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Effect of different processing methods of hawthorn on the properties and emulsification performance of hawthorn pectin

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ABSTRACT

Five types of hawthorns were obtained using hot air drying (HH), vacuum freeze-drying (FH), Parched processing (PH), Charred processing (CH), and blackening (BH). Five types of pectins (HHP, FHP, PHP, CHP, BHP) were extracted and characterized based on a series of characterization methods. The results indicated that the esterification and molecular weight of BHP were the lowest, which were 30.92 % and 73.67 $\times$ 10^3 (g/mol), respectively. FHP had the highest apparent viscosity and molecular weight (464.42 $\times$ 10^3 g/mol). PHP and CHP differ in galacturonic acid, molecular weight, and monosaccharide composition depending on the time of processing. The emulsion of HHP had the best stability, and the emulsification properties of FHP, PHP, and CHP also showed better performance compared to BHP. In conclusion, our results showed that different processing methods of hawthorn affected the physicochemical properties of pectin, and pectin with specific properties could be obtained by choosing the appropriate processing method.

1. Introduction

Pectin has attracted remarkable attention due to its unique properties, functions, and activities (Wan et al., 2021). At present, pectin derived from citrus peel and apple pomace is considered to have commercial value (Chen et al., 2021). The properties of pectin are associated with its structure, molecular weight, and degree of esterification (Chen et al., 2021), which strictly depend on plant resources (Banerjee et al., 2017). Although pectin exists in many plant tissues, new sources of pectin may provide new properties. Hawthorn (*Crataegus* spp.) is mainly distributed in North America, Europe, and Central Asia in the northern hemisphere (Cuevas-Bernardino et al., 2016), especially in China. Previous research found the pectin content of hawthorn fruit was relatively high (about 9.94 %) (Chen et al., 2019). Moreover, hawthorn pectin is increasing more research attention on account of its better accessibility and multifunctional properties than other cultivated plants (Zhu et al., 2015). Hawthorn pectin has the characteristics of high viscosity and its emulsification and stability are significantly better than that of citrus pectin (Cuevas-Bernardino et al., 2016).

Hot air-dried hawthorn, Freeze-dried Hawthorn, Parched hawthorn, Charred hawthorn, and Blacken hawthorn are currently the main dried hawthorn products in the Chinese market. Five processed products of hawthorn can be obtained by hot air drying, vacuum freeze-drying, 'Paozhi', and blackening (Li, Chen, et al., 2020; Tomás Barberán, 2007; Chao et al., 2022). Numerous studies have shown that different processing methods have a great influence on the physicochemical properties and biological functions of crude polysaccharides extracted from fruits and vegetables (Kong et al., 2015). Recent studies have indicated that the physicochemical and biological properties of the biomacromolecules (date fiber concentrates, finger citron polysaccharides, and bitter gourd polysaccharides) were influenced by the drying method used (Borchani et al., 2011; Wu, 2015; Yan et al., 2019). Pectin is a natural heteropolysaccharide that is easily affected by the processing methods of plant resources and causes changes in structure and function (Geerkenset al, n.d.). Comparing the effects of natural drying and freeze-drying on papaya pectin, the pectin extracted from the freeze-dried papaya had a high yield, high molecular weight, and good thermal stability (Ramos-Aguilar et al., 2015). At present, the research on hawthorn pectin mainly focuses on extraction, purification, and functional properties. However, there were no or few reports about the influences of different processing methods of hawthorn on the characteristics of hawthorn pectin.

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This study aims to investigate the effects of different processing methods of hawthorn on the functional properties and structure of pectin. The properties of pectins were characterized by the degree of esterification, monosaccharide composition, molecular weight distribution, etc., moreover, the rheological properties and emulsifying properties of pectins were also compared. The results obtained in this work will provide a scientific foundation for understanding the relationship between the processing method of plant resources and the structure and properties of pectin.

2. Materials and methods

2.1. Materials

Hawthorn fruits were supplied by Laiwu Wanbang Food Co., Ltd. (Shandong, China). Corn germ oil was bought from Longda Food Co., Ltd. (Shandong, China). All other chemical agents employed in this work were of analytical grade and the experimental results of this study were all calculated on a dry basis.

2.2. Preparation of hawthorn with different processing methods

Hot air-dried hawthorn: Fresh hawthorn was washed and sliced into pieces (0.4 cm thickness), then stored in an electric blast drying oven (101-OA, Longkou Electric Furnace Factory, Yantai, China) at 60 °C until the final moisture content reached 0.12 ± 0.02 g H_2O/g d.w (Liu et al., 2020).

Freeze-dried hawthorn: Fresh hawthorn was cut into slices (0.4 cm thickness) and then fast frozen to −30 °C using the LJ-6W freezer (Wuxi Guanya Thermostatic Refrigeration Technology Co., Ltd., Wuxi, China), and the completely frozen hawthorn slices were put into the vacuum freeze drier (TFDSO.25, Zhongfu Cold Chain Equipment Co., Ltd., Yantai, China) and freeze-dried for 24 h (90 °C, 8 h; 80 °C, 8 h; 55 °C, 6 h) until the final moisture content reached to 0.12 ± 0.02 g H_2O/g d.w (Qin et al., 2019; Wu, 2015).

Parched hawthorn: Hawthorn slices (0.4 cm thickness) was put into a drum rotary roaster machine (BM-30, Xiyuan Machinery Equipment Co., Ltd., Zhengzhou, China), then heated and fried at 190 °C until the surface is burnt brown and the inside is reddish-brown, and the final moisture content of parched hawthorn were 0.12 ± 0.02 g H_2O/g d.w.

Charred Hawthorn: Hawthorn slices (0.4 cm thickness) was put into a drum rotary roaster machine (BM-30, Xiyuan Machinery Equipment Co., Ltd., Zhengzhou, China), then heated and fried at 190 °C until the surface is charred black and the inside is burnt brown, and the sample moisture was 0.05 ± 0.03 g H_2O/g d.w.

Blacken Hawthorn: Washed hawthorn fruits have removed the nucleus and divided into three stages black in high and low temperature test chamber (YNK/T-50, Suzhou unique environmental test equipment Co., Ltd.). In the first stage, the temperature was 90 °C, and the time was 24 h. In the second stage, the temperature was reduced to 80 °C and lasts for 24 h. In the third stage, the temperature was constant at 70 °C until the final moisture content was 0.12 ± 0.02 g H_2O/g d.w.

2.3. Pectin extraction

The samples were firstly mixed and stirred with deionized water at a ratio of 1:20. After that, the samples were placed in a water bath at 90 °C with constant stirring for 2 h, then cooled down immediately. The supernatant was obtained by centrifugation at 4500 rpm for 10 min, cooled down to room temperature, and concentrated to 1/2 of the original volume by the rotary evaporation. The ethanol concentration in the system was adjusted to 75 % (v/v) by adding 95 % (v/v) ethanol to the supernatant and precipitated at 4 °C for 12 h. The pectin precipitation was gained using centrifugation at 4500 rpm for 10 min. Afterward, the precipitation was washed using 95 % (v/v) ethanol 2 times. The samples were then dialyzed using dialysis bags (3.5 g/mol, Yuanye Biotechnology, Shanghai, China) at 4 °C for 48 h to remove impurities. After treatment of concentrated and freeze-dried, five hawthorn pectin samples were obtained, namely: HHP, FHP, PHP, CHP, and BHP.

