DESIGNING A COMPOSITE FILMS BASED ON CARBON QUANTUM DOTS AND FURCELLARAN

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Abstract

Composite films based on furcellaran (FUR) and carbon quantum dots (CQDs) has been obtained by casting method. The effects of CQDs films as nanofiller on optical, physical, mechanical and microstructural properties of furcellaran films were evaluated. The synthesized composites were characterized using Scanning Electron Microscopy (SEM), Fourier-transform infrared spectroscopy (FT-IR) and ultraviolet-visible spectroscopy (UV-Vis). The results from scanning electron microscopy (SEM) confirmed that the composite films have homogeneous and compact structure, with no fractures or cracks. Tensile strength (TS) and elongation at break (EAB) values increased with the increase of CQDs concentration. The UV-Vis results confirmed that composite films exhibited enhancement of photosensitivity. The FUR/CQDs composite films have high potential to be used in many applications.

Keywords: Furcellaran, carbon dots, composite film

1. INTRODUCTION

Recently, polysaccharides-, proteins- and lipids- based films have been examined as an alternative for plastic packaging materials [1]. These bio-based films and coating offer excellent biocompatibility and biodegradability. However, biopolymer-based films have limitations: lower mechanical and water properties. This type of films are also used as carriers of active agents, such as essential oils [2], plant extracts [3] or nanostructures. In this work, we focused on the formation of nanocomposite films based on furcellaran and carbon quantum dots. Furcellaran is a polysaccharide with negative charge, which is composed of a fragment of (1 → 3) β-D-galactopyranose with a sulphate group at C-4 and (1 → 4) -3,6-anhydro-α-D-galactopyranose [4]. Carbon quantum dots, as a new class of photoluminescence (PL) nanoparticles, have been studied due to its excellent photostability, biocompatibility and low toxicity. Recently, there has also been a number of studies which investigated various nanocomposite films with quantum dots, including chitosan, gelatin [5], starch [6] and carboxymethyl cellulose [7]. Moreover, there are some reports on the application of carbon quantum dots such as photo catalysts, nanomaterials in medicine [8], sensors [9] and so on. To the best of our knowledge, no research work has been reported on the formation of nanocomposite films using furcellaran and carbon quantum dots. In this study, we described preparation of furcellaran films (FUR) containing carbon quantum dots (CQDs). Furcellaran was used as a polymer matrix and CQDs as nanofiller. The FUR/CDQs nanocomposite films were characterized using SEM, FT-IR and UV-Vis analysis. Physical and mechanical properties of nanocomposite films were also tested.

2. METHODOLOGICAL BASES AND EXPERIMENTAL PART

2.1. Chemicals

Furcellaran was provided by Est-Agar AS (Karla village, Estonia). All other chemicals were of analytical grade and purchased from Sigma-Aldrich (St. Louis, MO, USA).

2.2. Preparation of carbon quantum dots (CQDs)

Citric acid monohydrate (2.1 g) was dissolved in 45 ml of MilliQ water. Then, 3,3´-diamino-N-methyl-dipropylamine (mdpta) (1.7 ml) was slowly dropped into the solution with stirring. Water was added to 50 ml. 2 ml of the solution was heated in glass vials in microwave (130 °C) (Multiwave3000, Anton-Paar GmbH, Graz, Austria).

2.3. Preparation of nanocomposite films

Furcellaran films (FUR or control film) were prepared using a solution casting method. 1 g of FUR powder was dispersed in 100 ml of deionized water. Following this, glycerol (0.5 ml), as a plasticizer, was added into film-forming solution and stirred at 50 °C for 30 min. For the preparation of nanocomposite films, the CQDs (1, 3, 5, and 10 wt. % based on furcellaran) were added to the furcellaran solution following the same procedure as above. Finally, each film-forming solution (50 ml) was poured into petri dish (dimeter 90 mm) and transferred under fume hood and dried for 24 h. The dried films were peeled off from the petri dishes and conditioned at 20 °C and 50 % relative humidity in desiccators before evaluating.

2.4. Characterization

Thickness The manual instrument Mitotuyo, no. 7327 (Kawasaki, Japan) was used to measure the film thickness. Five measurements were taken from each type of films and averaged.

Water behaviors Water behaviors (WC- water content and WS- solubility) were examined according to our previous work [10].

Mechanical properties Tensile strength (TS, MPa) and elongation at break (EAB, %) of films were examined using a texture analyzer TAxT2i Stable Micro System (Surrey, UK). Mechanical properties were calculated according to the following equations:

$$\mathrm{TS\ [MPa]} = \frac{F_{max}}{\mathrm{S}} \quad (1)$$

$$EAB[\%] = \frac{L_f}{L_0} x100 \quad (2)$$

where TS - tensile strength [MPa], F_{max} - breaking load [N] and S - an area of the film cross-section [mm]; EAB-elongation at break; L_f - final length of the film sample at the point of break, L_0 - initial length of the film sample.

