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Fish gelatin films containing aqueous extracts from phenolic-rich fruit pomace

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ABSTRACT

The aim of the work was to study the feasibility of using aqueous extracts from rowanberry, blue-berried honeysuckle, and chokeberry pomace for the formulation of fish gelatin films with antioxidant and antimicrobial activity as well as improved mechanical and water barrier properties. The predominant phenolic components in rowanberry and chokeberry extracts were hydroxycinnamates, and in blue-berried honeysuckle extract anthocyanins. Although the gelatin film itself showed antioxidative activity, addition of blue-berried honeysuckle extract increased it 3-fold. Unlike the films containing 1.2 mL of extract, the films with increased extract volume possessed strong antimicrobial properties against *E. coli*, *P. fluorescens*, *S. aureus*, *L. innocua*. Films plasticized with glycerol at 15 and 17.5% did not increase the mechanical strength in the presence of all extracts tested, but at 20%, a positive effect of each extract on mechanical strength was observed. None of the extracts affected the water barrier properties of the films.

1. Introduction

Nowadays, there is not only a considerable interest in the use of natural polymers for environmentally friendly food packages as an alternative for non-biodegradable plastics, but also due to the possibility of obtaining active packaging materials. That latter can be achieved by incorporation into the polymer matrices natural additives displaying variety of valuable features, including antioxidant and/or antimicrobial properties.

The bioactive compounds can be extracted from many plant origins. The borage seeds and leaves (Gómez-Estaca, Giménez, Montero, & Gómez-Guillén, 2009b), oregano and rosemary (Gómez-Estaca, Bravo, Gómez-Guillén, Alemán, & Montero, 2009a; Gómez-Estaca, Montero, Fernández-Martín, Alemán, & Gómez-Guillén, 2009c), green tea (Hong, Lim, & Song, 2009; Li, Miao, Wu, Chen, & Hang, 2014), cinnamon, clove, star anise (Hoque, Benjakul, & Prodpran, 2011), ginger (Li et al., 2014), ginseng (Norajit, Kim, & Ryu, 2010), seaweed (Rattaya, Benjakul, & Prodpran, 2009) extracts rich in polyphenolic compounds, as well as various essential oils were incorporated into protein and polysaccharide films and their activity and functional properties were studied. By-products of agro-food industry can also be a source of bioactive compounds. Due to health benefits of fruit products, their consumption is steadily rising, creating a substantial amount of fruit by-products. Especially in the winemaking industry, a large mass of solid by-products is produced and some papers on the properties of polymeric films enriched with commercial extracts from grape seeds (Li et al., 2014; Sivarooban, Hettiarachchy, & Johnson, 2008) and wine grape pomace (Cerruti et al., 2011; Corrales, Han, & Tauscher, 2009; Deng & Zhao, 2011; Ferreira, Nunes, Castro, Ferreira, & Coimbra, 2014) have been published. Other fruit pomaces, for instance these from berries processing can also be used as source of bioactive compounds. According to Struck, Plaza, Turner, and Rohm (2016), the processing of berries into juice results in approximately 70 80% of target product and 20 30% of by-product. Due to the high level of polyphenolic compounds in berry pomaces (De Ancos, Colina-Coca, González-Peña, and Sánchez-Moreno (2015) they can be effectively used. However, reports on the films incorporated with them are rather scarce.

Polyphenolic compounds of various plant species include simple phenolic, phenolic acids, lignans, lignins, coumarins, flavonoids, stilbenes, flavonolignans, and tannins (Dewick, 2002). Polyphenolic composition of fruits, especially fruit berries, is different from that from other plant materials, as it is rich in bioactive polyphenols belonging to the anthocyanin group (Burdulis et al., 2009; Cisowska, Wojnicz, & Hendrich, 2011), which have been considered the most valuable components.

In the presence of plant extracts, mechanical and barrier characteristics of biopolymeric films can be changed as a result of interactions between biopolymer and polyphenolic compounds. Data on improving (Hong et al., 2009; Hoque et al., 2011; Sivarooban et al., 2008), worsening or on lack of changes (Gómez-Estaca et al., 2009b; Gómez-Estaca et al., 2009c; Gómez-Guillén, Ihl, Bifani,

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Silva, & Montero, 2007; Kim et al., 2006) of tensile strength of the films containing plant or herb extracts were reported. Different directions of changes of water vapour permeability (WVP) of these films were also evidenced (Gómez-Guillén et al., 2007; Hong et al., 2009; Hoque et al., 2011). Thus, in the formulation of active packaging films their functional properties must be taken in to account.

Waste from the food industry can constitute the source of polymers for food packages. Among proteins, gelatin obtained from fish offal like skins is very often used as the main component of polymer matrix (Alfaro, Balbinot, Weber, Tonial, & Machado-Lunkes, 2015; Staroszczyk, Pielichowska, Sztuka, Stangret & Kołodziejska, 2012). However, due to the hydrophilic character of gelatin, the functional properties of gelatin films are poorer than of those obtained from traditional synthetic polymers (Krochta & de Mulder-Johnston, 1997), so their application as packaging materials is still limited.

The purpose of the presented work was to study the possibility of using extracts from the pomace of some berry fruits for the formulation of gelatin films with antioxidant activity as well as improved mechanical and water barrier properties. It has been assumed that interactions of gelatin with polyphenolic compounds from fruit extracts will exert a positive effect on the functional properties of the films.

2. Materials and methods

2.1. Materials

Fish gelatin was obtained from Norwegian farmed salmon skins as described by Kołodziejska, Skierka, Sadowska, Kołodziejski, and Nieciowska (2008). Rowanberry (*Sorbus aucuparia* L.), blue-berried honeysuckle (*Lonicera caerulea* L. var. *edulis*) and chokeberry (*Aronia melanocarpa*) came from local plantations. HPLC grade methanol, formic acid (98 100%) and Folin Ciocalteu phenol reagent (FC) were obtained from Merck (Darmstadt, Germany). Quercetin-3-*O*-galactoside, cyanidin-3-*O*-glucoside, L-ascorbic acid, 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (Trolox), 2,2 -azinobis(ethyl-2,3-dihydrobenzothiazoline-6-sulfonic acid) diammonium salt (ABTS) and 2,2-diphenyl-1-picrylhydrazyl (DPPH) were purchased from Sigma-Aldrich (Saint Louis, MO, USA), and chlorogenic acid from Extrasynthese (Geney Cedex, France).

