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ORIGINAL RESEARCH

Comparative study on the physical entrapment of soy and mushroom proteins on the durability of bacterial cellulose bio-leather

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Abstract This study aimed to develop eco-friendly bacterial cellulose (BC) bio-leather with improved durability using plant-based proteins, namely soy protein isolate (SPI) and mushroom protein (MP), which were physically entrapped inside the BC, respectively. The amounts of the plant-based proteins were determined by evaluating the tensile strength of BC bio-leather, and were found to be 20 wt% and 50 wt% of BC for SPI and MP, respectively. The enhanced properties of mechanical strength and durability of BC bio-leather were measured in terms of changes in water resistance, tensile strength, flexibility, crease recovery, and dimensional stability. The durability of BC was improved after the entrapment of proteins, and moreover, the durability of BC entrapped with plant-based proteins was further improved by the addition of glycerol. Especially, BC entrapped with MP and glycerol had better water resistance, tensile strength, flexibility, and crease recovery compared to cowhide leather. The chemical and physical structures of BC bio-leathers were studied using Fourier transform-infrared spectroscopy, X-ray diffraction, field-emission scanning electron microscopy, and energy dispersive X-ray spectroscopy analyses. From the results, it was confirmed that BC entrapped with MP and glycerol could be a suitable leather substitute.

Keywords Bacterial cellulose · Bio-leather · Plant-based protein · Soy protein isolate · Mushroom protein · Durability

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Introduction

Leather is a natural fabric material obtained from skins of animals (Stepanova et al. 2017). The treatment process of leather is highly complicated with various steps (Zarlok et al. 2014). Especially, tanning is an essential treatment process in the leather industry since it prevents the degradation of leather, and thus, the quality of leather can be maintained for a long period of time (Sudha et al. 2009). In the tanning process, however, toxic chemicals such as metal salts and hexavalent chromium are used, and the decomposition of protein wastes causes serious odor (Kanagaraj et al. 2006). Moreover, the supply of the leather is currently decreasing due to the animal protection movements, and the demand for artificial leather or eco-friendly bio-leather is increasing with the advent of vegans (Kim et al. 2017).

Bio-leather is a sustainable biomaterial derived from natural sources such as plants and microorganisms, making it environmentally friendly and biodegradable, thus helping reduce textile waste (Garcia and Prieto 2019). According to the previous study, the general sources for bio-leather include natural latex, pineapple, mushroom, jellyfish, and bacterial cellulose (BC) (Kim et al. 2017; De Santa Costa et al. 2017). This study is focused on BC to develop the bio-leather.

BC is an eco-friendly cellulose material produced by *Acetobacter xylinus* (Kim et al. 2020a). Since BC is made of a fibrous three-dimensional nanostructure, it has excellent advantages as a bio-leather: It possesses high purity, high crystallinity and polymerization degree, and good water-holding capacity (Kim et al. 2020b); Altering the fermentation conditions can result in BC with excellent moldability, biodegradability, and biocompatibility (Song et al. 2020); Moreover, unlike animal leather, additional processes such as tanning and graining are not necessary for BC bio-leather.

However, the high water-holding capacity of BC has several drawbacks. Its hydrophilicity causes poor rehydration and durability of BC bio-leather, and when exposed to moist or wet conditions, BC loses its shape and strength (Song et al. 2020).

In this study, to overcome these aforementioned drawbacks, BC bio-leather is modified by physical entrapment of proteins, which are naturally derived materials, and are non-toxic and biodegradable (Wang et al. 2016). Proteins have shown to improve the mechanical properties of the cellulose composite material owing to their structural properties and high molecular binding potential (Ou et al. 2004; Zhou et al. 2008). Among them, this study is focused on plant-based proteins such as soy protein isolate (SPI) and mushroom protein (MP). SPI and MP contain polar amino acids having carboxyl and amide groups so that they can easily react with the hydroxyl groups in BC, making it easily modifiable (Tian et al. 2018; Senapati and Sarkar 2014; Kayode et al. 2015). In addition, they are inexpensive and can be easily obtained due to their abundance (Xu et al. 2019; Tian et al. 2016). Previous studies have also used SPI to modify BC (Zhang et al. 2020; Guo et al. 2018; Liu et al. 2017; Wang et al. 2017). However, in previous studies mentioned above, BC was ground or smashed, mixed with SPI, and then freeze-dried or dried to become a stabilized film or foam. These modification methods are complicated because they require additional steps to change the shape of BC. Instead, the physical entrapment method is employed in this study to entrap proteins directly inside BC without changing the shape of BC. This method not only improves the durability of BC, but also minimizes the modification process of BC.

