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Starch-based films with incorporated apple peel and chokeberry polyphenols

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Abstract

The aim was to prepare biodegradable starch-based films with active substances, and to examine the influence of temperature (80, 90, 99 °C), plasticizer (glycerol 1, 2, 4 %), and incorporation of phenolic compounds form apple peel and chokeberry on the properties of the films. The hygroscopic nature of glycerol affected the film properties. With the increase in glycerol content the water content, water solubility, and water vapor permeability of films significantly increased, while the swelling degree and hardness significantly decreased ($p<0.05$). Temperature did not have a significant influence on film properties. Phenolic compounds from apple peel and chokeberry increased the water solubility of films, and the loss of weight in water, in some cases significantly ($p<0.05$). The increase in hydrophilicity of films after the addition of phenolic compounds could be suggested, which affected the higher solubility and weight loss in the water. However, phenolic compounds decreased the swelling degree of films, in some cases significantly ($p<0.05$). The denser structure of films with the addition of phenolic compounds can be suggested, which caused the swelling degree to decrease. All films were biodegradable in water (the weight loss 18-38 %). The properties of starch-based films need to be studied and adjusted further for packing foods.

Keywords: active films; biodegradable films; phenolic compounds; *Aronia melanocarpa*; *Malus domestica*;

Introduction

Traditional plastic materials have good characteristics for packaging of foods. However, due to their impact on the environment, research is trying to find environmentally friendly materials, easily biodegradable, with good characteristics for packaging. Starch is intensively studied for the production of biodegradable films that could, at least in some areas, replace traditional plastic materials (Luo et al., 2022; Miao et al., 2021; Mendes et al., 2020). It has a good film-forming ability, it is inexpensive and non-toxic (Miao et al., 2021), and it creates transparent films with efficient barrier characteristics (Falcão et al., 2022). Due to the sensitivity to water and weak mechanical properties, pure starch is often combined with some other materials to improve its properties (Falcão et al., 2022). Such combinations are starch with sodium carboxymethyl cellulose (Lin et al., 2022), starch with MgO nanoparticles (Luo et al., 2022), starch with sodium alginate and gum Arabic (Xiao et

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al., 2022), or starch with whey proteins (Shivani, 2022). For example, the addition of MgO nanoparticles improved the tensile strength of starch films, decreased the water solubility, and the water vapor permeability (Luo et al., 2022). Whey protein enhanced the tensile strength, elongation at break of starch films, however, they increased the water vapor permeability (Shivani, 2022). Films based on starch or combinations of starch with other materials are biodegradable in soil (Luo et al., 2022), or in vegetable compost (Mendes et al., 2020).

Active substances can be incorporated into films based on starch. Such active films can actively participate in extending the shelf-life of packaged foods, and in increasing its quality. As active substances, many natural materials have been used, such as tea polyphenols (Luo et al., 2022; Miao et al., 2021; Zhang et al., 2021), thyme essential oils (Shivani, 2022), or apple polyphenols (Lin et al., 2022). Active substances can be obtained from the waste in food processing industries (Dhillon et al., 2013). Results have shown that these active films can be successful in packing various foods. Films made from cassava starch and sodium carboxymethyl cellulose with incorporated apple polyphenols showed antioxidant potential and prevented the oxidation of packed chicken meat (Lin et al., 2022). Films made from starch, MgO nanoparticles and tea polyphenols showed antioxidant and antimicrobial activities, and maintained the quality of packed foods such as bananas, strawberries and grapes (Luo et al., 2022). Films made from thyme essential oil nanoemulsion, tamarind starch, and whey proteins delayed the ripening process of tomatoes (Shivani, 2022). Active substances incorporated into films are an effective way to increase the desirable characteristics of films, and improve their ability to maintain packed foods. However, active, biodegradable films are still under intensive investigation. Biodegradable films need to achieve good and appropriate mechanical and barrier properties, and active substances should achieve the release in the food in order to be used for various foods (Westlake et al., 2022).

In this work, the aim was to study certain parameters (temperature and amount of glycerol) of the process of preparation of starch-based films with active substances, and how these parameters affect the properties of the films. Starch-based films were prepared at different temperatures (80, 90 and 99 °C), with different amounts of plasticizer (1, 2, and 4 % glycerol), and phenolic compounds from apple peel and chokeberry were incorporated into films as active substances. Several of their properties were determined (thickness, water content, swelling degree, water solubility, water vapor permeability, and hardness).

