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Hydrophobization, smoothing and barrier improvements of cellulose nanofibril films by sol-gel coatings

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Abstract

Single layer films from cellulose nanofibrils on a plastic support were coated with sol-gel coated with inorganic-organic copolymers (ORMOCER®s), consisting of inorganic Si-O-Si based networks combined with ceramic (Al-O- and Zr-O-) groups and special organic fluoroalkyl chain containing functional groups. Sol-gel coatings decreased the surface hydrophilicity and water vapor transmission rate. The water contact angle of uncoated films was 24°, indicating high affinity between water and the cellulose nanofibrils. All sol-gel coatings tested increased the surface hydrophobicity with the contact angles ranging between 54 and 102°. The water vapor transmission rates were varying between 230 and 410 g/m²/day. With UV curable highly organically crosslinked coating, the water vapor transmission rate was decreased by 77% as compared to uncoated film. The uncoated film had oxygen transmission rates of 0.7 and 107 cc/m²/day at 50% and 80% RH, respectively. At high humidity conditions, the films tend to swell thus allowing permeation to increase. Sol-gel coatings significantly improved the oxygen barrier properties especially at 80% RH. The transmission rates were varying between 0.4 and 0.5 cc/m²/day (50% RH) and between 51 and 86 cc/m²/day (80% RH).

Keywords: cellulose nanofibrils, sol-gel, film, coating

Introduction

Bioeconomy, also referred to as green economy aims for sustainable development with decreased environmental impact. The bioeconomy should be based less on fossil raw materials and more on biomass-derived renewable resources. Replacing the fossil-based films in packaging, transportation and printing industry with bio-based materials might give an advantage due to not only more sustainable image, but also improved properties. Current trends in the packaging and transport industry are towards lighter weight materials for reduction of raw material use, transportation costs, and the amount of waste [1]. Biopolymers such as cellulose, pectin, xylan, starch or chitosan are considered to be environmentally sustainable alternatives for synthetic packaging materials [2]. For example, cellulose nanofibrils (CNFs) are among the most promising innovations especially due to its excellent oxygen and mineral oil barrier properties [3-5]. However, the moisture resistance of most sustainable biopolymers is still insufficient, thus moisture absorption and excessive water vapor permeation through packaging degrades the

quality of food and other goods, resulting in short shelf-lives, increased costs and more waste [6]. Several approaches have been attempted for improving the moisture tolerance of CNF films. In spite of the efforts made by surface silylation [7-8], paraffin wax [3], aluminium oxide (Al_2O_3) [9], alkyl ketene dimer (AKD) [10] and cellulose fatty acid ester coatings [11], or grafting with hydrophobic dodecyl gallate [12], crosslinking [13], compounding with nanoclays [14] or impregnation with walnut oil [15], there is still a need for a more powerful method for hydrophobization of CNF films in a cost effective way. Meanwhile the markets for printed electronics, organic photovoltaics and biosensors are rapidly growing. The research activities on sustainable and environmentally sound raw materials especially in printed electronics have increased globally due to remarkable population growth together with limited biophysical resources. The CNF films are potentially utilized in certain printed electronics applications [16-19]. The requirements for surface smoothness and dimensional stability at high humidity, however, are demanding in most of these applications so that the traditional CNF films cannot fulfil them sufficiently. The surface roughness, which is more or less a natural feature of any surface formed from imperfect dispersions, may be overcome by using additional coatings with low porosity. As monolayer biopolymer films rarely have competitive edge against synthetic films, the coated structures are necessary. By multilayer structures the barrier properties and smoothness of bio-based materials may be dramatically improved.

