A REVIEW OF BIOPOLYMER FILMS APPLICATION FOR SUSTAINABLE PACKAGING OF EDIBLE OILS

PREGLJED PRIMENE BIOPOLIMERNIH FILMOVA ZA ODRŽIVO PAKOVANJE JESTIVIH ULJA

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ABSTRACT

Lipid oxidation is a major cause of off-flavors and the loss of nutrients in fat-containing foods and oils. The prevention or retardation of those deteriorative reactions of oil during processing and storage is required. Commercially available synthetic packaging materials are causing serious environmental problems due to their non-degradability. To reduce environmental impacts associated with synthetic plastics, biopolymer materials have a great potential to be used instead. Further, biopolymers play an important role in food preservation because of their antioxidant and antimicrobial activities. The packing system is comprised of natural active materials that can improve the shelf life of oil-packed, minimize oxidation and improve mechanical, barrier and biological properties of biopolymer films. This paper aims to review currently available literature in the field of biopolymer materials application for packaging different types of edible oils.

Keywords: edible oil, oil oxidation, active packaging, biopolymer films.

REZIME

Jestiva ulja predstavljaju visoko nutritivan element humane ishrane, zbog izvora energije i visokog sadržaja liposolubilnih vitamina i esencijalnih masnih kiselina. Oksidacija nezasićenih masnih kiselina, koja je u velikoj meri zastupljena u jestivom ulju, je jedan od najvažnijih razloga koji ograničava rok trajanja proizvoda na bazi ulja i masti. Ovi prehrambeni proizvodi spadaju u grupu lako kvarljivih namirnica, te zahtevaju pažljiv odabir uslova skladištenja, pakovanja i čuvanja i potrebno im je zaštitno sredstvo protiv autooksidacije i hemijskog kvarenja tokom naznačenog roka trajanja. Iz navedenih razloga, ulažu se napore u razvoju aktivnih ambalažnih materijala, koji će sprečavajući interakciju kiseonika i ostalih uticaja spoljašnje sredine, doprineti produžetku roka trajanja proizvoda industrije ulja.

Polimerni ambalažni materijali, koji su na tržištu najčešće zastupljeni za pakovanje ove vrste proizvoda sintetisani su iz neobnovljivih izvora, sa dugim životnim ciklusom, te značajno opterećuju životnu sredinu. Kao alternativa upotrebi sintetskih polimera, koji imaju loš ekološki status je upotreba biorazgradivih polimera, koji sve više dobijaju na značaju, jer su po funkcionalnosti slični tradicionalnim polimerima, ali su ekološki podobniji. Biorazgradivi materijali, prirodnog porekla su razgradivi (biopolimeri), a poseduju i dobra barijerna svojstva, te imaju potencijal za pakovanje prehrambenih proizvoda osjetljivih na prisustvo kiseonika iz vazduha. Pored toga, biopolimeri su dobri nosioci aktivnih agenasa, te je moguće postići antioksidativni efekat pakovanjem ulja u različite biopolimerne filmove. U radu je dat pregled dosadašnjih istraživanja u oblasti primene biopolimernih materijala za pakovanje različitih vrsta jestivih ulja.

Ključne reči: jestivo ulje, oksidacija ulja, aktivna ambalaža, biopolimerni filmovi.

INTRODUCTION

Lipid oxidation is a process that results in rancidity and deterioration of fats and progresses via free-radical propagated chain reactions. The most common initiators of this reaction are singlet oxygen, heat and UV light. During the lipid oxidation, oxygen reacts with lipids in the chain of consequential reactions, which results in chemical composition change, organoleptic characteristics of oil and quality reduction. Lipid oxidation “in vivo” is associated with the health issues, such as coronary heart diseases, atherosclerosis, cancer and the aging processes (Schaich, 2020; Johnson and Decker, 2015). Antioxidants are compounds that can delay or reduce lipid oxidation in great amounts. These compounds can be a part of the oil itself otherwise they can be incorporated in packaging during the packing process.