2.4. Analysis of physical and chemical characteristics of hawthorn pectin

2.4.1. Hawthorn pectin yield

The formula for calculating the yield (M) of hawthorn pectin was as follows:

$$M(\%) = \frac{M_1}{M_0} \times 100\%$$

where the M_1 is the weight of pectin (g); M_0 is the weight of hawthorn raw material (g).

2.4.2. GalA content measurement

The *m*-hydroxyphenyl method reported by Kintner and Buren (1982) was applied to determine the GalA content of pectin. The standard curve was drawn with D-Gal A solution (0.1 mg/mL) as the standard.

2.4.3. Degree of esterification (DE)

The degree of esterification (DE) was obtained according to the formula based on the Fourier transform infrared spectroscopy (FT-IR) (Petkowicz et al., 2017):

$$DE\ (\%) = \frac{A_{1740}}{A_{1740} + A_{1630}} \times 100\%$$

where A_{1740} and A_{1630} are the peak area at 1740 cm^{-1} (esterified carboxyl groups) and the peak area at 1630 cm^{-1} (free carboxyl groups), respectively.

2.4.4. Protein content measurement

The Bradford method was used to determine the protein content in the hawthorn pectin sample (Bradford, 1976).

2.4.5. Chromaticity analysis of hawthorn pectin

Chromaticity of hawthorn pectin Chroma analysis was analyzed by CR-400 colorimeter (Konica Minolta, Japan). CIELAB coordinates (L*, a*, b*, ΔE*). The calculation formula of chromaticity value was as follows:

$$\Delta E^* = \left[(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2\right]^{1/2}$$

2.4.6. Molecular weight and distribution analysis of hawthorn pectin

The high-performance gel permeation chromatography (HPGPC) equipped with an LC-20A GPC system (Shimadzu, Japan) and a RID-10A differential refractive index detector was employed to determine the molecular weight (MW) and distribution of pectin samples. Three columns of the TSK guard column (3.5 cm × 4.6 mm), TSK gel column G5000 PWx1 and G4000 PWx1 (30 cm × 4.6 mm) were connected in series. The mobile phase consisted of 0.05 % NaN_3 (w/w) and 0.1 M $NaNO_3$ solution (Zainudin et al., 2018). Pectin samples (2 mg/mL) were dissolved with mobile phase and loaded on a tandem column and eluted for 100 min at a column temperature of 40 °C and a flow rate of 0.4 mL/min. In addition, P-28 pullulan was used as a standard to calibrate the Mw of the sample (Sun et al., 2020).

2.4.7. Monosaccharide composition analysis

The monosaccharide composition of the pectin samples was determined as previously described by Guo et al. (2014). The approximate percentages of the homogalacturonan (HG) and rhamnogalacturonan-I (RG-I) regions in pectin were evaluated based on the reported method (Hua et al., 2015).

$$HG\% = \frac{G/194 - R/164}{G/194} \times 100\%$$

$$RGI\% = \frac{R/164}{G/194} \times 100\%$$

where G is the content of GalA (%), and R is the content of Rha (%).

2.5. Structural characterization of pectin

2.5.1. Morphological analysis of hawthorn pectin

The dried pectin samples were fixed to the sample table covered with conductive adhesive tape and coated with a thin layer of gold (Wang et al., 2021). A scanning electron microscope (Inspect F50, FEI, USA) with an acceleration voltage of 10 kV and three magnifications (1.5 k×, 1.0 k×, and 5.0 k×) was applied to capture the microstructural changes of hawthorn pectin samples.

2.5.2. Fourier transform infrared spectroscopy (FT-IR) analysis

The pectin samples were incorporated with KBr (1:100) and compressed by a tablet press. The test was conducted by the IS50 FTIR spectrometer (Thermo Fisher Scientific, USA). Scanning was carried out in absorption mode, the resolution was 4 cm^{-1}, the frequency range was 4000–400 cm^{-1}, the cumulative scan number was 32 times, and the absorption spectrum was gained after denoising and baseline correction (Yang, Mu, & Ma, 2018).

2.5.3. X-ray diffraction analysis

The X-ray diffraction results of pectin were performed using an X-ray diffractometer (D8-focus, Bruker, Karlsruhe, Germany). The scanning range of the diffraction angle (2θ) of the pectin sample was from 5° to 45° with Cu Kα diffraction at a voltage of 40 kV, current 40 mA, using fractional scanning mode, each scanning angle was 0.02° (2θ) (Jiang et al., 2018).

2.6. Rheological behaviors

The freeze-dried pectin sample was dissolved in distilled water and mixed into a 2 % aqueous solution, then stirred for 2 h at room temperature to homogenize the sample solution. Rheological measurements were detected by the controlled stress rheometer equipped with a 20 mm flat disk (AR2000ex, TA Instruments, USA). The prepared samples (2 %) were subjected to steady-state shear measurement at 25 °C, and the sheer frequency range was 0.1–1000 s^{-1}. Dynamic viscoelasticity tests were used to determine the loss (G″, Pa) and storage (G′, Pa) moduli across the angular frequency range of 0.1–100 rad/s at 25 °C (Wang et al., 2021). An oscillatory strain sweep at a constant oscillation frequency of 1 Hz was performed to determine the linear viscoelastic region before the dynamic experiments. All oscillatory tests were performed at 0.5 % of the strain value (in the linear viscoelastic region).

2.7. Preparation of emulsion

The pectin samples were first dissolved in deionized water to make 10 mL of fully hydrated pectin solution (2 %) and then mixed with corn germ oil (10 mL). Then the mixture was homogenized at 14000 rpm for 2 min using a high-speed homogenizer (Ika-Ultraturrax T25 basic, Ika Works, Inc., Wilmington, NC, USA) to prepare emulsions (Zhang et al., 2021).

2.7.1. Emulsifying properties

Emulsifying capacity (EC) and emulsifying stability (ES) were evaluated by previous studies (Zhang et al., 2021). EC and ES were evaluated using the following equations:

Table 1
Chemical composition and molecular weight of pectin from hawthorn.

