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Research Article

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Direct Measurement of Surface Adhesion between Thin Films of Nanocellulose and Urea–Formaldehyde Resin Adhesives

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Graphical Abstract

When applying an adhesive to wood, the chemical heterogeneity of the wood cell walls makes it difficult to understand the contribution they make to the interfacial adhesion between the adhesive and the wood as the adhesion is a very complex physical and chemical phenomenon. This study, for the first time, directly measured the surface adhesion between cellulose, a major component of wood, and urea–formaldehyde (UF) resin adhesives. The adhesion between thin, smooth nanocellulose films, such as cellulose nanofibrils (CNFs), carboxymethylated nanofibrils (CM)–CNFs, and carboxylated cellulose nanocrystals (C–CNCs), and UF resins with two formaldehyde to urea (F/U) molar ratios of 1.0 and 1.6 was measured using two approaches: 1) direct measurement of the adhesion force between nanocellulose films and liquid droplets of the UF resins, and 2) calculation of the work of adhesion between films of the nanocelluloses and UF resins using the contact angle and the van Oss–Chaudhury–Good (OCG) method. The results show that the total surface energies, either between the different nanocelluloses or between the two UF resins are somewhat similar, indicating the similarity in their surface properties. However, the adhesion force and work of adhesion of 1.6 UF resins with different types of nanocellulose are higher than those of 1.0 UF resins, which shows that van der Waals forces are dominant in their molecular interactions. These results suggest that the adhesion between 1.6 UF resins and nanocellulose is stronger than that when 1.0 UF resins are used because the 1.6 UF resins have a more branched structure, smoother surface, and higher surface energy.

Keywords: UF resins, nanocellulose, adhesion force, work of adhesion, surface energy, van der Waals force

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1. Introduction

For a long time, wood has been used for many purposes, as a structural material in engineering, as a fuel, and in wood-based panels (Pereira Oliveira Moreira et al. 2020). In terms of wood-based materials, cellulose, a major component of wood, plays a pivotal role in their mechanical properties (Gibson 2012). Engineered wood products such as plywood, particleboard, and medium density fiberboard require adhesives to attach them together, which act as a binder between the wood components. The adhesion process in wood bonding is an extremely complex physical and chemical phenomenon that must be understood to obtain durable and excellent adhesion of wood-based products. One of the primary obstacles in understanding the wood adhesion is the heterogeneity of wood cell walls, which are composed of three major chemical components, cellulose, hemicellulose, and lignin. Despite the role they play in joining wood together, there is still a lack of understanding about the interaction that occurs between wood adhesives and wood components. To the authors' knowledge, the contribution that these biopolymers make toward wood adhesion is yet unknown. Hence, it is necessary to clarify the contribution that each wood component makes toward the adhesion to have better understanding of wood bonding, which consequently affects the performance of wood-based materials.

One of the most extensively used adhesives in wood-based panels is urea-formaldehyde (UF) resin. However, industrial UF resins are known to emit a high amount of formaldehyde, which has led to the necessary reduction of these emissions in industrial settings by decreasing the amount of formaldehyde present in the formulation, with the resulting materials being referred to as low formaldehyde-to-urea (F/U) molar ratio UF resins (Pizzi and Valenzuela 1994; Dunky 1998). Unfortunately, in the pursuit of low formaldehyde emissions, the low molar ratio (≤ 1.0) UF resins that have previously been prepared show poor adhesion to wood-based panels.

Recently, the crystalline domains in low molar ratio UF resins are responsible for the poor adhesion because they significantly reduce their cohesion by inhibiting the formation of 3D cross-links (Levendis et al. 1992; Wang et al. 2018; Wibowo et al. 2020a; Wibowo and Park 2021). Crystalline domains arise because of the formation of hydrogen bonds between linear molecules as a result of oxymethylene and branched methylene ether link cleavage (Wibowo et al. 2020b; Wibowo and Park 2021). This cleavage occurs because of the large amount of urea that requires to be added in the final stage of the synthesis of the UF resins to obtain materials that have low F/U molar ratios. However, high molar ratio (≥ 1.2) UF resins require the addition of only a small amount of urea in the final stage of their preparation, which results in the materials containing more branched molecules rather than their linear counterparts.

For decades, researchers have attempted to modify low molar ratio UF resins in various ways to enhance their cross-linking as well as their cohesion (Younesi-Kordkheili et al. 2014; Mahrdrdt et al. 2016; Esmaeili et al. 2017; Lubis et al. 2017; Wibowo and Park 2020). Typically, the mechanical and physical properties of the materials, such as their internal bonding, tensile shear strength, and thickness swelling, were evaluated to determine the effect that the modification has on the resins. However, the methods used to measure such properties do not directly measure the actual adhesion between wood and resins. The obtained results primarily reflect the combination of the cohesion and adhesion involved in bonding the wood together. Knowledge on the adhesion or interaction between wood and adhesives, particularly UF resins, is essential because the adhesives are responsible for the actual interaction between them, in addition to the cohesion of the adhesives themselves. However, on the one hand, wood cell walls are chemically heterogenous, which makes it difficult to conduct studies on the adhesion, which requires a smooth and homogenous surface (Gustafsson et al. 2012). Nevertheless, model surfaces of the

three primary biopolymers of wood cell wall, cellulose, hemicellulose, and lignin, make it possible to study the adhesion because of the convenient preparation of their smooth and homogenous surfaces (Kontturi et al. 2007; Ahola et al. 2008; Notley and Norgren 2010; Gustafsson et al. 2012; Hoeger et al. 2012; Hollertz et al. 2013; Carrick et al. 2014). Cellulose is the most abundant natural polymer on Earth; it is commonly found in plant cell walls and is a major component of wood (Stelte and Sanadi 2009; Sacui et al. 2014; Zhao et al. 2017). Cellulose is a polysaccharide that is composed of glucose monomers that are typically arranged in linear chains that are bound together via inter- and intramolecular hydrogen bonds (He et al. 2020; Tang et al. 2021). As mentioned above, cellulose is one of the most important wood biopolymers because of its presence being correlated with the strength of wood. Thus, this study is focused on the direct measurement of adhesion between cellulose, the major component of the wood cell wall, and the most extensively used wood adhesives, UF resins, which are prepared with two different F/U molar ratios of 1.0 and 1.6. To this aim, three types of nanocellulose are used in this study, namely, cellulose nanofibrils (CNFs), carboxymethylated nanofibrils (CM)-CNFs, and carboxylated cellulose nanocrystals (C-CNCs).

Generally, smooth and thin cellulose films that are suitable for wettability and adhesion studies are prepared using spin-coating or layer-by-layer (LbL) deposition methods (Lefebvre and Gray 2005; Kontturi et al. 2007, 2011; Ahola et al. 2008; Karabulut et al. 2012; Qi et al. 2012). For example, Ahola et al. prepared cellulose model films from both low and high charge density nanofibrils using a spin-coating method (Ahola et al. 2008). The results demonstrated that the charge density of the model surfaces affects their morphology, leading to average root mean squared (rms) roughness values of 4 and 2 nm, for low and high charge density nanofibrils, respectively. Furthermore, Karabulut et al. prepared smooth CM-CNFs films using a layer-by-

layer method (Karabulut et al. 2012). They fabricated pure CM–CNFs and hybrid conjugates of CM–CNF–dopamine films, which combine with polyethyleneimine (PEI) as an anchoring polyelectrolyte, to form smooth surfaces with average rms roughness values of 5 and 8 nm, for the pure CM–CNFs and hybrid CM–CNFs, respectively.