Materials and methods

Chemicals

Starch was a corn starch. Glycerol was obtained from Fagron d.o.o. (Donja Zelina, Croatia). Standards of phenolic compounds were purchased from Sigma-Aldrich (St. Louis, MO, USA) ((+)-catechin hydrate, (-)-epicatechin, quercetin-3-glucoside, chlorogenic acid, and neochlorogenic acid) and from Extrasynthese (Genay, France) (procyanidin B1, procyanidin B2, quercetin-3-galactoside, quercetin-3-rhamnoside, phloretin, phloretin-2'-O-glucoside, cyanidin-3-galactoside chloride, and cyanidin-3-glucoside chloride). Orto-phosphoric acid (85% HPLC-grade) was purchased from Fluka (Buchs, Switzerland), and methanol (HPLC grade) from J.T. Baker (Gliwice, Poland).

Samples and extract preparation

Apples ('Crimson crisp') were purchased from the local store, and peeled. The rest of the flesh from the peel was removed with the knife. Peel was dried in a fruit dryer and homogenized in a coffee grinder. Chokeberry (*Aronia melanocarpa*) was harvested in an orchard located in Orahovica (Croatia). Chokeberry was dried in the fruit dryer, homogenized with the coffee grinder. Both dry fruit samples were placed in plastic bags, vacuumed, and stored in a refrigerator (-18 °C) (no more than one week).

Dry fruit samples (5 g) and 100 ml of distilled water were put in a beaker. The beaker was put in an ultrasonic bath (RK 100, Bandelin Sonorex, Berlin, Germany) for 30 min and filtered. An aliquot of extract (1 ml) was additionally filtered (0.2 µm PTFE syringe filter), and analyzed with a reversed-phase high-performance liquid chromatography method (RP-HPLC method). The rest of the extract was used for the preparation of films.

Preparation of films

For the preparation of films, three different temperatures (80, 90 and 99 °C) and different amounts of plasticizer were tested (1, 2 or 4 %). Starch (2.5 g) and distilled water (100 ml) were put in beakers and then in a water bath with shaking (LSB Aqua Pro, Grant Instruments, Cambridge, UK) (60 min) at different temperatures (80, 90, or 99 °C). Next, glycerol was added (1, 2 or 4 %), mixtures were heated for additional 15 minutes, and then poured on Petry dishes. Films with fruit extracts were prepared with a similar procedure by using the chosen temperature 99 °C, and the amount of glycerol 1 and 2 %. The starch (2.5 or 5 g) and distilled water (80 ml) were put in beakers, and then in the water bath with shaking (45 min) at 99 °C. Next, 20 ml of fruit extracts were added, and the mixtures were additionally heated for 15 minutes. Then, glycerol was added (1 or 2 %), and the mixtures were heated for additional 15 minutes before pouring them on Petry dishes. Films were dried at room temperature.

Reversed phase high-performance liquid chromatography method (RP-HPLC)

Fruit extracts were analyzed on a 1260 Infinity II HPLC system consisting of a vialsampler, a quaternary pump, a diode array detector, a column Poroshell 120 EC C-18 (4.6 x 100 mm, 2.7 µm), and a Poroshell 120 EC-C18 4.6 mm guard-column (Agilent Technologies, Santa Clara, CA, USA). Mobile phases A (0.1 % H_3PO_4 in water) and B (100 % methanol) were used for the gradient that separated compounds (0 min 5 % B, 5 min 25 % B, 14 min 34 % B, 25 min 37 % B, 30 min 40 % B, 34 min 49% B, 35 min 50 % B, 58 min 51 % B, 60 min 55 % B, 62 min 80 % B, 65 min 80 % B, 67 min 5 % B, 72 min 5 % B). Compounds were identified by comparing UV/Vis spectra and retention times of peaks in extracts with those of authentic standards.

Characterization of films

Thickness and hardness

The thickness was measured at three places on the film (Mini digital thickness gauge). The hardness was determined by using shore hardness tester (Sauter, Balingen, Germany) (Shore A).

Water content (WC), swelling degree (SD) and water solubility (WS)

The WC, SD, and WS were determined according to Miao et al. (2021) with some modifications. Pieces of films were cut 1 x 1 cm, weighed (m_0), put in an incubator (IN 30 Memmert, Schwabach, Germany) (80 °C, 24 h) to dry, and weighed again (m_1). Next, they were put in plastic cuvettes containing 2 ml of water for 24 h, and weighed again (m_2). Films were dried once more (24 h, 80 °C) in the incubator, and weighed (m_3). WC, SD and WS were calculated according to the following equations:

$$WC\ (\%)= \frac{(m_0\text{-}m_1)}{m_0}\ 100$$

$$SD\ (\%)= \frac{(m_2\text{-}m_1)}{m_1}\ 100$$

$$WS\ (\%)= \frac{(m_1\text{-}m_3)}{m_1}\ 100$$

Biodegradability in water

According to the method by De Carli et al. (2022) with minor modifications, films were cut 1 x 1 cm, dried 24 h at 80 °C in the incubator, and weighed (m_1). Next, they were put in plastic cuvettes containing 2 ml of distilled water, for 48 h, dried for 24 h in the incubator (80 °C, 24 h) and weighed again (m_2). The biodegradability was calculated as the percentage of weight loss (WL):

$$WL\ (\%)= \frac{(m_1\text{-}m_2)}{m_1}\ 100$$

Water vapor permeability (WVP)