	HHP	FHP	PHP	CHP	BHP
Physicochemical indexes					
Yield (%)	9.14 ± 0.14^{d}	12.48 ± 0.27^{b}	9.67 ± 0.03^{d}	14.48 ± 0.44^{a}	10.74 ± 0.32^{c}
DE (%)	44.71 ± 3.64^{d}	45.24 ± 0.63^{c}	52.39 ± 2.14^{a}	46.50 ± 4.50^{b}	30.92 ± 0.80^{e}
Protein content (%)	2.59 ± 0.03^{c}	2.56 ± 0.03^{c}	2.72 ± 0.02^{a}	2.65 ± 0.03^{b}	2.69 ± 0.03^{b}
Molecular weight					
Mw (g/mol)	279.81 × 10^3	464.42 × 10^3	396.09 × 10^3	346.81 × 10^3	73.67 × 10^3
Mn (g/mol)	93.67 × 10^3	190.83 × 10^3	142.34 × 10^3	152.64 × 10^3	43.62 × 10^3
Mw/Mn	2.99	2.43	2.78	2.27	1.69
Monosaccharide composition					
Gal A (%)	69.09 ± 0.40^{e}	83.64 ± 0.15^{d}	93.28 ± 0.17^{c}	90.91 ± 0.55^{b}	70.56 ± 0.09^{a}
Rha (%)	1.24 ± 0.05^{b}	1.31 ± 0.03^{a}	1.19 ± 0.05^{b}	1.33 ± 0.07^{a}	1.34 ± 0.07^{a}
Ara (%)	1.78 ± 0.04^{a}	1.74 ± 0.08^{a}	0.67 ± 0.02^{b}	0.56 ± 0.03^{c}	0.10 ± 0.04^{d}
Xyl (%)	0.22 ± 0.00^{b}	0.23 ± 0.02^{b}	0.23 ± 0.01^{b}	Nd	0.42 ± 0.02^{a}
Gal (%)	0.80 ± 0.03^{b}	1.06 ± 0.04^{a}	0.68 ± 0.07^{a}	0.77 ± 0.15^{a}	1.52 ± 0.18^{a}
Glc (%)	0.56 ± 0.00^{c}	3.92 ± 0.00^{a}	Nd	Nd	0.99 ± 0.06^{b}
Sugar molar ratios					
HG (%)	97.88 ± 0.07^{c}	98.14 ± 0.04^{b}	98.48 ± 0.07^{a}	98.32 ± 0.04^{a}	97.74 ± 0.13^{c}
RGI (%)	2.12 ± 0.07^{a}	1.86 ± 0.04^{b}	1.52 ± 0.07^{c}	1.68 ± 0.04^{c}	2.26 ± 0.01^{a}
(Gal +Ara)/ Rha	2.10 ± 0.02^{a}	2.13 ± 0.05^{a}	1.14 ± 0.02^{b}	1.00 ± 0.08^{c}	1.16 ± 0.06^{b}

Results were presented in the form of means ± standard deviation (SD). Data with different letters in the same column are significantly different with $p < 0.05$. HHP, hot air-dried hawthorn pectin; FHP, freeze-dried hawthorn pectin; PHP, parched hawthorn pectin; CHP, charred hawthorn pectin; BHP, blacken hawthorn pectin. Degree of esterification (DE, %). Molecular weight (Mw), number-average Molecular Weight (Mn). Rhamnose (Rha), fucose (Fuc), arabinose (Ara), xylose (Xyl), galactose (Gal), and glucose (Glc). HG, homogalacturonan; RGI, rhamnogalacturonan-I.

$$EC\ (\%) = \frac{V_f}{V_i} \times 100$$

$$ES\ (\%) = \frac{V_t}{V_f} \times 100$$

where V_f is the volume of emulsion, and V_i is the total volume of the mixture. V_t was the volume of the emulsion after high-temperature culture and centrifugation.

2.7.2. Droplets size distribution and optical microscopy observation

A laser particle size analyzer (LS13320, Beckman Coulter, USA) was used to analyze the droplet size distribution of emulsion. 20 μL emulsion was placed on the microscope slide and carefully covered with a cover glass. The microstructure of the emulsion was observed at 25 °C using an IX73 fluorescence inverted microscope system (Tokyo, Japan) coupled with CapStudio image processing software. Photographs were taken using a 40× objective of the microscope and an exposure time of 10 ms (Wang et al., 2021).

2.7.3. Rheological properties

A controlled stress rheometer (AR2000ex, TA Instruments, USA) equipped with a 20 mm parallel plate configuration was used to test pectin emulsions at a concentration of 2.0 %. At 25 °C, the prepared samples were subjected to steady-shearing for a shear rate ranging from 0.01 to 1000 s^{-1}. The dynamic viscoelasticity test was consistent with the method used in 2.6.

2.8. Statistical analyses

Unless otherwise noted, the data in this paper were expressed as mean and standard deviation. Analysis of variance (ANOVA, pb0.05) was acquired by SPSS 21.0 and the figures were created using Origin8.0.

3. Results and discussion

3.1. Characteristics of pectin in hawthorn with different processing methods

3.1.1. Physicochemical property and yield

The extraction rates of HHP, FHP, PHP, CHP, and BHP (Table 1) were 9.14 %, 12.48 %, 9.67 %, 14.48 %, and 10.74 %, respectively, indicating that different processing methods had an effect on the extraction rate of hawthorn pectin. The higher extraction rate of FHP was the same as the results of previous studies (Qin et al., 2019). In the study of Yan et al. (2019), it was found that the extraction rate of bitter melon polysaccharides was higher after freeze-drying. Moreover, the breakage of covalent bonds during roasting led to the release of proteins, pectins, and fibers (Zhang et al., 2012). This could be the reason for the high extraction rate of CHP.

The GalA content of HHP, FHP, PHP, CHP, BHP was 69.09 ± 0.40 %, 83.64 ± 0.15 %' 93.28 ± 0.17 %, 90.91 ± 0.55 %, 70.56 ± 0.09 %, respectively (Table 1). The differences in the content of GalA for pectin might be an indication of structural variations of the pectin backbone or varying extractability of pectin due to different drying methods (Xu et al., 2020). Similar results have also been reported by Ma et al. (2013). *Ganoderma lucidum* polysaccharides, mushroom *Inonotus obliquus* polysaccharides, and mulberry leave polysaccharides obtained from the freeze-dried sample all had the highest level of GalA comparison with the other drying method (Fan et al., 2012; Ma et al., 2013; Ma et al., 2018), which might be related to the lower oxygen concentration and lower temperature in the freeze-drying process (Ma et al., 2013; Yuan et al., 2020).

From Table 1, different processing methods resulted in pectins with different degrees of esterification. Apart from PHP, the other four pectins were low methoxylated pectin. At the same processing temperature, the DE of CHP with a longer heating time was lower than that of PHP, indicating that prolonged heating time can reduce the DE of pectin. It was also found that the DE of hawthorn water-soluble pectin and alkali-soluble pectin decreased with increasing heating time, which was due to the de-esterification of pectin at high temperatures (Zhou et al., 2021). Meanwhile, such changes in the apparent structure of the raw material might be conducive to the different DE of CHP and PHP (Qin et al., 2019; Xu et al., 2021). A small amount (2.56 %–2.72 %) of protein was present in the HHP, FHP, PHP, CHP, and BHP, which was lower than (4.4 %) of hawthorn pectin obtained by Cuevas-Bernardino et al. (2016).

