The influence of different plasticizers on the mechanical properties of active edible bilayer films

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Abstract: In addition to potentially resolving environmental issues that come from plastic and food waste, active biodegradable packaging is being developed to increase the shelf life, quality, and safety of packaged food. In order to overcome the drawbacks of monolayer hydrocolloid-based coating, such as poor mechanical and barrier properties, the design of bilayer hydrocolloid-based coating has been structured using pullulan and gelatin. Sugar alcohols are widely used for the plasticizing of biopolymer-based films. The aim of this work is to investigate the influence of different sugar alcohols – xylitol, mannitol, and glycerol on the mechanical properties of pullulan/gelatin bilayer films. Among investigated plasticizers, glycerol has demonstrated the best plasticizing effect, giving a bilayer film with the value of elongation at break which is 66.5 and 88.4% greater than the same values for the bilayer films prepared using xylitol and mannitol. The formulation with glycerol has been applied for the preparation of active edible coating using the mixture of two hydrolats – lemongrass and curry plant. Obtained coatings have shown great potential for the improvement of packaged cheese shelf-life.

Keywords: active edible bilayer coating, Pullulan, Gelatin, sugar alcohols

1. Introduction

Edible films can be effective barriers that prevent unwanted mass transfers in foods and are also a *green* alternative to synthetic petroleum-based polymer packaging materials [1, 2]. In that way, they can help extend the shelf life of certain food products by providing a protective barrier against moisture and gases [3, 4]. Some edible packaging materials may contain added nutrients or functional compounds that make them active. Recently, there has been growing interest in research into the use of edible films containing natural preservatives in food protection [5]. The active compounds mostly are a variety of antioxidants, antimicrobials, probiotics, or other incorporated ingredients [1]. The

development of edible packaging is still in its early stages, and there may be things to overcome to find the right balance between the packaging's durability and its edibility.
The development of bilayer edible packaging films involves addressing various challenges, such as optimizing its mechanical strength, improving gas barrier properties, and ensuring it remains safe for consumers. The bilayer approach usually involves two edible materials with different functions. This paper aims to study the effect of various plasticizers (glycerol, xylitol, and mannitol) on the mechanical properties of active edible films based on pullulan and gelatin. Gelatin is an edible animal-originated protein with remarkable film-forming ability, biocompatibility, nontoxicity, and biodegradability which makes it ideal for food packaging applications [6]. Pullulan is an exopolysaccharide obtained from the fermentation of black yeast and is considered a promising material for edible films due to its film-forming properties, biodegradability, and biocompatibility. The interest in the use of pullulan for edible packaging is growing due to several advantages such as the lack of taste and odor, and the ability to create transparent, shiny, and flexible films with relatively low oxygen and lipid permeability. Both pullulan and gelatin are biodegradable materials and compatible with different food products, making the packaging environmentally friendly and safe for consumption.

2. **Experimental part**

2.1. *Materials*

Pullulan (M_w ~ 574 570 g/mol) was acquired from Avena Lab (Vršac, Srbija). Xylitol and mannitol were purchased from Sigma Aldrich, USA, while gelatin and glycerol were purchased from Centrohem.

2.2 Methods

The film-forming solutions were prepared by dissolving pullulan (10 wt%) and gelatin (4 wt%) in a mixture of curry plant (*Helichrysum italicum*) and lemongrass (*Cymbopogon citratus*) in a ratio of 1:1. The solutions were prepared with the addition of different types of plasticizers (xylitol, mannitol and glycerol) in the amount of 30 wt% per biopolymer weight. The bilayer film was produced using a solution-casting technique. After drying of pullulan-based film, the gelatin-based solution with the same plasticizer type was poured onto the surface of the pullulan film.
The chemical structure of obtained films was analyzed by Fourier-transform infrared spectroscopy (FTIR) (Thermo Fisher Scientific, MA, USA) operating in total reflectance attenuation (ATR) mode.
Mechanical properties of obtained bilayer films were investigated using the Instron Universal Testing Instrument Model 4301 (Instron Engineering Corp., Canton, MA) according to the ASTM standard D882-18. All tests were performed at a temperature of 23 ± 2 °C with an initial grip spacing set to 50 mm and a crosshead speed of 10 mm/min.
In order to investigate the ability of an active edible coating to prolong the storage time of cheese slices, the same were contaminated by inoculation with bacterial suspension after application of the edible coating in order to simulate the contamination during the

storage and distribution. The coating was applied by spraying on the cheese surface. Sampling and analysis were performed at regular time intervals during the 28 days.