Spectroscopic analysis Ultraviolet-visible (UV-Vis) spectroscopy was performed by using a UV-5500 spectrophotometer (Metash), in the wavelength range from 200 to 800 nm. FTIR spectra of film samples were determined using a MATTSON 3000 spectrophotometer (Madison, Wisconsin, USA). 32 scans were collected with 4 cm^{-1} resolution in the 600 - 4000 cm^{-1} wavelength range.

Scanning electron microscopy (SEM) For the documentation of the structure of films, a scanning electron microscope HITACHI S-3400 N (CA, USA) was used.

Statistical analysis Statistical analysis was performed with Statistica v12.0 software (StatSoft, Tulsa, USA). Differences were statistically significant at the $p < 0.05$ level.

3. RESULTS AND DISCUSSION

The furcellaran films (FUR, control) were transparent, flexible and homogenous. The nanocomposite films with CQDs (in concentration 1, 3, 5 and 10 %) were visually homogeneous with no bubbles, cracks or brittle areas (**Figure 1**).

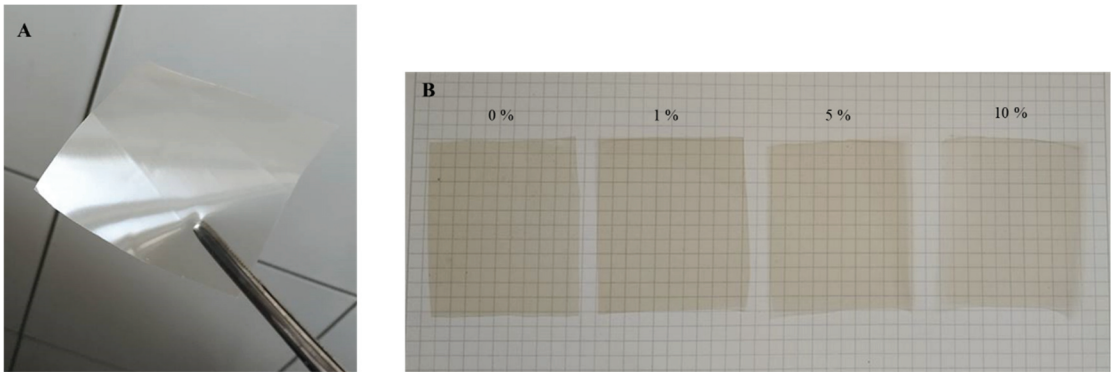

Figure 1 Appearance of nanocomposite FUR-based films with CDQs in different concentration (A) FUR films with 6 % CDQs, (B) FUR films with 0-10 % CDQs

Figure 2 shows SEM micrographs of the FUR/CQDs films. Uniform and smooth structure was observed for furcellaran films (**Figure 2A**), the presence of CQDs did not caused significant differences in the appearance of the films. SEM micrographs suggested the strong interaction between CQDs and furcellaran molecules.

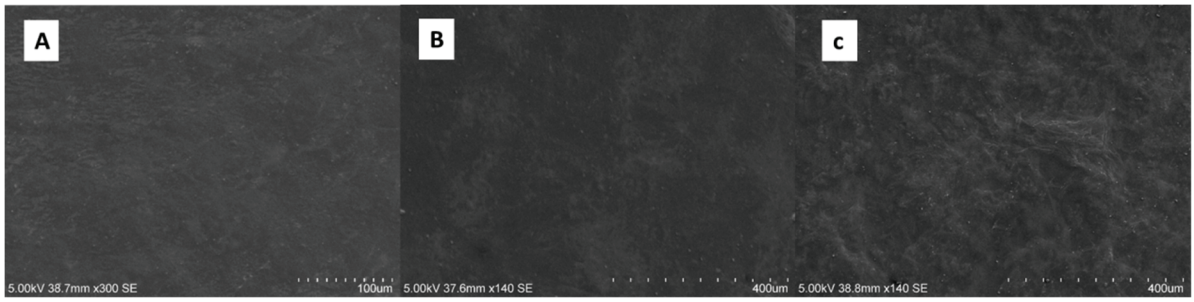

Figure 2 Scanning electron microscopy micrographs of the surface of films (A) control films, (B) FUR films with 5 % CDQs and (C) FUR films with 10 % CDQs