Usually, the interfacial adhesion of a cellulose model surface is measured using Johnson–Kendall–Roberts (JKR) contact mechanics, contact angle measurements, and more advanced methods such as atomic force microscopy (AFM) in the peak–force mode (Rundlöf et al. 2000; Eriksson et al. 2007; Gustafsson et al. 2012; Carrick et al. 2014; Lai et al. 2019). For example, Gustafsson et al. measured the work of adhesion between cellulose and other wood biopolymers using the JKR method and contact angle measurements (Gustafsson et al. 2012). They reported that the JKR work of adhesion was lower than that calculated from contact angle measurements because of the overestimation of the surface energies of the contact angle measurements. Furthermore, Lai et al. compared the JKR contact mechanics and AFM peak–force mode measurements combined with a colloidal probe technique to measure the interfacial adhesion between cellulose surfaces (Lai et al. 2019). They reported that the JKR adhesion values are higher than their proposed experimental values because the JKR model only considers the interactions between smooth surfaces at equilibrium, whereas their developed method considers a contact model of rough–rough interactions, devised by dividing the surface contacts into primary and secondary levels. Hence, the local individual contacts between rough surfaces were considered in their work.

However, in this study, the direct adhesion between nanocellulose and UF resins is determined by measuring the adhesion force (Sun et al. 2017; Wang et al. 2020a) between nanocellulose films and liquid droplets of the UF resins, as well as by calculating the work of adhesion between

the films of the nanocelluloses and UF resins using contact angles via the van Oss–Chaudhury–Good (OCG) method (van Oss et al. 1988; Gustafsson et al. 2012). These two methods were selected because of their convenience and simplicity. The adhesion force (F) between the UF resin droplets and nanocellulose films can be calculated using **Eq. 1**. F comprises two components: i) the surface tension force (F_s), which is the vertical component of the liquid–gas interfacial tension located along the perimeter of the triple contact line, and ii) the other is the capillary pressure force (F_L), which is caused by the curvature of the liquid because of the pressure difference (**Eq. 2**) across the liquid–gas interface for a stretched droplet (see **Scheme 1** for details). The combination of these two forces can be expressed using the following equation (Sun et al. 2017; Wang et al. 2020a):

$$F = F_s - F_L = 2\pi r \gamma \sin \theta - \pi r^2 \Delta P \quad (1)$$

where r is the base radius of a droplet that is in contact with the substrate, γ is the liquid–gas interfacial tension, θ is the contact angle, and ΔP is the Laplace pressure, defined as the pressure difference inside and outside the droplet. Note that ΔP can be either positive or negative, depending on the shape of the droplet. The contact angle at the maximum adhesion force (F_{max}) is the most stable contact angle, θ_{max} . All the stretched droplets are concave shaped; thus, ΔP can be expressed as follows:

$$\Delta P = \gamma \left(\frac{1}{D} - \frac{1}{R} \right) \quad (2)$$

where D and R are the principal radii of the droplet.

Scheme 1. An example of a UF resin droplet in its maximum adhesion state recorded at the retraction stage, where the contact angle (θ), droplet base radius (r), and principal radii (D and R) of the droplet are shown.

The work of adhesion between these two films can be calculated using the surface energy of each film, which can be determined using the OCG method. The surface energies of the different nanocelluloses and UF resin films were calculated according to the OCG method (van Oss et al. 1988; Gustafsson et al. 2012) (**Eq. 3**):

$$\gamma_{l,i}^{Tot}(1 + \cos \theta_i) = 2 \left(\sqrt{\gamma_{l,i}^{LW} \gamma_s^{LW}} + \sqrt{\gamma_{l,i}^+ \gamma_s^-} + \sqrt{\gamma_{l,i}^- \gamma_s^+} \right) \quad (3)$$

where θ is the contact angle between a droplet of a liquid and a solid; γ^{Tot} is the total surface energy; γ^{LW} is the Lifshitz–van der Waals (dispersive) component of the surface energy; γ^+ is the electron acceptor surface energy parameter; and γ^- is the electron donor surface energy parameter of the material. Hence, this method allows the surface energy to be split into its dispersive, γ^{LW} ; and polar component, acid, γ^+ , and base, γ^- , contributions. Because the OCG equation contains three unknown variables (γ_s^{LW} , γ_s^+ , and γ_s^-), this method requires the use of a minimum of three test liquids that have known surface tensions to solve the equation. As shown in **Scheme 2**, water, diiodomethane, and ethylene glycol are commonly used for this purpose.

Scheme 2. Schematic of the measuring of contact angles on nanocellulose and UF resin films using the probe liquids in the OCG method.

Furthermore, AFM and X-ray photoelectron spectroscopy (XPS) were used to determine the thickness, surface roughness, and chemical composition of the sample films. Moreover, Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and transmission electron microscopy (TEM) were also used to determine the chemical structures, diffraction patterns, and morphologies of the different nanocellulose samples, whereas gel permeation chromatography (GPC) was used to determine the molecular weights of the low and high molar ratio UF resins.

2 Experimental

2.1 Materials

Formalin (37 wt%) and extra pure grade urea (99 wt%) were obtained from Daejung Chemical, Korea. Extra pure grade NH_4Cl (99 wt%), NaOH (93 wt%), and aqueous formic acid (85 wt%) were purchased from Duksan Chemical, Korea. High-performance liquid chromatography (HPLC) grade dimethylformamide (DMF, 99.9%) and dimethyl sulfoxide (DMSO, 99.9%) used as the mobile phase for GPC analysis were obtained from Fisher Scientific and Duksan Chemical Korea, respectively. CNFs (1 wt%) and CM-CNFs (2 wt%) with a degree of substitution of 0.8 mmol/g were obtained from CNNT Co. Ltd in Suwon, Korea and Moorim Paper in Ulsan, Korea,

respectively. C-CNCs (0.45 wt%) with a degree of oxidation of 0.15 were prepared in the laboratory as per a previously reported method (Khanjanzadeh and Park 2021). CNFs were prepared using an aqueous counter collision method (Kondo et al. 2014), while both the CM-CNFs and C-CNCs were prepared via a chemical treatment (Gustafsson et al. 2012; Khanjanzadeh and Park 2021). Silicon wafer (p-type, Si 100 with a native oxide layer on top) was acquired from MTI Korea, Seoul, Korea. HellmanexTM III solution and poly(diallyldimethylammonium chloride) (PDADMAC) solution (20 wt%) with an average molecular weight of 200,000–350,000 was purchased from Sigma-Aldrich, USA. Moreover, HPLC-grade water, diiodomethane (99%), and ethylene glycol (99.8%) were purchased from Sigma-Aldrich, USA, and used in the contact angle measurements.

