International Journal of Biological Macromolecules 106 (2018) 681–691

Contents lists available at ScienceDirect

International Journal of Biological Macromolecules

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

Reuse of red algae waste for the production of cellulose nanocrystals and its application in polymer nanocomposites

Mounir El Achaby[a,*], Zineb Kassab[a], Adil Aboulkas[a,b], Cédric Gaillard[c], Abdellatif Barakat[a,d]

[a] Materials Science and Nanoengineering (MSN) Department, Mohammed 6 Polytechnic University (UM6P), Lot 660–Hay Moulay Rachid, 43150, Benguerir, Morocco
[b] Laboratoire Interdisciplinaire de Recherche des Sciences et Techniques, Faculté polydisciplinaire de Béni-Mellal, Université Sultan Moulay Slimane, BP 592, 23000 Béni-Mellal, Morocco
[c] UR BIA 1268 Biopolymères Interactions Assemblages, INRA, 44316 Nantes, France
[d] IATE, CIRAD, Montpellier SupAgro, INRA, Université de Montpelier, 34060, Montpellier, France

ARTICLE INFO

Article history:
Received 9 July 2017
Received in revised form 9 August 2017
Accepted 10 August 2017
Available online 16 August 2017

Keywords:
Red algae waste
Acid hydrolysis
Cellulose nanocrystals
Polymer composites

ABSTRACT

Red algae is widely available around the world and its exploitation for the production of agar products has become an important industry in recent years. The industrial processing of red algae generates a large quantity of solid fibrous wastes, which constitutes a source of serious environmental problems. In the present work, the utilization of red algae waste as raw material to produce high-quality cellulose nanocrystals (CNC) has been investigated, and the ability of the as-isolated CNC to reinforce polymer has been studied. Red algae waste was chemically treated *via* alkali, bleaching and acid hydrolysis treatments, in order to obtain pure cellulose microfibers and CNC. The raw waste and the as-extracted cellulosic materials were successively characterized at different stages of treatments using serval analysis techniques. It was found that needle-like shaped CNC were successfully isolated at nanometric scale with diameters and lengths ranged from 5.2 ± 2.9 to 9.1 ± 3.1 nm, and from 285.4 ± 36.5 to 315.7 ± 30.3 nm, respectively, and the crystallinity index ranged from 81 to 87%, depending on the hydrolysis time (30, 40 and 80 min). The as-extracted CNC were used as nanofillers for the production of polyvinyl alcohol (PVA)-based nanocomposite films with improved thermal and tensile properties, as well as optical transparency. It is shown that the addition of 8 wt% CNC into the PVA matrix increased the Young's modulus by 215%, the tensile strength by 150%, and the toughness by 45%. Additionally, the nanocomposite films maintained the same transparency level of the neat PVA film (transmittance of ~90% in the visible region), suggesting that the CNC were dispersed at the nanoscale.

1. Introduction

Cellulose is one of the most abundant matter on the earth, and widely used for various industrial applications, due to its unique properties such as renewability, biodegradability, high tensile strength and stiffness, cost effectiveness, light weight and environmental benefits [1,2]. Since its discovery and isolation by Anselme Payen in 1838, the structure and properties of cellulose have been largely studied and highlighted in the literature [1,3]. Cellulose is naturally present in plants, marine animals, marine biomass, fungi, bacteria, and invertebrates, among others [2,4]. From lignocellulosic materials, cellulose can be extracted in the form of fibers. It is considered to be water-insoluble compound and can plays an important role in maintaining the structure of a plant cell wall [2,3].

Using top-down processes, cellulose can be extracted from cellulose-rich materials in various forms including fibers, microfibers, microfibrills, nanofibers and nanocrystals [2,4,5]. Cellulose nanocrystals (CNC) is the nanoscale form of cellulose which can be produced in various morphological shapes such as sphere-like, rod-like, ribbon-like, or needle-like shape, having a compact structure of ordered cellulose chains stabilized by inter and intra-molecular hydrogen bonding, which make very interesting solid crystalline nanoparticles with unique characteristics [6–9]. Starting from pure cellulose fibers, CNC can be extracted by various methods such as acid hydrolysis, TEMPO-mediated oxida-

---

* Corresponding author.
E-mail address: mounir.elachaby@um6p.ma (M. El Achaby).

http://dx.doi.org/10.1016/j.ijbiomac.2017.08.067
0141-8130/© 2017 Elsevier B.V. All rights reserved.

tion, mechanical disintegration and enzyme-assisted hydrolysis [5,10]. Among these methods, acid hydrolysis process represents the most effective method, where the cellulose fibers are subjected to concentrated acid to hydrolyze the amorphous domains of the cellulose chains and leave the crystalline domains unaltered [7]. In this context, the sulfuric acid has been extensively used for CNC extraction, however, hydrochloric, phosphoric and hydrobromic acids have also been reported for such purposes [3]. The sulfuric acid hydrolysis is a simple process and it requires shorter reaction time than other processes [2]. Additionally, this process produces CNC with functionalized surface, high crystallinity and good colloidal stability in water [3]. Unfortunately, this process has some drawbacks for large scale production, such as serious large water usage, equipment corrosion, and generation of huge amount of waste [5]. It should be noted that, the physico-chemical properties of CNC are strongly related to the nature of the bio-sourced raw materials and the hydrolysis conditions such as time, temperature, agitation and acid concentration [3,9].

