Journal of Industrial and Engineering Chemistry 18 (2012) 1122–1127

Contents lists available at SciVerse ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec

Fabrication of hydrophobic self-assembled monolayers (SAM) on the surface of ultra-strength nanocellulose films

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ARTICLE INFO

Article history:
Received 21 September 2011
Accepted 3 January 2012
Available online 11 January 2012

Keywords:
Cellulose nanofibrils
Nanocellulose film
SAM
Water contact angle
Tensile properties
XPS

ABSTRACT

Nanocellulose (NC) films with extremely high tensile properties after high-pressure homogenization and chemical modification with perfluoroctyltriethoxysilane (PFOTES) were prepared by a solution-immersion method. The tensile properties of the treated NC films were significantly increased by the self-assembled monolayer (SAM) formation on the surface. With increasing the PFOTES concentration, the water contact angle (WCA) of the NC films increased up to 130.1°. The slope of the decaying WCA of the treated NC films decreased with increasing the immersion time and PFOTES concentration. XPS data shows that fluorine atoms by the SAM formation are obviously present on the surface of the NC films.

1. Introduction

Comprehensive research related to cellulose nanofibrils (CNFs) has been done in the domain of their preparation, characterization, chemical modification and potential applications. The CNFs are derived by shearing and impact forces through a homogenizing process [1–4]. Through the homogenization process, the cellulose bundles are split and moderately degraded inducing micro-fibrillated cellulose strands with diameter of 10–100 nm and lengths of hundreds of nanometer. The CNFs possess a few interesting properties, such as highly expanded surface area and very high aspect ratio (L/D) [5]. In the previous study, the suspension of the CNFs was converted to nanofilms by dilution and dispersion in water and by vacuum filtration [4]. The nanofilms prepared by controlling the pass numbers and degree of polymerization (DP) through the high-pressure homogenizer showed the extremely high tensile strength and modulus up to 212 MPa and 10.8 GPa, respectively.

The CNFs are hydrophilic, with great potentials to form interfibrillar hydrogen bonds and strong thin films. The CNFs can also be modified so that their surface becomes hydrophobic, thereby applying to packaging, specialty paper, or membranes. Sizing processes are performed to impart resistance to the penetration of liquids to paper by the use of wet-end additives such as a rosin acid sizing agent, Alkyl Ketene Dimer (AKD), Alkenyl Succinic Anhydride (ASA), and by surface sizing with modified starches [6]. On the other hand, the formation of self-assembled monolayer (SAM) on the paper surface is a new technology to convert the hydrophilic properties of the papers to the hydrophilic [7]. Hydrophobic SAM in water contact angle (WCA) of >110° on the surface of paper was formed with perfluorodecyltriethoxysilane (PFDTES), methyloctadecyldichlorosilane (MODDCS) and dimethyl-dichlorisilane (DMDCS) by a solution-immersion method [4].

Many factors such as porosity, surface roughness, pH value, moisture content, temperature and hydrophobicity influence the degree to which papers resist penetration by fluids [8]. The hydrophobicity of materials is typically evaluated with water contact angle (WCA), which provides an adverse measure of wettability [9,10]. When the WCA is higher than 90°, the materials are conventionally defined as hydrophobic [11]. In general, hydrophobicity is achieved by lowering the surface free energy. For the chemical modification, fluorine is the most effective element to lower the surface free energy due to a small atomic radius and the biggest electronegativity among all atoms [12]. When the fluorine is replaced by other elements such as C and H, the surface free energy decreases in the order of $-CH_2- > -CH_3 > -CF_2- > -CF_2H > -CF_3$ and the $-CF_3$ groups on the surface gives the lowest surface free energy of the materials [13].

X-ray photoelectron spectroscopy (XPS) is one of the most effective methods for surface analysis of paper and fibers [14,15]. The XPS analysis of cellulose materials is basically confined to the

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1226-086X/$ – see front matter
doi:10.1016/j.jiec.2012.01.001

topmost 10 nm of the surface of materials. In addition, the XPS analysis is useful in evaluating the surface content of lignin and extractives [16–18]. Besides, the method can be successfully applied in the characterization of fiber surface with chemical modification [19,20].

Although a number of researches on hydrophobicity of pulps and fibers have been published, there are few reports on characteristics of wettability at the NC films made of CNFs. The objective of this study was to investigate the hydrophobic behavior (i.e., water contact angle and sessile droplet method) of the silane treated NC films as a function of silane concentration and solution-immersion time. The effects of silane concentration and solution-immersion time on the mechanical properties, morphology, and surface characteristics were also examined.

