



Stereoselectively water resistant hybrid nanopapers prepared by cellulose nanofibers and water-based polyurethane

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ABSTRACT

Cellulose nanopapers, known for excellent mechanical properties, loses 90% of their stiffness in the wet conditions. In this study, we attempt to improve the wet mechanical properties of cellulose nanopaper by incorporating polyurethane by a novel and ecofriendly method. Water based PU was dispersed along with CNFs in water and hybrid nanopapers were prepared by draining water under vacuum followed by forced drying. These hybrid nanopapers have a gradient interpenetrating structure with PU concentrated towards one side and CNFs towards the other, which was confirmed by scanning electron microscopy, x-ray photoelectron spectroscopy and contact angle measurements. Because of this, the nanopapers are water resistant on one surface (PU rich side) and hydrophilic on the other (cellulose rich side), making them stereoselectively water resistant. When wetted with water on the PU side, the hybrid nanopaper with 10% PU is able to retain 65% modulus; on the other hand, the reference retains only 10% of the modulus. Similar results are seen in the tensile and the yield strength. Additionally, the hybrid nanopapers have higher elongation and improved thermal stability. The reported material is relevant to the applications such as flexible electronics and transparent displays.

1. Introduction

Non-degradable plastic materials have dominated the world of materials for almost a century, which until recently, was proudly addressed as the age of plastics. Plastics evolved as a corrosion free, lightweight, durable material for non-structural applications (Greene & Tonjes, 2014). Characteristics with such a stark contrast to corroding and expensive metals skyrocketed their popularity, making them mandatory for everyday materials. In course of modernization and progress, they became irreplaceable. As the population grew, so did the demand and supply of the plastics. The perils of plastics were ignored for a long time. However, during last couple of decades, it has been realized that such materials are damaging our environment on a massive scale. Plastics are one of the major pollutants produced by us. Plastic has created (and is still creating) a massive amount of landfill deposits. If not lying dormant under the ground, plastics will be floating in the oceans for a long time (Barnes, Galgani, Thompson, & Barlaz, 2009). There is no easy way to get rid of such ultra-stable materials. The hailed durability of plastics is, in fact, a curse in terms of sustainability and environmental protection. Additionally, the crude oil resources are depleting faster than ever (Gamadi, Elldakli, & Sheng, 2014). It has become a matter of paramount interest among the material scientists to

find environment- friendly alternatives for the everlasting plastics. A common trend is to combine the synthetic plastic with renewable polymer to obtain a new environment-friendly polymeric material (Kim & Park, 1999; H. J. Lee, Lee, Lim, & Song, 2015).

In search of renewable materials, researchers have refocused on the cellulose, which is the most abundant polymer in the world. Cellulose, a biodegradable polymer, was a major source material for a long time much before industrial revolution (in the form of paper and wood). In search of alternative, new eco-friendly materials, it received a head start as its chemistry is well-documented and understood. Additionally, it was found that nanoscale, cellulose offers exciting opportunities for functional materials (Klemm et al., 2011; Shun Li, Qi, & Huang, 2018). Cellulose, present in form of well-arranged crystallites in amorphous matrix of hemi-celluloses and lignin, is the vital structural element of wood. It has been estimated that elastic modulus of cellulose crystal can be as high as 100–160 GPa (Eichhorn et al., 2010; Mittal et al., 2018). Such fascinating properties of a natural material have persuaded researchers to use this ancient material in their modern research. Nanocellulose has started an exciting field of research with promising future, but it is certainly not devoid of challenges.

As any new field of research, nanocellulose has brought its own roadblocks, which need to be crossed. The major one was large-scale

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production in a cost effective way— as grinding pulp to nanosized fibers was a slow and energy consuming process. The problem was solved by using energy-efficient production which involved use of physical, chemical or enzymatic pretreatment of cellulose pulp, followed by homogenization (grinding) (Isogai, 2018; Klemm et al., 2011). Once the feasible production methods were established, the attention was focused on the various aspects of material and its potential uses. One such product is self-standing 100% cellulose film called nanopapers, which are prepared by draining water from cellulose nanofibers (CNFs). They are fascinating as they are known to have an elastic modulus of 10–20 GPa and a strength of 200 MPa (Henriksson, Berglund, Isaksson, Lindström, & Nishino, 2008; Sehaqui et al., 2012), which is unheard of in case of a polymeric material. It has been suggested that in the future, nanopaper will find use in high-end applications such as packaging (Sehaqui, Zimmermann, & Tingaut, 2014), electronic displays (Sehaqui et al., 2014), flexible electronics (Koga et al., 2014), lithium ion batteries (Chun, Lee, Doh, Lee, & Kim, 2011), and transformers (Huang, Zhou, Zhang, & Zhou, 2018).

