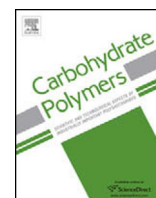




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Engineered pigments based on iridescent cellulose nanocrystal films

Raphael Bardet^{a,b}, Francine Roussel^c, Stéphane Coindeau^c,
Naceur Belgacem^{a,b}, Julien Bras^{a,b,*}^a University of Grenoble Alpes, LGP2, F-38000 Grenoble, France^b CNRS, LGP2, F-38000 Grenoble, France^c Materials Characterization Center, Grenoble INP, Pagora 461, rue de la papeterie 38402, Saint-Martin-d'Hères, F-38000 Grenoble, France

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ABSTRACT

A simple method to produce biobased iridescent pigments from cellulose nanocrystal (CNC) films is reported. The process consists of forming nanostructured films from a CNC liquid-crystalline suspension and an appropriate dry grinding. The features of the iridescent pigments are described; they have a flake-like morphology with a thickness of 25 μm . However, because of the presence of sulfate groups, thermal degradation and high redispersion in water occur, which affect the iridescent property of these biobased pigments. To overcome such limitations, two post-treatments are proposed. The sulfate ester groups are removed from the iridescent pigments with vacuum overdrying. The mass loss of iridescent pigment in water is reduced with an increase of the ionic strength in the aqueous medium by NaCl addition. These post-treatments have proven to be efficient and engineered pigments based on CNC films can be used to add anticounterfeiting features to packaging manufactured by classical paper techniques or extrusion.

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1. Introduction

Over the last two decades, major current environmental issues have actively contributed to the emergence of two important scientific fields: nanotechnology with the development of innovative and efficient materials (Cao & Wang) and sustainable products from nonfood raw materials (Mohanty, Misra, & Drzal, 2002). At the crossroads, nanocellulose is one of the most promising biobased nanomaterials, as exhibited by the significant and increasing number of research institutes or industrial companies focusing on it.

Nanocellulose displays outstanding properties, including a high surface area (250 m^2/g), a high aspect ratio (>50) and a Young's modulus greater than that of Kevlar. Moreover, this nanomaterial has been demonstrated to be promising for the reinforcement of barriers and to improve the mechanical properties of composites (Dufresne, 2010; Siró & Plackett, 2010). In comparison to inorganic nanomaterials, it also presents several advantages, such as a low density (1.5 g/cm^3) and a reactive surface that makes its chemical functionalization possible (Lin & Dufresne, 2014; Moon, Martini, Nairn, Simonsen, & Youngblood, 2011). Different types of nanocellulose are available, including cellulose nanocrystals (CNCs) and cellulose nanofibers (CNFs), depending on its isolation treatment,

i.e., whether a chemical treatment or mechanical disintegration is used, respectively.

This study will focus only on the self-organization properties of CNCs; however, more detailed information about the production, characterization and utilization of both CNFs and CNCs can be found in a recent book (Dufresne, 2012) or reviews (Eichhorn et al., 2010; Habibi, Lucia, & Rojas, 2010; Moon et al., 2011).

Recent works (since the year 2010) not only describe the characterization and production of CNC but increasingly frequently address its end use in smart applications, such as for controlling drug release (Jackson, Letchford, Wasserman, Ye, Hamad, & Burt, 2011), as an aerogel for insulation (Heath & Thielemans, 2010), as a stimuli-responsive material (Mendez et al., 2011) and as a photonic film (Shopsowitz, Hamad, & MacLachlan, 2011). Indeed, there is a growing interest at the industrial level with the recent construction of the first CNC processing plants and the growth of the patent portfolio since the year 2008 (Charreau, Foresti, & Vazquez, 2013).

Derived from the well-known property of CNCs to display liquid-crystalline behavior in water (Gray, 1994) and non-aqueous suspensions (Heux, Chauve, & Bonini, 2000), one outstanding application is the manufacturing of iridescent materials as patented in 1995 (Revol, Godbout, & Gray, 1995). Revol and Gray were the first to report that the self-organization can be preserved by simple evaporation (Revol, Godbout, & Gray, 1998). Since then, several scientific publications, conferences and patents have been created, as recently summarized in a book chapter (Abitbol & Cranston, 2014).

* Corresponding author at: University of Grenoble Alpes, LGP2, F-38000 Grenoble, France. Tel.: +33 0 4 76 82 69 15.

E-mail address: julien.bras@grenoble-inp.fr (J. Bras).

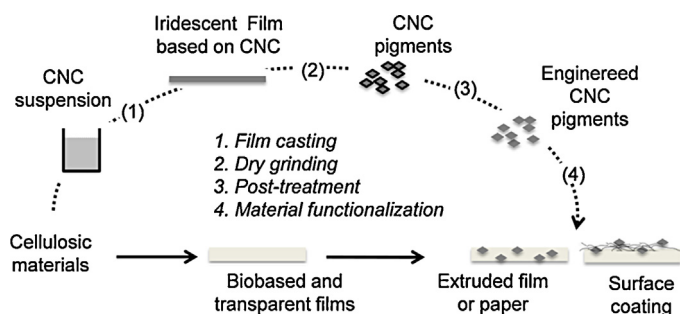


Fig. 1. The proposed approach for engineering pigments from solid iridescent films based on CNCs.

Even if this nanostructured material is indisputably promising, end applications appear to be limited to the lab scale because a processing technique that can be completed within one day is required for manufacturing iridescent films. Continuous and fast production processes, such as surface treatment, extrusion, lamination, or paper-like techniques, cannot preserve the structural coloration property. In addition, CNC as a starting material is not cost-efficient enough to compete with other materials that are able to display similar photonic properties, and iridescent films based on CNC are usually very brittle and difficult to process.

