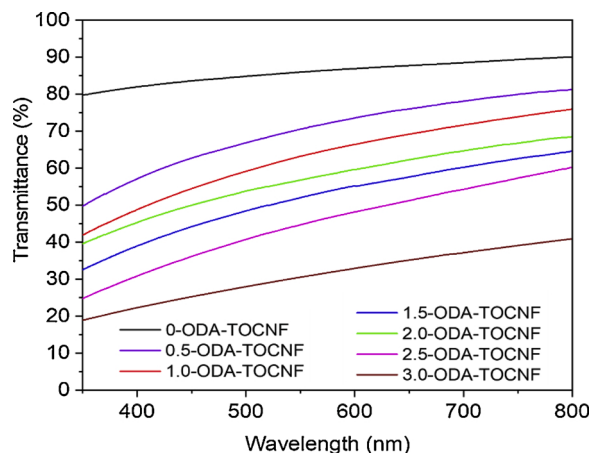


Fig. 6. UV–vis spectra of self-standing x-ODA-TOCNF films.

hardness, the tensile strength, the elongation at break, and the Young's modulus, with film thickness are shown in Fig. 7 and Table 1. In the dry condition (relative humidity 50 %), as the ODA/carboxyl ratio increased, the pencil hardness, tensile strength, and Young's modulus decreased. In contrast, the elongation at break improved upon modification by ODA. These results suggest that the modification by ODA degrades the rigidity of the films via the hydrophobic effect. The aggregations in the films could cause the stress concentration which degraded the mechanical strength: The ODA moieties in the nanofibers could cause defects in the films (see Figs. 4). In the wet condition, the tendency of mechanical properties was similar to that in the dry condition; however, the tensile strength and Young's modulus significantly decreased, and the elongation at break became longer. These changes suggest that the mechanical strength of the dry films was significantly supported by the hydrogen bonding between remaining $-OH$, $COOH$, N^+H_3 , and amide groups.

3.2. Surface properties of ODA-TOCNF films

3.2.1. Hydrophobicity and oil repellency of ODA-TOCNF films

The hydrophobicity of the films was evaluated by the water contact

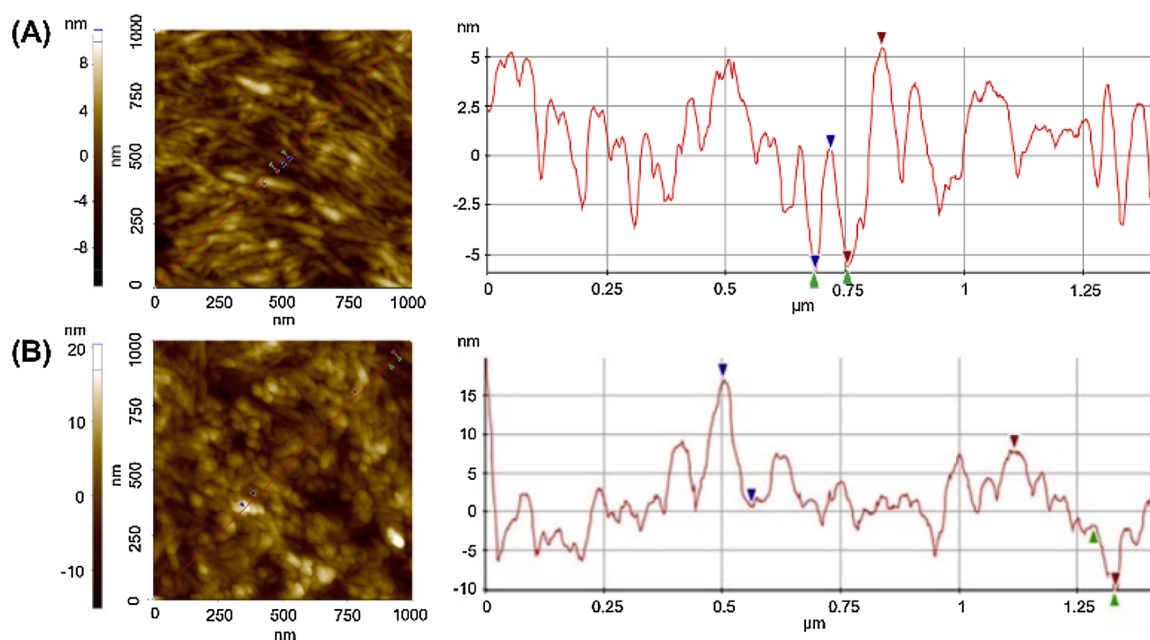


Fig. 5. AFM images (left) and their cross-sectional analyses (right) of (A) TOCNF and (B) 2.5 ODA-TOCNF.