The water vapor permeability (WVP) was determined according to the ASTM method (E96). Pieces of films were cut (3 x 3 cm). Plastic cuvettes with an opening 1 x 1 cm were filled with water with a small air pocket above the water. Films were sealed on top of cuvettes and put in a desiccator with hygrometer for the recording of relative humidity and temperature (Sicco Mini 2 Premium, Bohlender, Grünsfeld, Germany). The surface area of films (A) was 1 cm^2. Cuvettes sealed with films were weighed after 1, 2, 3, 4, 5, 6, 22, and 23 h. Inside the cuvettes the relative humidity (R_1) was 100 % (1 if expressed as a fraction), and in the desiccator at 26 °C relative humidity (R_2) mean value was 51,2 % (0.512 expressed as a fraction). The determined saturation vapor pressure (S) at 26 °C was

3365 Pa. The graph, mass of cuvettes (g) vs time (h), was created. Water vapor transmission (WVT) was calculated according to the slope of the line in the graph which represents the weight change through time (G/t), and according to the surface area $_A$. It was expressed in (g/h m^2)

$$WVT = \frac{\left(\frac{G}{t}\right)}{A}$$

Permeance was calculated according to the following equation and expressed in (g / s m^2 Pa)

$$Permeance = \frac{WVT}{S(R_1 - R_2)}$$

WVP was calculated according to the following equation, and expressed as g m / m^2 s Pa

$$WVP = Permeance \ x \ thickness$$

Statistical analysis

Extracts were analyzed two times with RP-HPLC, and the amounts of phenolic compounds were calculated as mean values ± standard deviation. Where possible, results were analyzed with post-hoc Tukey test with 95 % significance, and principal component analysis (Minitab LLC., State College, PA, USA).

Results and discussion

The effect of temperature and glycerol on the film properties

Table 1 shows properties of films prepared at three different temperatures (80, 90 and 99 °C) with different amounts of glycerol (1, 2 and 4 %). The amount of starch was the same, 2.5 %. The thickness of films was from 0.083 to 0.183 mm. According to literature, films prepared from various starches had similar thickness, 0.116 to 0.123 mm (Miao et al., 2021), 0.091 to 0.154 mm (Luo et al., 2022), 0.05 to 0.15 mm (Mendes et al., 2020). Films from this study contained 5 to 23 % of water. Again, water content in films made from various starches was similar, 20 to 24 % (Miao et al., 2021), or between 11 and 15 % (Luo et al., 2022). Films had a very high swelling degree, from 98 to 189 %. Values published in the literature were lower, from 37 to 41 % (Miao et al., 2021). Starches prepared earlier were modified porous starches (Miao et al., 2021). These modifications resulted in lower values of swelling degree than in our study in which we used pure starch. Furthermore, films from this study were soluble in the water. After 24 h in the water, their water solubility was from 22 to 59 %. Those values are somewhat similar to those published in literature, 15 to 16

Table 1 Properties of films prepared at different temperatures and with different glycerol content

T ˚C	Glycerol %	Thickness mm	WC %	SD %	WS %	H
80	1	0.083	8.3	162.0	22.0	22.1
80	2	0.123	17.6	129.7	32.3	20.2
80	4	0.180	11.4	98.1	50.7	18.4
90	1	0.097	5.3	188.9	23.5	24.7
90	2	0.130	17.4	122.6	36.8	22.8
90	4	0.163	15.9	137.7	58.6	10.1
99	1	0.123	6.9	163.8	25.2	20.9
99	2	0.143	22.6	107.8	33.1	18.9
99	4	0.183	17.7	117.7	54.0	11.2

WC – water content, SD – swelling degree, WS – water solubility, H – hardness (shore A), (starch 2.5 % in each film)

Table 2 Differences in properties of films according to different glycerol content and different temperature

T °C	WC	SD	WS	H		Glycerol %	WC	SD	WS	H
80	a	a	a	a		1	b	a	c	a
90	a	a	a	a		2	a	b	b	ab
99	a	a	a	a		4	a	b	a	b

Results from Table 1 were analyzed with post-hoc Tukey test with 95 % significance. Different letters in a column represent significant difference. WC – water content, SD – swelling degree, WS – water solubility, H – hardness (Shore A)

% (Miao et al., 2021), 15 to 20 % (Luo et al., 2022). The hardness of films was from 10 to 25 (Shore A).