Impregnating, hydrophobizing, oleophobizing and barrier agents commonly used are typically applied by a simple coating method. While substances with long alkyl chains are often sufficient for water repellent effects (hydrophobicity), fluorinated alkyl chains are usually necessary to achieve oil and fat repellency (oleophobicity) as well as water repellency. Moreover, for establishing desirable barrier properties, a highly densified network or a high degree of crosslinking in the coating material is an essential prerequisite. Sol-gel processing with the relevant alkoxysilyl or alkoxy metal compounds is a well-established method to build up these elements in a solution. Finally, wet coatings containing these elements can be processed by known wet chemical techniques and will be cured at moderate temperatures or by using UV light to initiate the organic polymerization of incorporated reactive groups. The basic technology, which was also used for coatings in the present study, is schematically illustrated in Figure 1.

The resulting materials exhibit properties between inorganic and organic polymers. Owing to the wide range of possible combinations and variations of inorganic and organic components, these materials can be used in many applications, for example, in wear resistant coatings for plastics [20], functional coatings on glass [21], sensor coatings for gas detection [22], corrosion protection layers for metals [23], coatings for microelectronic devices [24] and anti-static and easy-to-clean coatings [25].

In the present work, CNF coated plastic supports were further coated with sol-gel coatings and coating characteristics and barrier performances were examined. The overall goal is to develop an economically viable production method for lightweight structures based on sustainable materials with added value properties.

I: organically-functionalized siloxane => film formation, adhesion, polarity, conductivity, surface energy, flexibility

II: inorganic oxides => mechanical, thermal, chemical stability, rigidity

III: organic polymer chains => film curing, flexibility, cross-linking

Figure 1. Synthesis of inorganic organic hybrid ORMOCER® coating materials via sol-gel process and their features.

Materials & Methods

Cellulose nanofibrils (CNF) and CNF films

A native never dried birch kraft pulp was used to produce CNF. Mechanical disintegration was carried out with a fluidizer to obtain a fibre slurry. It was immersed in water at 1.7% consistency and dispersed using a Diaf dissolver 100 WH (Denmark), at 700 rpm for 10 minutes. Pre-refinement of the suspension was performed three times in a grinder (Supermasscolloider MKZA10-15J, Masuko Sangyo Co., Japan) at 1500 rpm. The pre-refined fibre suspension was fibrillated further in a Microfluidics fluidizer M-7115-30 (USA) three times at a pressure of 1800 bar. The appearance of the final fibre slurry was a viscous and translucent gel with a solid content of 1.91%, pH 7.26, electrical conductivity of 195 μ S/cm and the residual fibre amount of 39 pcs/mg. Rheological characteristics of the fibre slurry were analysed with a rheometer Anton Paar MCR301 with ST22-4V vane spindle at 0.5% consistency. The fibre slurry exhibited a storage modulus of 6.76 Pa, a loss modulus of 0.87 Pa and an apparent viscosity of 241 mPa s at 600 rpm.

A patented SutCo-concept [26] was employed to produce CNF films. The dispersion included 30% of sorbitol (D-sorbitol, Sigma-Aldrich). It was first homogenized by mixing with Diaf dissolver (100 WH, Denmark) for 30 min at 300 rpm and then with SpeedMixer (DAC 110.1 VAC-p, Hauschild) for 2 min at 1500 rpm at a reduced pressure to prevent formation of gas bubbles. After that it was cast onto a plastic support using a specific feeding head. At the feeding head the dispersion

formed an even and uniform wet layer. Spreading and adhesion between the support and the dispersion were controlled by plasma treatment. Vetaphone Corona-Plus (Type TF-415, CP1C MKII 2.0 kW, Denmark) equipped with argon/nitrogen plasma-unit was used for increasing the surface energy of the plastic support. After drying overnight at ambient conditions, dry CNF films with thickness of $37 \pm 1 \mu\text{m}$ were delaminated from the plastic support and cut into A4-sized sheets.

Sol-gel coatings

In the present study, inorganic-organic copolymers (ORMOCER®s) were used for combining the above properties with suitable coating materials for CNF films. Essential components of these types of materials are the inorganic Si-O-Si based networks which can be combined with ceramic (such as Al-O-, Ti-O- or Zr-O-) and specific organic fluoroalkyl chain containing functional groups. The former will contribute to the high density of the resulting material exhibiting especially the barrier properties and the latter will be responsible for specific surface properties such as oleophobicity and hydrophobicity.

