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Extraction of Anthocyanins and its effect on Mechanical Properties of pH Sensitive-based Films: A Review

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ABSTRACT Owing to its pH sensitive properties, anthocyanins has been used as one of the materials to develop this intelligent food packaging. This paper reviews the extraction methods of anthocyanins that used to incorporate with the film matrix and the fabrication methods of the pH sensitive-based film. Generally, there are changes in the properties of the biopolymer films after the addition of anthocyanins due to the intermolecular interactions between anthocyanins and biopolymer molecules. These results may interfere the capability of the films. Hence, the intermolecular interactions should be extensively considered in fabricating a pH sensitive-based film. Some reinforcement should be added to improve the sensitivity of the films. Whereas the mechanical properties of the pH sensitive-based films can be enhanced by adding plasticizers or mixing with different polymers.

KEYWORDS: pH sensitive film; Intelligent packaging; Anthocyanins
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Review Article

INTRODUCTION

In recent past, the functions of food packaging are classified into four categories such as protection, containment, communication and convenience (Yam *et al.*, 2005). However, they are not adequate for today's quality standards. None of them can provide an actual time information about the freshness of the food to consumer. Generally, they are destructive, time-consuming and need extensive instrumentation (Shukla *et al.*, 2016). Thus, new technologies are discovered in order to produce intelligent packaging which is suitable for consumers. The intelligent packaging is defined as a food packaging system that can monitor and inform the food conditions to consumers in real time (Pereira *et al.*, 2015). Besides, the major interests of intelligent packaging are simple, small size, non-invasive, non-destructive, great sensitivity, low costs, natural and consumer friendly (Shukla *et al.*, 2016). Intelligent packaging is classified into three types: time temperature, freshness and gas leakage indicators (Barska & Wyrwa, 2017). One of the examples of freshness indicators is acid-base indicator which is also known as pH indicator or visual pH indicator (Moradi *et al.*, 2019).

Generally, visual pH indicators consist of two important parts: a pH sensitive dye and a solid matrix that is used to immobilize the pH dye (Zhang *et al.*, 2014). The pH sensitive dye is classified into two classes: synthetic pigments and natural pigments. Synthetic pigments such as chlorophenol, bromocresol green and purple, bromothymol blue, methyl red, cresol red, and xylenol are prohibited in food applications as they are harmful to human beings (Zhang *et al.*, 2014). Thus, natural pH sensing dyes are selected in intelligent food packaging system (Pavai *et al*, 2015; Yoshida *et al.*, 2014). Natural dyes such as anthocyanins are chosen because they are easy to prepare, rarely toxic, and environmentally friendly (Calogero *et al.*, 2012; Zhang *et al.*, 2014). Anthocyanin is one of the examples of phenolic compounds, exhibits a colour sensitive property when applied to a wide pH range due to the presence of phenolic or conjugated structure. As the pH changes, the chemical structure of the anthocyanins will change which result in different colours (Shahid & Mohammad, 2013). Anthocyanins are extremely sensitive to pH fluctuations, and their chemical structures and colours shift dramatically in different buffer solutions. With a rise in pH value, the colour of anthocyanin-rich solutions changes from red to pink, purple/blue, and yellow as shown in Figure 1 (Yong & Liu, 2020). The structural alteration of anthocyanins, from red flavylium cation to purple/blue quinoidal base, colourless carbinol pseudobase, and yellow chalcone, is reflected in the colour variations of anthocyanin-rich solutions. To immobilize the natural pH dyes, a solid matrix that made from natural and biodegradable polymers are used. It plays an important role in sensitivity to lower the pH levels, response time between the appearance of distinctive colour and change of pH, reproducibility, and reversibility of fabricated pH indicator (Pourjavaher *et al.*, 2017). Moreover, chitosan, pectin, polyvinyl alcohol, starch and other different polymers have been used as the solid matrix (Maciel *et al.*, 2015; Yoshida *et al.*, 2014).

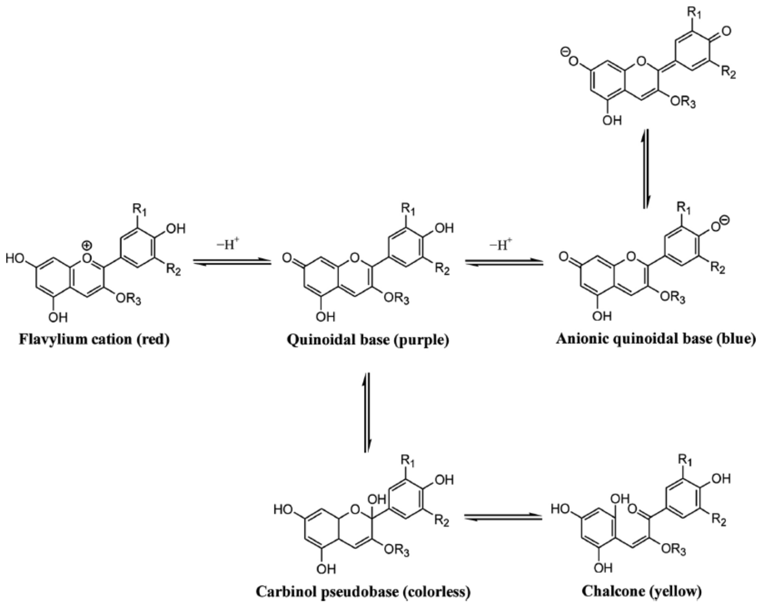

Figure 1. The structural transformation of anthocyanins-rich extracts in solutions (Yong & Liu, 2020).