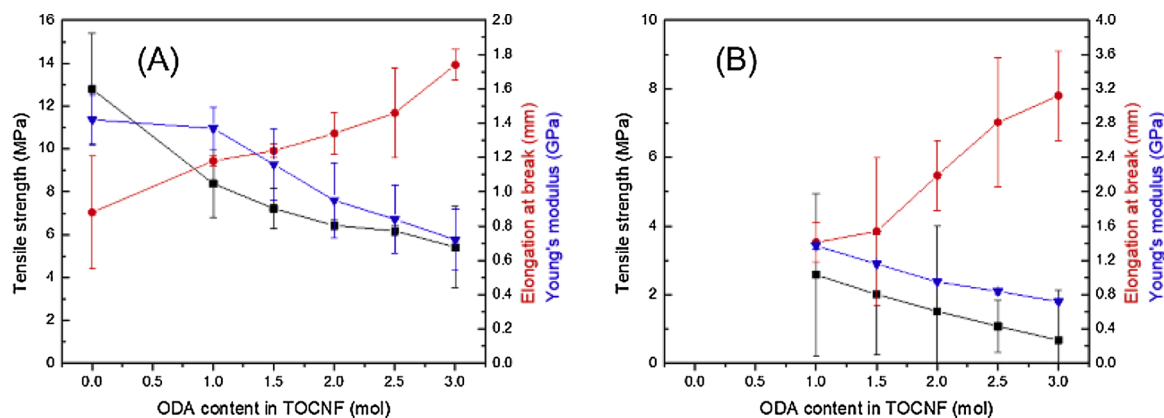


Fig. 7. Mechanical properties of x-ODA-TOCNF films in (A) dry condition and (B) wet condition.

Table 1

Mechanical properties of x-ODA-TOCNF films at room temperature in dry and wet conditions.

	Films Thickness (μm)	Pencil- Hardness	Tensile Strength (MPa)		Elongation at Break (mm)		Young's Modulus (GPa)	
			dry	wet	dry	wet	dry	wet
0-ODA-TOCNF	17	4H	12.79 ± 2.61	–	0.88 ± 0.33	–	1.42 ± 0.14	–
1.0-ODA-TOCNF	18	3H	8.38 ± 1.59	2.58 ± 2.37	1.18 ± 0.03	1.41 ± 0.23	1.37 ± 0.12	0.08 ± 0.04
1.5-ODA-TOCNF	19	3H	7.22 ± 0.95	2.01 ± 1.75	1.24 ± 0.04	1.54 ± 0.86	1.16 ± 0.21	0.05 ± 0.02
2.0-ODA-TOCNF	21	2H	6.43 ± 0.24	1.52 ± 2.48	1.34 ± 0.12	2.19 ± 0.41	0.95 ± 0.22	0.05 ± 0.01
2.5-ODA-TOCNF	23	2H	6.18 ± 0.23	1.08 ± 0.76	1.46 ± 0.26	2.81 ± 0.75	0.84 ± 0.20	0.05 ± 0.03
3.0-ODA-TOCNF	25	H	5.42 ± 1.89	0.68 ± 1.45	1.74 ± 0.09	3.12 ± 0.52	0.72 ± 0.18	0.04 ± 0.01

angle (WCA), as shown in Fig. 8A. The WCA of the 0-ODA-TOCNF film was 43.5° , which indicated the hydrophilic character of TOCNFs driven by the hydroxyl groups and carboxyl groups (Islam, Alam, & Zoccola, 2013). While the 0.5-ODA-TOCNF film, which had the lower ODA/carboxyl ratio in this study, exhibited a WCA of 80.2° , the films with higher amounts of ODA resulted in a higher hydrophobicity of up to 117° , which corresponds to the WCA of the densely packed ODA monolayer (Belman, Jin, Golan, Israelachvili, & Pesika, 2012). The long alkyl chains of the ODA moiety introduced onto the TOCNF film are thought to cause the hydrophobicity (Zheng & Lü, 2013), and more ODA resulted in a higher WCA. The surface roughness of the films could enhance the hydrophobicity by the lotus effect (see Fig. 4). Thus, the hydrophobicity of ODA-TOCNF films could be controlled by the ODA/carboxyl ratio.

