



Cellulose/microalgae composite films prepared in ionic liquids



Chenghu Yan^{a,1}, Ruihua Wang^{c,1}, Jiqiang Wan^b, Qinghua Zhang^a, Shengzhang Xue^a, Xia Wu^a, Jinming Zhang^{b,*}, Jun Zhang^b, Yunming Lu^d, Wei Cong^{a,*}

^a State Key Laboratory of Biochemical Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China

^b Beijing National Laboratory for Molecular Sciences (BNLMS), Key Laboratory of Engineering Plastics (KLEP), Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

^c College of Life Science and Technology, Beijing University of Chemical Technology, Beijing 100029, China

^d Shenzhen Ludebao Health Food. Co., Ltd, Shenzhen 518040, China

ARTICLE INFO

Article history:

Received 30 May 2016

Received in revised form 24 September 2016

Accepted 26 September 2016

Available online xxx

Keywords:

Cellulose

Microalgae

Composite film

Ionic liquids

Natural materials

ABSTRACT

Using 1-allyl-3-methylimidazolium chloride (AmimCl) as the solvent, cellulose/microalgae (C/M) composite films with microalgae content ranging from 19.14 to 78.83 wt% were prepared by solution-mixing and subsequent casting. The structure and properties were characterized by element analysis, Fourier transform infrared (FTIR) spectra, scanning electron microscopy (SEM), thermogravimetry, tensile test, hydrolytic degradation, and cell cultivation test. SEM and FTIR results indicated good compatibility between the microalgae and cellulose due to strong hydrogen bonding interaction. These composite films possessed good mechanical properties and thermal stability that are better than those of other microalgae based materials. The hydrolytic degradation rate of C/M composite films with microalgae content higher than 33.97% was faster than cellulose, and increased significantly with the increase of microalgae content. The cell culture experiments confirmed that the C/M composite films could support cell adhesion and proliferation, consequently exhibit good biocompatibility. Therefore, the C/M composite films can be considered as novel functional films with applications as biodegradable materials even in medical fields.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

In recent years, bio-based materials have gained much attention due to the environmental pollution by synthetic polymers and the depleting oil resources [1–5]. During the last few years, scientific interest is focused on biofuels and bioproducts from microalgae [6–8], while there are few reports on the potential application of microalgae in polymer materials. Microalgae protein can provide nourishment for cells. Moreover, clinical studies suggest that compounds in microalgae have therapeutic functions such as antiallergenic, antibacterial, antifungal, anti-inflammatory, antioxidant, and immune modulating properties [9–11]. Microalgae also contain high quantities of cellulose, hemicellulose, etc., and as a result can be considered as potential source for the production of useful cellulose fibers [12]. Therefore, microalgae may be promising candidate for the sustainable and affordable production of biodegradable materials.

Microalgae are difficult to be processed into materials with various shapes, due to their tiny cell sizes and high moisture sensitivity. In order to resolve these problems, the preparation of their composite materials is considered as a hopeful alternative for the use of microalgae [13–23]. Zhang et al. incorporated *Chlorella* or *Spirulina* into

polypropylene, polyethylene, and polyvinyl chloride, respectively, to create novel industrial materials and permanently capture CO₂ [13–16]. Mohanty et al. prepared biocomposite films of residual microalgae biomass with poly(butylene succinate) (PBS) and poly(butylene adipate-co-terephthalate) (PBAT) by extrusion and injection molding [17,18]. In addition, Morais et al. prepared nano structured scaffolds for tissue engineering by using biopolymers like polyethylene oxide (PEO) and polyhydroxybutyrate (PHB) incorporating *Spirulina* [22,23]. However, one of the most important factors influencing their application is the poor compatibility between the polar hydrophilic microalgae and the nonpolar hydrophobic polymer matrix, which reduced their ductility and increased their brittleness under tensile deformation [13–18]. Thus, further studies are necessary to improve the compatibility of microalgae with polymers in composite materials to obtain new microalgae-based composites with competitive mechanical properties.

Cellulose, which is the most abundant natural, renewable, biodegradable, non-edible low-cost source, is becoming one of the most used biomaterials due to its fascinating structure and mechanical properties and biocompatibility [24]. Nowadays, cellulose materials with different shapes and properties have been produced. Among them, blending cellulose with protein materials was a useful method to improve the biological properties of cellulose and the mechanical properties of protein materials. Some cellulose composites, such as cellulose/soy protein films, cellulose/casein films, cellulose/corn protein films and cellulose/egg white protein fibers, have been prepared with good

* Corresponding authors.

E-mail addresses: zhjm@iccas.ac.cn (J. Zhang), weicon@ipe.ac.cn (W. Cong).

¹ The first two authors contribute equally to this work.

Table 1
Composition of microalgae and microalgae residue.

Constitute (%)	Microalgae	Microalgae residue
Protein	43.7	50.5
Lipids	27.0	21.4
Carbohydrates	10.4	11.1
Ash	6.4	6.7
others	12.5	10.3

Table 2
Composition and thermal properties of C/M composite films.

Sample	W _N (%)	W _M (%)	W _{Pro} (%)	T _{onset} (°C)	T _{max} (°C)
Cellulose	0	–	0	308	334
C/M-20	1.51	19.14	9.36	284	314
C/M-40	2.68	33.97	16.73	275	300
C/M-60	4.30	54.50	26.85	267	294
C/M-80	6.22	78.83	38.86	262	292
Microalgae	7.89	–	49.31	233	278
Residue					330

mechanical and biological properties [25–30]. Thus, cellulose/microalgae (C/M) composites may be able to achieve good performance in terms of mechanical, biological and especially therapeutic functions.