The aim of this paper is to give an overview about the recent extraction methods of anthocyanins that used to fabricate pH sensitive-based films and their mechanical properties. This review paper is crucial as the guidance for other researcher to fabricate pH sensitive bio-film.

EXTRACTION OF pH INDICATOR

The extraction step of anthocyanins is the most important step in order to obtain a pH sensitive-based film. The most common method used is solvent-extraction method. It is dependent on several factors, such as liquid-to-solid ratio, temperature, solvent type and concentration, time, pH and others (Navas *et al.*, 2012). Table 1 shows the anthocyanins extraction methods, extraction solvents used, and the total anthocyanins content obtained. The time consuming for sample preparation should minimize as much as possible to avoid oxidation or degradation of anthocyanins. High temperature (> 30°C) also should be avoided, not only during sample preparation, but also in all the steps of the anthocyanin extraction procedure to avoid the degradation of anthocyanins (Albuquerque *et al.*, 2018).

Generally, a mixture of acidified organic solvent or acidified water are used during extraction procedures (Table 1). Methanol, ethanol, acetonitrile, ethyl acetate or distilled water can also be used as the extraction solvent. Based on the previous study in Table 1, the organic solvent and water are usually acidified by hydrochloric acid (HCl) as anthocyanins are more stable in acidic conditions. The anthocyanins which extracted using alcoholic solvent are known as alcoholic anthocyanins extracts (Qin *et al.*, 2019; Choi *et al.*, 2017; Zhang *et al.*, 2020; Qin *et al.*, 2020). Whereas, the anthocyanins which extracted by using distilled water are known as aqueous anthocyanins extracts (Kanatt, 2020; Netramai *et al*., 2020; Peralta *et al*., 2019). Based on Table 1, alcoholic extraction is the most frequently selected method to extract anthocyanins compared to aqueous extraction.The extraction of anthocyanins with methanol is the most efficient compared to ethanol or water. However, ethanol or water are more preferred in food packaging due to the toxicity of methanol. Hence, ethanol is frequently used as the extractant of anthocyanins in food packaging system and this is shown in Table 1. Moreover, special care should be taken in acidified extractant to avoid the degradation of anthocyanins in strong acid media (Castaneda-Ovando *et al*., 2009).

Filtration and centrifugation steps are applied after extraction procedures. These steps are used to remove impurities or the pomace of the anthocyanin sources (Albuquerque *et al*., 2018). Besides, purification steps are also important to separate the co-extraction of non-phenolic substances such as organic acids, sugars, and proteins. The extraction methods used are able to co-extract other compounds as they are not selective for anthocyanins only. The most common purification technique is solid-phase extraction by using C18 or Sephadex cartridges. By increasing the polarity of the solvents, anthocyanins can be separated from the co-extracts (Albuquerque *et al*., 2018; Castaneda-Ovando *et al*., 2009). After that, the anthocyanins in powder formed are obtained by drying or freeze-drying process (Albuquerque *et al*., 2018). Furthermore, anthocyanins have been extracted by juice production (Luchese *et al*., 2017; Sun *et al*., 2019; Luchese *et al*., 2018b; Luchese *et al*., 2018c). Unlike solvent-extraction method, there is no any extraction solvent needed during the extraction process. Usually, the anthocyanins sources that used in juice production are fruits. The juice is produced by squeezing the fruits.

MECHANICAL PROPERTIES

Generally, mechanical properties of the pH sensitive-based films such as tensile strength (TS), elongation at break (EB), and Young's Modulus (YM) are tested. These properties are necessary to withstand external stress while maintaining its integrity (Hosseini *et al.*, 2013). The mechanical properties of pH sensitive-based films are shown in Table 2.

Tensile Strength

Tensile strength (TS) is defined as the optimum potential of the films to withstand the stress applied (Mushtaq *et al.*, 2018). Generally, the TS of the pH sensitive-based films increases with the addition of anthocyanins. This is due to the hydroxyl groups present in the anthocyanins which can interact with the biopolymer, forming hydrogen bonds, resulting in a better TS (Kanatt, 2020; Mushtaq *et al.*, 2018; Yong *et al.*, 2019; Wang *et al.*, 2019; Rawdkuen *et al.*, 2020; Zhang *et al.*, 2020; Qin *et al.*, 2019). In contrast, the TS decreases with the incorporation of anthocyanins has been reported due to the effect of intramolecular interaction between anthocyanins and biopolymer. The addition of anthocyanins reduced the intramolecular forces between the biopolymer molecules and increase the disorder of the biopolymer structure, resulting in decreasing the TS (Ma & Wang, 2016; Ge *et al.*, 2020; Chi *et al.*, 2020; Ezati & Rhim, 2020; Liu *et al.*, 2019b; Liang *et al.*, 2018; Netramai *et al.*, 2020; Prietto *et al.*, 2017; Sun *et al.*, 2020; Liang *et al.*, 2019; Yoshida *et al.*, 2014).

