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Flexible, highly transparent and iridescent all-cellulose hybrid nanopaper with enhanced mechanical strength and writable surface

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ABSTRACT

With the development of flexible electronic devices, there is increasing requirement for the inexpensive and environmental-friendly substrates. Cellulose paper has gained great attention because of its abundance, biodegradability and renewability. In this paper, we designed a hybrid nanopaper by introducing native cellulose nanofibrils (CNFs) into cellulose nanowhiskers (CNWs) matrix, which achieved a high optical transmittance while retaining iridescence under polarizing film. This nanopaper is less expensive than neat CNFs-based nanopaper and more feasible for large-scale production. Besides, our transparent hybrid nanopaper possesses the writable surface like regular paper. Compared with commercial paper, however, hybrid nanopaper shows superior optical properties and low surface roughness. The combination of these characteristics makes this nanopaper an excellent candidate for substrates of flexible electronic devices.

1. Introduction

Cellulose, known as the most abundant natural polymer on earth, has become an important renewable chemical resource to replace petroleum-based materials (Beck, Bouchard, & Berry, 2011; Ma, Zhou, Li, Li, & Ou, 2011). Wood cellulose fiber has been used for more than thousands years as an ingredient for making paper, which is a widely used material in everyday life. As it is renewable, environment friendly, scalable, light weight, mechanically flexible and disposable, cellulose paper is recently being explored as a promising sustainable substrate for use in electronic devices (Fang et al., 2011; Gao et al., 2013). Various electronic devices such as displays (Madaria, Kumar, & Zhou, 2011), transistors (Russo et al., 2011), batteries (Nyholm, Nyström, Mihranyan, & Strømme, 2011) and solar cells (Hu & Cui, 2012) have been reported to be printed on regular paper. However, regular paper is made of cellulose fibers with a diameter in the range of 20–50 mm, which results in a series of shortcomings such as the large surface roughness, porous structure, and optical opaqueness to hosting electronic devices on the surface of this material (Zhu et al., 2013).

Recently, considerable interest has been directed to cellulose nanofibrils (CNFs) since they are well known that cellulose nanofibers have a coefficient of thermal expansion (CTE) of 0.1 ppm/K and an estimated strength of 2–3 GPa (Guo, Chen, & Yan, 2013). Besides, CNFs are virtually free from light scattering, which makes it possible to prepare optically transparent nanopaper with strong tensile strength, a low CTE and a low surface roughness (Zhu et al., 2013). Reports on nanopaper and its applications have arisen in recent years, mainly focusing on engineered nanostructures of cellulose to fabricate transparent and flexible electronic devices, such as nanopaper organic light-emitting diodes (Zhang, Zhang, Lu, Wang, & Deng, 2012), conductive transparent paper (Jung et al., 2008), magnetic nanopaper (Li et al., 2013) and nanopaper lithium-ion batteries (Hu et al., 2013). However, it is a costly process to extract CNFs from wood fibers as it requires high energy consumption, expensive equipment, time-consuming procedure and low yield rate. Recently, in order to reduce the cost of nanopaper, Fang et al. (Fang et al., 2013) have prepared a kind of all-cellulose hybrid nanostructured paper with a writable surface, which has a superior smoothness and high optical transmittance.

Cellulose nanowhiskers (CNWs), another form of nanocellulose, are generated by removing the amorphous sections of purified cellulose source through acid hydrolysis (Klemm et al., 2011). CNWs consists of rod-like cellulose crystals with widths of 5–70 nm and lengths of 100–1000 nm (Xiong, Zhang, Tian, Zhou, & Lu, 2012). Under a certain condition, CNWs can self-assemble into an anisotropic chiral nematic liquid crystalline phase (Klemm et al., 2011). Comparing with the CNFs, the cost of CNWs is much lower since the preparation procedure is facile and time-saving and does not need the expensive professional mechanical equipment. Owing to the absence of amorphous sections, however, CNWs film is so fragile that it needs other nanofillers to enhance their mechanical

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properties (especially flexibility). As a new class of nanoreinforcement in green nanocomposites, CNFs has attracted great attention because of its unique characteristics such as high aspect ratio and good mechanical properties (Chen, Yu, Li, Liu, & Li, 2011a; Chen et al., 2011b; Chen, Yu, & Liu, 2011c). Therefore, it would be very interesting to combine the two kinds of nanocellulose materials.

In this manuscript, we demonstrate a flexible, highly optical transparent and iridescent CNFs/CNWs hybrid nanopaper that possesses a writable surface for flexible electronics. Furthermore, it is iridescent under polarizing film and less expensive than that of neat CNWs-based nanopaper. In our hybrid paper, CNFs was used as a nanoreinforcement to be incorporated into CNWs paper, which aims to improve the mechanical properties of iridescent CNWs paper and thus facilitate their applications. CNFs fills the spaces to decrease the light scattering that otherwise occurs in CNWs paper substrates. Compared with CNWs nanopaper, hybrid paper has a greater optical transparency and mechanical strength.