Active packaging materials can extend the shelf life of products by preventing the interaction of oxygen and other external impacts with the food inside the packaging. Therefore,

different materials that can carry active compounds or those that are active without additional compounds are constantly investigated.

Materials that are suitable for active compounds incorporation are biopolymer materials. These materials are becoming increasingly significant because they are functionally similar but environmentally better than synthetic polymer packaging materials. Biodegradable materials of natural origin (biopolymers) have strong barriers to different environmental conditions, that qualifies them for sensitive food products packing (Popović et al., 2013; Popović et al., 2018). A particularly interesting group of food products are the oil industry products, sensitive to the presence of oxygen, which is a catalyst for lipid oxidation, especially unsaturated fatty acids. This paper aims at presenting the findings in recent studies, regarding the characteristics of different biopolymer packaging materials and their potential to be applied for oil industry product packing in order to maintain the quality during the shelf life of the products inside the packaging.

Oil sustainability and lipid oxidation

Edible oils originating from various plant sources (such as sunflower, soybean and corn) contain a high percentage of polyunsaturated fatty acids, therefore they are globally recommended in the balanced human diet, due to their multiple beneficial effects on human health (Schaich, 2020; Guillen and Goicoechea, 2008). Except for their energy and biological value, fats and oils have good physical properties. Being a good medium for heat transfer oils and fats ensure uniform heating and frying. A modern way of life favors the production of fast food and takeaway food, which is popular not only because of its availability and time savings but also because of its unique sensory characteristics, which would not have a characteristic taste without oils and fats (Johnson and Decker, 2015).

Since ancient times, the deterioration of lipids has been a major problem in the storage of oils and fats. Lipid oxidation is a process that results in rancidity and deterioration of fats and progresses via free-radical propagated chain reactions. It is a process where free radical and non-radical types of oxygen react with lipids causing oxidative destruction of unsaturated and polyunsaturated fatty acids (Yildiz et al., 2021; Dimić, 2005).

The primary oxidation products (hydroperoxides and peroxides), formed by the autooxidation of oils and fats, are unstable, tasteless and odorless compounds. During further reactions, their decomposition occurs as well as the formation of secondary oxidation products, carbonyl compounds (aldehydes, ketones, various acids and others). Quality deterioration of oils and fats occurs due to the formation of secondary oxidation products that can produce a strong, unpleasant smell and taste even at low concentrations (Schaich, 2020; Shi et al., 2020, Shahidi and Zhong, 2005).

Possibility of oil oxidation-reduction using active packaging materials

The use of appropriate packaging materials, packaging and packing conditions can contribute to preserving the integrity of the product, its quality and sustainability and reduce changes that occur during transport, storage and even usage (Lazić and Popović, 2015). The study conducted by a group of authors, Lolis et al. (2020) showed that extra virgin olive oil packed in "bag in box" packaging has been protected from oxidation and undesirable changes during storage for 9 months, which is not the case with the same oil packed in a dark glass bottle. This research represents a forward step in relation to commercially available packaging for oil industry products. However, although the oxidation of olive oil has been successfully delayed, there is a problem of residual packaging waste, which is a major environmental problem. These facts lead to the conclusion that the use of biopolymer films, as environmentally friendly packaging materials, greatly reduces the harmful impact on the environment, because it decreases consumption of non-renewable sources, and there are many options for disposal and destruction of such a waste.

Considering both the ecological problem of synthetic polymer materials and consumers' demands for minimally processed food, that requires a longer shelf-life, active packaging has been developed (Faas et al., 2020). Active packaging aims to maintain or extend the shelf life of food. It includes active systems for removing oxygen from the product or its environment (oxygen scavengers), as well as systems for an active release, emission when there is a high concentration of undesirable compounds inside the package. The use of active

packaging has been shown to reduce microbial growth and improve the oxidative stability of oils (Yildirim et al., 2018).