Table 1. Extraction solvent used to extract anthocyanins and the total anthocyanins content obtained.

No.	Sources of Anthocyanins	Extraction Method	Solvent	Total Anthocyanins Content (TAC)	References
1	Blueberries (*Vaccinium corymbosum* L.)[a]	Juice production	n.d.	Powder with fruit bleaching: 31 Powder without fruit bleaching: 17.5	Luchese *et al*. (2017)
2	Fresh red radisha	Alcoholic extraction	Ethanol	303.4	Zhai *et al*. (2018)
3	Blueberries (Vaccinium corymbosum L.)[a]	n.d.	n.d.	Extracts with larger particle size: 17.4 Extracts with smaller particle size: 31	Luchese *et al*. (2018a)
4	Jamaica (Hibiscus sabdariffa) flower	Alcoholic extraction	Ethanol	n.d.	Toro-Marquez *et al*. (2018)
5	Purple and black ricea	Alcoholic extraction	Acidified ethanol	Purple rice extracts: 152 Black rice extracts: 245	Yong *et al*. (2019)
6	Red cabbage[f]	Alcoholic extraction	Ethanol, deionized water, HCl	86.67	Vo *et al*. (2019)
7	Haskap berries (*Lonicera caerulea* L.)[b]	Alcoholic extraction	Ethanol, HCl	264.46	Liu *et al*. (2019a)
8	Black carrote	n.d.	n.d.	6	Moradi *et al*. (2019)
9	Torch ginger	Alcoholic extraction	Ethanol, distilled water	44.8	Mei *et al*. (2020)
10	Red pitaya (*Hylocereus polyrhizus*) peel[c]	Alcoholic extraction	Ethanol	56	Qin *et al*. (2020)
11	*Echium amoenum* [d]	Alcoholic extraction	Methanol	1.93	Mohammadalinejhad *et al*. (2020)
12	Carrot[d]	n.d.	n.d.	10	Goodarzi *et al*. (2020)
13	Rosee	Alcoholic extraction	Ethanol	0.182	Kang et al. (2020)
14	Pomegranate flesh and peel extractsa	Alcoholic extraction	Acidified ethanol	Pomegranate flesh extracts: 63.9 Pomegranate peel extracts: 4.3	Liu et al. (2020)
15	Prunus maackii a	Alcoholic extraction	Acidified ethanol	1.8323	Sun et al. (2020)
16	Clitoria ternatea g	Aqueous extraction	Distilled water	32.60	Ahmad *et al*. (2020)
17	Butterfly peaf	Aqueous extraction	Distilled water	102.62	Netramai *et al*. (2020)
18	Red cabbage, purple sweet potatoa	Alcoholic extraction	Ethanol, HCl	Purple sweet potato: 4.20 Red cabbage: 2.42	Zhang *et al*. (2020)

[a] In milligrams per gram; [b] In grams per 100 grams; [c] In milligrams per 100 grams;
[d] In milligrams per 100 millilitres; [e] In milligrams per millilitre; [f] In milligrams per litre;
[g] In grams per millilitre

There are few factors which can affect the tensile strength of pH sensitive-based films. One of the factors is the anthocyanins content that incorporated into the films. The TS decreases with the increasing of anthocyanins content (Chi *et al.*, 2020; Ge *et al.*, 2020; Ma & Wang, 2016; Sun *et al.*, 2020; Liu *et al.*, 2019b; Qin *et al.*, 2019; Liang *et al.*, 2018; Liang *et al.*, 2019; Mei *et al.*, 2020). In contrast, an increase in TS with the increasing of anthocyanin content have been reported (Kang *et al.*, 2020; Wang *et al*., 2019; Qin *et al*., 2020; Liu *et al*., 2019a). Furthermore, excess anthocyanins decreased the TS as the agglomeration of the anthocyanins disrupt the homogeneity and compactness of the film network (Yong *et al*., 2019; Luchese *et al*., 2018a; Sun *et al*., 2019; Pourjavaher *et al*., 2017). The films' preparation and storage conditions also affect the TS of pH sensitive-based film. The films prepared at pH 5 show higher TS compared to other films. Where a decrease or an increase in the pH conditions during the preparation of films lead to a decrease in TS due to the weakening of interactions among the molecules caused by the addition of HCl or NaOH (Ma *et al*., 2017).