The chemical compositions of the selected coatings described in the present study are summarized in Figure 2. Table 1 summarizes detailed information of the sol-gel coatings. The components are presented after hydrolysis and condensation reactions as they are incorporated in the inorganic basic network. Wet coatings were applied onto the CNF films by a doctor blade applicator. UV curing was performed by using a mercury lamp for 20 s with approximately 5000 mJ/m^2 . Thermal curing was performed at 130°C for 1 h.

Scanning electron microscopy (SEM)

Sol-gel coated films were embedded in an epoxy resin, grinded and polished for the micro- and nano-structural observation. In addition, surfaces of the films were observed without embedding them in the epoxy resin. Before observation, an approximately 15-nm thick gold coating was sputter-deposited on the sample surface for avoiding charging-up due to electron irradiation. Field emission scanning electron microscopy (FE-SEM. SUPRA 35, Zeiss, Germany) was used for the observation.

Roughness

Wyko NT9100 Optical Profiling System determined the micro-roughness average (R_a) of the films. R_a is the arithmetic mean of the absolute values of the surface departures from the mean plane. It is a stable, easily implemented parameter, useful for detecting general variations in overall surface height characteristics. Magnification of 10.1×, mode: VSI and 1000 $\mu\text{m} \times 1000 \mu\text{m}$ scan area was used.

Gloss

Gloss of the coated surface was measured using a laboratory glossmeter (Zehntner, ZLR 1050, Hoelstein, Switzerland). Reflectance was measured at an incidence light angle of 75° from the normal to the sample surface. Gloss was reported as gloss units (GU).

VMc: UV curable, highly densified and crosslinked inorganic and organic network

VMc F: UV curable, highly densified and crosslinked inorganic and organic network, combined with an oleophobic fluoroalkyl chain

Gdi: UV curable highly organically crosslinked structure

Gdi F: UV curable highly organically crosslinked structure, combined with an oleophobic fluoroalkyl chain

G_A_SiAlZr: Thermally curable system based on highly densified inorganic Si-O/Al-O/Zr-O oxidic network

Figure 2. Chemical compositions of the sol-gel coatings. $\sim$ represents the inorganic network, and $\curvearrowright$ represents the organic polymerization.

Table 1. Composition formulae, names of components, and molar ratios.

Composition formula	Name of functional components	Molar ratio
VMc	Vinylsilane „V“	50
	Mercaptopropylsilane „Mc“	50
VMc_F	Vinylsilane „V“	48,5
	Mercaptopropylsilane „Mc“	48,5
	Fluoroalkylsilane „F“	3
Gdi	Glyceryldimethacrylate silane „Gdi“	100
Gdi_F	Glyceryldimethacrylate silane „Gdi“	97
	Fluoroalkyl silane „F“	3
G_A_SiAlZr	Glycidoxypylsilane „G“	45
	Aminosilane „A“	5
	Peralkoxylated silane „Si“	30
	Peralkoxylated aluminium „Al“	10
	Peralkoxylated zirconium „Zr“	10

Contact angle measurements

Water contact angles of the films were measured using CAM200 equipment (KSV Instruments, Finland) in test conditions of 23°C and 50% relative humidity (RH). For each measurement, the water sessile drops were placed on the surface of the sample, and images were recorded every second for 1 min. The water contact angle of each sample was measured at 3-5 different positions, and the average value was calculated.

Oxygen permeation

The standard ASTM D3985 was employed for the measurement of an oxygen transmission rate using Oxygen Permeation Analyser Models 8001 and 8011 (Systech Instruments Ltd, UK). Films of 50 cm² were tested at the conditions of at the temperature at 23°C and the humidity at 50% and 80% RH. The test gas used was 100% oxygen.