The addition of antioxidant agents can improve control and slow down the oxidation process in fat-rich food. If antioxidants are incorporated into the matrix of packaging material, a gradual release of antioxidant agents into the product is achieved. Thus, there is no need for the unnecessary addition of synthetic antioxidants, which are effective but limited due to side effects harmful to human health (Anbinder et al., 2015). Various studies have shown the effectiveness of natural antioxidants, such as polyphenols, flavonoids and carotenoids, in delaying and slowing down oxidative changes in edible oils (Nishad et al., 2021; Faas et al., 2020; Stoll et al., 2019).

Biopolymers for edible oils packaging

The use of packaging materials based on biopolymers in the food industry is being constantly researched for several reasons. These materials originate from renewable sources; there is a possibility of producing active/edible packaging and these materials are, in most cases, biodegradable. Different types of biopolymers (proteins and polysaccharides) are available as by-products of the agricultural and food industries, so the possibility of combining and synthesizing new biopolymer materials is various (Popović et al., 2018; Popović et al., 2020). Natural molecules, such as biopolymers, are good carriers of natural active agents, so it is possible to incorporate them into biopolymer film's matrix, to sustain the quality of the packed product. In this regard, the potential of biopolymer films to overcome the problem of limited stability and shelf life of edible oils has been recognized.

Polysaccharides and proteins can be used divided, as mono materials, or as composite materials in combination with lipids to produce biodegradable packaging materials. Table 1 shows a variety of biopolymer materials and their possibility to be used for different edible oils packing and preserving the quality of the products packed.

Protein biofilms have been shown to be a good barrier to oxygen (Popović et al., 2012; Lolis et al., 2020), the primary cause of oxidative changes in products with high oil content. Numerous research (Nilsuwan et al., 2019; Hasan et al., 2020; Huang et al., 2020) showed that biopolymer films can effectively delay oxidative changes and reduce rancidity, compared to open-box or commercially packaged oil, because in that way a direct contact of oil with synthetic plastic materials is avoided, where the transition of certain toxic additives into oil is possible. Popović et al. (2019) examined the influence of biopolymer mono and duplex materials based on pumpkin oil cake on flaxseed oil stability. The results showed no significant changes in oil quality during 30 days, so it can be concluded that biopolymer films based on pumpkin oil cake are suitable material for oil packaging and other products sensitive to oxygen presence. Besides this protein-rich by-product, studies have shown that active biopolymer films can be successfully formed from pumpkin protein isolate, with excellent barrier properties against gases and antioxidant activity, without the addition of active agents (Popović et al., 2012). This is possible due to the antioxidant activity of structural and reserve proteins and peptides, which are precisely the carriers of the structure of those biodegradable films (Popović et al., 2013).

Lipid-based films have the highest resistance degree to moisture migration compared to protein and polysaccharide films, but they are difficult to apply due to their thickness and greasy surface. A group of authors has reported (Wang et al., 2019; Otabor et al., 2019) flaxseed oil to be used for composite

films formation, which are based on chitosan and potato protein. In that way, the addition of flaxseed oil contributes to an excellent moisture barrier and elastic and durable films formation, due to the high percentage of polyunsaturated fatty acids in flaxseed oil, which absorb oxygen from the air.

Packaging based on acetylated starch and starch with pea proteins can provide protection to soybean and olive oil for up to 3 months (Huntrakul et al., 2020). The addition of vegetable proteins to starch reduced the shrinkage of starch films and improved their thermal stability. The possibility of film blowing has also been improved, as well as the barrier properties, necessary for packaging products with high oil content. In studies of other authors (Stoll et al., 2019; Wang et al., 2019; Hasan et al., 2020) the addition of active components (anthocyanins, eugenols and carotenoids) significantly reduced the oxidation of packaged oil, compared to materials without active agents or commercial materials.