Elongation at Break

The optimum potential of the films to resist changes in the film length is known as elongation at break (EB) (Zhai *et al.*, 2018). The incorporation of anthocyanins into the film matrix can increase the EB of the films due to the interaction of anthocyanins with biopolymer which improve the compatibility of the films and resulting in enhanced extensibility (Rawdkuen *et al.*, 2020; Prietto *et al.*, 2017; Sun *et al.*, 2020; Liu *et al.*, 2020; Qin *et al.*, 2020; Zhang *et al.*, 2020; Qin *et al.*, 2019; Sun *et al.*, 2019). However, anthocyanins also decreased the EB of the films as it can reduce the intramolecular bonding between the biopolymer molecules. The biopolymer structure will become disorder, results in decreasing EB (Kanatt, 2020; Luchese *et al.*, 2018a; Liu *et al.*, 2019b; Netramai *et al.*, 2020; Yoshida *et al.*, 2014; Liu *et al.*, 2019a).

The anthocyanins content may influence the EB value. The increasing of anthocyanins content caused EB to decrease (Qin *et al.*, 2019; Chi *et al.*, 2020; Liang *et al.*, 2018; Sun *et al.*, 2019). In contrast, the EB increases as the concentration of incorporated anthocyanins increases (Pourjavaher *et al.*, 2017; Wu *et al.*, 2019; Ge *et al.*, 2020; Ma & Wang, 2016; Wang *et al.*, 2019; Yong *et al.*, 2019; Sun *et al.*, 2020; Liang *et al.*, 2019; Qin *et al.*, 2020; Liu *et al.*, 2019a). Furthermore, the pH sensitive-based films prepared in different pH conditions influenced the EB value because the presence of HCl and NaOH that used to obtain acidic and alkaline conditions may interfere the film matrix, resulting in a decrease of EB value (Ma *et al.*, 2017).

Young's Modulus

The stiffness (ratio between stress and strain) of a material at the elastic level of the tensile test is known as Young's Modulus (YM). Generally, YM increases with the addition of anthocyanins into the film matrix (Kurek *et al.*, 2018; Kang *et al.*, 2020) due to the formation of hydrogen bonds between anthocyanins and biopolymers. In contrast, the YM decreases with the addition of anthocyanins are found (Liu *et al.*, 2019b; Pourjavaher *et al.*, 2017; Mei *et al.*, 2020; Yoshida *et al.*, 2014) due to the addition of anthocyanins which causing the compact structure of film matrix become weaken.

Table 2. Mechanical properties of pH sensitive-based films.

No.	Anthocyanins sources	Biopolymer Film Matrix	Tensile Strength		Elongation at break		Young's Modulus		References
			CF	Antho-films	CF	Antho-films	CF	Antho-films	
1	Black soybean seed coat	Chitosan	14.83[a]	20.64-23.24[a]	44.87[b]	61.71-73.88[b]	n.d.		Wang *et al.* (2019)
2	Red cabbage	*Artemisia sphaerocephala Krasch. Gum / carboxymethyl cellulose sodium*	33.43[a]	30.27-23.57[a]	55.87[b]	58.47-66.27[b]	n.d.		Liang *et al.* (2019)
3	Purple and black rice	*Chitosan*	21.32[a]	Purple rice extracts: 26.48-21.46a Black rice extracts: 24.39-18.76a	36.22[b]	Purple rice extracts: 42.26-57.06[b] Black rice extracts: 51.13-61.16b	n.d.		Yong *et al.* (2019)
4	*Lycium ruthenicum* Murr	Cassava starch	12.08[a]	13.66-12.98[a]	3.87[b]	3.98-3.33[b]	n.d.		Qin *et al.* (2019)
5	*Black rice bran*	Chitosan/oxidised chitin nanocrystal	33.60[a]	30.25-20.32[a]	18.82[b]	19.26-27.38[b]	n.d.		Wu *et al.* (2019)
6	*Prunus maackii juice*	k-carrageenan/ hydroxypropyl methylcellulose	18.76[a]	22.92-18.93[a]	3.16[b]	3.64-4.75[b]	n.d.		Sun *et al.* (2019)
7	*Haskap berries (Lonicera caerulea L.)*	Fish gelatin	42.5[a]	46.7-51.5[a]	2.96[b]	2.87-3.69[b]	n.d.		Liu *et al.* (2019a)
8	*Lycium ruthenicum* Murr.	*k*-carrageenan	20.07[a]	6.49[a]	391[b]	182.25[b]	0.25[c]	0.07[c]	Liu *et al.* (2019b)
9	Alizarin	Chitosan	30.6[a]	29.1[a]	48.3[b]	54.4[b]	1.65[c]	1.53[c]	Ezati & Rhim (2020)
10	Grape skin powder	*k*-carrageenan/ hydroxypropyl methylcellulose	20.96[a]	18.89-14.25[a]	19.65[b]	17.70-11.30[b]	n.d.		Chi *et al.* (2020)
11	Butterfly pea	*Gelatin*	7.0[a]	2.4[a]	78[b]	210[b]	n.d.		Rawdkuen *et al.* (2020)
12	Pomegranate flesh and peel extracts	*k*-carrageenan	24.73[a]	Flesh extracts: 30.13-23.82[a] Peel extracts: 27.52-30.94[a]	13.82[b]	Flesh extracts: 20.28-17.28[b] Peel extracts: 19.68-22.29[b]	n.d.		Liu *et al.* (2020)
13	Torch ginger	Sago starch	5.00[d]	4.41-4.26[d]	48.55[b]	71.55-85.14[b]	82.48[a]	78.15-73.96[a]	Mei *et al.* (2020)
14	Butterfly pea	Carboxymethyl cellulose/ *k*-carrageenan	0.40[a]	0.33[a]	91.14[b]	87.23[b]	n.d.		Netramai *et al.* (2020)
15	Amaranthus leaf	PVA/gelatin	15.8[a]	19.2[a]	129[b]	105[b]	n.d.		Kanatt (2020)
16	Rose	PVA/okra mucilage polysaccharide	26.5-34.2[a]	34.9-36.0[a]	n.d.		3.2-9.6[c]	8.5-11.1[c]	Kang *et al.* (2020)
17	Black rice bran	Gelatin/oxidized chitin nanocrystals nanocomposite	9.44[a]	4.26-2.53[a]	115.3[b]	126.33-141.67[b]	n.d.		Ge *et al.* (2020)