Water vapor permeation

A water vapor transmission rate of the films was determined gravimetrically using a modified ASTM-E-96B procedure “wet cup method”. Samples with a test area of 30 cm² were mounted on circular aluminum cups (68-3000 Vapometer EZ-Cups; Thwing-Albert Instrument Company) containing distilled water (100% RH). The cups were stored in test conditions of 23°C and 50% RH and weighed periodically until a constant rate of weight reduction was attained. Climaveneta climate control system (Italy) model AXO 10 controlled both temperature and humidity conditions in an environmental chamber. Humidity gradient is the driving force for water molecules to diffuse within a material. In this test, 100/50% RH gradient was used.

Results & Discussion

CNF films consist of networks of individual or bundled CNFs. High pressure homogenization was used to separate the individual CNFs. Feed solutions were pumped from the inlet reservoir and pressurized by an intensifier pump to high pressure of 1800 bar and fed three times through fixed geometry chambers. Within the chambers the high pressures forced fibril networks to form turbulent and opposing jets, which contributed to mixing in nanometer scale, minimizing diffusion limitation. A diameter of single CNFs is typically a few nanometers whereas the lengths may be up to several micrometers. Between the junction points of the fibril network, some open voids and porosity may exist. Additional fibrillation leads into a finer fibril structure which improves the surface smoothness of the films. SEM images at the surfaces and the cross-sections of the sol-gel coated CNF films are shown in Fig. 3. As can be seen, the surface nano-roughness of the uncoated CNF film was considerably higher than those of all coated films. The individual CNFs on the surface were well-covered with the relatively dense and homogeneous coating layers. The nanoscale morphologies of the coatings, however, slightly differentiated from each other. Based on the cross-sectional images the layer thickness of the coatings and the CNF films were 2-4 μm and 22-27 μm , respectively. They are based on localized observations and it is difficult to define representative thickness values, especially when the observed values are significantly varied. Therefore, data analysis per thickness was not attempted. The adhesion between the coatings and the support was generally good. The cracks consistently appeared in the cross-sectional images in Fig. 3 were most likely created during the preparation of the epoxy embedded samples due to shrinkage of the epoxy during curing.

Figure 3. Scanning electron microscopic images of the surface topography (a) and cross-section (b) of the sol-gel coated CNF films as follows: (1) no coating, (2) VMc, (3) VMc F, (4) Gdi, (5) Gdi F and (6) G_A_SiAlZr. The sol-gel coatings are marked with an arrow.

Figure 4. Surface topography of the sol-gel coated CNF films measured with Wyko NT9100 Optical Profiling System. Magnification of 10.1 $\times$, mode: VSI and 1000 μm $\times$ 1000 μm scan area was used.

Table 2. Water contact angle, gloss and roughness of the sol-gel coated CNF films.

Coating	Coating grammage (g/m ²)	Water contact angle after 30 sec. (°)	Gloss 75° (GU)	Roughness average R _a (nm)
no coating	-	24	79.2	621
VMc	5.6	71	104.0	353
VMc F	3.5	102	102.1	431
Gdi	6.2	71	29.8	1010
Gdi F	1.9	99	98.7	813
G_A_SiAlZr	7.6	54	92.4	496

Surface topography of the sol-gel coated CNF films is shown in Fig. 4, measured with Wyko NT9100 Optical Profiling System. Regarding the micro-roughness, the results were somewhat different. Based on the optical profilometry, the surface smoothness was clearly improved only with VMc, VMc F and G_A_SiAlZr coatings. Especially the inorganic/organic networks also efficiently increased the gloss-value. Gdi was suffering from both high micro-roughness (Fig. 4 Gdi) and low gloss-value probably (Table 2) due to unsuitable drying conditions.

A variation of the measured coating grammage in Table 2 can be associated with wetting characteristics of the coatings applied on to the CNF films. When fluorine is included in the coatings such as VMc F and Gdi F, the coating grammage tends to be lower probably due to a mismatch of the surface tensions between the fluorine containing coating materials and the CNF film surfaces. However, the coating grammage of Gdi F (1.9 g m⁻²) seems too low, since the density of the Gdi F coating would be lower than 1 g cm⁻³. It may be due to macroscopic unevenness of the Gdi F coating.

