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ORIGINAL ARTICLE

Development of Biocompatible Film Fabricate from Polylactic Acid Incorporating Roselle Calyx Extract and Halloysite Nanoclay

Shahriyar Sheykhi[1], Tahereh Sadeghi[2], Neda Sadat Aghayan[*3], Nima Abdoli Kamali[*4], Stella Abigail[5]

[1] *Department of Food Science and Technology, Faculty of Agriculture, University of Tabriz, Tabriz P.O. Box 51666-16471, Iran*

[2] *Department of Food Science and Technology, Science and Research Branch, Islamic Azad University, Tehran, Iran*

[3] *Department of Food Science and Technology, Shahrood Branch, Islamic Azad University, Shahrood, Iran*

[4] *Food Health and safety ,Faculty of Health, Qazvin University of Medical Science*

[5] *Research Group for Nano-Bio Science, Division of Food Technology, National Food Institute, Technical University of Denmark, Lyngby, Denmark*

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ABSTRACT: The development of biocompatible packaging is a fine replacement for using of synthesis film. The purpose of the presentation investigation was to prepare and characterize biocompatible film. The active films were fabricated from polylactic acid (PLA) containing roselle calyx extract (RCE) and roselle calyx extract (RCE)/halloysite nanoclay (HNC). The incorporation of HNC and extract improved the functional characteristics of films. RCE and HNC/RCE incorporated films represented lower oxygen permeability (OP) than control film, 1.82 $\times10^{-18}$, 1.41×10^{-18}, and, 3.61×10^{-18} $m^2\ s^{-1}\ Pa^{-1}$ respectively. Water vapor permeability (WVP) and thickness of PLA film, PLA/RCE, and PLA/RCE/HNC film were estimated as follows: 3.61×10^{-14}, 2.5×10^{-14}, and 1.46×10^{-14}kg m $m^{-2}s^{-1}Pa^{-1}$; 0.18, 0.21, and 0.22 mm respectively. The tensile strength and young modulus of the films increased from 47.91 to 62.83 MPa and 9.4 to 17.4 MPa respectively by the addition of extract and RCE/HNC into the biodegradable film. This investigation illustrated films based on PLA incorporated RCE/HNC and RCE has positive functional properties for applications in natural film packaging.

INTRODUCTION

Destruction of the environment caused by synthetic plastics is a global concern in the current decade. Greenhouse effects and water contamination challenges are enhanced by synthetic packaging and they threaten human life[1]. Thus, the fabrication of biofilms is becoming increasingly essential. Biofilms would not release dangerous compounds into the environment, while after degradation, they would improve soil nutrients [2, 3]. To substitute non-biodegradable plastics, notably in food packaging, there is an enormous need for plastics created from biopolymers, also commonly known as bioplastic [4]. Different kinds of biopolymers have been applied for the preparation of biodegradable films such as starches, gelatin, whey protein, soy protein,

*Corresponding author: nedaaghayan@yahoo.com;nima.abdoli.kamali@gmail.com (N. Sadat Aghayan; N. Abdoli Kamali)
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polylactic acid, gluten, CMC, etc[5, 6].

Polylactic acid belongs to polyester category that can be created either by chemical method or carbohydrate fermentation technique applying the monomer of lactic acid. Due to its moderate water resistance, fine mechanical properties, high transparency, availability, low price, and biocompatibility, polylactic acid has applications in natural film, textiles, tissue engineering, and pharmaceutical industry[7]. The mentioned polymer is a degradable material that contributes to a healthy environment by being free of waste disposal challenges and greenhouse effects [8]. The film characteristics of PLA have been estimated in previous investigations and findings illustrated that PLA can produce films with excellent appearance properties. However, PLA film is sensitive to oxygen molecules and water vapor transmission [9].

Nanoparticles including metal nanoparticles (ZnO, TiO_2, nanoclay, Ag, Au, etc.) have attracted many studies because of their barrier, electrical, mechanical, and antibacterial properties [10]. Halloysite nanoclay (HNC) is a hydrated polymorph composed of phyllosilicate and clay (kaolin group). $Al_2Si_2O_5(OH)_4$, is the chemical formula of the mentioned nanoparticle and it is a tubular nanostructure. The inner layer is composed of Al_2O_3, while the outside layer of the nanoparticle is composed of SiO_2 [11].

HNC is applied to different applications, such as food packaging, wastewater treatment, drug delivery, and catalysis [12]. Due to its variety of properties, for example, a tubular nanostructure, high stability, biodegradability, low cost, and suitable mechanical characteristics, HNC in biopolymer has high advantage and may eventually substitute expensive carbon nanotubes in the fabrication of multifunctional nanocomposites [13, 14].