[a] In megapascal; [b] In percentage; [c] In gigapascal;[d] In pascal or Newton per meter square; CF is control film; Antho-films is anthocyanin incorporated films.

CONCLUSION

Recently, the applications of pH indicative films are growing in food packaging industry as it is selected as an active and intelligent packaging to monitor the food quality. In most of the study, alcoholic extraction method was the mostly employed method to extract the anthocyanin. Since the mechanical properties of biopolymer films are poor compared to the synthetic polymers, the addition of plasticizer and/or combining different type of polymer can improve the mechanical properties of the films.

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REFERENCES

[1] Ahmad, A. N., Lim, S. A. & Navaranjan, N. 2020. Development of sago (*Metroxylon sagu*)-Based Colorimetric Indicator Incorporated with Butterfly Pea (*Clitoria ternatea*) Anthocyanin for Intelligent Food Packaging. *Journal of Food Safety*, 40(4), e12807.

[2] Ahmad, N. A., Heng, L. Y., Salam, F., Zaid, M. H. & Hanifah, S. A. 2019. A Colorimetric pH Sensor Based on *Clitoria* sp and *Brassica* sp for Monitoring of Food Spoilage Using Chromametry. *Sensors*, 19(21), 4813.

[3] Albuquerque, T. G., Silva, M. A., Oliveira, M. B. & Costa, H. S. 2018. Analysis, Identification, and Quantification of Anthocyanins in Fruit Juices. *In:* Rajauria, G. & Tiwari, B. K. (eds.). *Fruit Juices*. London: Academic Press.

[4] Barska, A. & Wyrwa, J. 2017. Innovations in the Food Packaging Market Intelligent–packaging–A review. *Czech Journal of Food Sciences*, 35(1), 1-6.

[5] Calogero, G., Yum, J.-H., Sinopoli, A., Di Marco, G., Grätzel, M. & Nazeeruddin, M. K. 2012. Anthocyanins and Betalains as Light-Harvesting Pigments for Dye Sensitized Solar Cells. *Solar Energy*, 86(5), 1563–1575.

[6] Castaneda-Ovando, A., Pacheco-Hernandez, M. D., Paez-Hernandez, M. E., Rodriguez, J. A. & Galan-Vidal, C. A. 2009. Chemical Studies of Anthocyanins: A review. *Food Chemistry*, 113(4), 859-871.

[7] Chi, W., Cao, L., Sun, G., Meng, F., Zhang, C., Li, J. & Wang, L. 2020. Developing a Highly pH-Sensitive κ-Carrageenan-Based Intelligent Film Incorporating Grape Skin Powder via a Cleaner Process. *Journal of Cleaner Production*, 244, 118862.

[8] Choi, I., Lee, J. Y., Lacroix, M. & Han, J. 2017. Intelligent pH Indicator Film Composed of Agar/Potato Starch and Anthocyanin Extracts from Purple Sweet Potato. *Food Chemistry*, 218, 122-128.

[9] Ezati, P. & Rhim, J.-W. 2020. pH-Responsive Chitosan-Based Film Incorporated with Alizarin for Intelligent Packaging Applications. *Food Hydrocolloids*, 102, 105629.

[10] Ezati, P., Tajik, H., Moradi, M. & Molaei, R. 2019. Intelligent pH-Sensitive Indicator Based on Starch-Cellulose and Alizarin Dye to Track Freshness of Rainbow Trout Fillet. *International Journal of Biological Macromolecules*, 132, 157-165.

[11] Hosseini, S. F., Rezaei, M., Zandi, M. & Ghavi, F. F. 2013. Preparation and Functional Properties of Fish Gelatin–Chitosan Blend Edible Films. Food Chemistry, 136(3-4), 1490-1495.

