BIOPOLYMER FILMS PROPERTIES CHANGE AFFECTED BY ESSENTIAL OILS ADDITION

PROMENE KARAKTERISTIKA BIOPOLIMERNIH FILMOVA UZROKOVANE DODATKOM ESENCIJALNIH ULJA

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ABSTRACT

Biopolymer films can be used as packaging materials in the food industry, when they contribute to a better mechanical integrity of packaged foods and act as barrier to various environmental agents. The greatest disadvantage regarding biopolymer films application are poor barrier characteristic, which is a consequence of their high hydrophilicity; their mechanical and physico-chemical properties are considered to be a moderate disadvantage. This paper presents the effects of chemical modifications, such as the addition of hydrophobic components (essential oils), to the properties of biopolymer films. Except that the addition of essential oils significantly affects the mechanical, barrier and physico-chemical properties of biopolymer films, in this way, biopolymer films become active and exhibit antimicrobial and antioxidant action. Changes in the mechanical and barrier properties of various biopolymer films have been observed in particular, with and without the addition of oil in different concentrations.

Keywords: biopolymer films, mono- and composite films, essential oils, characteristics

REZIME

Oblast biopolimernih materijala je u fokusu naučnih istraživanja poslednjih nekoliko decenija. Biopolimerni filmovi mogu koristiti kao ambalažni materijali u oblasti prehrambene industrije, kada doprinose boljem mehaničkom intergritetu upakovanih namirnica i deluju kao bariera prema raznim agensima spoštašnice sredine. Najveći nedostatak u primeni biopolimernih filmova su slabe barjerne osobine prema vodenoj pari, što je posledica njihove visoke hidrofilnosti, a umerenim nedostatkom se smatraju njihove mehaničke i fizičko-hemijske osobine. U ovom radu su prikazani uticaji hemijskih modifikacija, u vidu dodatka hidrofnih komponenta matriksu biopolimernih filmova, kao što su esencijalna ulja, na osobine biopolimernih filmova. Esencijalna ulja su prirodne aromatične komponente dobijene iz biljnog materijala i smatraju se zdravstveno bezbednim, tako da se mogu koristiti u oblasti jestive aktivne ambalaže. Osim što dodatak esencijalnih ulja značajno utiče na mehaničke, barjerne i fizičko-hemijejske osobine biopolimernih filmova, na ovaj način biopolimerni filmovi postaju aktivni i ispoljavaju antimikrobno i antioksidativno delovanje sa ciljem očuvanja kvaliteta upakovanih sadržaja. Biopolimerni filmovi, kao nosači esencijalnih ulja, imaju efekat matrice za inkapsulaciju, što se ogleda u minimalnim potrebnim dozama primenjenoj esencijalnoj ulja, ograničenom isparljivosti i kontrolisanom oslobađanju aktivnih komponenata. Ovaj pregledni rad prikazuje objavljene rezultate iz oblasti različitih biopolimernih filmova, kako monoofilmsa, tako i kompozitnih, kojima su dodata esencijalna ulja sa ciljem unapređenja osobina. Prikazane su promene mehaničkih i barjerneh osobina različitih biopolimernih filmova, bez i sa dodatkom ulja u različitim koncentracijama.

Ključne reči: biopolimerni filmovi, mono- i kompozitni filmovi, esencijalna ulja, karakteristike.

INTRODUCTION

Biopolymer films represent an interesting alternative to conventional plastic materials, which is why they have been investigated extensively (Šuput et al., 2015; Popović et al., 2018). Biopolymer film is usually produced from food-derived ingredients using wet or dry manufacturing process and it is defined as free-standing sheet that can be placed on or between food components (McHugh, 2000; Šuput et al., 2015). Films are applied on the product like wrapper or among the layers or can be used as covers, packaging or layer separation (Ribeiro-Santos et al., 2017). In addition, most of them are classified as Generally Recognized as Safe (GRAS) (Ruiz-Navajas et al., 2013). The most common materials for the formulation of biopolymer films are polymers obtained from biomass such as the agro-polymers from agro-resources (polysaccharides, proteins and lipids), and the combination of these allows for producing blends of improved characteristics (Fabra et al., 2009; Popović et al., 2018). Beside these, biopolymers could be obtained by microbial production, chemically synthesized using monomers obtained from agro-resources or polymers whose monomers and polymers are both obtained by chemical synthesis from fossil resources (Vieira et al., 2011). Edible films should provide a barrier to moisture, oxygen and solute movement from the food (Bourtoom, 2008; Šuput et al., 2016a). Along with their usage, environmental impact has been lowered, as these films and coatings can be consumed with the food, while additional external packaging can be limited (Ganiari et al., 2017). Consuming biopolymer films along with food product, provides additional nutrients, improved sensory characteristics and quality of the protected product (Rojas-Grau et al., 2007). What is most important is that biopolymer films have a high potential to carry active ingredients: anti-browning agents, colorants, flavors, nutrients, spices, antimicrobial and antioxidant compounds that can extend product shelf-life, improve the organoleptic properties and food nutritional value (Ganiari et al., 2017; Šuput et al., 2016b). The active function of edible films and coatings is reflected in the protection food products from oxidation and microbiological failure, which leads to improving the quality and improving the safety of the packaged product (Kim et al., 2012; Lee et al., 2012). Essential oils are aromatic components derived from plant materials and are considered health-safe so that they can be used in the edible active packaging to promote antimicrobial and antioxidant activity (Burt, 2004). Edible films,
as carriers of essential oils, have a matrix effect for an encapsulation that is reflected in the required minimum doses of the essential oils, limited volatility and controlled and gradual release active ingredients from the food surface (Bonilla et al., 2013). In general, the major components of EOs are the main responsible for their biological properties, but it is known that the minor compounds can also contribute for it and they can exhibit a synergetic activity (Burt, 2004). Properties of the essential oil, the amount used, the use of plasticizer and the polymer matrix affect the properties of an active packaging that incorporates essential oils (Ghanbarzadeh and Oromiehi, 2008; Ramos et al., 2013).