2.2 Synthesis of UF resins with different molar ratios

Low and high F/U molar ratio (1.0 and 1.6) UF resins were prepared via an alkaline–acid–alkaline three-step reaction. Formalin solution was first poured into a four-neck glass reactor, adjusted to pH 8.0 using sodium hydroxide (NaOH, 20 wt%), and then heated to 40 °C. Urea was subsequently added into the reactor to give an initial F/U molar ratio of 2.0. The mixture was then heated to 90 °C and the pH was maintained at 8.0 for 1 h to allow the addition reaction to proceed. Then, the temperature and pH were adjusted to 80 °C and 4.6, respectively, to facilitate the condensation reaction. The reaction was terminated when a target viscosity of ‘J–K’ scale was reached based on readings using a bubble viscometer (VG 900, Gardener-Holdt, Columbia, South Carolina, USA) and the pH was adjusted back to alkaline (8.0–8.2). Furthermore, a certain amount of urea was added into the glass reactor to obtain a final F/U molar ratio of 1.0 or 1.6 and the temperature was maintained at 60 °C for 20 min. Subsequently,

the resins were cooled to 25 °C and the pH was adjusted to ~8.2. The resins were then stored at room temperature for 24 h prior to their analysis.

2.3 Properties of the UF resins

The viscosity, non-volatile solid content, and gelation time of the UF resins with different molar ratios of 1.0 and 1.6 were determined as per a method used in a previous work (Wibowo et al. 2020a). The apparent molecular weights of the 1.0 and 1.6 UF resins were measured using GPC (YL9100, Younglin, Gyeonggi-do, Korea). Note that 1% UF resin solutions were prepared by dissolving each sample in a mixture of 10% DMSO and 90% DMF and placing them in an oven at 50 °C for 3 h. Subsequently, the mixtures were injected into the GPC instrument after filtration through a 0.45-μm-sized filter. The columns used in this characterization technique were KD 801, 802, and 806 M (SHODEX, Showa Denko K.K., Tokyo, Japan). Polyethylene glycol (PEG) with a molecular weight (M_w) of between 106 and 25,200 Da (Polymer Standards Service GmbH, Mainz, Germany) was used for calibration standards. The weight-averaged M_w , number molecular weight (M_n), and polydispersity index (PDI) of the resins were calculated using the YL-Clarity Version 6.1.0.130 software (Younglin, Gyenggi-do, Korea).

2.4 Attenuated total reflection-FTIR (ATR-FTIR) spectroscopy

ATR-FTIR measurements were conducted using a Bruker Alpha FTIR spectrometer (Bruker Optics GmbH, Ettlingen, Germany) to determine the functional groups of the different CNFs, CM-CNFs, and C-CNCs nanocellulose samples. Solid suspensions of each of the nanocellulose materials were freeze-dried, ground into a fine powder, and then measured using the

spectrometer for 32 scans in the wavelength range of 400–4000 cm⁻¹ at a resolution of 4 cm⁻¹.
The spectrum of each sample was then normalized using a min–max normalization.

2.5 X-ray diffraction (XRD) analysis

XRD patterns of the different CNFs, CM–CNFs, and C–CNCs nanocellulose samples were analyzed using a multipurpose diffractometer (Malvern Panalytical, UK) equipped with a CuK α radiation source ($\lambda = 0.15406$ nm). For analysis, the solid suspensions of the different nanocellulose materials were freeze-dried and ground into a fine powder. These samples were then scanned at room temperature from 0° to 50° with a step of 0.02°/min. Moreover, the crystallinity of the samples was estimated using the peak deconvolution method from XRD patterns. The sharp crystalline peaks in the patterns correspond to cellulose I reflections (1 1 0), (1 $\bar{1}$ 0), (0 1 2), and (2 0 0), and the broad peak corresponding to amorphous material were fitted using a pseudo-Voigt function instead of the commonly used Gaussian function. As pointed out by French et al., the simple and very broad Gaussian peak does not adequately represent amorphous cellulose (Ling et al. 2019; French 2020). In addition, the curve deconvolution representation of the amorphous fraction cannot reach the minimum intensity of the observed data at about 18.5°. Furthermore, the crystallinity of each sample was calculated as follows:

$$Crystallinity (\%) = \frac{Sc}{St} \times 100 \quad (4)$$

where Sc represents the area of the crystalline domain and St is the area of the total domain (crystalline + amorphous).

2.6 Transmission electron microscopy

The morphologies of the CNFs, CM–CNFs, and C–CNCs were analyzed using TEM (JEM-2100 F, JEOL, Japan), where the samples were prepared using a previously described method (Khanjanzadeh and Park 2021). Briefly, each sample was diluted with water to a concentration of 0.01 wt%. Then, small amounts of the diluted samples were dropped on copper grids and dried at room temperature. Subsequently, the samples were stained by placing a drop of 3% uranyl acetate solution on the grids to intensify the contrasts of the images. Any excess stain solution was absorbed using filter paper and the samples were then left to dry at room temperature.

2.7 Atomic force microscopy

Prior to AFM analysis, different UF resins and nanocellulose films were first prepared using a spin-coating method. Briefly, Si wafers were cut to a size of $1 \times 1 \text{ cm}^2$ and cleaned with 2% Hellmanex solution at room temperature for 120 min. The Si substrates were then rinsed in deionized water and dried inside a clean desiccator in a fume hood. The cleaned substrates were then placed in 0.1% PDADMAC for 1 h. Subsequently, the pre-treated substrates were rinsed in deionized water and dried inside a clean desiccator in a fume hood. Finally, 1.0 or 1.6 UF resins mixed with 0 or 3% NH_4Cl and 0.1 wt% of the CNFs, CM–CNFs, and C–CNCs nanocellulose samples were spin-coated onto the Si wafer substrates at 3000 rpm for 30 s. Furthermore, the resins films were then cured at 105°C for 3 h in an oven, whereas the nanocellulose films were dried at 50°C for 3 h. The morphologies of all the sample surfaces were then imaged using AFM (Park NX20, Park Systems Corp., Suwon, Korea). Images were acquired in non-contact mode at a nominal resonance frequency of 290.5 kHz, a Q-factor of 574.8, a scan rate of 1.00 Hz, and a set-point of 7.0 nm. The rms surface roughness (R_q) was calculated from the average of six $10 \times 10 \text{ }\mu\text{m}$ areas using XEI software (4.3.4 version, Park Systems Corp.). The thickness of films is

determined by measuring the height difference between the top surface of the sample film and the Si substrate surface at four different locations (Yokota et al. 2007). Thus, the film thickness was measured at two locations, namely, the edge and middle of the films. To measure the middle thickness, a section of the films was scratched off with the tip of a pair of tweezers wrapped in tissue that was dipped in 1 N HCl prior to their use (Sczech and Riegler 2006). AFM images showing the thickness measurements are provided in the supplementary information (**Fig. S1**).