[12] Ge, Y., Li, Y., Bai, Y., Yuan, C., Wu, C. & Hu, Y. 2020. Intelligent Gelatin/Oxidized Chitin Nanocrystals Nanocomposite Films Containing Black Rice Bran Anthocyanins for Fish Freshness Monitorings. *International Journal of Biological Macromolecules*, 155, 1296–1306.

[13] Goodarzi, M. M., Moradi, M., Tajik, H., Forough, M., Ezati, P. & Kuswandi, B. 2020. Development of an Easy-to-Use Colorimetric pH Label with Starch and Carrot Anthocyanins for Milk Shelf Life Assessment. *International Journal of Biological Macromolecules,* 153, 240-247.

[14] Kanatt, S. R. 2020. Development of Active/Intelligent Food Packaging Film Containing Amaranthus Leaf Extract for Shelf Life Extension of Chicken/Fish during Chilled Storage. *Food Packaging and Shelf Life,* 24, 100506.

[15] Kang, S., Wang, H., Xia, L., Chen, M., Li, L., Cheng, J., Li, X. & Jiang, S. 2020. Colorimetric Film Based on Polyvinyl Alcohol/Okra Mucilage Polysaccharide Incorporated with Rose Anthocyanins for Shrimp Freshness Monitoring. *Carbohydrate Polymers,* 229, 115402.

[16] Kurek, M., Garofulic, I. E., Bakic, M. T., Scetar, M., Uzelac, V. D. & Galic, K. 2018. Development and Evaluation of a Novel Antioxidant and pH Indicator Film Based on Chitosan and Food Waste Sources of Antioxidants. *Food Hydrocolloids,* 84, 238–246.

[17] Liang, T., Sun, G., Cao, L., Li, J. & Wang, L. 2018. Rheological Behavior of Film-Forming Solutions and Film Properties from *Artemisia sphaerocephala* Krasch. Gum and Purple Onion Peel Extract. *Food Hydrocolloids,* 82, 124–134.

[18] Liang, T., Sun, G., Cao, L., Li, J. & Wang, L. 2019. A pH and NH_3 Sensing Intelligent Film Based on *Artemisia sphaerocephala* Krasch. gum and Red Cabbage Anthocyanins Anchored by Carboxymethyl Cellulose Sodium Added as a Host Complex. *Food Hydrocolloids,* 87, 858–868.

[19] Liu, J., Wang, H., Guo, M., Li, L., Chen, M., Jiang, S., Li, X & Jiang, S. 2019b. Extract from *Lycium ruthenicum* Murr. Incorporating κ-Carrageenan Colorimetric Film with a Wide pH–Sensing Range for Food Freshness Monitoring. *Food Hydrocolloids,* 94, 1–10.

[20] Liu, J., Yong, H., Liu, Y., Qin, Y., Kan, J. & Liu, J. 2019a. Preparation and Characterization of Active and Intelligent Films Based on Fish Gelatin and Haskap Berries (*Lonicera caerulea* L.) Extract. *Food Packaging and Shelf Life,* 22, 100417.

[21] Liu, Y., Zhang, X., Li, C., Qin, Y., Xiao, L. & Liu, J. 2020. Comparison of the Structural, Physical and Functional Properties of κ-Carrageenan Films Incorporated with Pomegranate Flesh and Peel Extracts. *International Journal of Biological Macromolecules,* 147, 1076–1088.

[22] Luchese, C. L., Abdalla, V. F., Spada, J. C. & Tessaro, I. C. 2018a. Evaluation of Blueberry Residue Incorporated Cassava Starch Film as pH Indicator in Different Simulants and Foodstuffs. *Food Hydrocolloids,* 82, 209–218.

[23] Luchese, C. L., Frick Pavoni, J. M., Spada, J. C. & Tessaro, I. C. 2019. Influence of Blueberry and Jaboticaba Agroindustrial Residue Particle Size on Color Change of Corn Starch Based Films Submitted to Different pH Values Solutions. *Journal of Renewable Materials,* 7, 235–243.

[24] Luchese, C. L., Garrido, T., Spada, J. C., Tessaro, I. C. & de la Caba, K. 2018b. Development and Characterization of Cassava Starch Films Incorporated with Blueberry Pomace. *International Journal of Biological Macromolecules,* 106, 834–839.

[25] Luchese, C. L., Sperotto, N., Spada, J. C. & Tessaro, I. C. 2017. Effect of Blueberry Agro-Industrial Waste Addition to Corn Starch-Based Films for the Production of a pH-Indicator Film. *International Journal of Biological Macromolecules,* 104, 11-18.

[26] Luchese, C. L., Uranga, J., Spada, J. C., Tessaro, I. C. & de la Caba, K. 2018c. Valorisation of Blueberry Waste and Use of Compression to Manufacture Sustainable Starch Films with Enhanced Properties. *International Journal of Biological Macromolecules,* 115, 955–960.