Unfortunately, cellulose processing is extremely difficult in general, because this natural polymer can neither be molten nor be soluble in conventional solvents due to its hydrogen bonding and partially crystalline structure [31]. Several solvent systems have been developed to dissolve cellulose materials, such as NaOH/CS₂ [32], lithium chloride/*N,N*-dimethyl acetamide (LiCl/DMAc) [33], *N*-methylmorpholine-*N*-oxide (NMMO) [34], phosphoric acid [35], LiOH/urea and NaOH/urea [36] and ionic liquids [37,38]. On account of the unique physicochemical properties such as negligible vapor pressure, high thermal stability, wide liquid range and tunable solvation properties [39,40], ionic liquids have gained increasing interest and have been used to develop new cellulose materials. Moreover, it has been reported that some ionic liquids, such as 1-butyl-3-methylimidazolium chloride (BmimCl) and 1-allyl-3-methylimidazolium chloride (AmimCl), also exhibit an outstanding capability for dissolving microalgae [41–44]. Thus, the employment of ionic liquids can provide a new approach to mix microalgae and cellulose at molecular level in an efficient way.

In this work, microalgae residue of *Nannochloropsis* after oil extraction was used to prepare cellulose/microalgae (C/M) composites. The C/M composite films with different microalgae content (0, 20, 40, 60, 80 wt%) were prepared in AmimCl by dissolution and regeneration method. The structure and properties of the composite films were investigated and discussed.

2. Experimental

2.1. Materials

The cellulose (cotton pulp) with a degree of polymerization (DP) of 620 and cellulose content above 98% was supplied by Hubei Chemical Company Limited (Xiangfan, China). *Nannochloropsis* was purchased from Yantai Hairong biotechnology Co, Ltd. The ionic liquid, AmimCl, was synthesized according to the literature [45] and the water content in the resultant ionic liquid was found to be less than 0.3% as measured by Carl-Fisher method. Cotton pulp and *Nannochloropsis* were dried at 80 °C under vacuum for 6 h prior to use. All other organic solvents were analytical reagents and used without further purification.

2.2. Preparation and characterization of microalgae residue

Microalgae residue was prepared by oil extraction from *Nannochloropsis*, which was carried out using *n*-hexane solvent by heating. A typical preparation procedure used is presented as follows: 20 g *Nannochloropsis* and 200 mL *n*-hexane were mixed in a round bottom flask. The flask was connected to a reflux condenser and put into an oil bath. Then the extraction was carried at 80 °C with vigorous stirring for 12 h. When the extraction was completed, the mixture was then centrifuged at 10,000 rpm for 5 min. The upper *n*-hexane layer containing the lipid was collected, and the under layer of microalgae residue was dried at 80 °C under vacuum overnight. The carbohydrate, protein, lipids and ash content in microalgae and microalgae residue were determined according to the Association of Analytical Communities (AOAC, Official Methods) [27,28]. The composition of microalgae and microalgae residue is shown in Table 1.

2.3. Preparation of C/M composite films

The C/M composite films with different microalgae residue content (0, 20, 40, 60, 80 wt%) were prepared in AmimCl by dissolution and regeneration method. A typical preparation procedure used is as follows: 0.2 g microalgae residue and 0.8 g cellulose were dispersed into 24.0 g AmimCl in a flask, and the mixture was stirred at 80 °C for 1.5 h to ensure a complete dissolution. The solutions were degassed in vacuum, then cast onto a glass plate and immediately coagulated in deionized water to make regenerated C/M composite films. To remove residual ionic liquid in samples, the films were further washed with distilled water at least three times until no Cl[−] ions were detectable by the AgNO₃ test. After drying in a vacuum oven at 80 °C for 12 h, the C/M composite films were obtained and kept in a desiccator prior to characterization.

2.4. Hydrolytic degradation of C/M composite films

A typical degradation procedure used is as follows. C/M composite films were placed in a closed bottle containing 5 mL phosphate buffer saline (PBS, pH 7.4) and kept at 37 °C for 35 days. One of the specimens was consecutively removed from the bottle with an interval of 5 days, washed with distilled water and dried in vacuum to a constant weight

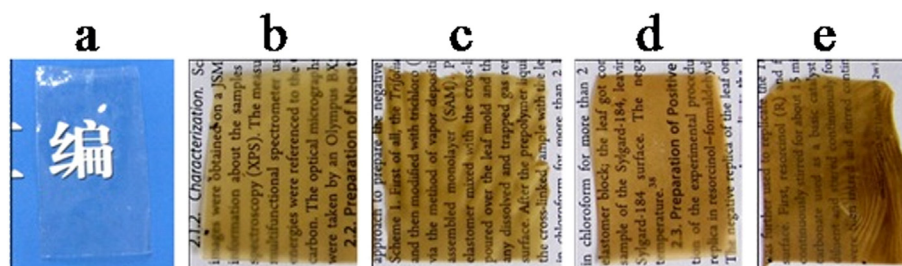


Fig. 1. Photographs of cellulose and C/M composite films. (a), regenerated cellulose film; (b), C/M composite film with 19.14% microalgae; (c), C/M composite film with 33.97% microalgae; (d), C/M composite film with 54.50% microalgae; (e), C/M composite film with 78.83% microalgae.

Download English Version:

<https://daneshyari.com/en/article/5478601>

Download Persian Version:

<https://daneshyari.com/article/5478601>

[Daneshyari.com](https://daneshyari.com)