3.1.2. Molecular weight and distribution

As shown in Table 1, comparing PHP and CHP, the Mw of CHP was lower. Li and Shah (2016) reported that polysaccharides could be thermally degraded during high-heat temperature treatment. Frying time could change the Mw of the polysaccharides from *Angelica Sinensis Radix*, attributing to the ability of polysaccharides to depolymerize, β-elimination, and reaggregate depending on temperature and heating time (Wang, Li, Chen, et al., 2019). The heating time of HHP and BHP was longer, and the Mw of BHP was also lower, which indicated that extending treatment time can reduce the Mw of pectin in high-temperature and acidic environments. This finding was proved by previous results reported by Wang, Li, Zhao, et al. (2019). FHP has a maximum Mw of 464.42 × 10^3 g/mol, indicating that freeze-drying has less effect on the Mw of pectin compared to other processing methods. This finding was in accordance with the results of Xu et al. (2021). It might be due to the fact that freeze-drying removes water from the raw material under vacuum sublimation, low temperature, and deoxygenation, minimizing degradation reactions (Karam et al., 2016). The polydispersity index (Mw/Mn) is often used to determine the molecular weight distribution width of polymers. The smaller the Mw/Mn was, the Mw distribution more concentrated (Kong et al., 2015). The Mw/Mn of BHP was 1.69, while the Mw/Mn of the other four pectins ranged from 2.27 to 2.99, indicating that BHP had the narrowest molecular weight distribution.

3.1.3. Monosaccharide composition

The content of neutral sugar and uronic acid of pectins was influenced by the processing method. Table 1 showed the galacturonic acid content and monosaccharide composition of the five pectins. The main component of hawthorn pectin is galacturonic acid (GalA), followed by other neutral sugars, mainly rhamnose (Rha), arabinose (Ara), and galactose (Gal). The type of neutral sugars in HHP, FHP, and BHP were the same, including Rha, Ara, Xyl, Gal, and Glc. PHP was no Glc, and CHP was no Xyl and Glc. The significant difference in the ratio and composition of the neutral sugars might be attributed to the temperature, time, and oxygen concentration of the five processing methods (Basanta et al., 2012; Huang et al., 2017; Nep & Conway, 2011; Wang, Li, Chen, et al., 2019; Xu et al., 2021; Zhao, Dong, et al., 2015). The low content of glucose and xylose in the pectin samples may be due to the presence of starch residues in the pulp or the presence of cellulose and hemicellulose attached to the pectin during pectin extraction (Yang, Mu, & Ma, 2018). And the ratio of galacturonic acid to rhamnose is an important characteristic of pectins and can be used to approximately assess the main types of pectin (homogalacturonan (HG) to rhamnogalacturonan-I (RGI)) (Yang, Nisar, et al., 2018). Five pectins with high galacturonic acid content indicated that HHP, FHP, PHP, CHP, and BHP were all HG pectin, and have a long main chain (Zhang et al., 2020). The HG region contents of the five pectins in Table 1 from highest to lowest were PHP (98.48 ± 0.07 %), CHP (98.32 ± 0.04 %), FHP (98.14 ± 0.04 %), HHP (97.88 ± 0.07 %), and BHP (97.74 ± 0.13 %), The proportion of HG regions of PHP, CHP, HHP, and BHP decreased with increasing heat treatment time, and Zhou et al. (2021) found that the "smooth regions" of hawthorn pectin were more sensitive to heat than the "hairy regions". Xu et al. (2020) showed that drying at 25–80 °C caused the decomposition of the smooth region in the pectin composition.

The molar ratio of (Ara + Gal)/Rha represents the branching degree and side-chain length of the RG-I fragment (Qin et al., 2019). From the data in Table 1, the ratios of the five pectins ranged from 2.13 ± 0.05 to 1.00 ± 0.08, indicating that they all had lower branching degrees and shorter side chains. The ratios of HHP, PHP, CHP, and BHP were lower than those of FHP, and the content of Ara gradually decreased from HHP to BHP, which showed that thermal processing reduced the (Ara + Gal)/Rha ratio of hawthorn pectin, indicating that the neutral sugar side chains of pectin were degraded, resulting in relatively shorter side chains of PHP, CHP, and BHP (Tan et al., 2020; Xu et al., 2021). Basanta et al. (2012) showed a significant loss of arabinose in pectins extracted by boiling water (Ps-HW, Ps-2-RHW), possibly indicating debranching of the hairy region (RG-I) and hydrolysis and β-elimination of side-chain glycosidic bonds due to heating.

Table 2
Color analysis of hawthorn pectin.

	HHP	FHP	PHP	CHP	BHP
ΔL*	−10.7 ± 0.26[b]	−9.9 ± 0.38[a]	−17.2 ± 0.35[c]	−25.4 ± 0.17[d]	−32.17 ± 0.05[e]
Δa*	3.47 ± 0.05[d]	4.03 ± 0.12[c]	5.00 ± 0.10[b]	5.36 ± 0.06[a]	5.03 ± 0.15[b]
Δb*	5.20 ± 0.36[c]	7.53 ± 0.47[b]	9.46 ± 0.45[a]	7.70 ± 0.10[b]	1.97 ± 0.15[d]
ΔE*	12.37 ± 0.12[e]	13.13 ± 0.06[d]	20.27 ± 0.12[c]	27.07 ± 0.12[b]	32.63 ± 0.06[a]

Results were presented in the form of means ± standard deviation (SD). Data with different letters in the same column are significantly different with $p < 0.05$. HHP, hot air-dried hawthorn pectin; FHP, freeze-dried hawthorn pectin; PHP, parched hawthorn pectin; CHP, charred hawthorn pectin; BHP, blacken hawthorn pectin.

3.2. Structural characteristics of pectin

3.2.1. Colorimetric analysis, surface morphology, and scanning electron microscopy

The colorimetric analysis of five hawthorn pectin was shown in Table 2, and the combination of the apparent morphological photographs could visually show that different processing methods affected the color of the pectin. Among them, the ΔL* values of HHP, PHP, CHP, and BHP gradually decreased. BHP had the lowest ΔL* value and FHP had the highest ΔL* value, it showed that among HHP, FHP, PHP, CHP, and BHP, FHP was whiter and brighter, while BHP was deeper and darker. When Δa* was a positive number, it indicated the degree of redness, as the value of Δa* increased, the degree of browning gradually deepened. It could be seen that PHP, CHP, and BHP all have browned, and CHP has a deeper degree of browning than PHP. PHP has the largest Δb* value, indicating that PHP has the yellowest color. The ΔE* values represent the total color difference of the pectins. Combining the data in Table 2 and Fig. 1, it could be seen that the ΔE* values gradually increased from HHP to BHP, HHP had the lightest color, and BHP had the darkest color. Monsoor (2005) found significant differences in the color of soybean pectin samples prepared by different drying methods, and the L*, a*, and b* values of pectin prepared by oven drying were the lowest, this was similar to the results of the present study.

The appearance of five pectins had a flake-like appearance at a magnification of 150×, but there were differences in morphology (Fig. 1). The lamellar structures of HHP and BHP were more complete, and smooth surfaces were observed for HHP at greater magnification, while pores and depressions existed on the surface of BHP. The lamellar gaps of PHP were larger and the surface was rippled, and the lamellae of CHP were thicker and had a smooth surface. The lamellae of CHP were thicker and had a smooth surface. The denseness of the surface structure of *angelica* polysaccharides was related to the stir-frying time, and different stir-frying times caused changes in molecular weight, molecular spacing, and interconnections (Wang, Li, Zhao, et al., 2019). The lamellae of FHP were less convoluted and had a rough surface with granular projections. Studies have found that mulberry leaf polysaccharides are affected by temperature, causing irreversible damage in cells, more active components are released due to structural integrity and internal collapse, resulting in smooth and rough surface morphology of mulberry leaves polysaccharides (Ma et al., 2018).