[27] Ma, Q., Ren, Y., Gu, Z. & Wang, L. 2017. Developing an Intelligent Film Containing *Vitis amurensis* Husk Extracts: The Effects of pH Value of the Film-Forming Solution. *Journal of Cleaner Production,* 166, 851–859.

[28] Ma, Q. & Wang, L. 2016. Preparation of a Visual pH-Sensing Film Based on Tara Gum Incorporating Cellulose and Extracts from Grape Skins. *Sensors and Actuators B: Chemical*, 235, 401–407.

[29] Maciel, V. B., Yoshida, C. M. & Franco, T. T. 2015. Chitosan/Pectin Polyelectrolyte Complex as a pH Indicator. *Carbohydrate Polymers*, 132, 537–545.

[30] Mei, L. X., Nafchi, A. M., Ghasemipour, F., Easa, A. M., Jafarzadeh, S. & Al-Hassan, A. 2020. Characterization of pH Sensitive Sago Starch Films Enriched with Anthocyanin-Rich Torch Ginger Extract. *International Journal of Biological Macromolecules*, 164, 4603-4612.

[31] Mohammadalinejhad, S., Almasi, H. & Moradi, M. 2020. Immobilization of *Echium amoenum* Anthocyanins into Bacterial Cellulose Film: A Novel Colorimetric pH Indicator for Freshness/Spoilage Monitoring of Shrimp. *Food Control*, 113, 107169.

[32] Moradi, M., Tajik, H., Almasi, H., Forough, M. & Ezati, P. 2019. A Novel pH-Sensing Indicator based on Bacterial Cellulose Nanofibers and Black Carrot Anthocyanins for Monitoring Fish Freshness. *Carbohydrate Polymers*, 222, 115030.

[33] Mushtaq, M., Gani, A., Gani, A., Punoo, H. A. & Masoodi, F. A. 2018. Use of Pomegranate Peel Extract Incorporated Zein Film with Improved Properties for Prolonged Shelf Life of Fresh Himalayan Cheese (Kalari/kradi). Innovative Food Science & Emerging Technologies, 48, 25–32.

[34] Navas, M. J., Jimenez-Moreno, A. M., Bueno, J. M., Saez-Plaza, P. & Asuero, A. G. 2012. Analysis and Antioxidant Capacity of Anthocyanin Pigments. Part IV: Extraction of Anthocyanins. *Critical Reviews in Analytical Chemistry*, 42(4), 313-342.

[35] Netramai, S., Kijchavengkul, T., Kham-ngam, C., Sirinupong, P., Kwanmuang, S., Samsudin, H. & Lertsiri, S. 2020. Development of Colorimetric Film with Butterfly Pea (*Clitoria ternatea* L.) Extract for Application in Intelligent Packaging. *The 22nd Food Innovation Asia Conference 2020 (FIAC 2020) Future Food Innovation for Better Health and Wellness*. 18-20 June, 2020, Bangkok, Thailand.

[36] Pavai, M., Mihaly, J. & Paszternak, A. 2015. pH and CO_2 Sensing by Curcumin-Coloured Cellophane Test Strip. *Food Analytical Methods*, 8(9), 2243–2249.

[37] Peralta, J., Bitencourt-Cervi, C. M., Maciel, V. B. V., Yoshida, C. M. P. & Carvalho, R. A. 2019. Aqueous Hibiscus Extract as a Potential Natural pH Indicator Incorporated in Natural Polymeric Films. *Food Packaging and Shelf Life*, 19, 47–55.

[38] Pereira, V. A., de Arruda, I. N. Q. & Stefani, R. 2015. Active Chitosan/PVA Films with Anthocyanins from *Brassica oleraceae* (Red Cabbage) as Time-Temperature Indicators for Application in Intelligent Food Packaging. *Food Hydrocolloids*, 43, 180–188.

[39] Pourjavaher, S., Almasi, H., Meshkini, S., Pirsa, S. & Parandi, E. 2017. Development of a Colorimetric pH Indicator based on Bacterial Cellulose Nanofibers and Red Cabbage (Brassica oleraceae) Extract. Carbohydrate Polymers, 156, 193-201.

[40] Prietto, L., Mirapalhete, T. C., Pinto, V. Z., Hoffmann, J. F., Vanier, N. L., Lim, L., Dias A. R. G. 2017. Zavareze, E. D. 2017. pH-Sensitive Films Containing Anthocyanins Extracted from Black Bean Seed Coat and Red Cabbage. *LWT-Food Science and Technology*, 80, 492-500.

[41] Qin, Y., Liu, Y., Yong, H., Liu, J., Zhang, X. & Liu, J. 2019. Preparation and Characterization of Active and Intelligent Packaging Films Based on Cassava Starch and Anthocyanins from *Lycium ruthenicum* Murr. *International Journal of Biological Macromolecules*, 134, 80-90.

[42] Qin, Y., Liu, Y., Zhang, X. & Liu, J. 2020. Development of Active and Intelligent Packaging by Incorporating Betalains from Red Pitaya (*Hylocereus polyrhizus*) Peel into Starch/Polyvinyl Alcohol Films. *Food Hydrocolloids*, 100, 105410.