**Biopolymer film function and properties**

Main functions of edible films are to act as barriers against gas or vapors, oils and solutes; provide structural protection to prevent mechanical damage during transportation, handling and display; and protect food against oxidation, microbial growth and other chemical reactions (Salgado et al., 2015). They also could enhance the visual and tactile features of food products and to carry active substances (Han and Scanlon, 2014).

The type of prevailing molecule in the network structure of the biopolymer determines the basic physico-mechanical and barrier properties, and thus the application of packaging of

### Table 1. Essential oils addition effect on properties of biopolymer films

<table>
<thead>
<tr>
<th>Biopol. matrix</th>
<th>Added EO</th>
<th>Concentration</th>
<th>Effect</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starch</td>
<td>Basil</td>
<td>0.1g/g starch</td>
<td>- Insignificant effect on mechanical properties</td>
<td>Bonilla et al., 2013</td>
</tr>
<tr>
<td>Citric acid</td>
<td></td>
<td></td>
<td>- OP significantly reduced by the addition of all active components</td>
<td>Souza et al., 2013</td>
</tr>
<tr>
<td>α-tocopherol</td>
<td></td>
<td></td>
<td>- The most pronounced antioxidant activity in the α-tocopherol samples</td>
<td>Souza et al., 2013</td>
</tr>
<tr>
<td>Starch</td>
<td>Cinnamon</td>
<td>0.4g/100g</td>
<td>- TS value decreased with the EO addition</td>
<td>Šuput et al., 2016b</td>
</tr>
<tr>
<td>EO</td>
<td></td>
<td>0.6g/100g</td>
<td>- EB value increased with the EO addition</td>
<td>Šuput et al., 2016b</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.8g/100g</td>
<td>- WVP value increased with the EO addition</td>
<td>Šuput et al., 2016b</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>- Confirmed antimicrobial activity for <em>P. commune</em>, <em>E. amstelodami</em></td>
<td>Šuput et al., 2016b</td>
</tr>
<tr>
<td>Starch</td>
<td>Oregano</td>
<td>0.5%-2%</td>
<td>- EOs addition positively affected film swelling (decreased), mechanical properties (TS decreased while EB increased) and WVP (decreased along with EO addition).</td>
<td>Šuput et al., 2016b</td>
</tr>
<tr>
<td>Black cumin</td>
<td></td>
<td></td>
<td>- Oregano EO was more effective in terms of biological activity.</td>
<td>Šuput et al., 2016b</td>
</tr>
<tr>
<td>EO</td>
<td></td>
<td></td>
<td>- FTIR results pointed to quantitative law dependency between amount of EO and spectra absorption values.</td>
<td>Šuput et al., 2016b</td>
</tr>
<tr>
<td>Gelatin</td>
<td>Oregano</td>
<td>0.2-0.6</td>
<td>- TS and EB increased with EO addition</td>
<td>Norajit et al., 2010</td>
</tr>
<tr>
<td>Lavender EO</td>
<td></td>
<td></td>
<td>- Lavender EO promotes change in WVP, due to its high hydrophobic nature.</td>
<td>Norajit et al., 2010</td>
</tr>
<tr>
<td>Alginates</td>
<td>Red ginseng</td>
<td>0.5 g/ml</td>
<td>- The addition of ginseng decreased TS and elastic modulus and increased the EB.</td>
<td>Norajit et al., 2010</td>
</tr>
<tr>
<td>White ginseng</td>
<td></td>
<td></td>
<td>- The presence of ginseng did not significantly affect the WVP.</td>
<td>Norajit et al., 2010</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>- No differences in moisture contents of all film samples.</td>
<td>Norajit et al., 2010</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>- White ginseng film presented the highest free-radical scavenging activity.</td>
<td>Norajit et al., 2010</td>
</tr>
<tr>
<td>Chitosan</td>
<td>Rosemary</td>
<td>0.5 v/v</td>
<td>- The solubility and water gain decreased by EO incorporation because of the interaction between hydrophilic groups.</td>
<td>Abdollahi et al., 2012</td>
</tr>
<tr>
<td>EO</td>
<td></td>
<td>1.0 v/v</td>
<td>- EO improved the film transparency</td>
<td>Hromiš et al., 2015</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.5% v/v</td>
<td>- Films containing EO showed more antibacterial activity and total phenol content.</td>
<td>Hromiš et al., 2015</td>
</tr>
<tr>
<td>Chitosan</td>
<td>Caraway</td>
<td>0.025-0.100</td>