3. **Results and discussion**

Figure 1 shows the FTIR spectra of Pull, Gel, and bilayer Pull/Gel film with incorporated hydrolats. The broad peak with the center at 3342 cm^{-1} in the FTIR spectrum of neat Pull is attributed to OH stretching. The overlapping of N-H and OH stretching vibrations of amino acids in gelatin results in a broad absorption band between 3600 and 3000 cm^{-1} (Figure 1b). Two peaks between 2900 and 2800 cm^{-1} in spectra of neat biopolymers are attributed to C-H stretching. In the spectrum of bilayer film with hydrolats and plasticizers (Figure 1c), there are three peaks in this range. A peak at 1646 cm^{-1} corresponds to an O-C-O bond in Pull, while the absorption band at 1631 cm^{-1} in the spectrum of Gell corresponds to CO stretching. The band at 1547 in the spectrum of Gel and bilayer film is attributed to NH bending and C-N stretching. Stretching of the COO- group appears as a weak peak at 1453 cm^{-1} in both spectra (Figure 1b and c).

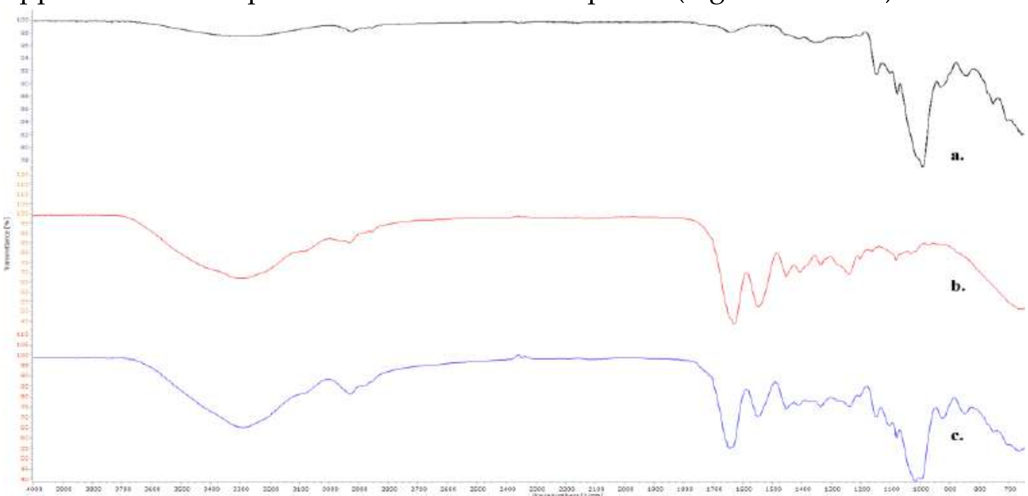

Figure 1. FTIR spectra of a) Pull, b) Gel, c) bilayer Pull/Gel-g film.

In comparison to the monolayer films (Pull and Gel), bilayer films possess improved values of tensile strength (TS), and elongation of break (EB) in comparison to the neat Gel (Table 1). Among investigated plasticizers, glycerol has demonstrated the best plasticizing effect, resulting in the bilayer film (Pull/Gel-g) with an EB value that is 65.8% greater than the EB value of bilayer film prepared with xylitol as plasticizer (Pull/Gel-x), and even 88.4% higher EB value in comparison to the EB value of bilayer film prepared with mannitol (Pull/Gel-m).

Table 1. Tensile strength (TS) and elongation at break (EB) for edible bilayer films with different plasticizer type.

Samples	**Tensile strength (N/mm^2)**	**Elongation at break (%)**
Pull	14.23	25.60

Gel	15.34	8.23
Pull/Gel-x	32.20	9.12
Pull/Gel-m	30.45	8.6
Pull/Gel-g	31.45	15.12

Pull/Gel active coating exhibited a reduction in bacterial concentration for 50% at day 3, and complete elimination of *S. aureus* cells at day 14, demonstrating the efficiency against this pathogen and the potential to be applied for prolongation of cheese slices' shelf-life.

3. Conclusions

Bilayer active edible films based on Pull and Gel with glycerol as a plasticizer have shown the best mechanical properties (the greatest EB value) in comparison to the films prepared with xylitol and mannitol as plasticizers. The obtained formulation has demonstrated potential in the application for the packaging of cheese slices, enabling the prolongation of the shelf-life of this food product.

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