2.8 XPS analysis

An XPS system (Nexsa, Thermo Fisher Scientific, Massachusetts, USA) was used to determine the chemical compositions of the different nanocellulose model surfaces. For quantitative elemental analysis, low-resolution scans at a pass energy of 80 eV and 1 eV steps were used to analysis the C_{1s}, O_{1s}, and Si_{2p} regions, whereas high-resolution scans at a pass energy of 20 eV and 0.1 eV steps were used to obtain detailed chemical analysis of the samples (Ahola et al. 2008). High-resolution XPS spectra were used to deconvolute the C–C, C–O, O–C–O, and O–C=O peaks using a Gaussian function.

2.9 Maximum adhesion force and work of adhesion measurements

The maximum adhesion force (F_{max}) values of droplets of the UF resins with different molar ratios on the different nanocellulose films were measured using a tensiometer (DCAT 25, Data Physics Instruments GmbH, Filderstadt, Germany). For measurements, a liquid droplet was placed on an RG 2 Du Noüy ring and pressed onto the respective solid film surface. Then, the liquid droplet was pulled off and a force–distance curve was recorded automatically during this procedure. The surface of a film sample was moved upward toward the UF resin droplet at a

speed of 0.5 mm/s, which was then reduced to 0.2 mm/s when the film sample surface came into contact with the surface of the droplet. After reaching the compression distance (0.1 mm), the film sample was retracted at a constant speed of 0.2 mm/s until the droplet was detached from the surface of the film sample. F_{max} was measured at the θ_{max} identified from a typical recorded image (**Scheme 1**) and represented by the peak of a force–distance plot. Then, the F_{max} value was calculated based on **Eq 1**. This experiment was repeated three times for each sample. Furthermore, the work of adhesion (W_{12}) between the nanocellulose and UF resin films was calculated using the following equation (Gustafsson et al. 2012; Carrick et al. 2014):

$$W_{12} = 2 \left(\sqrt{\gamma_1^{LW} \gamma_2^{LW}} + \sqrt{\gamma_1^+ \gamma_2^-} + \sqrt{\gamma_1^- \gamma_2^+} \right) \quad (5)$$

where γ_1 and γ_2 are the surface energies of the nanocellulose and UF resin films, respectively, which were determined using the OCG method and from contact angles (**Eq 3**). Static contact angle measurements were performed using the same tensiometer, using HPLC-grade water, diiodomethane, and ethylene glycol. The contact angles were measured using the sessile drop method, with the measurements repeated three times for each sample. The reported contact angles were recorded after at least 20 s to obtain values that were as stable as possible without any significant influence from the penetration of the liquid into the film (Gustafsson et al. 2012; Carrick et al. 2014). The contact angles were used to calculate the surface energies of the nanocellulose and UF resin samples according to the OCG method (van Oss et al. 1988) (**Eq 3**). The surface tensions, including the dispersive, acid, and base components, of the three probe liquids used in this experiment were obtained from the literature (van Oss 1993; Cwikel et al. 2010; Jafarzadeh et al. 2011).

Table 1. The surface energies (mJ m^{-2}) of the three liquids used for the contact angle measurements (van Oss 1993; Cwikel et al. 2010; Jafarzadeh et al. 2011).

Probe liquid	γ^{Tot}	γ^{LW}	γ^{AB}	γ^{+}	γ^{-}
Diiodomethane	50.8	50.8	0	0	0
Water	72.8	21.8	51	25.5	25.5
Ethylene glycol	48	29	19	1.92	47

3. Results and Discussion

3.1 Physical and chemical properties of the UF resins and nanocellulose samples

The properties and characteristics of the UF resins are closely related to their F/U molar ratio. Usually, high F/U molar ratio UF resins have better properties than those with lower ratios, as has been explained in many reports published in the literature (Park and Jeong 2011; Park et al. 2013; Wibowo et al. 2020a). As presented in **Table 2**, the viscosities and molecular weights of the samples increase as their molar ratios increase from 1.0 to 1.6, indicating that the 1.6 UF resin contains bigger molecules than the 1.0 UF resin, which is primarily attributed to the formation of more branched molecules in the former. The amount of urea added at the end of the synthesis procedure, particularly in the case of the 1.0 UF resin, results in the formation of linear molecules that have a low viscosity and molecular weight. It has been revealed that the addition of an excess of urea to the synthesis under the alkaline condition might split oxymethylene and branched methylene ether linkages into linear molecules in the UF resins (Wibowo et al. 2020b; Wibowo and Park 2021). The formation of linear molecules contributes to the crystalline domains because they are responsible for the ordered arrangement, maintained by hydrogen

bonds that form between the linear molecules, as has been reported in a previous work (Wibowo et al. 2020a; Wibowo and Park 2021). These crystalline domains inhibit the formation of a 3D network and consequently decrease the reactivity and adhesion of the UF resins. The degradation in the reactivity of the resin of the sample with a F/U molar ratio of 1.0 was demonstrated by a significant increase in its gelation time compared with that of the resin with a 1.6 F/U molar ratio. Moreover, the high amount of free formaldehyde present in the 1.6 UF resin is capable of facilitating the curing of the sample, thus resulting in a shorter gelation time, because it acts as a bridge that connects the oligomers formed in the pre-cured resin (Wibowo and Park 2020).

Table 2. Properties of the two UF resins with different F/U molar ratios.

F/U molar ratio	Non-volatile solids content (%)	pH	Specific gravity	Gelation time (s)	Viscosity (mPa s)	Mw (g/mol)	Mn (g/mol)	PDI
1.0	57.9 ± 0.2	8.1	1.21	145.0 ± 1.0	147.5 ± 1.1	578	369	1.56
1.6	53.0 ± 0.3	8.3	1.20	57.3 ± 1.0	215.0 ± 1.0	762	475	1.60

To understand the adhesion between a UF resin and cellulose, the chemical properties of the cellulose need to be understood. Thus, different types of nanocellulose were characterized to evaluate the influence of chemical property and morphology to their surface adhesion with UF resins. **Fig. 1** shows the FTIR spectra and XRD patterns of the different nanocellulose samples. It can be seen that the functional groups in the CNFs, CM-CNFs, and C-CNCs samples are somewhat similar. For example, they all feature a broad hydroxyl peak at 3600–3000 cm⁻¹ in their FTIR spectra, as they primarily comprise hydrogen-bonded hydroxyl groups (Leng and Pan 2019). However, in the case of the CM-CNFs, the FTIR peak shapes are different and of a lower