The main component of roselle calyx is carbohydrates [15]. H. *sabdariffa*, commonly known as roselle, is a recognized tropical shrub that is native to the African continent and is cultivated in Asian countries (Malaysia and India)[16]. Roselle hibiscus is safe, biodegradable, and abundant in anthocyanin colorants. The anthocyanin colorant of roselle can sense and represent pH changes with various colors [17].

The addition of roselle extract to biodegradable film as an additive could enhance mechanical quality, and barrier properties and also create another positive effect in films such as increasing hydrophobic behavior[18, 19].

In the presentation investigation, HNC/RCE was applied as additives to fabricate PLA biocompatible film. The active films based on PLA were studied for their thickness, mechanical, and barrier behavior.

MATERIALS AND METHODS

Roselle calyx extract

The method for extracting hibiscus was followed according to Giusti, et al. [20] with slight modification. Roselle calyx powder (1g) and 15 mL of ethanol were combined and HCl was added to get the suspension's pH to just 2. To obtain the final extract the mixture was heated for 1h at 55°C and then centrifuged for 5 min. With a rotary evaporator of the Hei-VAP model, the solvent was eliminated at 50°C.

Biocompatible film fabrication

The casting process was used to create PLA/RCE/HNC films with small changes to the method described by Rhim, et al. [21]. About 5 g of PLA resins were dissolved in 100 ml of chloroform to create a PLA-based solution, which was then stirred for 4 h.

After adding around 0.5 g of extract to 5 mL of chloroform the mixture homogenized in an ultrasonic homogenizer. PLA/HNC film was achieved by adding 1% (w/w) of HNC to PLA solution. At 25°C PLA/HNC mixture was agitated for 16h. The nano-solution was submerged in an ultrasonic bath for 55 min. Nano-suspension was combined with the extract solution. The final solution with RCE/HNC was cast on plastic casting plates and then dried for 40 min at 70 °C.

The thickness of the film was estimated using a micrometer (INSIZE, 25A- 3109, Iran) with a nearest of 0.01 mm. Five various regions of biocompatible film based on PLA were estimated.

Barrier properteis properties

The oxygen permeability of edible films was estimated using the time-lag technique [22]. The test was created of 2 tanks, feed and permeate (53.43 cm^3), coupled to a permeation cell. The mentioned complex was put in a thermostatic cubicle. The test membrane separated permeate and feed chamber of permeation cell. Initially, both compartments were emptied the membrane PLA film was created to contact the feed at 0-2 bar. The derivative of the pressure of permeate within a low pressure change was used to evaluate permeate flow rate.
WVPs of biodegradable films were evaluated gravimetrically according to ASTM standard E96-80, at 25 °C and 52% ΔRH conditions [13]. The WVP experiment was repeated at least four times for active films

Mechanical properties

The mechanical characteristics of PLA containing RCE and RCE/HNC were estimated by an Instron (Zwick material testing machine, UK) equipped with a crosshead speed of 10 mm/min and a load cell of 5000 N, according to ASTM standard D882–18 [23]. The samples were cut from the casted biocompatible films. Samples were conditioned at 24C and 50 RH for 24 h. The mean of triplicate for each natural film based on PLA was recorded.

Statistical analysis

Data were estimated using an ANOVA test to evaluate significant differences between functional properties of films based on PLA ($p < 0.05$) using Minitab software (21.4.2 Chicago, UAS).

RESULTS AND DISCUSSION

Barrier properties and thickness of active film

Decrease in the gas permeability is a favorable property when developing film packaging where fine barrier characteristics are desired to decrease oxygen and water vapor travel between outside packaging and packaged food [24, 25].