3.2.2. FT-IR analysis

The spectra of five pectin samples were consistent except for some different band intensities (Fig. 2A). Broadband appears between 3600 cm^{-1} and 3000 cm^{-1} centered at about 3330 cm^{-1}, this is due to the stretching vibrations of O—H groups induced by intermolecular and

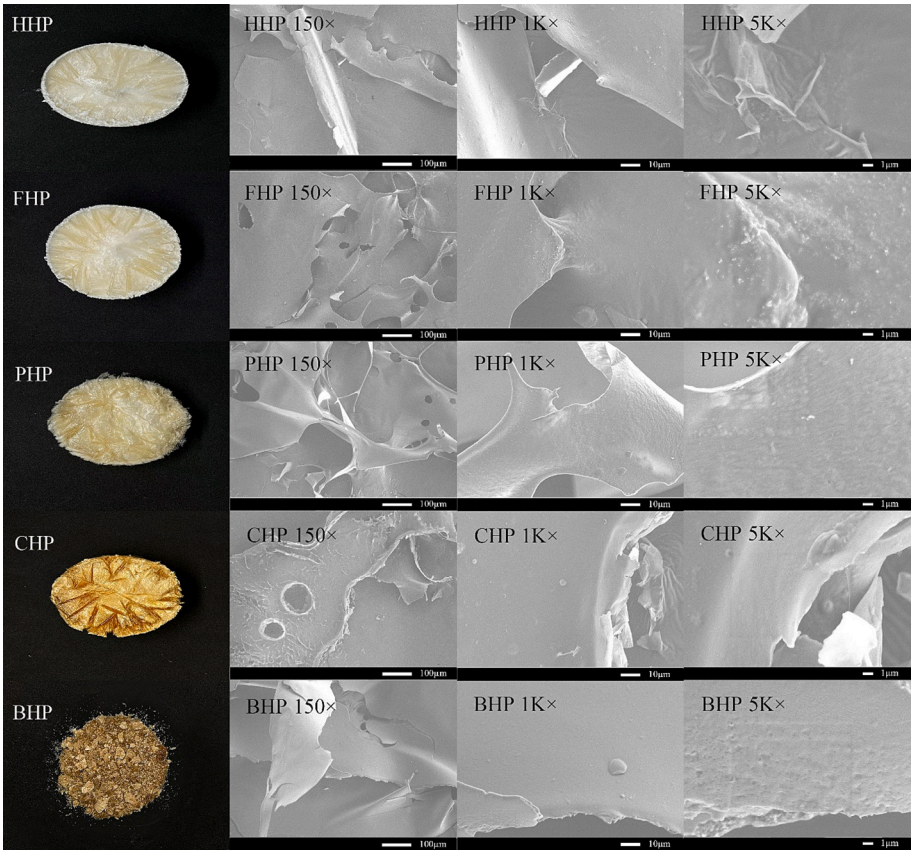

Fig. 1. Digital photos and Surface morphological images of HHP, FHP, PHP, CHP, BHP (HHP, hot air-dried hawthorn pectin; FHP, freeze-dried hawthorn pectin; PHP, parched hawthorn pectin; CHP, charred hawthorn pectin; BHP, blacken hawthorn pectin).

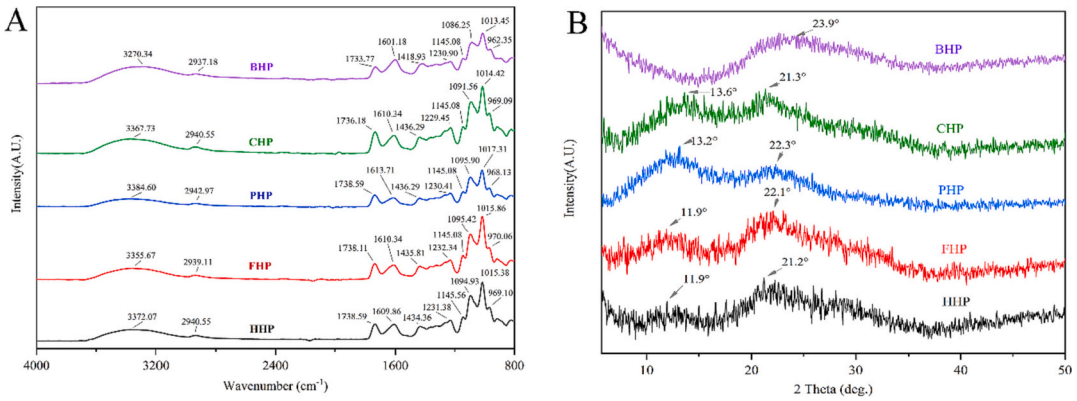

Fig. 2. FTIR spectrum (A), XRD pattern (B) of HHP, FHP, PHP, CHP, BHP (HHP, hot air-dried hawthorn pectin; FHP, freeze-dried hawthorn pectin; PHP, parched hawthorn pectin; CHP, charred hawthorn pectin; BHP, blacken hawthorn pectin).

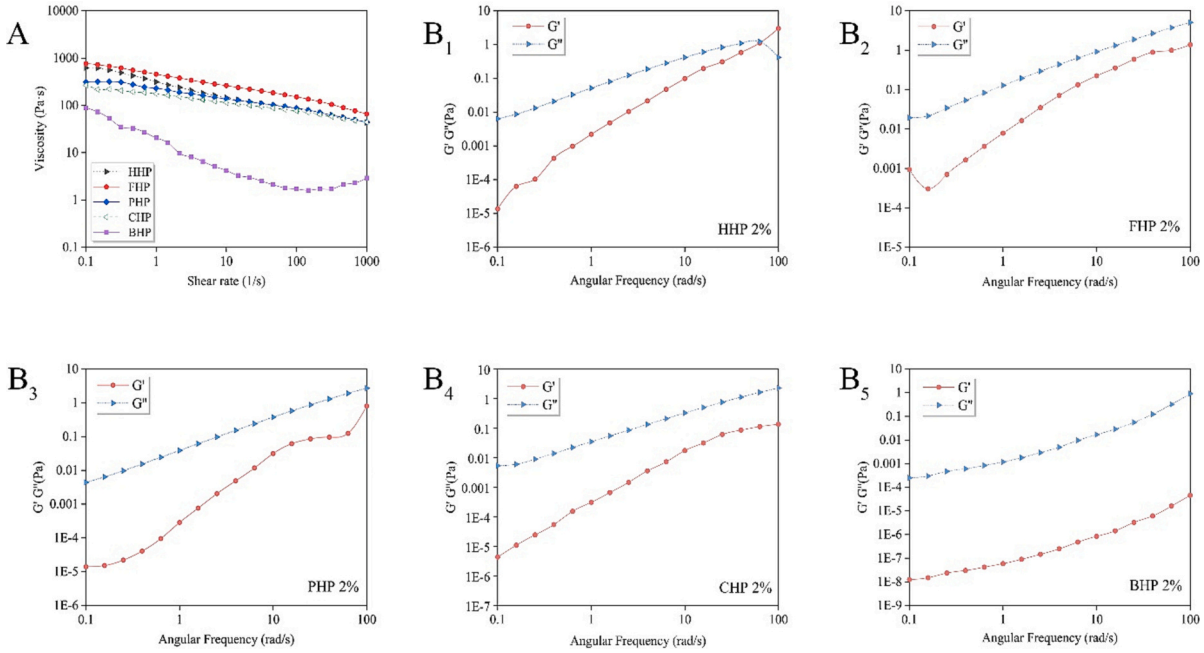

Fig. 3. Apparent viscosity(A) and rheological behavior(B_{1-5}) of HHP, FHP, PHP, CHP, BHP (HHP, hot air-dried hawthorn pectin; FHP, freeze-dried hawthorn pectin; PHP, parched hawthorn pectin; CHP, charred hawthorn pectin; BHP, blacken hawthorn pectin. G′, storage modulus; G″, loss modulus).