Bags for sesame oil packing were made of a composite film based on carrageenan derivatives and glucomannan konjac (Ganesan et al., 2019). The combination of those materials contributed to the improvement of mechanical properties, as well as to the improvement of the moisture permeability. Also, during the three months of storage, no significant changes in phytosterol content of sesame oil were noticed, which is evidence of active compounds' influence on the oil and its oxidative stability.

Since olive oil is very popular among consumers, due to its pleasant aroma and taste, fatty acid content (mainly oleic acid) and the presence of natural antioxidants (phenols and tocopherols), researchers are intensively searching for the application of biopolymer films for olive oil packaging. In the study conducted by Yildiz et al. (2021), the addition of gallic acid to the pea flour-based film successfully delayed the oxidation of packaged olive oil. The percentage of primary oxidation products was reduced by 28%, because gallic acid, in addition to its anti-carcinogenic and antimicrobial effect, also has a significant antioxidant effect. The hydrophobicity of the films was increased by 36-40%, compared to films without the addition of gallic acid.

Similarly, by examining the influence of lignin as an active material in combination with soy proteins for soybean oil packaging, the delay of oxidative changes up to 75%, because of their possibility to block UV radiation (Mohammad et al., 2019). Lipid oxidation of soybean oil was successfully delayed even by the use of green tea extract in the composite matrix of LLDPE and thermoplastic starch (Panrong, 2019).

Moreover, it is possible to improve the mechanical, barrier and biological properties of composite films based on casein and Na-alginate by adding nanoparticles. This composite film was found to protect the coconut oil from oxidation, by packing it in bags made of this composite material (Gautam and Mishra, 2017).

Table 1. Various biopolymer materials with active compounds for preserving different types of edible oils.

Type of biopolymer material	Type of packed oil	Reference
Sugar palm starch-chitosan films carrying extra virgin olive oil	Extra virgin olive oil	Hasan et al. (2020)
PLA films with carotenoid extracts	Sunflower oil	Stoll et al. (2019)
Egg white protein/ κ -Carrageenan composite film	Soybean oil	Huang et al. (2020)
Cassava starch films with pea protein	Soybean oil and olive oil	Huntrakul et al. (2020)
Fish gelatin monolayer and bilayer films incorporated with epigallocatechin gallate	Chicken skin oil	Nilsuwan et al. (2019)
Gelatin films with anthocyanins complexes	Olive oil	Wang et al. (2019)
Composite film from carrageenan derivate and konjac glukomannan	Sesame oil	Ganesan et al. (2019)
Pumpkin seed oil cake films, mono and duplex	Linseed oil	Popović et al. (2019)
Sodium alginate-pectin/casein films with copper nanocomposite	Coconut oil	Gautam and Mishra (2017)
Pea flour films with gallic acid	Olive oil	Yildiz et al. (2021)
Thermoplastic starch and green tea blends with LLDPE films	Soybean oil	Panrong et al. (2019)
Soybean protein films with two types of lignin	Fish oil and soybean oil	Mohammad et al. (2019)

CONCLUSION

Since the products of the oil industry are highly nutritious and have multiple benefits for human health, it is necessary to preserve the characteristics of the packaged products within the declared shelf life. This can be achieved by reducing the diffusion of oxygen into the oil-packed. Usage of modern packaging materials and modern packing techniques can minimize oil oxidation. Packing system with natural active materials has been more effective due to the possibility to reduce the promotion of primary lipid oxidation products in great amount, providing safety and security during storage and transportation with zero drawbacks for the product. In comparison with commercially available materials for oil packaging, biopolymers are biodegradable and eco-friendly. Protein-based biopolymer films with lipid components have been found to show the best results in reducing oxygen migration into the oil-packed. In this regard, active biopolymer materials are intensively investigated and optimized aiming to produce packaging material with functional properties that can best contribute to the purpose-retard oil oxidation and prolong the shelf life of oil industry products.

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