[43] Rawdkuen, S., Faseha, A., Benjakul, S. & Kaewprachu, P. 2020. Application of Anthocyanin as a Color Indicator in Gelatin Films. *Food Bioscience*, 36, 100603.

[44] Shahid, M. & Mohammad, F. 2013. Recent Advancements in Natural Dye Applications: A Review. *Journal of Cleaner Production*, 53, 310-331.

[45] Shukla, V., Kandeepan, G., Vishnuraj, M. R. & Soni, A. 2016. Anthocyanins Based Indicator Sensor for Intelligent Packaging Application. *Agricultural Research*, 5(2), 205-209.

[46] Sun, G., Chi, W., Xu, S. & Wang, L. 2020. Developing a Simultaneously Antioxidant and pH-Responsive κ-Carrageenan/Hydroxypropyl Methylcellulose Film Blended with *Prunus maackii* Extract. *International Journal of Biological Macromolecules*, 155, 1393–1400.

[47] Sun, G., Chi, W., Zhang, C., Xu, S., Li, J. & Wang, L. 2019. Developing a Green Film with pH-Sensitivity and Antioxidant Activity Based on κ-Carrageenan and Hydroxypropyl Methylcellulose Incorporating *Prunus maackii* Juice. *Food Hydrocolloids*, 94, 345-353.

[48] Toro-Marquez, L. A., Merino, D. & Gutierrez, T. J. 2018. Bionanocomposite Film Prepared from Corn Starch With and Without Nanopackaged Jamaica (*Hibiscus sabdariffa*) Flower Extract. *Food and Bioprocess Technology*, 11, 1955–1973.

[49] Vo, T.-V., Dang, T.-H. & Chen, B.-H. 2019. Synthesis of Intelligent pH Indicative Films from Chitosan/Poly(vinyl alcohol)/Anthocyanin Extracted from Red Cabbage. *Polymers*, 11(7), 1088.

[50] Wang, X., Yong, H., Gao, L., Li, L., Jin, M. & Liu, J. 2019. Preparation and Characterization of Antioxidant and pH-Sensitive Films Based on Chitosan and Black Soybean Seed Coat Extract. *Food Hydrocolloids*, 89, 56-66.

[51] Wu, C., Sun, J., Zheng, P., Kang, X., Chen, M., Li, Y., Ge, Y., Hu, Y. & Pang, J. 2019. Preparation of an Intelligent Film based on Chitosan/Oxidized Chitin Nanocrystals Incorporating Black Rice Bran Anthocyanins for Seafood Spoilage Monitoring. *Carbohydrate Polymers*, 222, 115006.

[52] Yam, K. L., Takhistov, P. T. & Miltz, J. 2005. Intelligent Packaging: Concepts and Applications. *Journal of Food Science*, 70(1), R1-R10

[53] Yong, H. & Liu, J. 2020. Recent Advances in the Preparation, Physical and Functional Properties, and Applications of Anthocyanins-Based Active and Intelligent Packaging Films. *Food Packaging and Shelf Life*, 26, 100550.

[54] Yong, H., Liu, J., Qin, Y., Bai, R., Zhang, X. & Liu, J. 2019. Antioxidant and pH-Sensitive Films Developed by Incorporating Purple and Black Rice Extracts into Chitosan Matrix. *International Journal of Biological Macromolecules*, 137, 307–316.

[55] Yoshida, C. M. P., Maciel, V. B. V., Mendonca, M. E. D. & Franco, T. T. 2014. Chitosan Biobased and Intelligent Films: Monitoring pH variations. LWT-Food Science and Technology, 55(1), 83–89.

[56] Zhai, X., Li, Z., Zhang, J., Shi, J., Zou, X., Huang, X, Zhang, D., Sun, Y., Yang, Z., Holmes, M., Gong, Y. & Povey, M. 2018. Natural Biomaterial-Based Edible and pH-Sensitive Films Combined with Electrochemical Writing for Intelligent Food Packaging. *Journal of Agricultural and Food Chemistry*, 66, 12836-12846.

[57] Zhang, J., Zou, X., Zhai, X., Huang, X., Jiang, C. & Holmes, M. 2019. Preparation of an Intelligent pH Film Based on Biodegradable Polymers and Roselle Anthocyanins for Monitoring Pork Freshness. *Food Chemistry*, 272, 306–312.

[58] Zhang, K., Huang, T.-S., Yan, H., Hu, X. & Ren, T. 2020. Novel pH-Sensitive Films Based on Starch/Polyvinyl Alcohol and Food Anthocyanins as a Visual Indicator of Shrimp Deterioration. *International Journal of Biological Macromolecules*, 145, 768-776.

[59] Zhang, X., Lu, S. & Chen, X. 2014. A Visual pH Sensing Film Using Natural Dyes from *Bauhinia blakeana Dunn*. *Sensors and Actuators B: Chemical*, 198, 268-273.