High density of hydroxyl groups on the CNF film surface results in increased hydrophilic behavior which can be measured with water contact angle measurements. The water contact angle of unmodified CNF surface was 24°, indicating very high affinity between water and the surface (Table 2). All sol-gel coatings clearly increased the surface hydrophobicity with the contact angles varying between 54° and 102°. Oleophobic fluoroalkyl chains improved the hydrophobicity of both VMc and Gdi coatings. A thermally curable coating from an inorganic Si-O/Al-O/Zr-O oxidic network only slightly increased the water contact angle. Overall, the hydrophobic effects on CNF films were comparable to plasma silylation and walnut oil impregnation [8,15].

Oxygen and water vapor transmission rates of the sol-gel coated CNF films are summarized in Table 3. CNF films are typically excellent barriers against oxygen permeation. The uncoated CNF film had oxygen transmission rates of 0.7 and 107 cc/m²/day at 50% and 80% RH, respectively (Table 3). The results were comparable to regenerated cellulose films and other studies of CNF at elevated humidity [6,10,27-33]. During drying the CNFs are closely packed which reduced the free volume and efficiently prevented the oxygen permeation. Large surface area and high polarity of nano-sized fibrils resulted in enhanced fibril-to-fibril attraction especially at lower humidity. Due to the hydrogen bonds the movement of fibrils was restricted efficiently preventing the oxygen permeation. The barrier properties of cellulosic films are sensitive to moisture variations. Water molecules diffuse into the structure and break the hydrogen bonds that hold the chains together. At high humidity conditions, the CNF films tend to swell, increasing permeation. Sol-gel coatings

efficiently improved the oxygen barrier properties especially at 80% RH. The transmission rates were varying between 0.4 and 0.5 cc/m²/day (50% RH) and between 51 and 86 cc/m²/day (80% RH), respectively. By using G_A_SiAlZr coating, the oxygen transmission rate was decreased by 52% at 80% RH as compared to uncoated CNF film. Water vapor transmission rates through cellulosic films are typically high due to strong hydrophilic nature of these materials. The penetrating water molecules break intramolecular hydrogen bonds which enables plasticization and swelling of the matrix polymer finally resulting in increased moisture permeation. Water vapor transmission rates of uncoated CNF films were comparable to previously reported bleached softwood and hardwood CNF films [6] and regenerated cellulose and chitosan films [10,34]. Sol-gel coatings efficiently decreased the moisture permeability. The water vapor transmission rates were varying between 230 and 410 g/m²/day and with Gdi coating, the transmission rate was decreased by 77% as compared to uncoated CNF film. The water vapor transmission rates were lower than with cellulose fatty acid ester coated, plasma silylated or walnut oil impregnated CNF films [8,11,15], but not as good as with beeswax and paraffin wax coated microfibrillated cellulose (MFC) films [35], alkyd resin/CNF coated kraft paper [36] or shellac/MFC coated paperboard [37].

Table 3. Oxygen and water vapor transmission rates of the sol-gel coated CNF films.

Coating	OTR at 23°C, 50% RH (cc/m ² /day)	OTR at 23°C, 80% RH (cc/m ² /day)	WVTR at 23°C, 100/50% RH (g/m ² /day)
no coating	0.7	107	990
VMc	0.5	74	240
VMc F	0.5	86	370
Gdi	0.4	78	230
Gdi F	0.5	77	260
G_A_SiAlZr	0.5	51	410

Conclusion

Sol-gel coated CNF films were prepared to examine coating properties and oxygen and water permeability. Sol-gel coatings exhibited relatively dense and homogeneous coating layers with sufficiently strong adhesion to the CNF coatings, and improved the technical performance of the CNF films. Especially the moisture resistance and surface hydrophobicity were improved due to inorganic-organic copolymer coatings (ORMOCER®s). The results of this study will contribute to the development of the techno-economically feasible production methods for lightweight structures based on sustainable materials with added value properties.

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