To evaluate the surface properties of ODA-TOCNF films in contact with oil, the contact angle of the films with oleic acid, which is a main component of sebum, was measured (Fig. 8B). The surface of the 0-ODA-TOCNF film showed the lowest oleic acid contact angle (hereafter, OCA) (22.5°). The OCA increased as a result of ODA modification, and the highest OCA (62.3°) was measured for the 2.5-ODA-TOCNF film, which was significantly higher than that in the previous report using non-fluorinated compounds (Siriviriyannun & Imae, 2014). The 3.0-ODA-TOCNF film resulted in a low OCA of 57.1° , and this decline could be due to the surface roughness of this film (Fig. 4). As oleic acid is the main component of sebum, the high OCA value indicates the high anti-fingerprint. This behavior can be contrasted with the increasing hydrophobicity observed with WCA described above.

The slipping behavior of hexadecane on the films was also measured (Fig. 8C). On the 0-ODA-TOCNF film, hexadecane spread flatly. This behavior could be explained by the high surface energy of the dried TOCNF film and the affiliative interaction of hexadecane with organic moieties in the cellulose. On the other hand, the ODA-TOCNF films prevented the hexadecane from spreading on the film. With a tilt angle of 10° , the oil (hexadecane) drop slipped off the films without trails, except for the 0.5-ODA-TOCNF film and the 3.0-ODA-TOCNF film. This oil repellency was observed even on the film with the 1.0-ODA-TOCNF

film, which exhibited moderate hydrophobicity (WCA of 95.4°). The decrease in oil repellency of the 3.0-ODA-TOCNF film with the highest ODA/carboxyl ratio, which demonstrated the highest hydrophobicity (WCA of 117°), suggested that the oil repellency of ODA-TOCNF films could not be simply explained by the hydrophobicity of the film surface. Recently, a similar oil repellency of a silica layer partially alkylated by alkylsilanes was reported (Urata, Cheng, Masheder, & Hozumi, 2012). The long alkyl chains on the silica layer could undergo conformational changes freely when their density was sufficiently low, and then the surface state was adjusted to minimize the energy gap between the wet and dry conditions, which decreased the pinning of oil drops on the surface (Urata et al., 2014). By TEMPO oxidation, carboxyl groups were introduced on every second glucose unit on the surface, and the ODA moiety was only partially bound to these carboxyl groups (Fig. 1A). The large distance between the ODA moieties on the films at a moderate modification could result in flexible conformational changes of the alkyl chains and thus oil repellency. When the TOCNF film was densely covered with ODA (the 3.0-ODA-TOCNF film), the flexibility of the ODA moiety and thus the oil repellency decreased. From viewpoints of practical usage, the oil repellency of the ODA-TOCNF films was also demonstrated with edible oils (Fig. S1 in the supporting information). The oil repellency should be further investigated in both of the theoretical and practical aspects in the future.

Then, the antifingerprint properties of the ODA-TOCNF films were tested by ZnO powder. After pressing a finger onto the films, ZnO powder was sprinkled on the films to visualize the sebum remaining on the surfaces (Fig. 8D). While the 0-ODA-TOCNF and the 0.5-ODA-TOCNF films adsorbed sebum, the x-ODA-TOCNF films ($x = 1.0$ – 2.0) demonstrated strong antifingerprint properties. The 2.5- and 3.0-ODA-TOCNF films did not prevent sebum adsorption, but the sebum-ZnO powder was easily cleaned by brushing, which suggests that the interaction between the film surface and the sebum was weak.