<td>- Films with ginger EO were less resistant and less stretchable although lipid–protein interactions led to more resistant and stretchable films in case of cinnamon EO.</td>
<td>Ateres et al., 2010</td>
</tr>
<tr>
<td>Beeswax</td>
<td></td>
<td></td>
<td>- TC and TS value decreased with the EO addition</td>
<td>Hromiš et al., 2015</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>- Cinnamon EO affected the optical properties more markedly than ginger EO. Cinnamon EO considerably affected the colour and whiteness index.</td>
<td>Hromiš et al., 2015</td>
</tr>
<tr>
<td>Soy protein isolate</td>
<td>Cinnamon</td>
<td>0.2-0.6</td>
<td>- Films with EO addition were less resistant to breakage, more flexible and more opaque with lower gloss.</td>
<td>Shojae-Aliaabadi et al., 2013</td>
</tr>
<tr>
<td>Ginger EO</td>
<td></td>
<td></td>
<td>- Films incorporated with EO showed good antioxidant properties (dose–dependant).</td>
<td>Shojae-Aliaabadi et al., 2013</td>
</tr>
<tr>
<td>k-carrag.</td>
<td><em>Satureja hortensis</em></td>
<td>1%-3%</td>
<td>- WV barrier properties were improved considerably upon the addition of EO.</td>
<td>Sanchez-Gonzalez et al., 2009</td>
</tr>
<tr>
<td>HPMC</td>
<td>Tea tree</td>
<td>0.5%–2%</td>
<td>- The higher the EO content, the lower the WVP and the moisture sorption capacity.</td>
<td>Sanchez-Gonzalez et al., 2009</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>- EO addition leads to a significant decrease in gloss and transparency and a decrease in the tensile strength and elastic modulus.</td>
<td>Sanchez-Gonzalez et al., 2009</td>
</tr>
<tr>
<td>Sunflower oil cake</td>
<td>Parsley</td>
<td>0.25%-1%</td>
<td>- With the EO addition, TS values decrease, and the EB values increase (films become less firm, stretchy and more elastic).</td>
<td>Lazić et al., 2018</td>
</tr>
<tr>
<td>Rosemary EO</td>
<td></td>
<td></td>
<td>- The WVP values decrease with the addition of parsley EO. The addition of rosemary EO influenced the WVP increase - Films with added EO represent a good barrier at wavelengths smaller than 400 nm (UV region).</td>
<td>Lazić et al., 2018</td>
</tr>
</tbody>
</table>

*EB* – elongation at break; *EO* – essential oil; *HPMC* - hydroxypropyl methylcellulose; *OP* – oxygen permeability; *TS* – tensile strength; *WVP* – water vapour permeability
certain types of products. For the production of edible biopolymer films, components are classified into three categories: hydrocolloids (proteins and polysaccharides), lipids (fatty acids, acylglycerols and waxes) and composites (may be a combination of several hydrocolloids or hydrocols and lipids) (van Tuil et al., 2000; Šuput et al., 2017). Hydrocolloid-based films can be applied when the barrier to water is not crucial. These films have excellent barrier properties for gases and lipids. Most have good mechanical characteristics and are used to improve the structural integrity of fragile and brittle products. Most do not affect the sensory properties of the packaged product (Giancone, 2006).

Polysaccharides are natural polymers made up of monosaccharide and/or disaccharide units and represent suitable material for the formation of edible films and coatings, as they exhibit excellent mechanical, structural and barrier properties towards gases, but in the presence of moisture these good properties worsen due to the hydrophilic nature of the polymer and show very poor barrier characteristics to water vapor (Falgueiras et al., 2011; Šuput et al., 2016a).

Proteins consist of amino acids linked by peptide bonds. The mechanical properties of protein-based biodegradable films are excellent, due to the unique structure of the protein molecule that provides a wider range of functional properties, and especially the high potential of intermolecular networking. In protein films, a large number of bonds can be formed at different positions in molecules (Ou et al., 2005). Due to the large number of reactive polar groups and the extensive interaction between polymer chains of proteins, formed films have impressive barrier characteristics for gases, compared with synthetic films (Bourtoom, 2008).