In this context, this study proposes to overcome these limitations by manufacturing pigments from iridescent CNC films and then incorporating them within flexible and transparent films, as described in Fig. 1. Such strategy has been recently patented (Bardet et al, 2014). In the first part, the CNCs and the iridescent film were characterized. Then, the optimized procedure for manufacturing the pigment with dry grinding is described. The chemical and morphological features of the pigments are also summarized. In addition to the elaboration and characterization of the ground pigment, two main drawbacks that limit the industrial application of such pigments are addressed, i.e., the low thermal stability due to surface sulfate groups and the water sensitivity. For this, various treatments are also investigated, i.e., obtaining engineered iridescent pigment based on CNCs.

2. Experimental

2.1. Materials

The starting material for producing iridescent solid films is commercial cellulose nanocrystals (CNCs) delivered as a dry powder. It was purchased from Celluforce (Canada) and isolated from wood pulp by sulfuric acid hydrolysis.

CAB (CAB-381-20, Eastman Chemical CompanyTM, USA) is a thermoplastic polymer based on cellulose. The butyryl, acetyl and hydroxyl contents are 37.0, 13.5 and 1.8 wt%, respectively, with a molecular weight of 70,000 g/mol. The CAB used has a glass transition temperature of 141 °C and a melting point ranging from 195 to 205 °C, as reported by the supplier.

NaCl solutions were prepared by dissolving salt purchased from Sigma-Aldrich (France) in deionized water.

2.2. Methods

2.2.1. Manufacturing of the iridescent solid film

After being diluted to 5.0 wt%, the CNC suspension was submitted to a dispersion energy of 1 kJ/g using a 200-Watt sonication probe (Sonifier[®] S-250A, Branson, USA), to obtain a homogeneous dispersion. Films were obtained by simple evaporation of the suspension. Approximately 200 ml of the suspension was gently poured into a rectangular glass container (40 × 30 cm²) and

evaporated at room conditions (23 °C, 50% RH) over 24 h. An iridescent film based only on CNCs with an average thickness of approximately 75 μm (basis weight of approximately 100 g/m²) was obtained.

2.2.2. Iridescent-pigment preparation

Approximately 10 g of the iridescent film was previously cut into small pieces (0.5 × 0.5 cm²) with a knife mill (GM300, Retsch, Germany) and then dry-crushed using an ultracentrifugal mill (ZM 200, Retsch, Germany). To separate the finest and coarsest elements, the ground materials were successively screened between two sieves of 60 and 270 mesh.

2.2.3. Nanoparticle characterization

Individual nanoparticles were imaged using atomic force microscopy, AFM, (Nanoscope III[®], Veeco, Canada). All samples were previously diluted at 10⁻⁴ wt%, and a drop of 0.2 ml was deposited onto freshly cleaved mica substrates and dried overnight under room conditions. Each sample was characterized in tapping mode with a silicon cantilever (OTESPA[®], Bruker, USA) at four different locations with a scanning area of 3 × 3 μm². Both topographical and phase images were captured, and the AFM images were subjected to first-order polynomial flattening to reduce the effects of bowing and tilt. Only the most representative images were presented in this study; however, the morphological dimensions were calculated as an average of at least 50 individual nanoparticles.

Dynamic light scattering (DLS) was used to measure the size of the nanoparticles (Vasco[®] I, Corduan Technologies, France). All of the samples were previously diluted in DI water at 10⁻² wt%. A cumulative method was used, and two parameters were taken into account: the hydrodynamic diameter (z^*) and the polydispersity index (PDI). For each sample, 10 acquisitions were performed, and each measurement was replicated three times.

The electrophoretic mobility of the CNCs was measured using a zeta potential analyzer (Zeta 2000, Malvern, UK). The CNC suspensions were diluted to approximately 0.05 wt% in deionized water in the presence of a NaCl solution to maintain a constant ionic strength (500 μS/cm). The reported zeta potential corresponded to the average value of ten measurements.

The sulfur (%S) content was determined by inductively coupled plasma atomic emission spectroscopy (iCAP 6300 ICP Spectrometer, Thermo Scientific, USA). The analysis was performed at the "Institut des Sciences Analytiques" (CNRS, France). Each elemental analysis (EA) was duplicated and averaged. The surface-charge density was estimated from the sulfur content and assuming the geometrical dimensions obtained from AFM:

$$\sigma \text{ (e/nm}^2\text{)} = \frac{M_{\text{SO}_3} \times \%S \times \text{Na}}{S_{A:V} / d_{\text{Cell}}}$$

where M_{SO_3} corresponds to half of the sulfate ester molecular weight, %S is the sulfur content, Na is Avogadro's constant, $S_{A:V}$ refers to the surface-to-volume ratio and d_{cell} corresponds to the density of the cellulose crystals.

The thermal degradation of the investigated samples was monitored by thermogravimetric analysis (TGA, using the thermogravimetric analyzer STA 6000[®], Perkin Elmer Instruments, England). The weight-loss and heat-flow curves were recorded for a 30 mg subsample at a heating rate of 10 °C/min in the temperature range of 30–950 °C under oxidizing atmosphere (air). The analyses were duplicate and averaged.

The X-ray diffraction (XRD) patterns were obtained with an X-ray diffractometer (PANalytical[®], X'Pert PRO MPD). The operating conditions for the refractometer were Cu K α radiation (1.54 Å), a 2 θ Bragg angle range between 5 and 60°, a step size of 0.067° and a

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