To determine the antimicrobial activity of the films, the following bacterial strains were used: *Escherichia coli* K-12 PCM 2560 (NCTC 10538) and *Staphylococcus aureus* PCM 2054 (ATCC 25923) from Polish Collection of Microorganisms, Ludwik Hirszfeld Institute of Immunology and Experimental Therapy of the Polish Academy of Sciences (Wrocław, Poland), *Pseudomonas fluorescens* WSRO 121 from the Collection of Dairy Cultures of Department of Microbiology, University of Warmia and Mazury (Olsztyn, Poland), and *Listeria innocua* DSM 20649 from the German Collection of Microorganisms and Cell Cultures (Braunschweig, Germany).

2.2. Preparation and modification of films

2.2.1. Preparation of aqueous extracts from fruit pomaces

To obtain fruit extracts, a typical home juice extractor (Omega, Harrisburg, PA, USA) was used. Fruit berries were washed, placed in the juice extractor operating according to the producer's manual, and after squeezing out the juice, the fruit pomaces were freeze-dried and granulated using laboratory grinder (ZBPP, Poland). The efficiency of juice pressing depended on the type of fruit tissue and was about 46, 78, and 57% for rowanberry, blue-berried honeysuckle and chokeberry, respectively. Then, the fruit pomaces were added to water to the final concentration of 0.2 g per 1 mL of water, stirred during 20 min at 40 °C, and centrifuged at 7730 × *g* for 10 min at 20 °C to remove water-insoluble residue. The dry weight of the aqueous extracts from fruit pomaces was determined according to the Association of Official Analytical Chemists methods (AOAC, 1990) and it was 10.1, 6.4 and 4.4% (w/w) for rowanberry, blue-berried honeysuckle and chokeberry, respectively. The obtained aqueous extracts from fruit pomaces were kept in sterile sample tubes and stored in a refrigerator at 4 °C.

2.2.2. Determination of antioxidant activity of fruit pomace extracts by spectrophotometric methods

The colorimetric determination of antioxidant activity was performed by the standard methods employing ABTS, DPPH, and FC indicators as described earlier (Kusznierewicz et al., 2012). The antioxidant activity of fruit pomace extracts was calculated based on standard lines generated for Trolox and expressed as Trolox equivalents (TE) (mg of TE per 1 mL of extract).

2.2.3. On-line profiling of antioxidants in fruit pomace extracts by HPLC with post-column derivatisation

For antioxidants analyses, the HPLC-DAD system (Agilent Technologies, Wilmington, DE, USA) was connected with a Pinnacle PCX Derivatisation Instrument (Pickering Laboratories Inc., Mountain View, California, USA) and a UV VIS detector (Agilent Technologies, Wilmington, DE, USA). Chromatographic separation was carried out using Agilent Eclipse XDB, C-8, 4.6 × 150 mm, 3.5 m column. The mobile phase contained aqueous 4.8% v/v formic acid (A) and methanol (B). The linear gradient applied was 5 50% B in 30 min at a flow rate of 0.8 mL/min. The injection volume of all samples was 4 L. The post-column derivatisation with ABTS reagent was done according to Kusznierewicz, Piasek, Bartoszek, and Namiesnik (2011). The percentage contribution of the particular separated analyte to the antioxidant activity of extracts was estimated on the assumption that 100% is the sum of the negative peak areas integrated in chromatograms obtained after derivatisation with ABTS.

2.2.4. Qualitative and quantitative determination of antioxidants in fruit pomace extracts by HPLC-DAD-MS

The parameters of resolution of phytochemicals were identical with those described for on-line antioxidants profiling. MS parameters were described in Kusznierewicz et al. (2012). Individual compounds were identified by comparing their retention times and UV-VIS and MS spectra with those for standards or on the basis of available literature data. The quantification of the analytes for which standards were available was performed with external calibration curves, whereas that for analytes for which standards were lacking by reporting the measured chromatographic area in the calibration equation of the reference standards (hydroxycinnamates were quantified as chlorogenic acid, anthocyanins were quantified as cyanidin-3-*O*-glucoside; flavonols were quantified as quercetin-3-*O*-galactoside).

2.2.5. Film preparation

Two types of film-forming dispersions with addition of fruit pomace aqueous extracts were prepared. In the first approach, extracts from three different pomaces were added in equal volume (1.2 mL), and in the second approach, different volumes of each extract (14.0 mL from rowanberry, 7.5 mL from blue-berried honeysuckle and 10.0 mL from chokeberry) were added to the gelatin solution containing 1 g of protein. In the former case the amount of extract addition provided a different contribution of the antioxidant activity to the film, it was 6, 9, and 7.2 mg of TE, and in the latter case the

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amount of extract addition was calculated ensuring the same input of antioxidant activity to the film, amounting to 40 mg of TE. In both cases distilled water was added to get 20 mL of final volume of film-forming dispersion, which then was poured on a polyester surface and dried at room temperature for 24 48 h. Selected films were plasticized with glycerol at a concentration of 15, 17.5, and 20% of the substrate mass. The average thickness of the films was 0.0603 ± 0.0009 mm.

2.3. Determination of film properties

2.3.1. Antioxidant activity

The stock solution of ABTS was prepared in aqueous $Na_2S_2O_8$ solution (2.45 mmol/L) to reach a concentration of 7 mmol/L and left in the dark at ambient temperature. Under such conditions, the concentration of ABTS radical reaches a maximum after 6 h and is stable for >2 days. The stock solutions of ABTS were diluted before measurements with water to display an absorbance of 0.7 at 734 nm. The diluted ABTS solution (4.5 mL) was mixed with either solutions of Trolox (30 L) to generate standard line or pieces of films (10 mg), centrifuged at 3005 × *g* for 10 min at 4 °C (Thermo Scientific Heraeus Megafuge, Karlsruhe, Germany) after 20 min, and the absorbance was measured in a cuvette at 734 nm with the use of a spectrophotometer (Jenway, 6305, Essex, UK). The antioxidant capacity of the films studied was expressed as mg of TE per each film prepared.

