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Development of Bio-Based Chitosan Films with Incorporated Chestnut Extract

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Abstract **–** Hydrolysable tannins have prominent biological activity and thus their industrial application is gaining importance in many fields. This study explored the possibility for the utilization of a commercially available chestnut extract (CE) as an active component in chitosan-based films intended for food packaging. Therefore, a set of chitosan-based films with incorporated CE was prepared and evaluated regarding physicochemical properties. The estimated total phenolic content (*TPC*) has revealed a maximal value of 19.5 mg_{GAE} g_{film}^{-1}. Moreover, the moisture content (*MC*) in the films has decreased (from 29.6% to 18.6%), while tensile strength (*TS*) has increased (from 13.5 MPa to 48.5 MPa) after the incorporation of CE. The observed coherence between *TPC* and evaluated properties has been confirmed by the existence of strong negative and positive linear correlations in the case of *MC* and *TS*, respectively. In large, CE extract was found to be a promising candidate as an active component in chitosan-based films.

Keywords: Chitosan; Chestnut extract; Total phenolic content; Moisture content; Tensile strength; Food packaging.

1. Introduction

In the contemporary society, plastic waste is a serious environmental burden that presents a planetary boundary threat [1]. Bearing in mind the fact that single-use food packagings are one of the biggest sources of plastic waste, additional efforts should strive towards the utilization of alternative food packaging systems such as polymer-based films/coatings. Chitosan, a partly deacetylated derivative of biomass-based polymer chitin, is a prominent candidate for the preparation of a broad palette of eco-friendly materials, including those intended for food packagings [2].

Chitosan is a biocompatible, biodegradable, and non-toxic biopolymer whose characteristics highly depend on its degree of deacetylation and molecular weight [2]. It is endowed by a good film-forming capacity that makes chitosan one of the most sought biopolymers for the preparation of environment-friendly films for food protection [2]. The films' antioxidant and/or antimicrobial properties could be significantly boosted by the incorporation of various plant-based active components, thus helping in the extension of the shelf life of perishable foods [2, 3]. The most recent studies have attempted the utilization of extracts/essential oils stemming from different parts of apricot (*Prunus armeniaca*) [3], mango (*Mangifera indica*) [4], hop (*Humulus lupulus*) [5], etc.

European chestnut (*Castanea sativa*) represents very important three in agro and forestry economy [6]. Industrial tannin extracts obtained from the chestnut wood have prominent antioxidant activity [6], and as such are interesting candidates as active components in chitosan-based films. Thus, the aim of the study was to explore the possibility to use CE as an active component in chitosan-based films. The films were evaluated in terms of *TPC* as well as its correlation with *MC* and *TS*.

2. Material and Methods

2.1. Material

High molecular weight chitosan (310-375 kDa; ≥75% deacetylated), lactic acid (purity ≥85%), Folin-Ciocalteu´s phenol reagent, and gallic acid were purchased from Sigma-Aldrich (Steinheim, Germany), while glycerol was from Pharmachem Sušnik (Ljubljana, Slovenia). CE (CasTan) was from Tanin Sevnica (Sevnica, Slovenia). Milli-Q® water was used throughout all experiments.

2.2. Preparation of chitosan-based films

Chitosan was dissolved in 1.0% (v/v) aqueous solution of lactic acid to reach the final concentration of 1.5% (w/v), and glycerol was added as a plasticizer in the concentration of 30% w/w (based on the mass of chitosan) [5]. The mixture was stirred overnight at 1000 rpm and 24 °C, and vacuum-filtered through two layers of medical gauze. The addition of CE powder [0.0% (control), 0.1%, 0.5%, and 1% (w/v)] was followed by 2 min long homogenization on Ultra-Turrax® T50 (IKA, Staufen, Germany) at 6000 rpm. Prepared film-forming solutions (FFS) were then left overnight to get rid of the bubbles and to stabilize the foam. Finally, the sticky foam and remaining bubbles were carefully removed from the mixtures using a laboratory spatula. The FFS were cast in polyurethane Petri dishes (~0.32 mL cm^{-2}) and dried at 40 °C for 48 h. Obtained films were labelled based on the CE concentration in the FFS as CE_0.0 (control), CE_0.1, CE_0.5, and CE_1.0. The films' thicknesses were measured by a digital thickness gauge (Mitutoyo, Aurora, USA).

2.3. Total phenolic content

The *TPC* value of chitosan-based films was estimated using Folin-Ciocalteu´s (FC) phenol reagent according to the protocol described elsewhere in the literature [5]. The results were expressed as the mass of gallic acid equivalent (GAE) per mass of the film.

2.4. Moisture content

MC in chitosan-based films was determined by oven-drying of rectangular film samples (~1 cm^2) with a known mass at 105 °C for 24 h. *MC* (%) was calculated from the difference between initial and dry mass of the samples [5].

2.5. Tensile strength

TS was determined by testing rectangular film samples (8 cm × 2 cm; gage length segment 6 cm) on the XLW Auto Tensile Tester (Labthink® Instruments, Jinan, China) equipped with a 100 N load cell, at a crosshead speed of 25 mm min^{-1}. It was calculated by dividing the load with the average original cross-sectional area in the sample gage length segment.

2.5. Statistical analysis

Statistical analysis was performed using the one-way ANOVA ($p < 0.05$) followed by Tukey's HSD post-hoc test, whereby different letters in the graphs indicate significantly different mean values. All experiments were done in triplicates and the results were expressed as the mean ± standard deviation.