Until recently CNC have been largely extracted from lignocellulosic materials (biomass containing cellulose, hemicellulose and lignin as the main substances) using various cellulose rich bio-sourced materials such as wood, straw, cotton, sisal, flax, ramie, bamboo pulp, coconut husk, rice husk, and sugarcane bagasse, among others [3,9]. More recently, CNC were successfully extracted from marine biomass such as posidonia oceanica ball and leaves [11,12] and Gelidium elegans [10]. Marine biomass, especially algae derivatives, contains low amounts of natural physicochemical barriers, making the cellulose accessible without a severe chemical treatment. It also contains a higher yield of carbohydrates and grows faster than typical terrestrial lignocellulosic biomass [10,13,14]. Marine biomass is, thus, considered to be a potential source for the production of cellulose fibers and its derivatives such as CNC.

Marine algae are categorized mostly into several main groups based on their photosynthetic pigmentation variations, i.e. green, blue-green, red, brown and golden algae [15]. There are about 55 000 kinds of algae species but only a dozen are commercially cultivated worldwide, with 27.1% of all known species of marine plants are red algae. Concerning chemical composition, red algae consist mostly of polysaccharides, small amounts of proteins, traces of lipids, and inorganic materials. The body of red algae contains large amounts of mucilaginous materials such as agar or carrageenan. The exploitation of red algae, especially *Gelidium sesquipedale*, for the production of agar products has become an important industry in recent years [16]. It generates a large quantity of solid fibrous wastes which cause serious environmental problems [17]. Indeed, this algae waste (AW) is available in large amount and its valorization for the production of high value-added materials is not developed yet. However, the AW has been directly applied as soil conditioner and/or fertilizer in many coastal regions around the world [18–20], and can be reused as biosorbents for heavy metals [21,22]. After the extraction of Agar-Agar, the remaining AW mostly consists of 87.4% of organic matter of which 31.60% is made up of proteins and 54.95% of total sugars, which include lignocellulosic fibers [17]. This renders AW a good bio-sourced material for the production of cellulose derivatives, such as highly crystalline CNC, for advanced composite materials development, which is the main objective of the present work.

The use of CNC as reinforcing fillers in polymer-based nanocomposites has attracted a lot of attention in the field of nanotechnology. It has been widely demonstrated that the incorporation of CNC into biopolymers can result in nanocomposite materials with high mechanical, optical, thermal, and barrier properties [23]. This is possible because of CNC's special morphology (generally needle like-shape), structure (ordered cellulose chains), large specific surface area ($\sim$250–500 m^2/g), low density, high crystallinity, high tensile strength (7.500 GPa), and very high elastic modulus (approximately 100–140 GPa) [7,9]. Additionally, CNC possess abundant hydroxyl groups on their surfaces, making them hydrophilic nanomaterials, which may facilitate their dispersions within water-soluble polymer matrices [7].

The aim of the current work is to explore the re-valorization of red algae waste (fibrous residue of red algae after extraction of agar-agar product) for the isolation of CNC using the same chemical treatments that are largely used for CNC isolation from typical terrestrial lignocellulosic materials, e.g. alkali, bleaching and sulfuric acid hydrolysis treatments [23–25]. CNC were extracted at various hydrolysis times (30, 40 and 80 min), in order to investigate the influence of extraction time on the yield, morphology, size, crystallinity, thermal stability of the resulting CNC. This parameter was selected because it was identified as one of the most important parameters for obtaining CNC using the acid hydrolysis treatment [26–28]. After their successful extraction, the as-obtained CNC were successfully characterized in terms of their physico-chemical properties, and used as nanoreinforcing fillers for polymer nanocomposites development, using polyvinyl alcohol (PVA) as a polymeric matrix. PVA is a material with technological potential as a biodegradable polymer. It has wide commercial applications due to its unique chemical and physical properties. This polymer is nontoxic, highly crystalline, and water-soluble polymer that has good film-forming ability and hydrophilic properties, which arise from the presence of —OH groups on its macromolecular chains, which could be useful to link the functional groups of CNC, leading in the formation of hydrogen bonds. The PVA-CNC nanocomposites were produced thought solvent casting method and characterized regarding their thermal, transparency and mechanical properties.

2. Materials and experimental detail

2.1. Materials

Unpurified algae waste (AW) (Moisture = 9.11%; ash = 14.13%), which is generated from industrial processing of agar-agar production, was provided by SETEXAM Company localized in Kenitra City in Morocco. The PVA polymer (Mw 31,000–50,000) and all the analytical grade chemicals used for extraction, bleaching, and hydrolysis were purchased from Sigma–Aldrich and used without further purification.

2.2. Production of cellulose fibers

CNC were successfully extracted from AW by alkali and bleaching treatments followed by an acid hydrolysis process, as described in our previous works [23,24,29]. The as-received AW samples were first cut into small pieces ($\leq$2 cm), which were ground using a precision grinder equipped with a 2 mm sieve screen (RETCH SM 100). The ground AW fibers were washed with distilled water for 1 h at 60 °C under mechanical stirring. Then, the prewashed AW fibers were treated three times with a 4 wt% NaOH solution at 80 °C for 2 h under stirring. The resulting alkali-treated algae waste (ATAW) was bleached 3 times at 80 °C for 2 h with a solution made up of equal parts (v:v) of acetate buffer (27 g NaOH and 75 mL glacial acetic acid, diluted to 1 L of distilled water) and aqueous sodium chlorite (1.7 wt% $NaClO_2$ in water), resulting in pure white colored cellulose fibers, defined as bleached algae waste (BAW). The overall steps of CNC extraction and digital images of each obtained products are presented in Fig. 1.

2.3. Isolation of CNC

The as-produced bleached algae waste (BAW) was submitted to a sulfuric acid hydrolysis to isolate CNC. The acid hydrolysis was