2.3.2. Mechanical properties

Tensile strength (TS) and elongation at break (E) of the films were determined according to ASTM method D 882 00 (ASTM, 2001) with a model 5543 Instron Universal Testing Machine (Instron Co., an ITW Company, Canton, MA, USA). Initial grip separation and cross-head speed were set at 50 mm and 10 mm/min, respectively. TS was calculated by dividing the maximum load by the initial cross-sectional area of the sample and expressed in MPa. E was calculated as a ratio of the elongation at the point of sample rupture to the initial length of a sample as a percentage. Strips of film samples (15 by 100 mm) were conditioned for 48 h at 25 °C and 50% relative humidity (RH) before determination of TS and E.

2.3.3. Water vapour permeability (WVP)

WVP of each film was determined according to the American Society for Testing and Materials (ASTM) method E 96 95 (ASTM, 1995). The films were conditioned for 24 h at 25 °C and 50% RH before determination. The film samples were mounted on cups filled with water. The cups were placed, at 25 °C and 50% RH in a desiccator. The weight of the cups was measured at 1 h intervals during 8 h. Simple linear regression was used to estimate the slope of weight loss vs. time plot.

WVP was calculated from the formula:

$$WVP = (WVTR \times L)/\ p,$$

where water vapour transmission rate (WVTR) is the slope/film area ($g/m^2 \cdot h$), L is the film thickness (mm), and p is the partial water vapour pressure difference (kPa) between the two sides of the film.

2.3.4. Solubility in water

Before the solubility measurements, the film squares 30 × 30 mm were dried until constant weight. Then the film squares were immersed in 10 mL of distilled water and the system was shaken in a water bath (GLS Aqua Plus, Grant Instrument, Cambridge, UK) at 40 strokes/min for 24 h at 25 °C. The samples were then filtered by cotton wool and 5 mL of filtrate was weighed, and dried at 105 °C. The solubility of the films was calculated by applying the formula:

$$R = m_r/m_f \text{ x } 100\%$$

where R is the solubility of the film [%], m_f is the initial weight of the film sample [mg], and m_r is the weight of solubilized sample [mg].

2.3.5. Antimicrobial activity

The bacterial cultures in stationary phase were prepared by inoculating 100 mL of trypticase soy broth with 100 L liquid culture (at stationary phase of growth) and incubating at 37 °C (*E. coli, S. aureus*) or at 28 °C (*L. innocua, P. fluorescens*) for 24 h with shaking.

Determination of antimicrobial activity of films was performed according to Ko, Janes, Hettiarachchy, and Johnson (2001). 15 L of bacterial suspension (10^5 CFU/g) was placed on film discs (22 mm in diameter and 0.02 g in weight) and these discs were incubated for 24 h at ambient temperature. After the incubation, the film discs were placed into sterile plastic tubes, diluted with PBS, and homogenized for 1 min at 10000 rpm. The solution was decimally diluted with PBS and plated in duplicate on plate count agar. The plates were incubated at 37 °C (*E. coli, S. aureus*) and at 28 °C (*P. fluorescens, L. innocua)* for 24 h, and CFU/g was then determined.

2.4. Statistical analysis

The data obtained were statistically analyzed by one-way analysis of variance to determine significant differences among samples, using STATGRAPHICS version 2.1 (Statistical Graphics Corporation, USA). Significance was accepted at $p < 0.05$.

3. Results and discussion

3.1. Characterisation of the antioxidant composition and activity of fruit pomace extracts

Plant pomace is usually composed of remaining carbohydrates, dietary fibre, and small amount of proteins. Besides, numerous studies have shown that fruit pomace is also a rich source of polyphenolic compounds, therefore making them a good source of natural antioxidants (De Ancos et al., 2015).

Three standard tests were applied to assess the antioxidant activity of aqueous extracts of pomace obtained from rowanberry, blue-berried honeysuckle, and chokeberry, namely ABTS assay, DPPH assay and FC assay (Fig. 1). The extract from pomace of blue-berried honeysuckle revealed the highest, and that from rowanberry the lowest, antioxidative activity expressed as mg of TE per 1 mL of extract. It has been already shown that extraction of polyphenolic compounds from pomace is extremely affected by the solvents used, and these organic ones, such as ethanol, methanol and acetone, are more effective than others (Boeing et al., 2014; Spigno & De Faveri, 2007; Spigno Tramelli & De Faveri, 2007). The organic solvents, however, have not been widely used by fruit juice manufacturers due to safety concerns, processing costs and consumer reluctance towards food products exposed to chemicals. Hence, in the present study, water as extraction medium was proposed. Although water decreased the yield and antioxidant power of the obtained extracts, and for this reason the determined antioxidants activities of extracts were lower than these presented in literature (Oszmiański & Lachowicz, 2016), such approach seems to by a more environmentally friendly to extract the antioxidants from berry pomace than the use of organic solvents.

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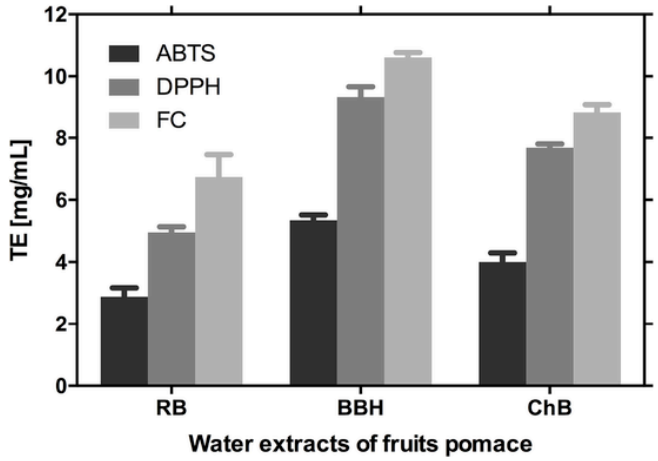

Fig. 1. Total antioxidant activity of rowanberry (RB), blue-berried honeysuckle (BBH) and chokeberry (ChB) pomace aqueous extracts determined by ABTS, DPPH and FC spectrophotometric tests and expressed as mg of Trolox equivalents per mL of extract. The results are the mean ± SD of three independent determinations.