3. Results and discussion

3.1. Preparation of chitosan-based films

Obtained films were robust, stable, compact and easily-peeled off from Petri dishes. The films had a pale-brown to a dark-brown shade that was increasing in intensity along with increasing the amount of CE. The thicknesses of the samples were 86 ± 1 μm, 67 ± 2 μm, 78 ± 1 μm, and 84 ± 1 μm for CE_0.0, CE_0.1, CE_0.5, and CE_1.0, respectively.

3.2. Total phenolic content

The *TPC* value is of high importance due to its relation to the antioxidant activity as well as other physicochemical properties of the films. The results of a crude estimation of *TPC* are depicted in Fig. 1.

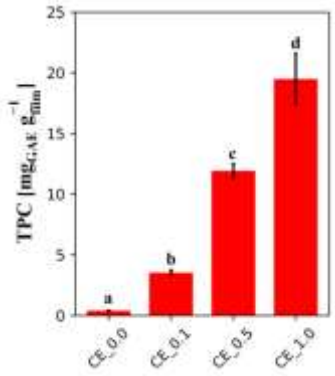

Fig. 1: Total phenolic content in chitosan-based films.

The *TPC* value was gradually increasing with the increase of CE concentration in chitosan-based films (Fig. 1). Accordingly, *TPC* in CE_0.0 was negligibly small (only 0.4 mg_{GAE} g_{film}^{-1}), presumably due to the reaction between the FC reagent and $–NH_2$ functional groups from chitosan [5 and ref. therein]. In the blended films, *TPC* was 3.5 mg_{GAE} g_{film}^{-1}, 11.9 mg_{GAE} g_{film}^{-1}, and 19.5 mg_{GAE} g_{film}^{-1} for CE_0.1, CE_0.5, and CE_1.0, respectively (Fig. 1). By comparison, analogous chitosan-based films containing a supercritical CO_2 hop extract had *TPC* of 1.5 mg_{GAE} g_{film}^{-1}, 7.0 mg_{GAE} g_{film}^{-1}, and 10.5 mg_{GAE} g_{film}^{-1} [5].

3.3. Moisture content

MC content significantly affects the film performances [5]. Therefore, this parameter was determined by the gravimetric method and the results are summarized in Fig. 2.

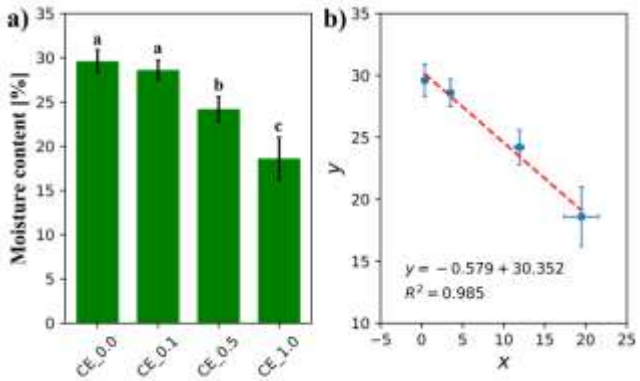

Fig. 2: Moisture content in chitosan-based films: a) moisture content; b) correlation between *TPC* (x-axis) and *MC* (y-axis).

As compared to the control film, the values of *MC* have decreased after the incorporation of CE (Fig. 2a). The control sample (CE_0.0) had 29.6% of water, while other three samples had 28.6% (CE_0.1), 24.2% (CE_0.5), and 18.6% (CE_1.0). The increased hydrophobicity of chitosan-based films was assumed to be due to intermolecular interactions between chitosan and incorporated tannins that prevent the establishment of chitosan-water hydrogen bonds [5]. This assumption is reinforced by the existence of a strong negative correlation between *TPC* and *MC* (Fig. 2b).

3.4. Tensile strength

Sufficient strength of the film material is crucial in providing mechanical integrity during transport and storage of food. The results of the films' *TS* are presented in Fig. 3.

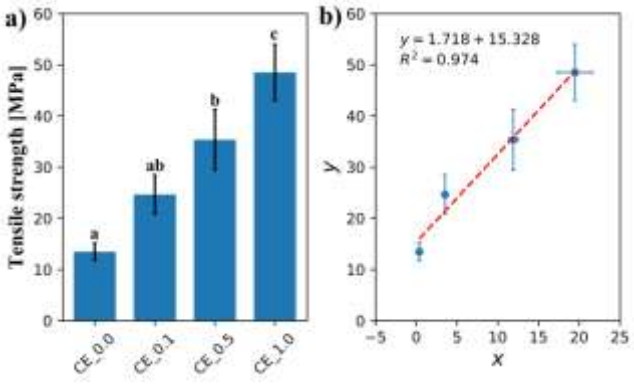

Fig. 3: Tensile strength of chitosan-based films: a) tensile strength; b) correlation between *TPC* (x-axis) and *TS* (y-axis).

The evaluated films have revealed *TS* from 13.5 MPa (CE_0.0) to 48.5 MPa (CE_1.0) (Fig. 3a). The presence of CE has heightened the films' resistance, in all probability due to the interactions between incorporated tannins and chitosan. This was additionally confirmed by the existence of a strong positive correlation between *TPC* and *TS* (Fig. 3b). For instance, the presence of a hop extract in chitosan-based films has diminished their resistance, most likely due to a lower number of –OH groups in the hop's α-acids and β-acids that can interfere with chitosan [5], as compared to tannins from CE. Thus, CE is supposed to acts as a cross-linker.

4. Conclusion

A possibility for the utilization of CE as the active ingredient in chitosan-based films has been successfully tested. The film with the highest tested concentration of CE had *MC* of 18.6% and *TS* of 48.5 MPa. It has been clear from the correlations between *TPC* and *MC* (negative correlation) as well as between *TPC* and *TS* (positive correlation) that films' physicochemical properties can be tailored by adding a proper amount of CE.

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