intramolecular hydrogen bonds in the GalA backbone (Kpodo et al., 2017). Weak absorption peaks were observed near 2940 cm^{-1} due to the stretching and bending vibrations of CH_2 and CH_3 (Jiang et al., 2020). The absorption peaks in the wavelength range between 1730 cm^{-1}-1740 cm^{-1} and 1630 cm^{-1}-1600 cm^{-1} were the characteristic peaks of pectin, It is caused by the C—O stretching vibration of methyl esterified carboxyl group and the asymmetric stretching vibration of free carboxyl group C═O, the area ratio of these two peaks reflects the DE of pectin (Munoz-Almagro et al., 2017). C═O elongation and bending vibration of C—OH groups were observed near 1436 cm^{-1} (Chen et al., 2021), and the peak near 1230 cm^{-1} was caused by —CH_3CO stretching. In addition, the asymmetric C—O—C stretching vibration appears near 1145 cm^{-1} (Sun et al., 2020; Yuan et al., 2020). Absorption peaks at 1095 cm^{-1} and 1017 cm^{-1} illustrated the presence of pyranose and furanose in the pectin (Jiang et al., 2018). The peak at 969 cm^{-1} belonged to the asymmetric C═O stretching vibration (Qin et al., 2019). Five pectins had no signal near 1651 cm^{-1} and 1555 cm^{-1}, indicating that the protein content in pectin was low (Kpodo et al., 2017).

3.2.3. XRD analysis

As shown in Fig. 2B, HHP, FHP, PHP, and CHP all showed two broad diffraction peaks, while BHP had only one broad diffraction peak, which demonstrated that five pectins had amorphous or semicrystalline structures (Xu et al., 2021). The diffraction peaks of HHP and FHP were around 11.9° and 21.2°-22.3° at 2θ, respectively, and the first diffraction peaks of PHP and CHP were at around 13.2° at 2θ, and BHP only had one diffraction peak at 23.9°. Previous studies have found that drying methods significantly affect the structure and crystallinity of polysaccharides (Caparino et al., 2012; Kong et al., 2015; Xu et al., 2021). The results showed that different processing methods will affect the crystallization properties of pectin. In particular, after the blackening of hawthorn, the crystallinity of pectin decreased. It was found that most natural polysaccharides existed in a microcrystalline or amorphous structure, and no obvious crystal structure was formed, which provided strong evidence for the results of this study (Kong et al., 2015).

3.3. Rheological analysis

Fig. 3 showed the flow curves of five pectin solutions under stable

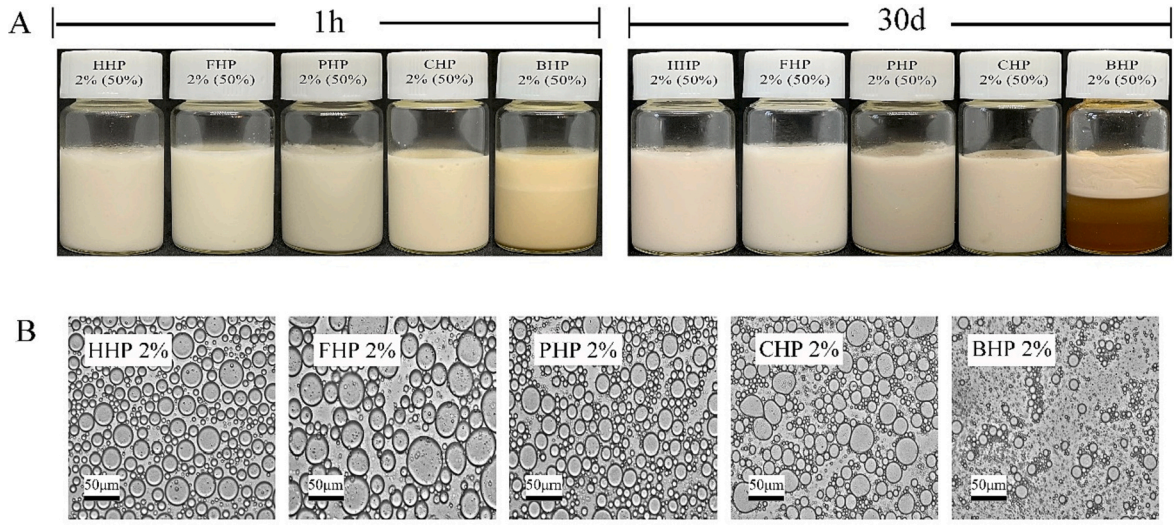

Fig. 4. Digital photos (A) and Optical micrographs (B) of oil-in-water emulsions stabilized by five hawthorn pectin (HHP, hot air-dried hawthorn pectin; FHP, freeze-dried hawthorn pectin; PHP, parched hawthorn pectin; CHP, charred hawthorn pectin; BHP, blacken hawthorn pectin).

shear conditions. The solutions of HHP, FHP, PHP, CHP, and BHP showed the characteristics of non-Newtonian fluids, the apparent viscosity decreased with an increase in the shear rate, indicating a typical shear thinning behavior (Wang et al., 2021). BHP had weaker shear resistance compared with the other four pectins, the shear-thinning fluidity was related to the disentanglement of molecular chains in solution (Fu et al., 2020). Under a high shear rate, the degree of entanglement between pectin macromolecular chains was reduced (Yuan et al., 2020), and molecules were more likely to reorient following the flow direction, resulting in a decrease in apparent viscosity (Zhang et al., 2021). When the shear rate was 0.1, FHP had the best apparent viscosity, while BHP had the lowest apparent viscosity. The results of Xu et al. (2020) also showed that the pectin extracted from freeze-dried okra pods had the highest viscosity among the five drying technology. FHP had the maximum viscosity, speculating that the big molecular weight increased the interaction of pectin polysaccharides. Similar results were gained by Ma et al. (2013). Studies have shown that molecular weight and its distribution had a strong influence on the viscosity of pectin polysaccharides, and the molecular weight is related to the apparent viscosity (Zhang et al., 2013). In the study of Xu et al. (2020), the molecular weight and the viscosity of okra pectin gained freeze-dried samples are the highest, which is consistent with the results of this study.