Phenolics compounds in aqueous extracts from rowanberry, blue-berried honeysuckle, and chokeberry pomace were analyzed by HPLC-DAD-MS. The chromatograms of separated compounds, recorded at 270 nm, present in the extracts are shown in the upper panel of Fig. 2, and in the bottom panel, profiling by post-column derivatisation, are revealed which of the detected components are redox active. The HPLC-DAD analysis and UV -VIS spectra revealed the presence of vitamin C, hydroxycinnamates, flavonols, as well as anthocyanins in berries extracts samples. The peaks exhibiting high UV-absorbing properties were then identified by LC-MS, based on their mass spectra and available literature data (Kusznierewicz et al., 2012; Kylli et al., 2010). Mass spectra of the phenols detected in the extracts provided data about their molecular weights and constitutive units. In the negative ion mode, mass spectra of polyphenols usually showed molecular ions as a main peak $[M\text{-}H]^-$ (Table 1), while in the positive ionisation, mass spectra revealed fragmentation patterns characterized either by a major molecular ion peak $[M+H]^+$ or sodium adduct $[M+Na]^+$. Additionally, in the case of almost all glycosides, the loss of sugar moiety was observed (Table 1). These assignments were then confirmed by comparison of HPLC-DAD retention times and UV spectra, and with those of authentic standards when available. In Table 1 the content of major compounds detected in pomace extracts are also presented, and in Fig. 2, the abundance of individual groups of polyphenols are illustrated as bar graphs. In the case of extract from rowanberry pomace chlorogenic acids were the dominating constituent, their content amounted to 0.61 mg/mL. Another group were flavonols, mainly quercetine glycosides, content of which was 0.20 mg/mL. The data reported in available literature are also showing that the main phenolics in rowanberry fruits are hydroxycinnamates and flavonols (Kylli et al., 2010). In the case of blue-berried honeysuckle extract anthocyanins were the predominant phenolic component, while in the case of extract from chokeberry pomace the content of this group of flavonoids was two times smaller. In turn, the content of chlorogenic acids was about 3 times higher in chokeberry than blue-berried honeysuckle extract, amounting to 0.35 and 0.10 mg/mL, respectively. The amount of flavonols was similar in these two extracts and ranged between 0.10 and 0.15 mg/mL. These data calculated on dry weight of pomace present lower levels of phenolics than former findings (Kylli et al., 2010; Oszmiański & Lachowicz, 2016; Struck et al., 2016). The observed differences probably result from different medium applied for extraction, as in the presented results, unlike as in those referred, the water was used for the extraction of phytochemicals. The lack of any organic solvent in extraction medium probably prevented the isolation of less polar phenolics from the pomace. Especially anthocyanins could remain in the pomace to a great extent because they are less water soluble than other polyphenols.

Over the past two decades, a number of analytical methods measuring total antioxidative activity have been developed, one of them

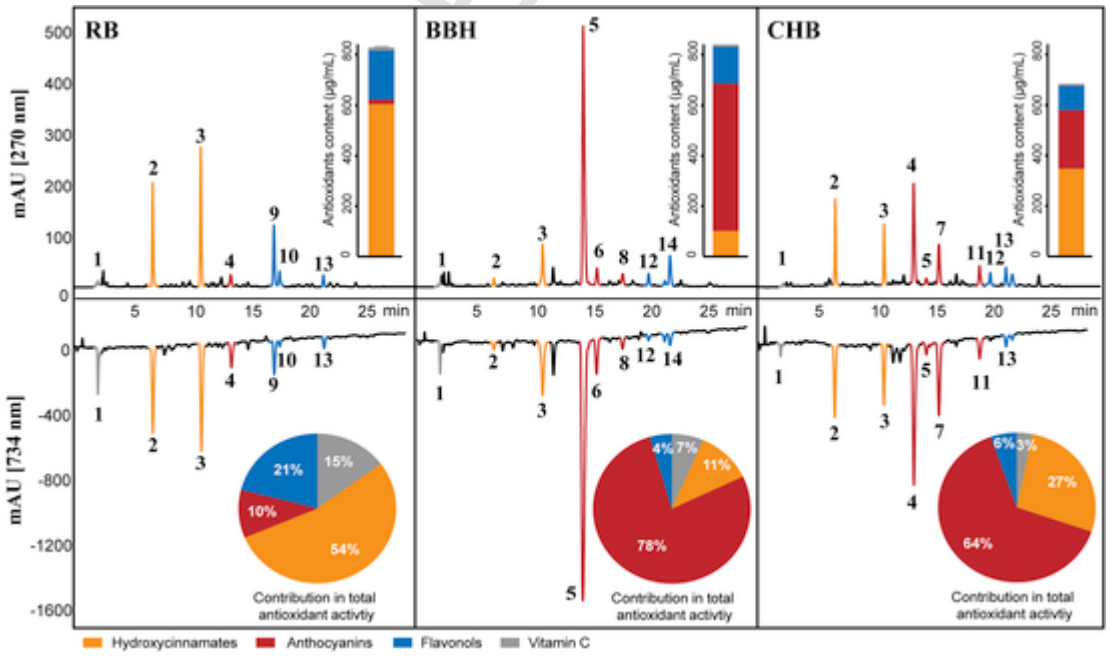

Fig. 2. Sample of HPLC-DAD chromatograms of rowanberry (RB), blue-berried honeysuckle (BBH) and chokeberry (ChB) pomace aqueous extracts (top chromatograms at 270 nm) along with profiles of antioxidants detected online with ABTS reagent (bottom chromatograms at 734 nm). The content of major groups of bioactive compounds (calculated as g of compound per mL of extract) combined with contribution of each group to the antioxidant activity (% of total) were presented as bar and pie graphs, respectively. For identity of peaks, see Table 1. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

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Table 1
Composition and content of antioxidants detected in aqueous extracts from rowanberry (RB), blue-berried honeysuckle (BBH) and chokeberry (ChB) pomace compiled with chromatographic and spectrometric data. The results are the mean ± SD of three independent determinations.

