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Switchable photoluminescence liquid crystal coated bacterial cellulose films with conductive response

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ABSTRACT

Three different low molecular weight nematic liquid crystals (LCs) were used to impregnate bacterial cellulose (BC) film. This simple fabrication pathway allows to obtain highly transparent BC based films. The coating of BC film with different liquid crystals changed transmittance spectra in ultraviolet–visible region and allows to design UVC and UVB shielding materials. Atomic force microscopy results confirmed that liquid crystals coated BC films maintain highly interconnected three-dimensional network characteristic of BC film and simultaneously, transversal cross-section scanning electron microscopy images indicated penetration of liquid crystals through the three-dimensional network of BC nanofibers. Investigated BC films maintain nematic liquid crystal properties being switchable photoluminiscence as a function of temperature during repeatable heating/cooling cycles. Conductive response of the liquid crystal coated BC films was proved by tunneling atomic force microscopy measurement. Moreover, liquid crystal coated BC films maintain thermal stability and mechanical properties of the BC film. Designed thermoresponsive materials possessed interesting optical and conductive properties opening a novel simple pathway of fabrication liquid crystal coated BC films with tuneable properties.

1. Introduction

Cellulose is one of the most abundant natural polymer which paid increasing attention of many scientists and engineers. Special interest is focused on bacterial cellulose (BC) due to their impressive properties such as high crystallinity, water holding capability, high porosity as well as biodegradability and remarkable biocompatibility (Abeer, Amin, & Martin, 2014; Almeida et al., 2014; Barud, Caiut, Dexpert-Ghys, Messaddeq, & Ribeiro, 2012; Fu, Zhang, & Yang, 2013; Gutierrez, Fernandes, Mondragon, & Tercjak, 2012; Hoenich, 2006; Iguchi, Yamanaka, & Budhiono, 2000; Klemm, Schumann, Udhardt, & Marsch, 2001; Lin et al., 2013; Qiu & Netravali, 2014; Shi, Zhang, Phillips, & Yang, 2014; Yano et al., 2005; Zhang et al., 2013; Zhu, Fang, Preston, Li, & Hu, 2014). These interesting properties of BC, consisted of interconnected three-dimensional nanofibers network, lead to their wide range of application in electronic (Gutierrez, Fernandes, et al., 2012; Lee, Buldum, Mantalaris, & Bismarck, 2014; Lin et al., 2013; Zhang et al., 2013, 2014), tissue engineering (Fu et al., 2013; Lin et al., 2013), medicine (Hoenich, 2006; Klemm et al., 2001), drug delivery (Abeer et al., 2014; Almeida et al., 2014) and food packaging (Shi et al., 2014) among others.

Nowadays, many research groups have searched for novel strategies of fabrication composite materials based on BC matrix (Bulota, Tanpichai, Hughes, & Eichhorn, 2012; Galland et al., 2013; Shaha, Ul-Islama, Khattaka, & Park, 2013; Zhou et al., 2009). Different type of water-soluble polymeric materials (Barud et al., 2011, 2012; Brown & Laborie, 2007; Castro et al., 2014; Gea, Bilotti, Reynolds, Soykeabkeaw, & Peijs, 2010; Hebler & Klemm, 2009; Marins et al., 2011; Quero et al., 2010; Tercjak, Gutierrez, Barud, Domeneguetti, & Ribeiro, 2015) or inorganic nanoparticles (Barud et al., 2015; Dal'Acqua et al., 2015; Gutierrez, Fernandes, et al., 2012; Gutierrez, Fernandes, Mondragon, & Tercjak, 2013; Gutierrez, Tercjak, Argal, Retegi, & Mondragon, 2012; Jian et al., 2014; Li et al., 2009; Liu, Yang, Wang, Shi, & Jiang, 2012; Olsson et al., 2010) were employed to develop novel composites with tuneable properties which combine the exceptional properties of BC and physicochemical properties of polymeric materials or optical, electrical, magnetic or antibacterial properties of inorganic nanoparticles. Different preparation pathways such as in-situ biosynthesis, immersion of

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BC membrane in solution with polymer materials or inorganic nanoparticles, impregnation and coating were explored to fabricate BC based composites with fascinating properties and wide range of application possibilities (Barud et al., 2011, 2015; Brown & Laborie, 2007; Castro et al., 2014; Dal'Acqua et al., 2015; Gea et al., 2010; Gutierrez, Tercjak, et al., 2012; Gutierrez et al., 2013; Hebler & Klemm, 2009; Jian et al., 2014; Li et al., 2009; Marins et al., 2011; Olsson et al., 2010; Quero et al., 2010; Tercjak et al., 2015). On the other hand, low molecular weight nematic liquid crystals (LC) are organic molecules with interesting properties especially a large optic and dielectric anisotropy (Doane, Golemme, West, Whitehead, & Wu, 1988; Drzaic, 1988; Zhou, Collard, Park, & Srinivasarao, 2002). Consequently, LC are one of the most convenient materials to control light by changes in the alignment of their molecules with external stimuli such as an electrical field, a temperature gradient and light (Campbell, Tasinkevych, & Smalyukh, 2014; Doane et al., 1988; Drzaic, 1988; Ganesan, Wirges, Mellinger, & Gerhard, 2010; Tercjak, Gutierrez, & Mondragon, 2011; Tercjak, Gutierrez, Ocando, Peponi, & Mondragon, 2009; Tercjak, Serrano, & Mondragon, 2006; Zhou et al., 2002). For this reason, LC have been extensively combined with polymers to design novel materials for application in the field of thermo- and electro-optical devices, such as optical shutters, smart windows, optical sensors, memories and flexible displays (Doane, Vaz, Wu, & Zumer, 1986; Herod & Duran, 1998; Sumana & Raina, 2005). However, based on our knowledge low molecular weight nematic liquid crystals have never been used in combination with BC.