Except for BHP, the storage modulus (G′), and loss modulus (G″) of the other four pectins were getting closer with increasing frequency (Fig. 3), showing the characteristics of weak gels (dilute solutions), indicating processing methods might influence on the G′ and G″ of

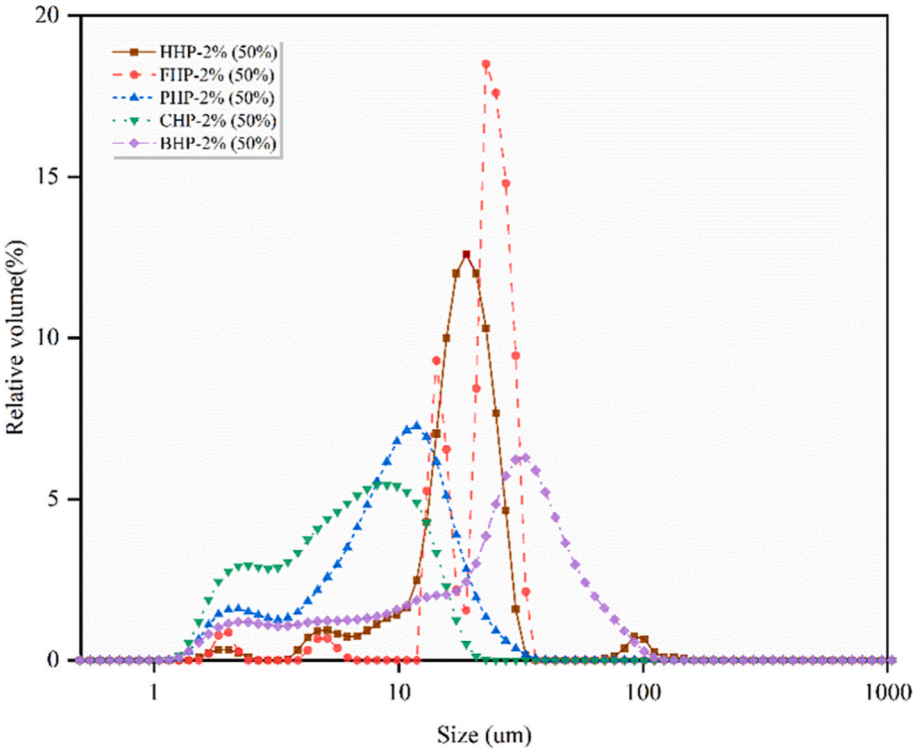

Fig. 5. Particle size distribution of five hawthorn pectin emulsions.

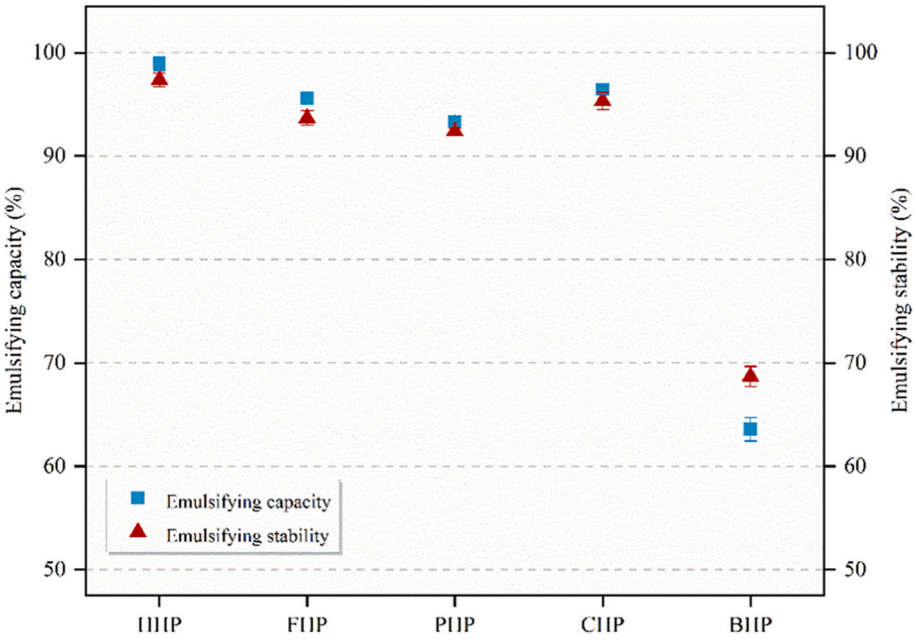

Fig. 6. Emulsifying capacity (EC) and emulsifying stability (ES) of five hawthorn pectin emulsions.

hawthorn. The results of this study were consistent with the previous results of the papers (Ramos-Aguilar et al., 2015; Yuan et al., 2020). The intersection point of G′ and G″ values reflected the viscoelastic properties of the material and is called the gel point (Gp). Except for HHP, there was no gel point in FHP, PHP, CHP, and BHP, Hou et al. (2012) found in a study of chitosan that the G″ and G′ of chitosan increased with the increase of frequency, and the G′ was lower than the G″, resulting in liquid-like behavior of the solution. It has been demonstrated that the presence of side chains could promote the entanglement and interaction of polymer molecules until a tighter conformation is formed, promoting hydrophobic interactions and hydrogen bonding (Sousa et al., 2015). The branched chains and RGI region of HHP were relatively high, which might be the reason for the gel-type nature of HHP.

3.4. Emulsifying properties of five pectin

3.4.1. Visual appearance and microscopic photos of five pectins stabilized emulsions

As shown in Fig. 4A, the BHP appeared to delaminate slightly after 1 h of preparation, but no significant phase separation occurred. After 30 d, except for BHP, the four pectin emulsions remained uniform and stable, and only BHP had phase separation, which indicated the emulsifying ability of HHP, FHP, PHP, and CHP were significantly better than that of BHP. Fig. 4B showed that the emulsions of HHP and FHP formed oil droplets of uniform size, while the emulsions of PHP, CHP, and BHP formed oil droplets of non-uniform size. Meanwhile, the emulsion of BHP appeared to coalesce. The difference in the emulsifying ability of the five pectins might be related to the difference in the physicochemical properties among the five pectins (N. et al., 2022). The study found that non-adsorbed pectins with lower molecular weights had a limited ability to alter the viscosity of the aqueous phase, possibly leading to a greater tendency for droplet movement and subsequent destabilization of the emulsion (Wan et al., 2019). The results gained by Schmidt et al. (2015) proved lower molecular weights may lead to pectin chains that are too short to entangle, resulting in stabilizing the droplets.

3.4.2. Particle size analysis of emulsion

As shown in Fig. 5, the emulsions of the HHP, FHP, PHP, CHP, and BHP showed a bimodal distribution. The emulsion particle sizes of PHP and CHP were smaller compared to the other three pectins, the droplet size distribution was wider compared to HHP and FHP, and the droplet size distribution of BHP was the widest, indicating that different processing methods affected the emulsion particle size. It has been suggested that the faster the emulsifier molecules cover the droplet surface during the homogenization process, the smaller the initial droplet size will be and accordingly have better emulsification ability (Cuevas-Bernardino et al., 2016). Previous studies have found that pectins with higher molecular weights do not adsorb properly in the oil-water phase, resulting in emulsions with larger droplet sizes (Cui et al., 2020). Wan et al. (2019) concluded that pectin emulsions with a wide particle size distribution and multiple peaks were not stable enough after droplet fragmentation. HHP pectin had a narrow and simple particle size distribution, and in combination with microscopic observation, HHP was found to form highly uniform and stable emulsions. Therefore, pectin emulsions with good emulsion stability can be prepared by selecting pectin with good viscosity through processing.