intensity compared with those of the other samples, indicating that it has fewer –OH groups due to these being replaced with negatively charged carboxymethyl groups ($-\text{CH}_3\text{COO}^-$), which can separate some hydrogen bonds via a charge repulsion effect. Another notable difference can be observed in the FTIR spectra at $\sim 1640\text{--}1590\text{ cm}^{-1}$. Typical asymmetric (1590 cm^{-1}) (Dos Santos et al. 2015; Melilli et al. 2020; Wu et al. 2021) and symmetric (1420 and 1217 cm^{-1}) (Melilli et al. 2020) vibrations associated with the carboxylate anion (COO^-) were detected in the spectra of both the CM–CNFs and C–CNCs samples, while only a weak band at 1640 cm^{-1} attributed to OH bending (Leng and Pan 2019) was observed in the spectrum of the CNFs. Nonetheless, OH bending was still detected and overlapped at the shoulder of the spectrum of the CM–CNFs, indicating that there are still certain similarities between the CNFs and CM–CNFs, with their only difference being in the abundance of negative charges. Interestingly, the absorption bands at $\sim 1107\text{ cm}^{-1}$ (anhydroglucose ring vibration) and 1053 cm^{-1} (C–O–C pyranose ring vibration) in the FTIR spectrum of the C–CNCs are more intense than those observed for the other samples, indicating that certain non-cellulosic amorphous material was removed during the oxidation of the samples, which consequently increased the crystalline cellulose content (Khanjanzadeh and Park 2021). These bands are of very weak intensity in the spectrum of the CM–CNFs, indicating that it may feature fewer crystalline domains. These results are supported by the XRD and crystallinity data shown in **Fig. 1b–c**. The XRD patterns of the nanocellulose samples feature four crystalline peaks associated with the $(1\ 1\ 0)$, $(1\ -1\ 0)$, $(0\ 1\ 2)$, and $(2\ 0\ 0)$ reflections typically associated with cellulose I and one broad peak at a 2θ angle of $\sim 18^\circ$ that can be attributed to an amorphous region (Nindiyasari et al. 2016). However, the peaks at $\sim 12^\circ$ and $\sim 20^\circ$ in the XRD pattern of the CM–CNFs are more intense in comparison, and are indicative of the cellulose II crystalline structure of the CM–CNFs (Bhandari et al. 2012). It thus appears that

some cellulose I has been converted to cellulose II and amorphous. However, the pattern of CM–CNFs is still dominated by the cellulose I reflections which is consistent with FTIR result. Furthermore, the C–CNCs have the highest crystallinity compared with the other samples, observed from its XRD pattern having the lowest intensity of the amorphous peak. This occurs because the strong acid used during the preparation of the C–CNCs removes most of the amorphous material from the sample, resulting in the presence of highly crystalline cellulose, as illustrated in **Scheme 3**. However, the CM–CNFs exhibit the lowest crystallinity, with its XRD pattern featuring the amorphous peak with the highest intensity. As mentioned in the FTIR results, the CM–CNFs may still contain some noncellulosic amorphous material. Moreover, another reason for the low crystallinity of this sample is the high degree of substitution of the carboxymethyl groups in the CM–CNFs, which contributes to the negative charge that induces electrostatic repulsion in this material. This leads to the destruction of hydrogen bonds, resulting in the CM–CNFs having a less ordered structure, as shown in **Scheme 3**. This result is in agreement with the published results of many studies in the literature, which report that the incorporation of carboxymethyl groups in a sample reduces the crystallinity of the cellulose (Bhandari et al. 2012; Doh et al. 2013; Dos Santos et al. 2015).

Fig. 1. (a) FTIR spectra and deconvoluted XRD patterns of the (b) CNFs, (c) CM–CNFs, and (d) C–CNCs.

Scheme 3 shows the schematic of the structures of the nanocellulose samples alongside their actual morphology exhibited in TEM images. The TEM images (**Scheme 3** and **Fig. S2**) clearly show the differences in the morphologies of the nanocellulose samples, particularly in their shape and size. For instance, the CNFs exhibit large web-like and highly entangled structures, while the CM–CNFs are relatively short and separated fibrils. Moreover, the TEM image of the

C–CNCs clearly displays their short needle-like whisker morphology. In agreement with these results, similar morphologies of nanocelluloses in the TEM images of different cellulose samples were observed in another report in the literature (Xu et al. 2013).

Scheme 3. Schematic of the structures of the different nanocellulose samples alongside their actual morphologies shown in the respective TEM images.

3.2 Morphologies of the UF resins and nanocellulose films

Table 3 lists the different UF resins and nanocellulose films fabricated using a spin coating method and their properties were measured. The results show that the R_q values of the UF resin films vary, depending on their molar ratio and addition of a hardener during their preparation. It can be observed that the 1.6 UF resins have smoother surfaces than those of the 1.0 UF resins,

415 regardless of level of hardener used in their preparation. It can be observed that the 1.0 UF resin
416 prepared using a hardener has the highest R_q value; however, the 1.6 UF resin prepared using a
417 hardener has the lowest R_q value. This is because the 1.0 UF resins features crystalline domains,
418 especially when cured with hardener, while the 1.6 UF resins are amorphous as has been
419 previously reported (Wibowo and Park 2021). The crystal domains of the 1.0 UF resins, which
420 are shown in the AFM image in **Fig. 2b** make the surface rough, resulting in the materials
421 exhibiting high R_q values. Moreover, as shown in **Figs. 2a** and **b**, the 1.0 UF resins have pores
422 distributed across their surfaces, which are not observed for the 1.6 UF resins shown in **Figs. 2c**
423 and **d**. These pores are formed by the evaporation of water from the sample, which might
424 contribute to the roughness of the 1.0 UF resins. It seems that the evaporation might occur in an
425 uneven manner from the 1.0 UF resins, probably because of the uneven distribution of the
426 crystalline domains in the 1.0 UF resins. This is supported by the fact that the pores are primarily
427 formed around the crystalline domains, as shown in **Fig. 2b**, which can be seen in the enlarged
428 image shown in **Fig. S3** in the supplementary information. These results are in line with those of
429 another study in the literature, which reported that semicrystalline poly(ethylene terephthalate)
430 (PET) has a higher roughness than the amorphous PET polymer (Junkar et al. 2009).
431 Furthermore, the nanocellulose films have various thicknesses and R_q values according to the
432 different nanocellulose types. As expected, the edge thickness is greater than the middle
433 thickness in all cases. This is attributed to the edge bead formation resulting from an increase in
434 the friction between the air and the substrate at the periphery, and a faster drying at the edge
435 during the rotation of the spin-coater (Atthi et al. 2009). Moreover, the obtained thickness and R_q
436 values of the nanocellulose films are in the range of or similar to the results previously reported
437 in the literature (Yokota et al. 2007; Ahola et al. 2008). However, the results for the CNFs are

worse than those of the CM–CNFs and C–CNCs, indicating that the negative charges attributed to the carboxymethyl (CH_3COO^-) or carboxylate (COO^-) ions have a significant repulsion effect during the manufacture of the film. These repulsive anion–anion electrostatic forces prevent their molecular agglomeration that occurs because of the formation of strong hydrogen bonds when the molecules are very close. It has been reported that highly charged nanocellulose has a dense and smooth surface structure (Ahola et al. 2008). This makes it easier to liberate fibrils from the structure, which results in smaller and more uniform dimensions. This is supported by the AFM images of the nanocellulose films with a scan size of $50 \times 50 \mu\text{m}$ (**Fig. S4** in the supplementary information). The structures of the CM–CNFs and C–CNCs films can be observed as being more uniform and denser (less open) compared to that of the CNFs film. Moreover, the CNFs film has a rougher surface with the presence of some big fibers, probably because of the aggregation or web-like morphology of the CNFs. However, interestingly, the C–CNCs film is very uniform, which is primarily related to the smaller size of the nanocellulose fibrils in this sample, as shown in **Scheme 3**, compared to in the other samples.