The temperature for the preparation of films did not have any significant effect on the properties of films (Table 2). The temperature of 99 °C was chosen for the preparation of films in the next experiments.

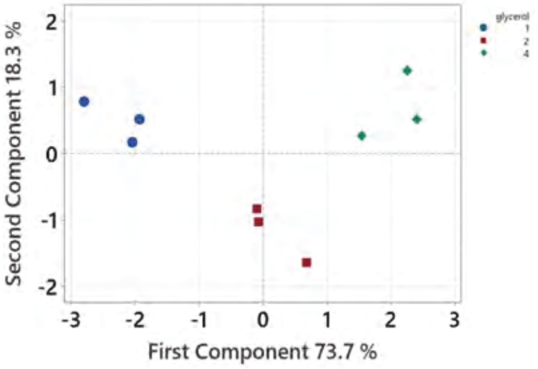

Figure 1 Principal component analysis of properties of films (water content, swelling degree, water solubility, hardness) prepared with different amounts of glycerol

Glycerol significantly affected all of the mentioned characteristics ($p<0.05$) (Table 2). Water content, and water solubility increased with the increase of glycerol content ($p<0.05$) (Table 1 and 2). Glycerol is miscible in water, hygroscopic, and attracts water molecules which is why more glycerol in films resulted in films with the higher water content. Similarly, higher glycerol content resulted in the higher solubility of films in the water. This can be explained by the fact that glycerol binds more water from the environment which affects starch to dissolve more easily. Moreover, higher glycerol content created flexible films with significantly lower hardness ($p<0.05$). Flexible films with more glycerol between starch polymers prevented the starch from swelling in the water which caused significantly lower swelling degree ($p<0.05$). The principal component analysis of all the mentioned properties (Figure 1) showed grouping of the results on the basis of glycerol content, which confirms its effect on films. 1 and 2 % of glycerol were chosen for the preparation of films in the next experiment, because the amount of 4 % gave too flexible films.

The effect of apple peel or chokeberry phenolic compounds on film properties

In the next experiment, we prepared films with phenolic compounds from apple peel and chokeberry incorporated within the structure of the film by using the chosen parameters: temperature (99 °C), percentage of starch (2.5 %), and the percentage of plasticizer (1 and 2 %). Films were additionally prepared with 5 % of starch. Extracts from apple peel and chokeberry were prepared in the water, and the amounts of phenolic compounds per mass of fruits extracted with the use of water are shown in Table 3. Apple peel contained flavan-3-ols (425 mg/kg fresh weight (fw)), dihydrochalcones (52 mg/kg fw), phenolic acids (42 mg/kg fw), flavonols (179 mg/kg fw), and anthocyanins (16 mg/kg fw). Chokeberry had more phenolic compounds. It contained phenolic acids (2083 mg/kg fw), flavonols (198 mg/kg fw), and anthocyanins (433 mg/kg fw). The amounts of phenolic compounds are lower than in earlier studies (Khanizadeh et al., 2008; Jakobek et al., 2020; Jakobek et al., 2021). Since extracts for our study were prepared only with the water, amounts are expected to be somewhat lower than in earlier studies where organic solvent such as methanol was used (Khanizadeh et al., 2008; Jakobek et al., 2020; Jakobek et al., 2021). We avoided organic solvents, because they need to be removed before the incorporation of fruit extract into the film. Instead we used just water which allows us to put extracts directly into the films without the additional procedure of removing organic solvent.

Table 3 The amount of polyphenols in apple peel and chokeberry

Polyphenols	Apple peel (mg/kg fw)	Chokeberry (mg/kg fw)
Flavan-3-ols		
procyanidinB1	11.2 ± 0.5	ni
(+)-catechin	34.1 ± 0.8	ni
procyanidin B2	192.9 ± 6.4	ni
(-)-epicatechin	186.5 ± 1.7	ni
total	424.6 ± 7.8	
Dihydrochalcones		
phloretin-2-glucoside	51.7 ± 0.1	ni
total	51.7 ± 0.1	
Phenolic acids		
neochlorogenic acid	ni	1251.4 ± 9.0
chlorogenic acid	41.6 ± 0.2	831.1 ± 18.4
total	41.6 ± 0.2	2082.5 ± 9.4
Flavonols		
quercetin-3-galactoside	48.9 ± 0.2	42.1 ± 0.3
quercetin-3-gucoside	27.4 ± 0.1	122.1 ± 0.8
quercetin derivative	31.0 ± 0.0	33.5 ± 0.0
quercetin-3-xyloside	49.0 ± 0.4	ni
quercetin-3-rhamnoside	23.0 ± 0.3	ni
Total	179.3 ± 1.0	197.7 ± 1.1
Anthocyanins		
cyanidin-3-galactoside	15.5 ± 0.2	212.1 ± 3.7
cyanidin -3-glucoside	ni	32.0 ± 0.8
cyanidin -3-arabinoside	ni	159.6 ± 3.8
cyanidin -3-xyloside	ni	28.9 ± 0.6
Total	15.5 ± 0.2	432.5 ± 7.2
TOTAL	712.7 ± 8.7	2712.7 ± 17.7