Peak number	Rt [min]	Positive ionisation (m/z)	Negative ionisation (m/z)	Mw	Name of compound	Content in fruit pomace aqueous extracts (g/mL)		
						RB	BBH	ChB
1	2.3	177 [M+H]	175 [M-H]	176	Vitamin C	11.00 ± 0.91	9.41 ± 0.81	0.03 ± 0.01
2	6.6	355 [M+H]	353 [M-H]	354	3-*O*-caffeoylquinic acid	237.34 ± 13.23	15.89 ± 1.21	191.92 ± 11.12
3	11.1	355[M+H]	353 [M-H]	354	5-*O*- caffeoylquinic acid	372.13 ± 22.21	87.64 ± 5.12	158.03 ± 9.22
4	13.7	287 [M + H-Gal], 449 [M+H]	447 [M-H]	448	Cyanidin-3-*O*-galactoside	21.19 ± 2.02	nd	177.02 ± 10.14
5	14.6	287 [M + H-Glu], 449 [M+H]	447 [M-H]	448	Cyanidin-3-*O*-glucoside	nd	544.66 ± 32.11	10.17 ± 1.55
6	15.8	287 [M + H-Rut], 595 [M+H]	593 [M-H]	594	Cyanidin-3-*O*-rutinoside	nd	33.88 ± 3.24	nd
7	15.9	287 [M + H-Ara], 419 [M+H]	417 [M-H]	418	Cyanidin-3-*O*-arabinoside	nd	nd	24.93 ± 1.45
8	17.1	301 [M + H-Glu], 463[M+H]	461 [M-H]	462	Peonidin-3-*O*-glucoside	nd	8.95 ± 0.56	nd
9	17.4	303 [M + H-diGlu], 649 [M+Na]	625 [M-H]	626	Quercetin-di-hexoside	123.51 ± 10.25	nd	nd
10	17.9	303 [M + H-diGlu], 649 [M+Na]	625 [M-H]	626	Quercetin-di-hexoside	29.35 ± 1.91	nd	nd
11	19.5	287 [M + H-Xyl], 419 [M+H]	417 [M-H]	418	Cyanidin-3-*O*-xyloside	nd	nd	24.81 ± 2.13
12	21.7	303 [M + H-Pen-Hex], 619 [M+Na]	595 [M-H]	596	Quercetin-hexoside-pentoside	5.28 ± 0.33	30.26 ± 2.32	31.63 ± 2.61
13	22.3	303 [M + H-Gal], 487 [M+Na]	463 [M-H]	464	Quercetin-3-*O*-galactoside	26.97 ± 1.70	36.51 ± 3.21	33.67 ± 2.88
14	24.6	303 [M + H-Rut], 633 [M+Na]	609 [M-H]	610	Quercetin-3-*O*-rutinoside	10.95 ± 1.01	81.15 ± 7.18	33.10 ± 3.11

nd - Not detected.

is based on the ability of an antioxidant to quench ABTS radicals. The same chemical reaction has been exploited for online HPLC-coupled method that enables profiling of antioxidants in complex mixtures following their chromatographic separation from the matrix. This approach has been applied for the detection of antioxidant phytochemicals in chromatographic profiles obtained for pomace extracts studied (Fig. 2, bottom chromatograms). The occurrence of antioxidants in eluate leads to negative peaks at 734 nm. Chromatographic profiling coupled with chemical post-detection not only reveals the individual reducing analytes, but also enables quantitation of their input into the antioxidant potential of the sample. In Fig. 2, the input of individual groups of polyphenols into the antioxidant activity of fruit pomace extracts are presented as a pie graph. In the case of rowanberry extract hydroxycinnamates were the predominant antioxidants as they provided 54% of contribution to the total antioxidant activity, while in the case of blue-berried honeysuckle and chokeberry extracts the main contributors to the total antioxidant activity were anthocyanins, 78% and 64%, respectively. The lowest impact on antioxidant activity of extracts had anthocyanins in rowanberry, flavonols in blue-berried honeysuckle, and vitamin C in chokeberry pomace.

3.2. Antioxidant properties of gelatin films containing aqueous extracts from fruit pomace

The antioxidant activity of films studied was determined with the use of spectrophotometric test and ABTS reagent prepared in water solution. In this method the samples of gelatin films were completely dissolved without any precipitation that could interfere with the measurement of absorbance of ABTS reagent. This approach enables to estimate the antioxidant activity of compounds derived from fruit extracts incorporated to the films as well as antioxidant potential of gelatin solely. In the case of alternative spectrophotometric reagents, i.e. Folin Ciocalteu or DPPH, addition of gelatin films direct to the reaction mediums resulted in problems in measuring the absorbance. To omit these problems, some authors suggest to prepare the methanolic extracts from films, and then to add them to the reaction solution (Siripatrawan & Harte, 2010; Tongnuanchan, Banjakul & Prodpran, 2012). The conduct that experiment in such a manner, however, enables only the determination of the antioxidant capacity of plant phytocomplex extracted with an organic solvent, thus eliminating the antioxidant activity exhibited by the material from which the film is made, for example gelatin.

The gelatin films without the extracts showed relatively high antioxidative activity (Fig. 3). Such activity of gelatin films, including fish and squid skin gelatin films, was found by other authors (Gómez-Estaca et al., 2009a; Gómez-Estaca et al., 2009c; Li et al., 2014). Addition of 1.2 mL of aqueous extract from rowanberry pomace to film-forming dispersion did not confer extra antioxidant capacity to the gelatin films. The antioxidative activity of gelatin films containing this extract was similar to that from gelatin films without extract (Fig. 3 A). Slight increase in antioxidative capacity was observed in the case of films containing extract from chokeberry pomace, but the antioxidative activity of films with blue-berried honeysuckle extract was about 3 times higher than that of the control sample. Furthermore, only in this latter case, the theoretical antioxidant potential was similar with that determined by means of ABTS test (Fig. 3 A). The lack of clear increase in antioxidative properties of gelatin films with extracts from rowanberry and chokeberry pomace can point to the instability of some polyphenols during

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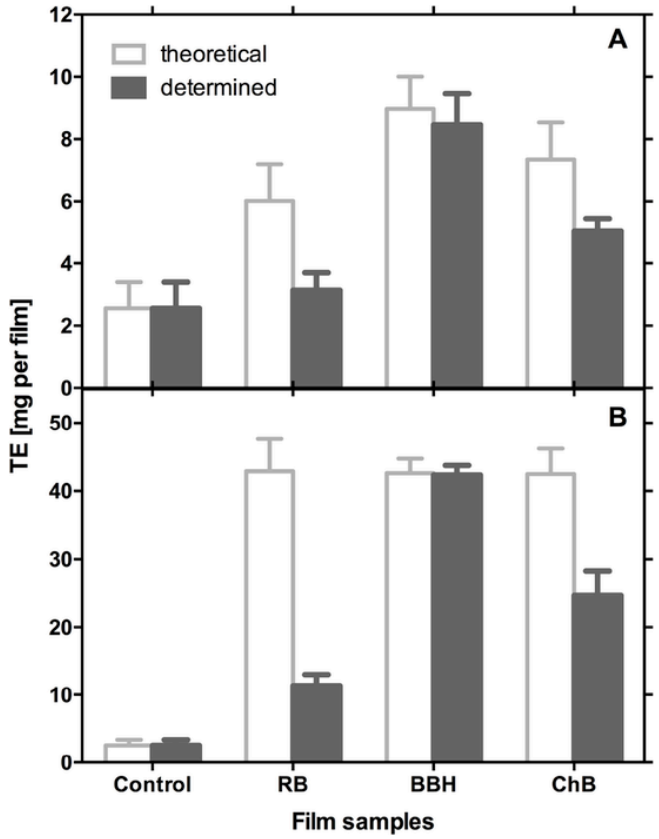