Taken above into account, in present work three low molecular weight liquid crystals, 4'-(hexyloxy)-4-biphenyl carbonitrile (HOBC), 4'-(hexyl)-4-biphenyl-carbonitrile (HBC) and multicomponent nematic mixture E7, were used for the preparation of LC coated BC films. UV–vis spectroscopy was used to study optical properties and transparency of the fabricated HOBC, HBC and E7 coated BC films. Structural properties and the dispersion of the liquid crystals on the surface of the BC film were studied employing atomic force microscopy and optical microscopy. Moreover, transversal cross-section of the coating was investigated to check profundity of the liquid crystals impregnation through three-dimensional BC nanofibers network. Photoluminescence properties of investigated liquid crystals coated BC films as a function of temperature were studied using spectrophotometer. Additionally, taken into account that nematic liquid crystals can have different respond to an applied voltage, tunneling atomic force microscopy measurement was employed to prove the effect of external stimuli on the liquid crystals coated BC films. Finally, mechanical properties were also studied using a material testing system (MTS).

2. Experiment

2.1. Materials

Two low molecular weight nematic liquid crystals used were 4'-(hexyloxy)-4-biphenyl carbonitrile (HOBC) and 4'-(hexyl)-4-biphenyl-carbonitrile (HBC) supplied by Sigma-Aldrich, and used without further purification. Additionally, low molecular weight nematic liquid crystal E7 supplied by Merck was also used without further purification. The thermal transitions of used LCs are shown in Table 1. These transitions were determinate by differential scanning calorimetry (DSC).

2.2. Production of BC inoculum

The strain used was *Gluconacetobacter xylinum* (ATCC 23760) supplied by André Tosello Foundation, Campinas-SP, Brazil. It was cultured in Hestrim-Schramm medium (HS medium) that contained D-glucose glycose, yeast extract, peptone, di-sodium hydrogen phosphate (Na_2HPO_4), citric acid, agar and purified water. Analytical grade chemicals were used as received. Before the bacterial strain inoculation the strain culture medium was sterilized and then was cultivated during 1 day at 28 °C in an air circulating oven as conditioning chamber.

Table 1
Crystal–nematic transition ($T_{C\text{-}N}$) and nematic–isotropic transition ($T_{N\text{-}I}$) of HBC, HOBC and E7 as determined by DSC.

Name	$T_{C\text{-}N}$ (°C)	$T_{N\text{-}I}$ (°C)
HBC	26	34
HOBC	59	76
E7	−10	58

2.3. Biosynthesis of bacterial cellulose

BC culture medium was prepared according to the method previously reported by us (De Salvi et al., 2014; Tercjak et al., 2015). 45 mL of culture medium and 5 mL of the inoculum was cultivated during 3 days in static conditions at 28 °C in a 250 mL Erlenmeyer flask in an air circulating oven. After this time, jelly-like BC pellicle was harvested and purified to eliminate the culture medium (to remove the cells and other impurities). The purification protocol was performed following the pathway published by Tercjak et al. (2015). Finally, purified BC pellicle was dried in order to obtain BC film.

2.4. LC/BC film preparation protocol

Considering practical applications of designed materials, we proposed an easy method which can also be applied over large-scale areas at ambient conditions relatively inexpensively. Thus, we fabricated LC/BC films by a simple painting process. The BC film was used as support (substrate, hold) for the LC coating. BC film substrates were painted with LC solution (3 wt% in chloroform) in order to get LC coated BC film. To ensure the same quantity of the LC used for painting, 1 mL of the LC solution was employed for preparation of each sample. Prepared LC/BC films were dried in a vacuum oven at 30 °C during 24 h. Additionally, elemental analysis was realized to determine LC content in LC/BC films. Table 2 shows the carbon (C), hydrogen (H) and nitrogen (N) contents of investigated materials.

2.5. Characterization techniques

Elemental Analysis of LC coated BC films was carried out using a Euro EA Elemental Analyzer made by EuroVector. Independent measurements were performed to measure C, H and N contents.

The optical properties of BC film and nematic liquid crystal coated BC films were studied using a UV-3600, Shimadzu UV-VIS-NIR spectrophotometer in the wavelength range of 200–800 nm. The average thickness of the samples used for this measurement was 20 ± 3 μm.

Fourier transform infrared spectra (FTIR) were carried out in a Nicolet Nexus Spectra equipped with a Golden Gate single reflection diamond ATR accessory and were taken with a 2 cm^{-1} resolution in a wavenumber range from 4000 to 400 cm^{-1}.

Table 2
Elemental analysis data of LC coated BC films.

Sample	C%	H%	N%
HOBC/BC	46.53	6.40	0.5
HBC/BC	45.26	6.42	0.3
E7/BC	45.89	6.34	0.28