Table 3. Film properties of different UF resins and nanocellulose samples.

Sample for film	Concentration (%)	Edge thickness (nm)	Middle thickness (nm)	Surface roughness, R_q (nm)
1.0 UF resins	+ 0% NH_4Cl	*		2.32 ± 1.03
	+ 3% NH_4Cl			4.48 ± 0.70
1.6 UF resins	+ 0% NH_4Cl			2.07 ± 0.40
	+ 3% NH_4Cl			0.58 ± 0.21
CNFs	0.1	39.79 ± 0.35	34.54 ± 1.17	7.52 ± 1.18
CM–CNFs	0.1	26.49 ± 3.40	9.75 ± 1.58	3.57 ± 0.19

C–CNCs	0.1	24.64 ± 0.20	7.19 ± 0.53	2.68 ± 0.38
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*The thickness of the UF resins could not be measured because their films are too thick for the AFM instrument.

Fig. 2(e–g) show clear images of the three types of nanocellulose films, in which the CNFs are less uniform and compact than the CM–CNFs and C–CNCs. These results are in good agreement with the film properties shown in **Table 3**, exhibiting that the CNFs film is thicker (both at the edge and middle) and has a higher R_q value compared with the CM–CNFs and C–CNCs. Moreover, abundant white spots and big fibers can be observed on the surface of the CNFs, thought to have formed because of the aggregation of the CNFs via hydrogen bonds and van der Waals forces, which might have occurred during their drying (Peng et al. 2012; Niu et al. 2018). During the drying of the CNFs, the forces resulting from the removal of water at high temperature may drive the molecular contact that facilitates the occurrence of the above forces (Peng et al. 2012). The aggregation of the CNFs can be clearly observed in the enlarged AFM image shown in **Fig. 2h**, which is very different from what is observed in the AFM images of the CM–CNFs and C–CNCs shown in **Fig. 2i–j**. Similarly, the agglomeration of CNFs on the smooth surface of PVA and Si wafer has been observed from AFM analysis (De Souza et al. 2017; Niu et al. 2018). Furthermore, the analysis of the coverage of the nanocellulose samples on the Si surface was evaluated using XPS to verify the AFM results.

Fig. 2. AFM images ($50 \times 50 \mu\text{m}$) of the films of the cured UF resins with the two molar ratios and hardener contents. (a) 1.0 UF resin, (b) 1.0 UF resin + hardener, (c) 1.6 UF resin, and (d) 1.6 UF resin + hardener. AFM images ($10 \times 10 \mu\text{m}$) of the different nanocellulose films: (e) CNFs, (f) CM-CNFs, and (g) C-CNCs and their color contrast AFM images ($1 \mu\text{m}^2$): (h) CNFs, (i) CM-CNFs, and (j) C-CNCs.

Low-resolution XPS (**Fig. S5**) was used to determine the chemical compositions of the nanocellulose model films and a Si wafer pre-treated with PDADMAC was used as a reference. In the XPS spectra, the highest intensity was generated by O_{1s} followed by C_{1s} and Si_{2p} , regardless of the nanocellulose type. However, for the reference film, the total intensity of Si_{2p} was higher than that of C_{1s} , indicating that the surface of the Si wafer might not be well covered.

Table S1 shows the quantitative chemical analysis related to the film coverage. The highest percentage of Si was detected in the reference film, but it was significantly decreased after the deposition of nanocellulose on the Si surface. As is consistent with the AFM analysis, the CM–CNFs and C–CNCs films contain a low Si content (<5%), indicating good sample coverage because of the uniform and compact distribution of the nanocellulose particles. However, the CNFs film shows the opposite, with a relatively high Si content (~10%). Nevertheless, compared with the percentage of Si in the reference (~30%), this value is good enough and still lower than that reported in another study in the literature (Ahola et al. 2008). These results indicate that, in general, the surface of all of the nanocellulose films show good coverage. Another notable difference between the samples is in their carbon content. The percentage of carbon in the CNFs is lower than that in the CM–CNFs and C–CNCs, primarily due to the CNFs having less film coverage also because of the absence of additional functional groups such as carboxymethyl (CH_3COO^-) or carboxylate (COO^-) groups that contain carbon atoms. The presence of several types of functional groups in the CNFs, CM–CNFs, and C–CNCs was confirmed from their high-resolution C_{1s} XPS spectra, shown in **Fig. 3**. These spectra display four typical peaks, namely, C1 (C–C, ~284 eV), C2 (C–O, ~286 eV), C3 (O–C–O or C=O, ~287 eV), and C4 (C–C=O, ~289 eV) (Niu et al. 2018). The C1, C2, and C3 peaks are detected in the spectra of all of the nanocellulose films, while C4 is only observed in the spectra of the CM–CNFs and C–CNCs. This is because only these nanocellulose samples feature functional groups that contain C–C=O. Moreover, only the C1 peak was detected in the spectrum of the reference film, reflecting the C–C bonds in the PDADMAC compound.

Fig. 3 Deconvolution of the high-resolution C_{1s} XPS spectra of the reference and nanocellulose films. (a) Si wafer + PDADMAC, (b) CNFs, (c) CM-CNFs, and (d) C-CNCs.

3.3 Adhesion force, wettability, and work of adhesion between the UF resins and nanocellulose films

Fig. 4 shows the typical force-distance curves of the adhesion force measurements between a droplet of the UF resins in the two molar ratios and the film surfaces of the nanocellulose

samples. **Fig. S6** shows the images taken at the maximum adhesion point of these curves. The measurement is divided into four stages: 1) approaching the film surface toward the liquid droplet until the surface of the film makes contact with the surface of the liquid droplet in an equilibrium; 2) retracting the film downward, which changes the state from an advancing to a receding one, and the adhesion force between the droplet and the film surface increases until maximum and the θ_{max} is reached; 3) stretching the film surface from the surface of the droplet by keep moving the solid film down; and 4) final detachment of the surface of the film sample from the surface of the droplet. The force value at the peak of the curve is referred as the maximum adhesion force (F_{max}), which represents the surface adhesion between a liquid droplet and a solid film surface (Sun et al. 2017). **Table S2** shows a summary of the experimental data of the adhesion force measurements. As expected, the 1.6 UF resins exhibit a higher adhesion force with the nanocellulose surface than the 1.0 UF resins, regardless of the nanocellulose type, as shown in the data in **Table 4**. According to the properties of the resins, as shown in **Table 2**, the 1.6 UF resins are more reactive, showing a shorter gelation time, and have a greater viscosity and M_w than the 1.0 UF resins. It is believed that these differences result in the stronger adhesion force of the 1.6 UF resins than the 1.0 UF resins with the surfaces of the nanocellulose samples. The adhesion forces between the UF resins and nanocellulose may be related to dispersion and dipole–dipole (hydrogen bonds) molecular interactions. A large molecular size is known to be a factor in the strong dispersion forces between molecules. Compared to smaller molecules, large molecules are more easily polarized. In other words, easier distribution of electrons around large molecules facilitates the formation of temporary dipoles, resulting in stronger molecular interactions. Furthermore, as shown in **Table 4**, among nanocellulose samples, CNFs exhibit the lowest F_{max} values with the two UF resins, while the other nanocellulose samples show similar

values. The reason for this can be attributed to the fact that both the CM-CNFs and C-CNCs have additional negative charges compared to the CNFs, which contribute toward the dipole-dipole forces between their molecules and the UF resins. Moreover, the aggregation and rough surface of the CNFs film may contribute to the lower adhesion force. However, the difference the $F_{\max}$ values of the samples is not great, therefore, it can be concluded that the adhesion forces between the UF resins with F/U ratios of 1.0 or 1.6 and the three types of nanocelluloses are relatively similar.