Extracts analyzed two times; ni – not identified

The properties of prepared films are shown in Table 4. The thickness of films (0.067 to 0.210 mm), their water content (7 to 19 %), and water solubility (16 to 38 %) agree with literature (Luo et al., 2022; Mendes et al., 2020; Miao et al., 2021). Again, the swelling degree (94 to 193 %) was higher than in earlier studies (Miao et al., 2021). After 48 hours in the water, films lost 18 to 38 % of their weight. Some other biodegradable materials such as chitosan-based films lost 46 % of their weight after 48 h in the water (De Carli et al., 2022), a little bit higher than our films. The weight loss of a film made from cassava starch with sodium carboxymethyl cellulose after 5 min in the water was 21 % (Lin et al., 2022). The hardness of films in this study was from 16 to 52.

Table 4 Properties of films prepared with the addition of apple peel and chokeberry polyphenols

Fruit	Starch %	Glycerol %	Thickness mm	WC %	SD %	WS %	WL %	H	WVP (10^{-11} g/m s Pa)
without	2.5	1	0.093	10.5	193.1	20.0	18.9	21.7	80.23
without	2.5	2	0.103	17.2	137.8	21.3	20.1	18.8	120.22
apple	2.5	1	0.103	12.9	95.7	34.6	30.5	23.9	87.12
apple	2.5	2	0.123	19.1	93.7	38.0	37.5	21.8	131.08
chokeberry	2.5	1	0.067	8.7	108.7	27.0	24.0	24.0	52.13
chokeberry	2.5	2	0.093	15.6	119.9	30.6	29.2	18.6	84.95
without	5	1	0.183	7.5	140.7	16.1	18.1	51.7	120.00
without	5	2	0.210	9.3	136.6	27.8	17.6	16.1	181.17
apple	5	1	0.120	7.3	110.7	23.7	24.7	26.1	71.00
apple	5	2	0.177	10.9	104.6	27.1	25.9	16.2	110.78
chokeberry	5	1	0.137	7.4	112.5	22.5	22.8	30.2	90.00
chokeberry	5	2	0.187	11.7	106.4	26.5	25.9	20.0	123.37

WC – water content, SD – swelling degree, WS – water solubility, WL-biodegradability expressed as weight los after 48 h in water, H – hardness (Shore A), WVP – water vapor permeability. Temperature was 99 °C

Table 5 Differences in properties of films according to the incorporation of fruit polyphenols

	WC	SD	WS	WL	H	WVP
glycerol						
1 %	b	a	a	a	a	b
2 %	a	a	a	a	b	a
Polyphenols	**2.5 % starch**					
without	a	a	b	a	a	a
apple	a	a	a	a	a	a
chokeberry	a	a	ab	a	a	a
	5 % starch					
without	a	a	a	b	a	a
apple	a	b	a	a	a	a
chokeberry	a	b	a	a	a	a

Results from Table 4 were analyzed with post-hoc Tukey test with 95 % significance. Different letters in a column represent significant difference. WC – water content, SD – swelling degree, WS – water solubility, WL-biodegradability expressed as weight los after 48 h in water, H – hardness (Shore A), WVP – water vapor permeability

Glycerol affected the properties of prepared films (Table 4 and 5). Higher glycerol content increased the water content ($p<0.05$), water solubility, and weight loss of films. In contrast, swelling degree and hardness ($p<0.05$) decreased. This agrees with the results for films prepared only with starch (Table 1) and already explained. The principal component analysis of properties shows grouping of the data based on the glycerol content (Figure 2), which confirms the mentioned differences. In addition, the higher amount of hygroscopic glycerol in films increased their WVP ($p<0.05$), probably due to easier transfer of water vapor through film (Table 4).