2. Materials and methods

2.1. Preparation of CNWs suspension

The CNWs suspension was obtained by acid hydrolysis of commercial cotton. About 5 g of commercial cotton was dispersed in 100 mL of sulfuric acid (64 wt%) at 45 °C under vigorous stirring for 60 min. The suspensions were then washed with deionized water using repeatedly centrifuge cycles (10 min at 12,000 rpm for a cycle) until the suspension reached neutrality. Finally, the samples were ultrasonic treated for 10 min in an ice bath. The resulted CNWs suspension was concentrated to 1.59 wt% by evaporation.

2.2. Preparation of CNFs suspension

Never-dried bamboo bleached fibers were used as cellulose source for preparing CNFs. The method to prepare CNFs is according to Chen et al. (Chen et al., 2011a, 2011b, 2011c). 100 mL solution containing purified cellulose fibers (0.1 wt%) was ultrasonically treated for 200 min with a common ultrasonic generator (JY99-II D, Ningbo Scientz Biotechnology Co., Ltd., China) at a frequency of 19.5–20.5 kHz. Then the upper CNFs suspension was collected.

2.3. Preparation of hybrid nanopaper

The mixed suspension containing different ratios of CNWs and CNFs was prepared by homogenization using a high shear mixer (IKA T18). This mixed suspension was filled into a diameter petri dish (90 mm) and allowed to evaporate over 48 h at ambient temperature to produce hybrid nanopaper. The thickness of each nanopaper was kept constantly at 50 ± 10 μm. The samples were coded as nanopaper-0, nanopaper-1, nanopaper-5, and nanopaper-10, according to the solid content of CNFs in the nanopapers at 0 wt%, 1 wt%, 5 wt%, and 10 wt%, respectively.

2.4. Characterization

2.4.1. Measurement of the thickness of nanopapers

The thickness of nanopapers was measured by using a micrometer (Lorentzen and Wettre, precision 1 μm). Each nanopaper was measured at least five different locations, which should be evenly distributed on the whole nanopaper. The mean value was used in the calculations to determine the mechanical test measurement.

2.4.2. Polarized light microscopy

An Olympus BH-2 optical microscope with 10 × objective lens was used to observe the iridescence in the nanopapers with the assistance of two polarized light filters. Samples were viewed under white light conditions.

2.4.3. Morphological investigation

The shape and size of the obtained CNWs and CNFs suspensions were analyzed by a transmission electron microscope (TEM, JEOL JEM-100CX, Japan) at 80 kV. Drops of dilute suspensions were deposited onto glow-discharged, carbon-coated electron microscopy grids; excess liquid was absorbed by a piece of filter paper. Furthermore, the nanopapers were fractured in liquid nitrogen to expose the middle part of cross sections for SEM observations by fixed on a metal stub using carbon tape and coated with gold.

2.4.4. UV-vis transmittance measurements

The optical transmittances of the films were measured from 350 to 900 nm using a Shimadzu UVmini-1240 spectrophotometer and were correlated based on the nanopaper thicknesses using the Lambert–Beer's law.

2.4.5. Wide-angle X-ray diffractions (XRD) analysis

Wide-Angle X-ray Diffractions were carried out by a Philips X'Pert X-diffractometer with Cu-Kα radiation operating at $\lambda = 0.1540$ nm (40 kV, 40 mA). Data were obtained in a 2θ scale from 5 to 50°.

The degree of crystallinity could be relatively expressed by the percentage crystallinity index (% CrI). (Habibi, Chanzy, & Vignon, 2006) The equation used to calculate the CrI was described by Segal et al. (Segal, Creely, Martin, & Comrad, 1959) as follows:

$$CrI(\%) = [(I_{002} - I_{am})/I_{002}] \times 100$$

where I_{002} is the counter reading at peak intensity at a 2θ angle close to 22° representing the crystalline part and I_{am} is the counter reading at peak intensity at 2θ close to 18° representing the amorphous part in cellulose.

2.4.6. Thermal Analysis

Thermal gravimetric analysis (TGA) was performed by using a TA-2000 analyzer (TA Instrument) under nitrogen purge with a flow rate of 100 mL/min. The scanning rate was 10 °C/min and the temperature range was from 40 to 600 °C.

2.4.7. Tensile strength tests

The tensile strength of the nanopapers was measured with a tensile testing machine (Instron 5567 Universal Testing Machine) fitted with a 100 N load cell at a crosshead speed of 1 mm/min. The samples were cut in the rectangular specimens with a width of 12 mm and length of 35 mm. The measurements were performed at 23 °C and relative humidity of 50%.

2.4.8. Water contact angel (WCA) measurements

The WCA was measured by a DSA 100 drop shape analysis system (Kruss Gmbh). The volume of the water droplet for each measurement was kept at 3×10^{-9} m^3.

3. Results and discussion

3.1. Polarized light microscopy

Fig. 1 shows the images of nanopaper-0 (Fig. 1a), nanopaper-1 (Fig. 1b), nanopaper-5 (Fig. 1c), and nanopaper-10 (Fig. 1d) observed in transmission between crossed polars in an optical microscope. Both nanopaper-0 and nanopaper-1 show remarkable iridescence and usual multidomain structure, which indicates the existence of chiral nematic structures in these nanopapers. However, it can be obviously observed that the color of nanopaper-5 in