Fig. 4. Typical force–distance curves recorded for the different molar ratios of UF resin droplets on the surfaces of the nanocellulose model films. (a) CNFs, (b) CM–CNFs, and (c) C–CNCs.

Table 4. Maximum adhesion force between two molar ratio UF resins and different nanocellulose films

Nanocellulose film type	$F_{\max}/\text{area (mN/mm}^2\text{)}$	
	1.0 UF resins	1.6 UF resins
CNFs	0.049*	0.055
CM-CNFs	0.053	0.059
C-CNCs	0.053	0.060

*All standard deviations are ≤ 0.001 , except for the CNFs vs 1.0 UF resins which is 0.0024 (see **Table S2**)

There are several factors that affect the surface wettability of a polymer, such as its molecular structure, M_w , PDI, surface topography, and surface roughness (Hirai et al. 2014). In this study, the effects of such factors on the wettability and surface energy were investigated. **Fig. 5** shows the contact angles of water and diiodomethane on the surfaces of the different UF resin films. It is clear from these images that there is a remarkable difference in the contact angles of water and diiodomethane. Thermosetting polymers such as cured UF resins, which are supposed to be hydrophobic (Yilgor et al. 2012), are more preferably wetted with diiodomethane rather than water. This is because diiodomethane is non-polar owing to its molecular symmetry, while water is a strong polar liquid. Although there is a slight difference in the magnitude of the contact angle between the UF resin films with different molar ratios and hardener levels, the 1.6 UF resins are more hydrophobic than the 1.0 UF resins, regardless of the level of hardener, as shown in **Fig. 5**. There are several reasons behind this behavior. The first reason is that the 1.6 UF resins have higher M_w values than the 1.0 UF resins. The second is that the 1.6 UF resins contain more

572 branched molecules and exhibit highly cross-linked structures when they are cured (Wibowo and
573 Park 2021). As expected, the greater the number of molecules in thermosetting resins, the higher
574 their water resistance. This is attributed to the high proportion of covalent bonds (methylene and
575 methyl ether linkages) that form in the chemical structure. The third reason is that the 1.6 UF
576 resins are amorphous with low R_q values, while the 1.0 UF resins are semicrystalline with high
577 R_q values. In general, the smoother the surface of a polymer, the lower its water contact angle,
578 which has been already discussed in some studies in the literature (Bikernian 1950; Wang et al.
579 2020b). In this case, the opposite is true, as the surface roughness of the 1.6 UF resins is lower
580 than that of the 1.0 UF resins. As mentioned above, there are various factors that affect the
581 wettability of a polymer surface. Thus, the dominant factors are possibly the chemical structure
582 and molecular weight in the case of the UF resins. Furthermore, these results are consistent with
583 another published study in the literature, which investigated the water contact angles of
584 thermosetting polyurethane films (Brzeska et al. 2017). They demonstrated that semicrystalline
585 linear polyurethane has a lower contact angle than amorphous cross-linked polyurethane that has
586 a smoother surface. In addition to the other contributing factors mentioned earlier, another
587 possible cause of this phenomenon is the micro- or nano-size pores present in the materials,
588 which has been explained in another report (Łojkowski et al. 2019). It appears that the numerous
589 pores in the 1.0 UF resin films (**Figs. 2a and b**) contribute to these materials having low water
590 contact angles. Furthermore, in the case of the addition of hardener, it seems that it makes the
591 resins slightly more hydrophobic. This is because the hardener facilitates the condensation
592 reaction, resulting in the formation of a long polymer that has abundant covalent bonding,
593 thereby leading to a high contact angle with water and a lower contact angle with diiodomethane.

Fig. 5. Example of water and diiodomethane contact angle measurements on different UF resins films. *H indicates that 3% NH₄Cl was used as a hardener.

The surface energy (γ), which is defined as the energy change divided by the change in the surface area, has become one of the fundamental parameters in polymer science (Gong et al. 2019). Various methods have been employed to estimate the surface energy of a polymer substrate, of which one of the most widely used methods is the measurement of contact angles for the OCG method (van Oss et al. 1988). The surface energies of the UF resins and nanocellulose films were calculated based on the contact angles of three different liquids on their surfaces, which are presented in **Table S3**. **Table 5** summarizes the results of the surface energy components obtained using the OCG method. From the data, it appears that the total surface energies (γ^{Tot}) of the UF resins and nanocellulose films are relatively similar, but the 1.6 UF resins have higher γ^{Tot} values than the 1.0 UF resins. It is clear for the results that γ^{LW} makes a more dominant contribution to the value of γ^{Tot} than γ^{AB} . As shown in **Table 5**, the value of γ^{LW} is much higher than γ^{AB} , primarily because of the large molecules and high amount of covalent

bonding in the cured UF resins and nanocellulose polymers. This shows that γ^{LW} increases as the molar ratio increases from 1.0 to 1.6, indicating that the 1.6 UF resins contain bigger polymers than the 1.0 UF resins. The dispersion interaction (γ^{LW}) depends on the polarizability of a molecule. The larger the polymer, the more polarized it is. Thus, the 1.6 UF resins that have higher M_w values have greater γ^{LW} values, which are consistent with the adhesion force measurements. It was found in another study that a high concentration of methylene linkages ($-\text{CH}_2-$) in paraffin wax and a decrease in its crystallinity resulted in higher surface energy (Pu and Severtson 2009), which is in line with the results in this work. However, the polar contribution denoted as γ^{AB} is higher in the 1.0 UF resins, which could be attributed to the materials mainly being composed of linear molecules that easily form hydrogen bonds (Wibowo et al. 2020b), either between the linear molecules or between the UF resin molecules and the water used for the contact angle measurements. Hydrogen bonding is considered to be a dipole–dipole force and makes a contribution to the polar interaction. Another notable difference can be observed in the individual acid (γ^+) and base (γ^-) surface energies, where γ^- is significantly higher than γ^+ , regardless of the molar ratios of the UF resins. The reason for this is that the UF resins consist of an abundance of electron donating groups, such as $-\text{C}=\text{O}$, $-\text{OH}$, and $-\text{NH}$. Thus, it can be concluded that even though the γ^{Tot} values of the UF resins are very similar, there are notable differences in their dispersive and polar surface energies because of their different chemical properties. Similarly, this phenomenon is observed for the nanocellulose materials. The γ^- values are significantly higher than the γ^+ values, indicating the presence of an abundance of electron donating groups in the nanocellulose structure. Interestingly, the γ^- values of the CM–CNFs and C–CNCs are higher than that of the CNFs, possibly due to the presence of anionic groups such as carboxymethyl (CH_3COO^-) or carboxylate (COO^-).