Phenolic compounds from apple peel or chokeberry did have some effect on the properties of films but not on all of them (Table 5). Water content and hardness in films prepared from 2.5 and 5 % of starch were similar, whether the films were prepared without added phenolic compounds or with added phenolic compounds from apple peel or chokeberry. The results from earlier studies vary. In films from starch, water content increased (Miao et al., 2021) or decreased (Luo et al., 2022) with the addition of tea polyphenols. In films from cassava starch/sodium carboxymethyl cellulose, the addition of apple peel decreased the water content (Lin et al., 2022). Earlier studies suggested that polyphenols in films made from starch can trap more water which can increase the water content (Miao et al., 2021) or, on the other hand, if the solid content is increased by the addition of polyphenols, the interactions with water molecules can be difficult which leads to the decrease in water content. Furthermore, earlier studies suggested physical interactions between phenolic compounds and starch, including hydrogen bonds, hydrophobic interactions and electrostatic interactions (Luo et al., 2022; Miao et al., 2021). Those physical interactions could be suggested between phenolic compounds from apple peel and starch, and between phenolic compounds from chokeberry and starch in prepared films. Phenolic compounds that interacted with starch, did not trap any more water in the films. Furthermore, the swelling degree decreased with the addition of apple peel or chokeberry polyphenols, however the decrease was significant only for films with 5 % starch (p<0.05). In films from starch prepared in earlier studies, the swelling degree was similar when tea polyphenols were added into the films (Miao et al., 2021). On the other hand, the swelling decreased when porous starch with tea polyphenols was added into the starch film, similar to our study, which was explained with a more compact structure of the created films (Miao et al., 2021). Likewise, a more compact structure with the addition of polyphenols that prevents swelling could be suggested for films in this study. Next, the addition of phenolic compounds increased the water solubility, however, significant only for materials from 2.5 % starch (p<0.05). Similarly, the weight loss after 48 h in the water increased with the addition of polyphenols, but significant only for films with 5 % starch (p<0.05). Increased water solubility and weight loss in the water can be explained by phenolic compounds bonded to starch with non-covalent physical interactions. They could have affected the hydrophilicity of films, as indicated in Lin et al. (2022), leading to easier solubility and weight loss in the water. Some studies reported different results. The addition of tea polyphenols did not affect the water solubility of starch films (Luo et al., 2022; Miao et al., 2021). Similarly, the addition of apple polyphenols did not affect the water solubility of cassava starch/sodium carboxymethyl cellulose films (Lin et al., 2022). On the other hand, the addition of propolis phenolic compounds decreased the water solubility of chitosan-based films (De Carli et al., 2022). The principal component analysis of the properties of films made without or with the addition of fruit extracts (Figure 2) shows the grouping of data, which might suggest that the described difference exists.

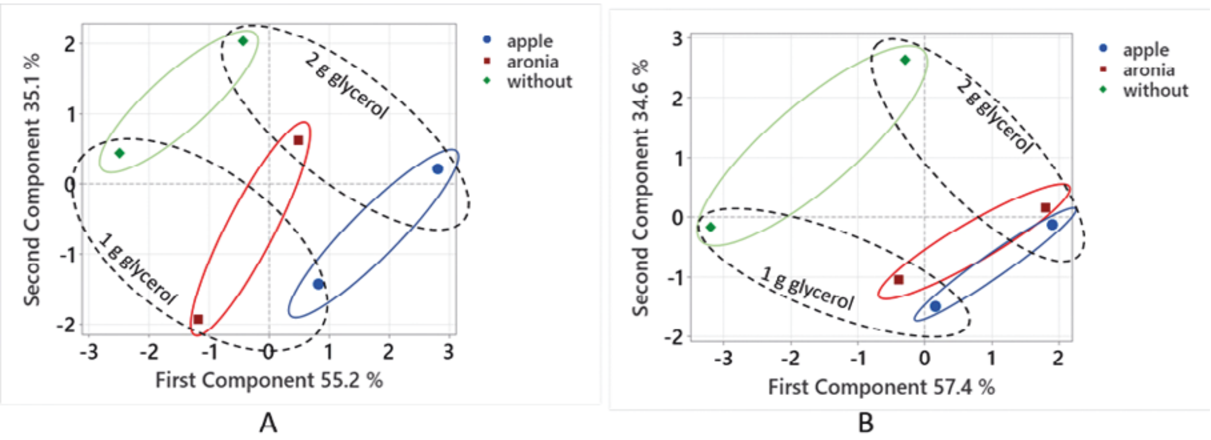

Figure 2 Principal component analysis of properties of films prepared without phenolic compounds and with added apple peel and chokeberry (aronia) phenolic compounds, with 2.5 % starch A) and with 5 % starch B). Properties that were analyzed are water content, swelling degree, water solubility, weight loss, hardness, and water vapor permeability