2. Experimental

2.1. Materials

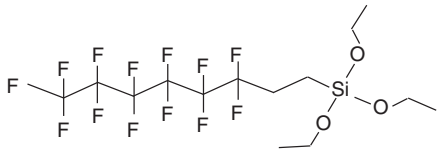
Cellulose powder (KC Flock, W-50) was used as a raw material for the preparation of the cellulose nanofibrils (CNFs). The cellulose powder (average particle size of about 45 μm and a bulk density of 0.15–0.20 g/cm^3) was purchased from Nippon Paper Chemicals Co., Ltd., Japan). 1H,1H,2H,2H-perfluoroctyltriethoxysilane (PFOTES) were obtained from Sigma–Aldrich (USA). The properties of the PFOTES are shown in Table 1. Anhydrous ethanol (99.8%) purchased from CARLO ERBA (Italy) was used in silane treatment with the CNFs. For NaOH solution preparation, de-ionized water was used.

2.2. Methods

2.2.1. Preparation of NC films

For alkaline treatment, cellulose powder of 2.5 g was loaded in 2% NaOH solution of 120 ml, then stirred for 1 h. The NaOH treatment was performed to increase the swelling of cellulose and to enhance the homogenization of cellulose. After washing the alkaline-treated cellulose with de-ionized water up to pH 7, cellulose was loaded in de-ionized water of 500 ml. Fibrillation of cellulose was conducted with a high-pressure homogenizer (M-110EH-30, Microfluidics, USA). The homogenization of cellulose was performed with 12 passes through interaction chambers of 87 and 120 μm at a pressure of 1400 bar. With the CNF suspension obtained after the homogenization, NC films were prepared over a filter paper on a Porcelain Buchner funnel by a vacuum filtration method. A wet NC film was inserted to two filter papers which were loaded under two stainless steel plates, then dried at 80 °C for 48 h under weight of a 10 kg steel in a dry oven. The thickness of the NC films was 35 μm.

Table 1
Properties of PFOTES used in this study.

	PFOTES
Chemical structure	
Chemical name	1H,1H,2H,2H-perfluorooctyltriethoxysilane
Molecular formula	$C_{14}H_{19}F_{13}O_3Si$
Molecular weight (g/mol)	510.36
Boiling point (°C)	272.4 °C at 760 mmHg
Density (g/cm^3)	1.351

2.2.2. Solution-immersion method

The nanofilms were cut into 20 mm × 40 mm pieces for water contact angle (WCA) and XPS analyses and 10 mm × 80 mm for tensile strength tests. The PFOTES of 50, 100, 200, 400, and 800 μl was added by a syringe into anhydrous ethanol of 20 ml, thus the concentrations of the PFOTES solution were 0.25, 0.5, 1, 2 and 4%, respectively. For silanization on the surface of the NC films, each NC film was immersed into the solutions at room temperature for 60, 120, 180 and 300 min, respectively. The NC films were picked up from the solutions, and washed carefully with 4× 40 ml ethanol to remove excess reagents. Then, the NC films were dried in the dry oven at 130 °C for 2 h to generate a stable self-assemble monolayer (SAM).

2.2.3. Mechanical properties

Tensile properties were measured according to ASTM D882. Tensile properties were conducted at a test speed of 10 mm/min using Universal Testing Machine (UTM, Zwick testing machine Ltd., UK). The distance between grips for the tensile tests was 50 mm. The mean value from 10 different specimens was obtained for each test sample.

2.2.4. Water contact angle (WCA) measurement

WCA measurement of the PFOTES-modified NC films was obtained using Phoenix 300 (SEO, Korea) contact angle analyzer applying a sessile drop method at an ambient temperature. During the WCA measurement, an NC film was loaded on the top of a workbench in front of a microscope and a 4 μl water droplet was placed on the surface of the NC film. The reported values are averages of 5 replicates observed on different locations of the NC film. Each water droplet images captured as image files was analyzed using Image-Pro® Plus. Additionally, the WCA measurements were conducted from 0 to 60 s in 10 s intervals for wetting behavior according to a sessile water droplet method.

2.2.5. X-ray photoelectron spectroscopy (XPS)

The surface characteristics of untreated and chemically modified samples (2.5 mm × 2.5 mm) were examined using the following analytical tools. XPS analysis was performed by means of a VG Scientific ESCA Lab. 2000 (UK). High resolution ESCA was used to evaluate the relative composition of the PFOTES-modified films and to estimate the presence of non-equivalent fluorine functionalities.

2.2.6. Data analysis

Statistical comparisons, based on a two-way analysis of variance (ANOVA), were performed to test the effects of the concentration of PFOTES, immersion period, and their interactions on the tensile strength, tensile modulus, and WCA of the NC films. A regression analysis was performed to establish the correlations between the WCA and wetting period at different concentrations of PFOTES.

2.2.7. Morphology

CNF suspension of 10 ml was dispersed in 50 ml acetone, and then a drop of the dispersed solution was placed on a cylindrical steel, air-dried, and then gold-coated (Edwards Sputter Coater, UK). Morphological study on the CNFs after the homogenization was performed using field-emission scanning electron microscope (FE-SEM, Supra 55VP, Carl Zeiss, Germany).

3. Results and discussion

3.1. Morphology

After 12 passes through the high-pressure homogenizer, the diameter of the CNFs ranged from 20 to 50 nm, when fibrillated