Table 5. The surface energies (mJ m^{-2}) calculated using the contact angle measurements of the materials, via the OCG method.

Film	γ^{LW}	γ^+	γ^-	γ^{AB}	γ^{Tot}
1.0 UF resins	44.76	6.8×10^{-4}	57.68	0.37	45.13
1.0 UF resin + H*	44.92	3.2×10^{-4}	45.36	0.24	45.16
1.6 UF resin	45.45	6.7×10^{-4}	42.56	0.34	45.79
1.6 UF resin + H	45.79	2.2×10^{-7}	35.24	0.01	45.80
CNFs	38.30	4.3×10^{-2}	55.45	3.08	41.38
CM-CNFs	40.82	2.7×10^{-3}	57.68	0.79	41.61
C-CNCs	41.17	3.6×10^{-2}	55.46	2.83	44.00

*H indicates that 3% NH_4Cl was added as a hardener.

Furthermore, the work of adhesion (W_{12}) values of the UF resins and nanocellulose films calculated from the surface energies using **Eq 5** are presented in **Table 6**. Consistent with the adhesion force results, the W_{12} values between the 1.6 UF resins and nanocellulose are higher than for the 1.0 UF resins, regardless of the nanocellulose type. As explained earlier, the greater M_w values of the 1.6 UF resins are related to the high γ^{LW} values and lead to higher γ^{Tot} and W_{12} values. This suggests that dispersion forces are dominant in the adhesion between the thermosetting UF resins and nanocellulose, which is in agreement with the results of another study (Gustafsson et al. 2012), which showed that van der Waals interactions play a dominant role in the adhesive interactions between lignin, cellulose, and hemicellulose. Furthermore, the smoother surfaces of the 1.6 UF resin films compared with those of the 1.0 UF resins may contribute to the higher W_{12} values. In summary, it can be concluded that the molecular

interactions between the 1.6 UF resins and different nanocellulose model surfaces are stronger than for the 1.0 UF resins as the 1.6 UF resins have more branched structures, smoother surfaces, and higher surface energies. In addition, the chemical structure, negative charge, and surface topography of nanocellulose materials also contribute to their adhesion with UF resins.

Table 6. Work of adhesion (W_{12} , mJ/m²) values between the different nanocellulose types and UF resin films.

Nanocellulose types	UF resin adhesives			
	1.0 UF resin	1.6 UF resin	1.0 UF resin + H*	1.6 UF resin + H
CNFs	86.12	86.53	86.01	86.22
CM–CNFs	86.62	87.22	86.61	87.09
C–CNCs	88.93	89.38	88.83	89.11

*H indicates that 3% NH₄Cl was used as a hardener.

4. Conclusion

In the present work, the adhesion between different nanocellulose materials and UF resin adhesives was directly measured. The adhesion forces between the nanocellulose films (CNFs, CM–CNFs, and C–CNCs) and liquid droplets of the UF resins (1.0 and 1.6 F/U), and the work of adhesion values between films of the nanocellulose materials and UF resins using contact angle measurements and calculated via the van Oss–Chaudhury–Good method were determined. The results show that the interactions between the 1.6 UF resins and nanocellulose materials are stronger than those of the 1.0 UF resins, which is proven from its greater adhesion force and work of adhesion values with the different types of nanocellulose materials. This is attributed to

the 1.6 UF resins having a more branched structure (high M_w), being more reactive (short gelation time), with a smoother surface, and higher surface energy than their 1.0 UF resin counterparts. These properties contribute to the high value of dispersive surface energy (γ^{LW}), suggesting that van der Waals forces are mainly responsible for the adhesion interaction. Overall, the results of this study provide a new insight on understanding the interaction between the most widely used thermosetting wood adhesive, UF resins, and nanocellulose as the most major component in the wood cell wall. However, knowledge of the adhesion interaction of wood adhesive with other wood biopolymers such as lignin and hemicellulose are necessary to better understand the nature of the adhesion of wood when these biopolymers interact with the adhesive.

Supplementary Information

AFM images used in the measuring of the thickness of the samples (**Fig. S1**), TEM images of the different cellulose samples (**Fig. S2**), AFM images of the 1.0 UF resin + 3% NH_4Cl ($10 \times 10 \mu\text{m}$) and the different cellulose films (**Fig. S3** and **Fig. S4**), the low-resolution XPS spectra (**Fig. S5**) and their relative atomic concentrations of the cellulose films (**Table S1**), images of the adhesion force measurements taken at the maximum adhesion point (**Fig. S6**) with the experimental data of the adhesion force measurements (**Table S2**), and all of the contact angle values from the three different liquids (**Table S3**) related to this article are presented in the supporting information.

Author Contributions

All authors contributed equally to this manuscript.

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Compliance with ethical standards

Conflict of interest The authors declare no competing financial interest.

Ethical approval All applicable international, national, and/ or institutional guidelines for the care and use of animals were followed.

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Figures

Figure 1

(a) FTIR spectra and deconvoluted XRD patterns of the (b) CNFs, (c) CM-CNFs, and (d) C-CNCs.

Figure 2

An example of a UF resin droplet in its maximum adhesion state recorded at the retraction stage, where the contact angle (θ), droplet base radius (r), and principal radii (D and R) of the droplet are shown.

Figure 3

AFM images ($50 \times 50 \mu\text{m}$) of the films of the cured UF resins with the two molar ratios and hardener contents. (a) 1.0 UF resin, (b) 1.0 UF resin + hardener, (c) 1.6 UF resin, and (d) 1.6 UF resin + hardener. AFM images ($10 \times 10 \mu\text{m}$) of the different nanocellulose films: (e) CNFs, (f) CM-CNFs, and (g) C-CNCs and their color contrast AFM images ($1 \mu\text{m}^2$): (h) CNFs, (i) CM-CNFs, and (j) C-CNCs.

Figure 4

Schematic of the measuring of contact angles on nanocellulose and UF resin films using the probe liquids in the OCG method.

Figure 5

Deconvolution of the high-resolution C1s XPS spectra of the reference and nanocellulose films. (a) Si wafer + PDADMAC, (b) CNFs, (c) CM-CNFs, and (d) C-CNCs.

Figure 6

Schematic of the structures of the different nanocellulose samples alongside their actual morphologies shown in the respective TEM images.

Figure 7

Typical force–distance curves recorded for the different molar ratios of UF resin droplets on the surfaces of the nanocellulose model films. (a) CNFs, (b) CM–CNFs, and (c) C–CNCs.

Figure 8

Example of water and diiodomethane contact angle measurements on different UF resins films. *H indicates that 3% NH₄Cl was used as a hardener.

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