The bold limitations of PLA film are high oxygen and water vapor permeability as indicated in Table 1. The OP and WVP of PLA/RCE/HNC edible film were lower than PLA/RCE and samples showed that the incorporation of extract/nanofiller greatly increased the barrier characteristics of the biocompatible film. Polylactic acid is composed of glassy biopolymers with high molecular weight, rigid and hard chains, and, high oxygen transmission [26]. The introduction of HNC significantly decreased the oxygen permeability (OP) of PLA films. HNCs filling the pores in the biopolymer can decrease transmission to oxygen [27].
In active film containing additives represented in Table 1 samples observed that significant reduction in WVP with incorporating HNC, because of the ‘tortuous path’ that increases in barrier characteristics, HNC contain platelets creates complex barriers to water vapor molecules [28]. Also, The decrease in WVP of PLA/RCE film and PLA/RCE/HNC film might be associated with interactions between extract and PLA [29]. The other work demonstrated that the increment in barrier properties of chitosan/guar gum/RCE/nano-ZnO film was associated with extract/nanoadditives added [30]. Similar findings of OP and WVP of the film were observed in previous investigations [16, 31].
Thickness is an important property of biocompatible films affecting WVP, OP, and tensile strength [32].
The thickness of the films is represented in Table 1. The thickness of PLA film, PLA/RCE film, PLA/RCE/HNC film were 0.18, 0.21 and, 0.22mm, respectively (Table 1).
The authors demonstrated that the increase in thickness of film for the biocompatible films with higher extract levels was due to the enhanced amount of solid content [33]. Another research represented that the increase in thickness of biodegradable film based on starch containing roselle extract (RE) is related to the additive incorporated [34]. Also, the addition of the RE into film based on alginate significantly enhanced the thickness of the active films which may associated with the conformational changes of natural molecule chains by the addition of RE [35].

Table 1. Thickness OP and WVP of PLA, PLA /RCE, PLA /RCE/HNC

Film sample	Thickness (mm)	OP×10^{-18}(m^2 s^{-1} Pa^{-1})	WVP×10^{-14}(kg m $m^{-2}s^{-1}Pa^{-1}$)
PLA	0.18±0.005b	3.61±0.21a	3.61±0.12a
PLA/RCE	0.21±0.005a	1.82±0.11b	2.05±0.1b
PLA/RCE/HNC	0.22±0.001a	1.41±0.08c	1.46±0.11c

Mean ± standard deviation values (n=4) of smart film followed by varied letters are significantly different (p<0.05)

Mechanical properties

The mechanical properties of PLA, PLA/RCE, and PLA /RCE/HNC films are indicated in Table 2.

Table 2 represented an increase in TS and YM of PLA/RCE film (58.9;14.06 Pa) and PLA/RCE/HNC film (62.83;17.4 Pa). The EB of the PLA film was 5.1%, and the value of PLA/RCE and PLA/RCE/HNC films was 4.17% and 3.61%, respectively. It was stated that the PLA/RCE/HNC film possessed higher TS and YM and lower EB as compared to PLA film (p< 0.05).

The findings showed that when incorporated HNC increased in TS, YM between (47.91-62.83)MPa and (9.4-17.4) GPa respectively appear in Table 2 due to the novel hydrogen bonding between HNC and biopolymer [36]. Also, the bold reason for these properties may be related to the high interfacial interaction between the biopolymer and HNC[24]. Similar results in YM and EB have been stated by Chikkatti, et al. [8] regarding increased YM and EB in active film incorporated with HNC.

The increase in TS and YM of the PLA containing extract can be attributed to the interaction between matrix and active compounds such as polyphenolics of roselle extract. Also, The behavior change of mechanical properties attributed to the incorporation of roselle extract into PLA film enhances the hydrogen bond with biopolymer molecules [37]. A similar tendency in TS and YM as affected by active agents such as polyphenol compounds was also observed in biocompatible film, including chitosan/guar gum incorporated RE film [30]. Other biodegradable films with black carrot [38] and bamboo extract[39] had similar tendencies.

Table 2. Mechanical properties of PLA, PLA /RCE, PLA /RCE/HNC

Film sample	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (GPa)
PLA	47.91.±2.69b	5. 1.±0.2c	9.4.±1.99b
PLA/RCE	58.9±3.01a	4.17±0.2b	14.06±1.47a
PLA/RCE/HNC	62.83±1.41a	3.61±0.16a	17.4±1.1a

Mean ± standard deviation values (n=4) of smart film followed by varied letters are significantly different (p<0.05).

CONCLUSIONS

In the presentation investigation, roselle calyx extract (RCE)/halloysite nanoclay (HNC) was used to produce biocompatible films based on polylactic acid. The results displayed that the oxygen and water vapor permeability of films based on PLA were significantly decreased by the incorporation of HNC/RCE. Findings illustrated that HNC/RCE could increase the film's thickness. In this research stated that with the incorporation of the HNC/RCE in the PLA film, the active film had a higher TS and YM, compared to the PLA film without additive. In summary, the PLA films containing RCE/HNC can be applied as film packaging and improve the mechanical and barrier properties of biocompatible film.

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Conflict of interests

The authors declare that there is no conflict of interest.

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