Water vapor permeability (WVP) of films is shown in Table 4. The permeability of films prepared with 2.5 % starch was from 52 to 131 10^{-11} g/m s Pa. Films prepared with 5 % starch had somewhat higher permeability (71 to 182 10^{-11} g/m s Pa). The WVP is an important characteristic of films. It shows how much water vapor can transfer from food into the environment through the film. This can lead to a decrease of the quality of packed food. The WVP are high for films in this study, and it can be seen that the values increased with the increase of glycerol in films. It can be suggested that glycerol attracts more water which can lead to higher WVP. Films made from starch in earlier studies had WVP up to 111.1 10^{-11} g/m s Pa (Mendes et al., 2020) similar to our study. Film made from potato starch had somewhat lower WVP, 17 10^{-11} g/m s Pa (Luo et al., 2022). However, films from starch are often combined with other polymers or additions to lower the permeability of water vapor. That is why some of those films are reported with lower permeability. Films from starch with added MgO nanoparticles and tea polyphenols (9-17 10^{-11} g/m s Pa) (Luo et al., 2022), films from porous starch with added tea polyphenols (24.4 to 26.4 10^{-11} g/m s Pa) (Miao et al., 2021), films from corn starch/sodium alginate/gum arabic (10 to 17 10^{-11} g/m s Pa) (Xiao et al., 2022) or films from cassava starch/sodium carboxymethyl cellulose with incorporated apple polyphenols (up to 8 10^{-11} g/m s Pa) (Lin et al., 2022), had lower values of WVP than in our study. Films made of pure starch, like in our study, are still more hydrophylic in nature which causes WVP to be higher than in films in earlier studies prepared with combinations of other polymeric materials with the starch. The addition of phenolic compounds did not have significant influence on WVP (Table 5).

Conclusion

Prepared films were 0.067 to 0.210 mm thick, and had 5 to 23 % of water. In the water, films were soluble (16 to 59 %), their swelling degree was 94 to 193 %, and they lost 18 to 38 % of their weight after 48 h in water. Higher glycerol content increased the water content, the water solubility and the loss of weight in water of starch-based films, and decreased swelling degree and hardness. Temperature did not have a significant effect on film properties. Phenolic compounds increased the solubility and the loss of weight in water. All films were biodegradable in water (18-38%). The properties should be additionally studied and adjusted for packing various foods.

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Filmovi na bazi škroba s polifenolnim spojevima iz kore jabuke i aronije

Sažetak

Cilj je bio pripremiti biorazgradive filmove na bazi škroba s aktivnim tvarima, te ispitati utjecaj temperature (80, 90, 99 °C), plastifikatora (glicerol 1, 2, 4 %) i polifenolnih spojeva iz kore jabuke i aronije na svojstva filmova. Higroskopna priroda glicerola utjecala je na svojstva filma. S povećanjem udjela glicerola sadržaj vode, topljivost u vodi i propusnost vodene pare filmova značajno su se povećali, dok su se stupanj bubrenja i tvrdoća značajno smanjili ($p<0,05$). Temperatura nije imala značajan utjecaj na svojstva filma. Polifenolni spojevi iz kore jabuke i aronije povećali su topljivost filmova u vodi i gubitak težine u vodi, u nekim slučajevima značajno ($p<0,05$). Moglo bi se sugerirati povećanje hidrofilnosti filmova nakon dodatka polifenolnih spojeva, što je utjecalo na veću topljivost i gubitak težine u vodi. Međutim, polifenolni spojevi smanjili su stupanj bubrenja filmova, u nekim slučajevima značajno ($p<0,05$). Može se sugerirati gušća struktura filmova s dodatkom polifenolnih spojeva, što je uzrokovalo smanjenje stupnja bubrenja. Svi filmovi bili su biorazgradivi u vodi (gubitak težine 18-38 %). Svojstva folija na bazi škroba potrebno je dodatno istraživati i prilagođavati za pakiranje hrane.

Ključne riječi: aktivni filmovi; biorazgradivi filmovi; polifenolni spojevi; *Aronia melanocarpa*; *Malus domestica*;