Table 1 Physical properties of furcellaran films with CQDs

Concentration of CQDs*	Physical properties of FUR/CQDs				
	Thickness (mm)	Water content (%)	Solubility (%)	Tensile strength (MPa)	Elongation at break (%)
0 %	0.10±0.01^{a}	24.54±1.66^{a}	100.00±0.00^{a}	4.44±0.74^{a}	54.77±2.75^{a}
1 %	0.10±0.01^{a}	21.48±0.57^{b}	100.00±0.00^{a}	3.99±0.75^{a}	54.09±3.80^{a}
3 %	0.10±0.01^{a}	22.39±0.45^{b}	100.00±0.00^{a}	5.28±0.76^{b}	56.29±4.40^{a}
5 %	0.10±0.01^{a}	21.65±0.29^{b}	94.18±1.97^{b}	5.91±0.74^{b}	56.16±4.02^{a}
10 %	0.10±0.01^{a}	22.00±0.65^{b}	60.55±1.95^{c}	8.94±0.37^{c}	56.34±2.31^{a}

* Values are expressed as mean ± standard deviation. Different letters in the same rows indicate significant differences ($p < 0.05$).

Table 1 shows the effect of incorporation CQDs on physical properties of FUR films. The thickness of films was not affected significantly by addition of CQDs. Reduced solubility of nanocomposite films is related to strong interaction between polysaccharide and CQDs. The incorporation CQDs into FUR matrix caused reduction in water content. Tensile strength (TS) of nanocomposite films increase with increasing the CQDs concentration, and the values of elongation at break were at the same level. The increase in the TS value indicates the presence of increased stiffness of the film after the addition of CQDs.

The UV-Vis absorption spectra of FUR films, CQDs in the water, and FUR/CQDs films were shown in **Figure 3**. CQDs in the films absorbed radiation in the visible regions of 300-400 nm, which is related to strong fluorescence. The control film has no absorption above 300 nm, while increase in FUR films resulted in increase in peaks in the range 300-400 nm.

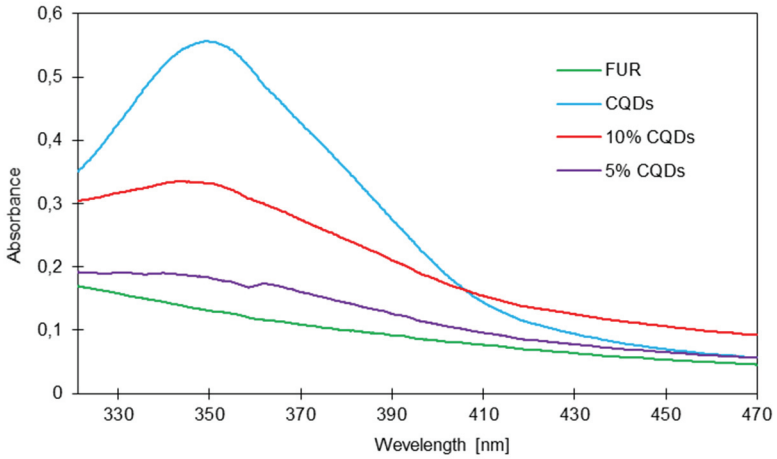

Figure 3 UV-Vis spectra of CQDs, FUR films and FUR films with different concentration of CQDs

The major bands in IR spectra of FUR films were observed at 841 cm^{-1} (-O-SO_3 stretching vibration at D-galactose-4-sulfate), at 920 cm^{-1} (C-O-O of 3,6-anhydro-D-galactose), at 1030 cm^{-1} (C-O stretch), at 1211 cm^{-1} (C-O bridge stretch), at 1632 cm^{-1} (water deformation), at 2923 cm^{-1} (C-H stretch), at 3267 cm^{-1} (O-H stretch). The spectrum of FUR-10 % CQDs film was similar to the bands of FUR, but there were new peaks: the band at 1734 cm^{-1} attributed to the C=O in ester group and 1629 cm^{-1} assigned to -COO- symmetric stretching. Thus, CQDs can interact with the functional group of FUR. According to You at al. [7], Javanakht and Namazi [6,11], the FT-IR analysis confirmed that incorporation of CQDs into polymer matrix modified intermolecular interaction.

4. CONCLUSION

The nanocomposite films were developed by adding CQDs in different concentration (1, 3, 5 and 10 %) to FUR matrix using the solution casting method. The incorporation CQDs into FUR matrix significantly influences water and mechanical properties of nanocomposite films. The furcellaran films with any concentration of CQDs were highly transparent and luminescent. The films with CQDs showed better UV-Vis light barrier properties, which make them good candidates as packaging materials. Excellent barrier properties against UV light were shown by FUR-10 % CQDs. FT-IR analysis confirmed the interaction between FUR and CQDs, by the presence of new bands in spectra. The results showed that CQDs can be used to improve the properties of furcellaran films. This study was preliminary research, so future studies on antimicrobial activity and toxicity test are required.

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