Lipids have been used for many years as protective coatings, but since they are not polymers, they have no ability to produce coherent independent films. They can improve the glow of the surface of the polymer and, since they are mostly non-polar substances, improve the barrier properties of the water. Film based on lipids are very difficult to apply because of their thickness and greasy surface, and they can have a pronounced taste on grease (van Tuil et al., 2000). Lipids are usually combined with other film-forming materials, such as emulsion particles or multilayer coatings in order to increase resistance to water vapor (Mehyar et al., 2012).

Recently, many research works have focused on composite or multicomponent films to explore the mandatory advantages of each component as well as to minimize their disadvantages (Kurek et al., 2014). The main goal of manufacturing composite films is to enhance mechanical and/or barrier properties (Hassan et al., 2018).

**Essential oils applied to biopolymer films**

Essential oils implementation in the film forming matrix could be carried out by applying emulsification/homogenization techniques, where fine emulsions of essential oils are obtained containing polymer at the continuous aqueous phase. In dried films, lipid droplets remain embedded into the polymer matrix, as can be observed by microscopic techniques (Atares and Chiralt, 2016). Table 1 shows the results related to essential oil addition effect on biopolymer films.

In order for a biopolymer film to have wider application, it must be resistant to the pressures that occur during transport, handling and application, thereby maintaining the integrity of the packaging and retaining the characteristics of the packaged food (Suput, 2016a). Biopolymer films structure is rigid and brittle due to the numerous interactions between polymer molecules (Krochta, 2002). Such a structure can be optimized by a wide spectrum of plasticizers (Suput, 2013; Suput, 2016a; Šuput, 2016c). Mechanical properties could, also, be enhanced by the addition of essential oils, which have the effect of plasticizers and thus attract water molecules. As a result of the presence of oil, the interactions of an essential oil-biopolymer occur instead of a biopolymer-biopolymer interaction (Shojaei-Alibadi et al., 2013). Many works have reported a decrease of TS of biopolymer films caused by lipid addition (Atares and Chiralt, 2016). Lipid incorporation into the film matrix induces a heterogeneous film structure featuring discontinuities (Zinoviadou et al., 2009). This affects the tensile properties of the films, depending on the characteristics of the lipid added.

The main functional characteristics of hydrophilic materials, which exactly biopolymer films obtained from hydrocolloids are, depend on their moisture content, as well as the relative humidity of the surrounding environment in which they are located (Chang et al., 2000). The addition of any component to the filmogenuous solution affects not only the mechanical properties, but also the barrier of the films (water vapor and gas permeability). The addition of plasticizers increases the hydrophilicity of the films, which in turn increases the water vapor permeability, while the addition of hydrophobic components (EO) reduces WVP. Reduction of water vapor permeability values is a consequence of hydrogen and covalent interactions between the structure of the bioplastic film and the polyphenolic oil components. These interactions prevent the availability of hydrogen groups to form hydrophilic linkages with water, which leads to a reduction in the affinity of the film to water (Suput, 2016a).

The WV transfer processes in films depend on the hydrophilic-hydrophobic ratio of the film constituents. The incorporation of hydrophobic EO into hydrophilic polymer matrices result in the WV barrier properties improvement (Atares and Chiralt, 2016). The physical state of the lipid and lipid distribution into the polymer matrix may affect WV barrier film efficacy. If the lipid droplets are smaller, they are more homogeneously distributed in the film matrix and the achieved WVP is lower (Perez-Gago and Krochta, 2001).

EO incorporation also can cause film transparency reduction. The EO addition implies decrease of light transmission, due to the light scattering at the interface of EO droplets imbedded in the film matrix. Consequently, an increase in opaqueness of films containing EOs was observed, which was affected by the type of EO (Atares and Chiralt, 2016).

**CONCLUSION**

Many studies have recognized biopolymer films as promising alternative toward synthetic packaging materials. Biopolymer films present good protection from various elements, while keeping quality and prolonging shelf life of packed product. They are naturally occurring, cheap and renewable. While investigating biopolymer sources, synthesis routes and obtained biopolymer film properties, many challenges had to be overcome. For this reason, a number of techniques have been developed to improve the properties of the obtained films. One of the film improvement directions goes toward essential oils application. EOs contribute to many benefits through their usage. Applying Eos to biopolymer matrices active packaging is achieved, with antioxidant and antimicrobial properties. But the application of lipophilic components (EO) also affects the other properties of films - mechanical, barrier, structural, optical, etc. This review contributes to a better understanding of the influence of added oils on the properties of biopolymer films through numerous examples and explained mechanisms of action.
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