4. Conclusions

Self-standing ODA-TOCNF films were prepared, and tests of the

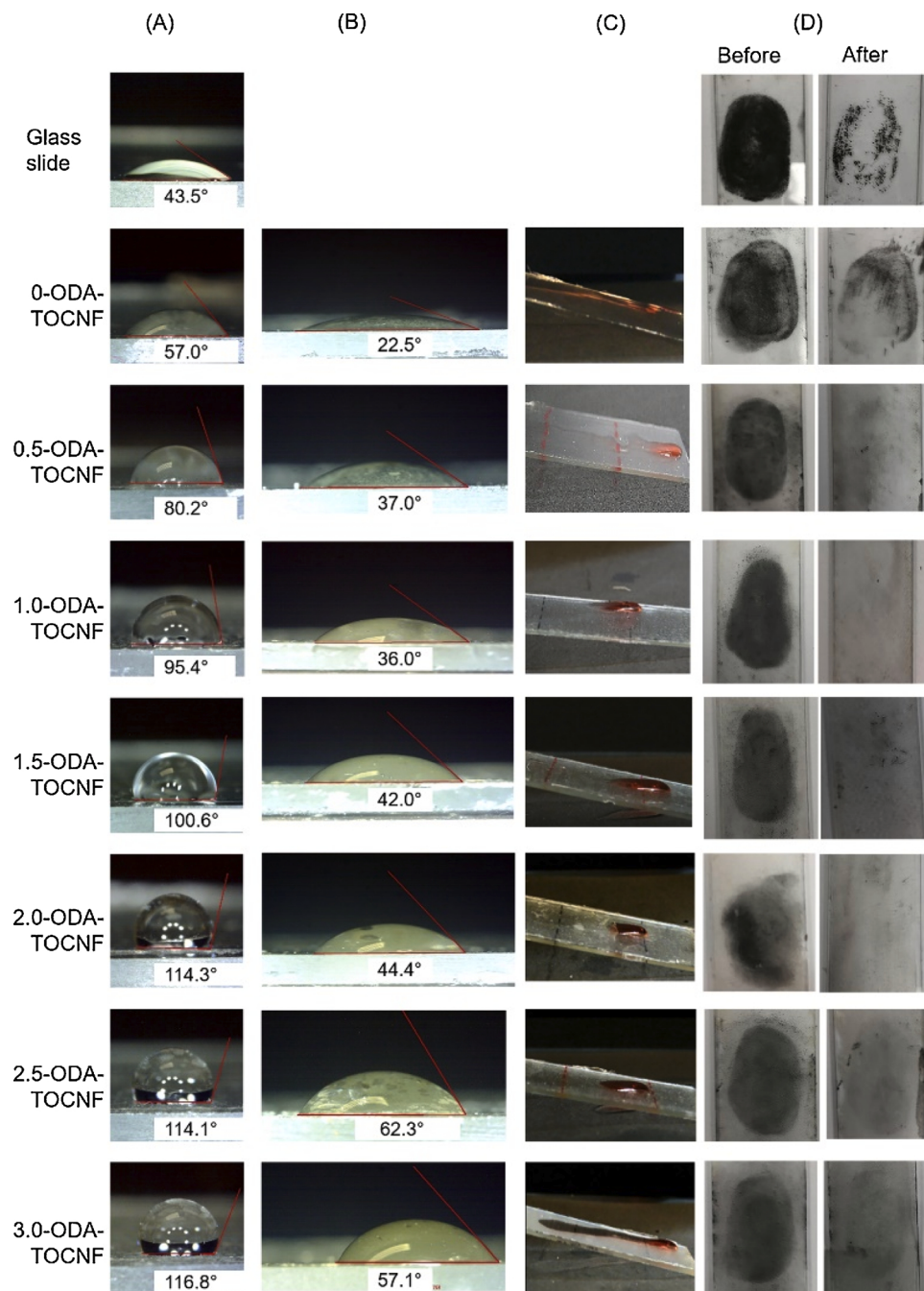


Fig. 8. (A) WCA, (B) OCA, (C) oil repellency test, and (D) antifingerprint property of glass slide and x-ODA-TOCNF films: the left side in 6D is before sprinkling with ZnO powder, and the right side in 6D is after brushing.

mechanical properties such as pencil hardness, tensile strength, elongation at break, and Young's modulus showed that the incorporation of ODA into TOCNF film improved the flexibility but reduced the rigidity and transparency of the TOCNF films. The haze and spots that appeared in the films were due to aggregation of ODA in the nanofibers, which could be formed in the dispersion. In this study, the improvement of the hydrophobicity and oil repellency of the cellulose-based nanofiber films was examined. The TOCNF film was derived with long alkyl chains via amidation with ODA. The introduction of ODA made the films hydrophobic, and improved oil repellency to hexadecane was observed. In particular, the dependence of the change in oil repellency on the ODA/carboxyl ratio suggested that there was an appropriate range of ODA/carboxyl ratio that would lead to oleophobicity. These results were consistent with the antifingerprint behavior of these films, which was

examined using a component of sebum: oleic acid. Moreover, the ODA-TOCNF films coated on glass demonstrated sufficient antifingerprint properties. These results could be used to develop films with enhanced oil repellence and oil removability without perfluorinated compounds, which can be applied for coating of screen and package/container of oily foods.

CRediT authorship contribution statement

Nattinee Krathumkhet: Writing - original draft, Writing - review & editing. **Masaki Ujihara:** Conceptualization, Writing - review & editing, Visualization, Supervision, Resources. **Toyoko Imae:** Writing - review & editing, Resources, Project administration, Funding acquisition.

Acknowledgments

The authors would like to acknowledge Yan-Rong Chen for her assistance for analyzing Tensile Tester. This study was financially supported by the National Taiwan University of Science and Technology Taiwan for the student scholarship, and by Ministry of Science and Technology (MOST), Taiwan (MOST 107-2221-E-011-067-).

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.carbpol.2020.117536>.

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