3.4.3. Emulsifying capacity (EC) and emulsifying stability (ES) of five pectin

Emulsifying capacity (EC) and emulsifying stability (ES) may be used to evaluate the emulsifying properties of pectin (Fig. 6). The ES and EC increased in the order of HHP > CHP > FHP > PHP > BHP, which revealed that HHP showed the best emulsifying properties and BHP the worst. This proved that the processing methods of hawthorn influence the emulsifying properties of hawthorn pectin. The ES and EC of five pectins were higher than that of commercial citrus pectin (EC:46.67 ± 2.35 %, ES: 64.28 ± 3.58 %), sugar beet pectin (EC:33.5 %), and *opuntia ficus indica* pectin (EC:26.9 %, ES: 14.31 %) (Bayar et al., 2016; Bayar et al., 2018; Ma et al., 2013). The emulsifying properties of pectin depend on the physicochemical properties of droplets (Li, Deng, et al., 2020; Xu et al., 2021). Funami et al. (2009) and Yang, Mu, and Ma (2018) proved emulsifying properties of pectin were proportional to the galacturonic acid concentration, acetyl group concentration, and molecular weight. Similar results were gained by Jiang et al. (2020). In addition, the presence of protein in pectin and the presence of arabinose, galactose in the lateral chains had a positive impact on the emulsifying properties of pectin (Bayar et al., 2016).

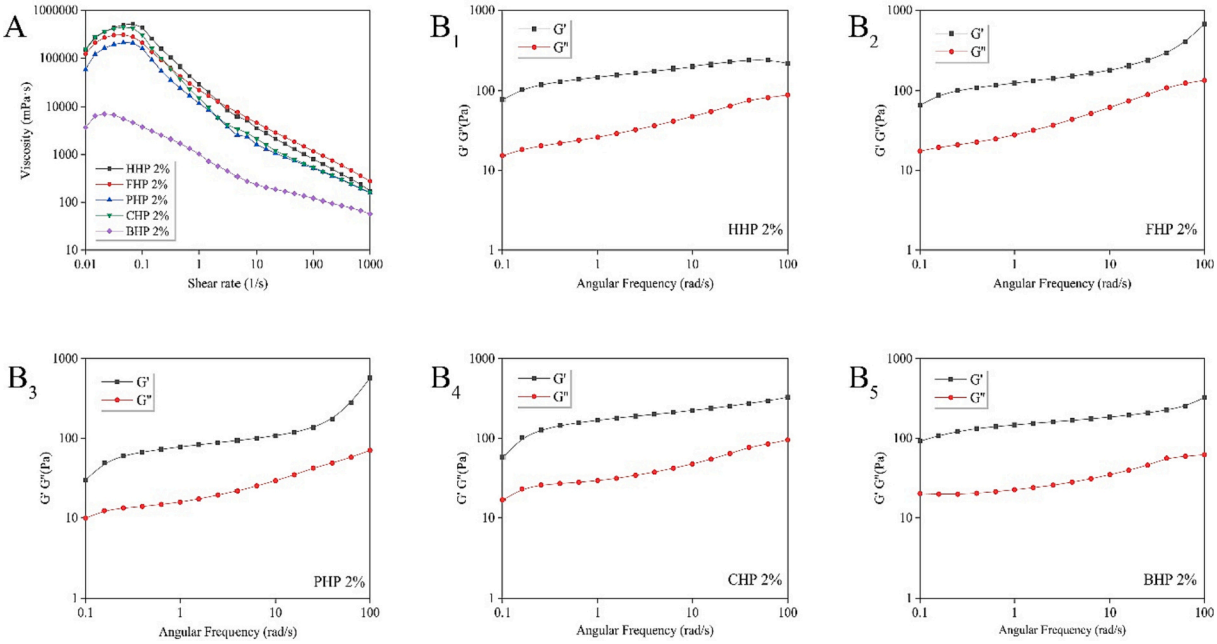

Fig. 7. Apparent viscosity(A) and rheological behavior(B_{1-5}) of HHP, FHP, PHP, CHP, BHP emulsions (HHP, hot air-dried hawthorn pectin; FHP, freeze-dried hawthorn pectin; PHP, parched hawthorn pectin; CHP, charred hawthorn pectin; BHP, blacken hawthorn pectin. G′, storage modulus; G″, loss modulus).

3.4.4. Influence of drying method on the rheological properties of pectin emulsions

As shown in Fig. 7, the emulsion of HHP, FHP, PHP, CHP, and BHP all exhibited shear thinning, that is, their apparent shear viscosity decreased with increasing shear rate. Similar results were found in a study by Zhao, et al. (Zhao, Wei, et al., 2015). Viscosity has a greater degree of influence on the stability of the emulsion, and higher viscosity can make the emulsion have better stability (Jiang et al., 2020). High viscosity polysaccharides reduced the fluidity of emulsions and impeded the movement or aggregation of droplets, thus improving the stability of emulsions (Ren et al., 2020). It was found that the reduction of molecular weight of polysaccharide emulsions could improve their interfacial properties and facilitate the formation of fine emulsions (Li et al., 2018). This may be the reason why HHP and CHP have lower molecular weight than FHP but higher apparent viscosity of emulsions. From Fig. 7, there was no crossover between energy G′ and the G″ of the five pectin emulsions, and all pectin emulsions exhibited rapid gel formation with a typical gel-like structure. According to previous reports, the longer the molecular chain of pectin with higher molecular weight, the more active binding sites, resulting in a permeable network structure with higher viscosity and elastic modulus (Cao et al., 2020).

4. Conclusions

HHP, FHP, PHP, CHP, and BHP were successfully acquired from different hawthorn processed products obtained by hot air drying, vacuum freeze drying, parched processing, charred processing, and blackening. The results revealed, that HHP, FHP, CHP, and BHP were all low-methoxy pectin apart from PHP. PHP and CHP had higher GalA content, FHP had high molecular weight, and BHP had the smallest molecular weight. In addition, Different processing methods of hawthorn had an effect on the physicochemical properties and emulsification properties of pectin. Especially, HHP had good emulsification ability and emulsification stability, however, BHP had poor emulsification properties performance. It was shown that the emulsification performance of high Mw pectin was better. HHP, FHP, PHP, and CHP had good emulsification performance and were suitable as natural emulsifiers. Low Mw pectin (BHP) can be obtained by blackening, while the specific application of low Mw pectin needed further study.

CRediT authorship contribution statement

Zhixin Li: Investigation, Methodology, Data acquisition and analysis, Writing-original draft; Jiarui Zhang: Data acquisition and analysis, editing; Hao Zhang, Data acquisition, Yuan Liu: Data acquisition, Chuanhe Zhu: Conceptualization, Supervision, Funding acquisition, Writing-review & editing.

Declaration of competing interest

The authors declare no conflict of interest related to the publication of this manuscript.

Data availability

Data will be made available on request.

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