Fig. 3. The antioxidant activity of gelatin films without (Control) and with addition of aqueous extracts from rowanberry (RB), blue-berried honeysuckle (BBH) and chokeberry (ChB) pomace determined by ABTS method (grey bars) and calculated theoretically as a sum of activities of gelatin and extracts (white bars). The antioxidant activity was expressed as mg of Trolox equivalents per each film studied. Panel A refers to film samples with addition of equal volume of fruit extracts (1.2 mL) and panel B refers to film samples with addition of fruit extracts with the same amount of Trolox equivalents (40 mg).

preparation of the films. On the other hand, it can indicate that some compounds included in these extracts could be engaged in interactions with the gelatin matrix, hence these extracts do not impart antioxidative activity to gelatine films. So, it was important to check the antioxidative potential of films formed from film-forming dispersion enriched with higher concentration of fruit pomace extracts and, additionally, added in amount that will provide the same value of antioxidative activity of 40 mg TE per each film. In this case significant increase in antioxidative potential of films containing blue-berried honeysuckle and chokeberry extract was evident (Fig. 3 B). Such clear effect was not apparent for film containing the rowanberry extract. The calculated theoretically antioxidant activity was similar to those determined in ABTS test again only for films with blue-berried honeysuckle extract. In the case of films with rowanberry and chokeberry extracts the determined values of antioxidant activity were much lower that these theoretical. However, these extracts differ from blue-berried honeysuckle extract in phenolics profile by higher levels of chlorogenic acids (Table 1). Furthermore, in the case of extract from rowanberry pomace, hydroxycinnamic acids were not only the dominating constituent but they also contributed to the highest level of the total antioxidant activity of that extract (Fig. 2). In the chokeberry extract hydroxycinnamic acids were dominating constituent, but the main contributors to the total antioxidant activity were not those acids but anthocyanins. In turn, in the extract from blue-berried honeysuckle pomace, anthocyanins were the predominant phenolic component as well as predominant antioxidants. As has been reported previously (Nallamuthu, Devi, & Khanum, 2015) due to the thermal instability of the chlorogenic acids thermal processing may reduce their total content by up to 90%, as in the case of the process of roasting coffee beans (Mills, Oruna-Concha, Mottram, Gibson, & Spencer, 2013). The antioxidant property of chlorogenic acid is attributed to its double bond conjugated catechol structure of the phenyl ring. High temperatures cause a breakage of the carbon carbon bonds in its molecules, resulting in their isomerization and degradation. Besides that, other chemical transformations may also occur, such as the formation of a lactone ring due to dehydration and formation of an intramolecular bond (Komes & Bušić, 2014). Hence, unlike the film with the extract from blue-berried honeysuckle, determined values of antioxidant activity of films with rowanberry and with chokeberry extract were much lower than those theoretical. However, that value of the latter films was higher than the former, as in that case anthocyanins instead of hydroxycinnamates were the main contributors to the total antioxidant activity.

3.3. Mechanical properties of gelatin containing fruit pomace aqueous extracts

Modification of gelatin films with blue-berried honeysuckle and chokeberry pomace extracts increased TS of unplasticized films by 38 and 23%, respectively (Table 2). Such effect was not observed in the case of gelatin films with extract from rowanberry pomace. Therefore, it can suggest that interaction of gelatin with anthocyanins included in extracts of blue-berried honeysuckle and chokeberry pomace improved the mechanical strength of films with those extracts.

All films, with and without extracts, had low elongation at break and plasticization of the material was necessary.

The incorporation of fruit pomace extracts into gelatin films plasticized with glycerol at concentration of 15 and 17.5% did not increase their TS or even decreased it, while at glycerol concentration of 20% positive effect of extracts on mechanical strength was observed in the case of all tested extracts. The film with extract from blue-berried honeysuckle pomace had the highest TS, but its flexibility was very low. The moderate mechanical properties, TS as well as E, characterized films with extract from rowanberry and chokeberry pomace. Some published data show improving of mechanical strength of protein or polysaccharide films with added extracts from plant material (Hong et al., 2009; Hoque et al., 2011; Siripatrawan & Harte, 2010; Sivarooban et al., 2008; Wu et al., 2013). According to these authors such effect is a result of polymer crosslinking with polyphenols via hydrogen bonds. Hydrophobic interactions are also taken in to account in the case of protein films and polyphenolic compounds (Hoque et al., 2011; Rattaya et al., 2009). As reported Siripatrawan and Harte (2010), in the chitosan films containing green tea extract apart of hydrogen bonds, covalent bonds could also be formed. On the other hand, lack changes of mechanical strength of polysaccharide and protein films, and even its decrease in presence of plant extracts, was also observed (Ferreira et al., 2014; Gómez-Estaca et al., 2009c, 2009; Gómez-Guillén et al., 2007; Kim et al., 2006; Li et al., 2014; Norajit et al., 2010; Wang et al., 2015). According to Gómez-Estaca et al. (2009b) and Li et al. (2014), the decrease of mechanical strength of gelatin films with extracts of polyphenols results from the weakening (by polyphenols) of protein-protein interactions that stabilize the protein network. Thus, the direction and stage of TS changes can depend on the origin of the extracts containing a diversity composition of polyphenolic compounds with different ability to interact with polymers as well as on their concentration in the film-forming solution.

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Table 2
Effect of aqueous extract from rowanberry (RB), blue-berried honeysuckle (BBH), and chokeberry (ChB) pomace on the functional properties of unplasticized and plasticized gelatin films (TS- mechanical strength, E elongation at break, WVP- water vapour permeability, R-solubility).