Folien auf Stärkebasis mit eingearbeiteten Apfelschalen- und Aronia-Polyphenolen

Zusammenfassung

Ziel war es, biologisch abbaubare Folien auf Stärkebasis mit Wirkstoffen herzustellen und den Einfluss der Temperatur (80, 90, 99 °C), des Weichmachers (Glycerin 1, 2, 4 %) und der Einarbeitung von phenolischen Verbindungen aus Apfelschalen und Aronia auf die Eigenschaften der Folien zu untersuchen. Der hygroskopische Charakter von Glycerin beeinflusste die Folieneigenschaften. Mit der Erhöhung des Glycerinanteils nahmen der Wassergehalt, die Wasserlöslichkeit und die Wasserdampfdurchlässigkeit der Folien signifikant zu, während der Quellungsgrad und die Härte signifikant abnahmen (p<0,05). Die Temperatur hatte keinen signifikanten Einfluss auf die Folieneigenschaften. Phenolische Verbindungen aus Apfelschalen und Aronia erhöhten die Wasserlöslichkeit der Folien und den Gewichtsverlust in Wasser in einigen Fällen signifikant (p<0,05). Die Zunahme der Hydrophilie der Filme nach dem Zusatz von Phenolverbindungen könnte darauf hindeuten, dass dies die höhere Wasserlöslichkeit und den Gewichtsverlust in Wasser beeinflusst hat. Die Phenolverbindungen verringerten jedoch den Quellungsgrad der Folien, in einigen Fällen signifikant (p<0,05). Die dichtere Struktur der Folien mit dem Zusatz von Phenolverbindungen lässt darauf schließen, dass der Quellungsgrad dadurch abnahm. Alle Folien waren in Wasser biologisch abbaubar (Gewichtsverlust 18-38 %). Die Eigenschaften der stärkebasierten Folien müssen weiter untersucht und für die Verpackung von Lebensmitteln angepasst werden.

Schlüsselwörter: aktive Folien; biologisch abbaubare Folien; Phenolverbindungen; *Aronia melanocarpa*; *Malus domestica*

Películas a base de almidón con polifenoles de cáscara de manzana y aronia

Resumen

El objetivo fue desarrollar películas biodegradables a base de almidón con sustancias activas, y examinar la influencia de la temperatura (80, 90, 99 °C), el plastificante (glicerol en concentraciones de 1, 2 y 4 %) y la incorporación de compuestos fenólicos de cáscara de manzana y aronia en las propiedades de las películas. La naturaleza higroscópica del glicerol afectó las propiedades de las películas. Con el aumento en el contenido de glicerol, el contenido de agua, la solubilidad en agua y la permeabilidad al vapor de agua de las películas aumentaron significativamente, mientras que el grado de hinchamiento y la dureza disminuyeron significativamente (p<0,05). La temperatura no mostró una influencia significativa en las propiedades de las películas. Los compuestos fenólicos provenientes de la cáscara de manzana y la aronia incrementaron la solubilidad en agua y la pérdida de peso en agua de las películas, en algunos casos de forma significativa (p<0,05). Se sugiere que el aumento de la hidrofilicidad de las películas tras la adición de compuestos fenólicos afectó la mayor solubilidad y pérdida de peso en el agua. Sin embargo, los compuestos fenólicos disminuyeron el grado de hinchamiento de las películas, en algunos casos significativamente (p<0,05). Se sugiere una estructura más densa en las películas con la adición de compuestos fenólicos, lo que provocó una reducción en el grado de hinchamiento. Todas las películas fueron biodegradables en agua (pérdida de peso del 18 al 38 %). Es necesario continuar estudiando y ajustando las propiedades de las películas a base de almidón para su aplicación en el envasado de alimentos.

Palabras claves: películas activas, películas biodegradables, compuestos fenólicos, *Aronia melanocarpa*, *Malus domestica*

Pellicola a base di amido con composti polifenolici da buccia di mela e aronia

Riassunto

L’obiettivo era quello di produrre pellicole biodegradabili a base di amido con sostanze attive e di esaminare l’impatto della temperatura (80, 90, 99 °C), dei plastificanti (glicerolo 1, 2, 4%) e dei composti polifenolici della buccia di mela e aronia sulle proprietà delle pellicole. La natura igroscopica del glicerolo ha influenzato le proprietà della pellicola. Con l’aumento della percentuale di glicerolo, il contenuto di acqua, l’idrosolubilità e la permeabilità al vapore acqueo delle pellicole sono aumentati in modo netto, mentre il grado di rigonfiamento e la durezza sono diminuiti in modo significativo (p<0,05). La temperatura non ha avuto effetti significativi sulle proprietà della pellicola. I composti polifenolici della buccia di mela e aronia hanno aumentato la solubilità e la perdita di peso in acqua delle pellicole, in alcuni casi in modo significativo (p<0,05). Si potrebbe ipotizzare un aumento dell'idrofilicità delle pellicole dopo l'aggiunta di composti polifenolici, cui si devono la maggiore solubilità e la maggiore perdita di peso in acqua. Tuttavia, i composti polifenolici hanno ridotto il grado di rigonfiamento delle pellicole, in alcuni casi in modo significativo (p<0,05). L'aggiunta dei composti polifenolici, che ha causato una diminuzione del grado di rigonfiamento, suggerisce una struttura più densa delle pellicole. Tutte le pellicole erano biodegradabili in acqua (perdita di peso 18-38%). Le proprietà delle pellicole a base di amido per l'imballaggio alimentare devono essere, in ogni caso, ulteriormente studiate e adattate.

Parole chiave: film attivi; pellicole biodegradabili; composti polifenolici; *Aronia melanocarpa*; *Malus domestica*