Despite such excellent properties and huge potential, nanopapers are still far away from commercialization. One of the major reasons being their poor performance under water (Benítez, Torres-Rendon, Poutanen, & Walther, 2013). When wetted with water, the nanopaper drastically loses its mechanical properties. It has been reported that the modulus of a soaked nanopaper reduces to 95% of the dry value (Sehaqui et al., 2014). Even in the presence of high humidity, the mechanical properties are heavily mitigated (Benítez et al., 2013). The reason behind this is that the cellulose molecule has pendant hydroxyl groups that make the surface hydrophilic. As a result, water seeps into the interfibrillar region of the nanopaper and causes the nanofibers to slide easily under external load leading to poor mechanical properties (Benítez et al., 2013). We found that this issue, understandably an important one, has rarely been discussed in literature. Sehaqui et al. modified nanofibers by grafting them with alkyl chains through esterification (Sehaqui et al., 2014). The presence of hydrophobic chains instead of hydrophilic hydroxyl group rendered the resulting nanopaper hydrophobic with 20-fold improvement in wet strength as compared to a reference. Recently, we used lactic acid modification to improve the water resistance and dimensional stability of nanopapers (Sethi, Farooq, et al., 2018). In this research, we hypothesized that using nanoscale polymer particles in tandem with cellulose nanofibers would be a possible way of preparing nanopapers with improved water resistance. It was decided to use water-based latexes as they are already stable in an aqueous suspension and have a nanoscale particle size (Product center coatings Covestro, 2018). The idea was to combine a renewable material (cellulose) with a synthetic polymer to prepare a superior hybrid material with minimal environmental impact. The structure was inspired by wood, which is more than 50% cellulose and still water resistant, due to the presence of lignin that gives it its extraordinary strength even in rain. Biomimicking is an interesting approach to prepare advanced materials. Nature has found a perfect way to make natural materials to particular standards. The key to commercialization of such materials can be in seeking inspiration from nature.

This paper presents a water-based method to prepare polyurethane (PU)–CNF hybrid nanopapers from a water based method. A commercially available PU dispersion (Bayhydrol® UH 240) and a CNF suspension was combined and water was drained to make nanopapers with PU concentration of around 1 wt.-%, 10 wt.-%, 30 wt.-% and 60 wt.-%. The morphology was analyzed by scanning electron microscopy. X-ray photoelectron spectroscopy (XPS) and contact angle measurements were used to characterize the surface properties. Tensile testing (dry and wet) was used to evaluate the mechanical properties and Thermogravimetric analysis (TGA) was used to evaluate the thermal stability. The papers prepared were significantly more water-resistant than the reference and were also thermally stable. The hybrid nanopaper containing relatively small amount (10 wt.-%) of non-

biodegradable polymer exhibited superior properties compared to reference nanopaper from pure CNF.

2. Materials and methods

Bayhydrol® UH 240 (henceforth, referred to as UH 240), an anionic surfactant based polyurethane dispersion was kindly provided by Covestro. The characteristics of UH 240 are provided in Table S1 (supplementary file). Cellulose nanofibers were prepared from softwood sulfite pulp provided by Stora Enso (Oulu, Finland). For grinding, pulp with a concentration of 1.6 wt.-% was fed to a Masuko grinder. The initial contact mode was 0-point, and the distance was gradually decreased from - 20 (3 passes), - 40 (4 passes), - 60 (5 passes) and - 90 (7 passes). The chemical composition of the reference pulp was 95.0 wt.-% cellulose, 4.2 wt.-% hemicellulose, 0.3 wt.-% lignin and 0.5 wt.-%. L-(+)-Lactic acid (80%) was purchased from Sigma-Aldrich.

2.1. Preparation of nanopaper

CNF suspension was diluted to a concentration of 0.2 wt.-% and UH240 was added to obtain a proportion of CNF to PU as 95:5, 80:20, 50:50 and 30:70. The CNF-PU suspension was mixed with a high speed ultraturrax at 10,000 rpm. Lactic acid (equal to amount of dry CNF) was used as additive to reduce the draining time. The sample was sonicated till the energy imparted was 300 J/ml. The details of this method is reported elsewhere (Sethi, Oksman, Illikainen, & Sirviö, 2018).

The nanopapers were prepared by filtering the suspension of CNFs and UH 240 through a Durapore PVDF membrane filter (Fisher Scientific, Pittsburgh, USA) with a pore size 0.65 µm. The vacuum was kept at 70 ± 5 kPa. Before filtration, the suspension was degassed under a vacuum of 70 kPa for half an hour. The wet CNF-PU sheet was peeled off from the PVDF membrane and kept between two steel mesh cloths (mesh size 70 µm), along with absorbent papers and carrier boards. The whole assembly was kept in compression molding at a temperature of 100 °C and a pressure of 5 MPa for 30 min. For composites with PU concentration higher than 50 wt.-%, PU was in a major phase and was infused into the steel mesh under higher temperature and pressure. Therefore, the pressure was reduced to 0.5 MPa to aid the film formation, once the film was dry, the steel mesh was removed and the films were compressed at 5 MPa for 30 min. The coding of the samples was done according to the amount of PU in the final film. It was observed that some PU was filtering through the PVDF membrane, perhaps due to its spherical morphology and the high vacuum. Therefore, the PU fraction was determined by calculating the increase in weight in comparison to the reference CNF film. The final samples were named as CNF(1)PU, CNF(10)PU, CNF(30)PU and CNF(60)PU, where the number in brackets refer to the actual concentration of PU in the film.

2.2. Characterization

2.2.1. Scanning electron microscopy

Zeiss Ultra Plus (Oberkochen, Germany) field emission scanning electron microscope (FE-SEM) was used for studying the morphology of hybrid nanopapers. The in-lens detector was used to collect signals from platinum coated samples after scanning the sample with an electron beam and an acceleration voltage of 5 kV.

2.2.2. X-ray photoelectron spectroscopy

Thermo Fisher Scientific ESCALAB 250Xi X-ray photoelectron spectroscopy (XPS) system was used for conducting chemical surface analysis. XPS spectra were collected using monochromatic Al K α (1486.6 eV) beam. Survey scan pass energy of 150 eV using 1 eV step and High-resolution scan pass energy of 20 eV was with 0.1 eV was used along with charge compensation by ion bombardment. The analysis chamber pressure was about 3 × 10⁻⁹ mbar.

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