Aqueous extract of fruit pomace	Concentration of glycerol [%]												
	0		15		17,5		20		0	15	17,5	20	0
	TS*	E*	TS*	E*	TS*	E*	TS*	E*	WVP [g ^{x}mm(kPa ^{x}h ^{x}m ^{2}) ^{1}]**				R [%]**
without extract	55.4 ^{bA}	1.2 ^{aA}	35.6 ^{cAB}	7.2 ^{bA}	55.4 ^{dB}	2.1 ^{aA}	7.1 ^{aA}	49.8 ^{cC}	1.08 ± 0.06 ^{abAB}	1.10 ± 0.06 ^{bA}	1.23 ± 0.04 ^{aA}	1.26 ± 0.05 ^{cA}	87.9 ± 1.32 ^{a}
RB	59.3 ^{cA}	2.3 ^{aB}	30.4 ^{aA}	42.7 ^{cC}	33.8 ^{aA}	20.8 ^{bC}	44.6 ^{bC}	15.7 ^{bB}	0.99 ± 0.08 ^{aA}	1.11 ± 0.06 ^{aA}	1.09 ± 0.05 ^{aA}	1.30 ± 0.02 ^{bA}	81.5 ± 6.52a
BBH	76.3 ^{cC}	2.6 ^{aB}	42.2 ^{aB}	4.6 ^{bA}	60.1 ^{cB}	5.3 ^{bAB}	50.3 ^{bC}	5.0 ^{bA}	1.23 ± 0.03 ^{aB}	1.14 ± 0.04 ^{aA}	1.22 ± 0.09 ^{aA}	1.23 ± 0.09 ^{aAB}	87.8 ± 1.35 ^{a}
ChB	68.2 ^{bBC}	2.5 ^{aB}	31.5 ^{aA}	33.5 ^{cB}	36.7 ^{aA}	10.3 ^{bB}	37.9 ^{aB}	13.9 ^{bB}	0.96 ± 0.03 ^{aA}	1.02 ± 0.09 ^{abA}	1.25 ± 0.03 ^{cA}	1.12 ± 0.05 ^{bcB}	89.3 ± 1.79 ^{a}

*and ** Mean value of 14 and 3, respectively, measurements. The values for columns (A-C) and for rows (a-d) followed by different letters differ significantly ($p < 0.05$).

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3.4. WVP and the solubility of gelatin films with fruit pomace aqueous extracts

The data presented in Table 2 show that none of the investigated extracts decreased WVP of unplasticized films. In films plasticized with glycerol at concentration of 20%, small increase of water barrier properties exerted chokeberry extract, the WVP of the film with this extract decreased by about 10% in comparison to plasticized films without the extract. The lack of changes in the WVP value was also reported for fish gelatin films with grape, ginger and gingko leaf (Li et al., 2014), oregano and rosemary (Gómez-Estaca et al., 2009c), and borage extracts (Gómez-Estaca et al., 2009b). In turn, Norajit et al. (2010) observed the increase in WVP of alginate films containing ginseng extract. However, some authors reported improving of water barrier properties of gelatin films in the presence of plant extracts (Gómez-Guillén et al., 2007; Hong et al., 2009; Hoque et al., 2011; Li et al., 2014; Rattaya et al., 2009). Siripatrawan and Harte (2010) revealed even a three times reduction in the WVP value of chitosan films with green tea extract, though in the case of fish gelatin films, the effect of such extract was much lesser, a decrease of WVP did not excide 20 30% (Hong et al., 2009; Li et al., 2014). The high decrease in the WVP value was reported for chitosan film with *Lycium barbarum* fruit extract (1:1, wt), a decrease of WVP in this case amounted to 40% (Wang et al., 2015), and for methyl cellulose films containing extracts from maqui berry fruit (1:0.3, wt.), a decrease of WVP in this case amounted to 55% (De Dicastillo, Rodríguez, Guarda, & Galotto, 2016). Certainly, many factors may influence the barrier properties of films, including type of polymer matrix, composition of polyphenols and their concentrations in the extract resulting from the origin of the plant material and conditions used in preparation of this extract. As was found by Gómez-Guillén et al. (2007), the direction of WVP changes of films can even depend on the ecotype of the plant from that bioactive compounds were obtained. The authors observed an increase in the WVP value of tuna-fish skin gelatin film with added aqueous extract from murta leaves ecotype Soloyo Grande by 33%, while from ecotype Soloyo Chico the decrease by 15%.

The fruit pomace aqueous extracts did not decrease the water solubility of the films (Table 2). The solubility of control film amounted to 88% and slightly deceased only in the presence of rowanberry extract; however, that difference was not statistically significant. Likewise, Hoque et al. (2011)noted only very small decrease in solubility fish skin gelatin films, from 96 to 92% when oxidized herb extracts were used. In turn, addition of oregano and rosemary extracts increased even two times the water solubility of fish gelatin films (Gómez-Estaca et al., 2009c). A slight increase in solubility showed also chitosan films with addition of grape pomace extract (Ferreira et al., 2014) and alginate films with addition of ginseng extract (Norajit et al., 2010). On the other hand, Wang et al. (2015) found that the water solubility of chitosan films with *Lycium barbare* fruit extract (0.4:0.6, wt) was decreased from 100 to 25%. Next, grape seed, ginger, gingko leaf and green tea extracts films did not reduce the water solubility of fish gelatin at 25 °C. At that temperature the solubility of control film amounted to 18%, while at 85 °C the solubility of films with ginger and grape seed extracts (95% of proanthocyyanidins) decreased from 74% to 52 and 45%, respectively (Li et al., 2014). So, the results obtained in the presented work and in the works of other authors confirm the statement mentioned above that the functional properties of films with bioactive compounds of plant origin are affected by many factors.

3.5. Antimicrobial properties of gelatin films with fruit pomace aqueous extracts

The data presented in Table 3 show that due to too low content of polyphenolic compounds, all films containing fruit pomace extracts in amount of 1.2 mL per film did not possess antimicrobial properties against *E. coli*, *P. fluorescens*, *S. aureus*, and *L. innocua*, when the test based on determination of reduction of the cells in bacterial population was used. Sivarooban et al. (2008) found that soy proteins films incorporated with grape seed extracts also did not affect surviving of *E. coli* O157:H7 and *Salmonella enterica* ser. Typhimurum. The authors noted some reduction in the case of Gram-positive *Listeria monocytogenes*, the number of bacteria decreased by 0.8 log cycle. On the other hand, antimicrobial properties of films with grape pomace extract against of *E. coli* and *L. innocua* were reported in the case of using of the test based on determination of bacterial growth inhibition (Deng & Zhao, 2011). Next *Gelidium corneum*-gelatin films with grapefruit seed extract decreased the number of *E. coli* O157:H7 and *L. monocytogenes* by about 2 and 3.3 log cycles, respectively (Hong et al., 2009). Lesser effect the authors observed for films containing green tea extract, reduction of both bacteria genera did not excide 1 log cycle.

When the content of polyphenolic compounds blue-berried honeysuckle and chokeberry pomace aqueous extracts in gelatin films increased, strong antimicrobial properties against Gram-negative *E. coli* and *P. fluorescens* and Gram-positive *S. aureus* and *L. innocua* was observed. The number of these bacteria decreased about 4 7 log cycles. Bacteria *S. aureus* were found to be more resistant to the gelatin films with both extracts than the others (Table 3). Antimicrobial activity of gelatin films with rowanberry pomace extract added at higher concentration was not tested due to their poor mechanical

Table 3
The antimicrobial activity of gelatin films with addition of aqueous extract from rowanberry (RB), blue-berried honeysuckle (BBH), and chokeberry (ChB) pomace against Gram-negative *E. coli* and *P. fluorescens* and Gram-positive *S. aureus* and *L. innocua.*

Aqueous extract of fruit pomace	Log cfu/mL [a]							
	Films with addition of equal volume (1.2 mL) of extract				Films with addition of extract with the same amount of TE (40 mg)			
	E. coli	P. fluorescens	*S. aureus*	L. innocua	*E. coli*	P. fluorescens	*S. aureus*	L. innocua
without extract	6.2 ± 0.18 [a]	6.1 ± 0.10 [a]	6.3 ± 0.16 [a]	5.9 ± 0.20 [a]	7.4 ± 0.16 [a]	7.7 ± 0.06 [a]	6.5 ± 0.08 [a]	7.2 ± 0.10 [a]
RB	6.4 ± 0.02 [a]	6.6 ± 0.23 [a]	6.4 ± 0.17 [a]	6.4 ± 0.20 [a]	nt	nt	nt	nt
BBH	6.0 ± 0.15 [a]	6.4 ± 0.19 [a]	6.2 ± 0.27 [a]	6.6 ± 0.14 [a]	0.4 ± 0.09 [c]	0.9 ± 0.04 [c]	2.4 ± 0,05 [b]	1.1 ± 0.05 [c]
ChB	6.2 ± 0.17 [a]	6.5 ± 0.18 [a]	6.2 ± 0.17 [a]	6.5 ± 0.13 [a]	2.5 ± 0.09 [b]	2.0 ± 0.10 [b]	2.7 ± 0.30 [b]	2.3 ± 0.06 [b]

nt not tested.
[a] Mean value ± standard deviation of 3 measurements. The values for a particular column followed by different letters differ significantly ($p < 0.05$).

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properties. The discrepancies of the reported data result first of all from differences in extract composition and concentration of antimicrobial compounds incorporated into polymer matrix. According to Sivarooban et al. (2008) the major group of compounds responsible for the antimicrobial properties of plant extracts is considered the phenolic fraction. However, depending on the origin of the plant, the extracts can differ in the profile of phenols and in antimicrobial activity of the particular phenols. Extracts from chokeberry and blue-berry honeysuckle pomaces contain hydroxycinnamates, anthocyanins and flavonols (Fig. 2). It was shown that these components demonstrate a broad spectrum of antimicrobial activity (Puuppone-Pimiä, Nohynek, Alakomi, & Oksman-Caldentey, 2005; Cisowska et al., 2011). Among them, in the highest concentration in both pomaces extracts, there are anthocyanins (Fig. 2), which are probably the most responsible for antimicrobial activity of the films. Especially, cyanidino-3-galactoside and cyanidino-3-glucoside, in chokeberry and blue-berry honeysuckle extracts, respectively, exert strong antimicrobial activity (Milenković Anđelković et al., 2015; Puuppone-Pimiä et al., 2001).

4. Conclusion

In our work we point to the potential of compounds contained in the troublesome waste products from the fish industry and fruit industry. They are usually thrown away, but can be successfully processed into valuable products. Gelatin obtained from fish offal like skins could be used as the main component of polymer matrix of food packaging materials, and fruit pomace received from the fruit processing - as a carrier of bioactive ingredients of these materials. Although in such a complex mixture of natural compounds there are interactions of its components, which can affect not only the functional properties of the obtained materials, still the materials with the addition of fruit pomace extracts are better than without it.

Unlike the extract form rowanberry pomace, these form blue-berried honeysuckle and chokeberry pomace were useful in the formulation of fish gelatin films with increased antioxidant activity and improved mechanical strength. However, the former was more effective than the latter. None of the used extracts affected the water barrier properties of the films. The thermal instability of hydroxycinnamate acids, the main bioactive compound of the rowanberry extract, probably contributed to the lack of clear increase in the antioxidative properties of films with that extract. In turn, the high antioxidant potential of films with blue-berried honeysuckle and chokeberry extracts resulted from the high content of anthocyannins combined with their high contribution to the total antioxidant activity in the case of the first extract, and the high contribution of anthocyannins to the total antioxidant activity in the case of the second extract. Films containing 1.2 mL of extract (6%) did not possess antimicrobial properties against *E. coli, P. fluorescens*, *S. aureus*, and *L. innocua*, while strong antimicrobial properties against each of them were observed when the extract volume was increased. It is assumed that interaction of gelatin with anthocyanins included in both extracts improved the mechanical strength of the films. However, in order to fully evaluate the influence of the tested extracts on the functional properties and biological activity of gelatin films it is necessary to study their physicochemical properties. Understanding of changes in these properties, which may occurre as a result of interactions with phenolic compounds, is essential not only from the scientific, but also from industrial and economical point of view. Therefore, the results of structural (XRD, FTIR) and thermal (TGA) studies are currently being analyzed and will be discussed in a separate paper.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.lwt.2019.108613.

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