Therefore, the aim of this study is to develop two types of eco-friendly BC bio-leathers by physically entrapping plant-based proteins, namely SPI and MP, respectively, and compare their durability. To enhance the processability of SPI and MP, glycerol was added (Tian et al. 2012). The amount of proteins is determined by observing the change in the tensile strength. Next, the durability and mechanical properties of BC bio-leathers are measured by parameters such as water resistance, tensile strength, etc. and compared with cowhide leather of similar thickness. Lastly, chemical and physical structures of BC bio-leathers are evaluated using Fourier-transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM), and energy dispersive X-ray spectroscopy (EDX).

Materials and methods

Materials

Glucose, hydrogen peroxide (H_2O_2, 34.5 %), sodium hydroxide (NaOH, beads), acetic acid, glycerol, and 1 N NaOH solution were purchased from Duksan Pure Chemical Co., Ltd. (Seoul, Korea). Kombucha SCOBY was obtained by GetKombucha (CO, USA). Yeast extract and peptone were obtained from BD Biosciences (San Jose, CA, USA). Soy protein isolate was purchased from Avention (Incheon, Korea). Shiitake mushroom powder (food grade) was purchased from The Yeondu (Uijeongbu, Korea). All chemical reagents were used as received.

Production of BC bio-leather

BC bio-leather was produced according to the procedure reported by Han et al. (2018) followed by washing, bleaching, and swelling pretreatments (Han et al. 2018; Song et al. 2017). Briefly, glucose was

used as a carbon source (20 g/L), and a mixture of peptone and yeast extract powders was used as a nitrogen source (5 g/L for each) to produce the HS medium. Kombucha SCOBY was added in the HS medium in a liquor ratio of 1:7 and statically cultured at 26 °C for 8 days to produce BC with a thickness of 1 cm. BC was then washed with 3 % NaOH solution at 25 °C for 90 min with shaking at 50 rpm, neutralized with distilled water, and adjusted to pH 3.0 using acetic acid for 30 min with shaking at 50 rpm. Subsequently, BC was bleached with a 5 % H_2O_2 solution at 90 °C for 60 min with shaking at 110 rpm, swelled with an 8 % NaOH solution in a liquor ratio of 1:10 (w/v) for 30 min in an ultrasonic bath (UC-20; JEIO TECH Co., Daejeon, Korea), and neutralized with acetic acid solution by adjusting the pH level of the solution to pH 3.0.

Physical entrapment of plant-based proteins in BC bio-leather

Plant-based proteins such as SPI and MP were entrapped inside the produced BC bio-leather separately. Figure 1 describes the production method of BC bio-leathers.

First, to determine the amount of SPI and MP, varied amounts of SPI or MP in the range of 10 to 60 wt% (weight %) of BC bio-leather were added to distilled water with a fabric-to-liquor ratio of 1:10. The determined amount of SPI and MP was evaluated by the change in the tensile strength of BC bio-leather according to ISO 13934-2:2014 (Tensile properties of fabrics—Determination of maximum force using the grab method). To find out whether the effects of amounts of SPI and MP on the tensile strength of BC bio-leathers were statistically significant or not, we calculated 95 % confidence intervals.

The 95 % confidence interval was calculated by the following Eq. (1):

$$95\%\,\text{confidence interval} = \bar{X} - 1.96\frac{\sigma}{\sqrt{n}} \le \mu \le \bar{X} + 1.96\frac{\sigma}{\sqrt{n}} \quad (1)$$

where $\bar{X}$ denotes the mean of samples, σ denotes the standard deviation, n denotes the number of samples, and μ denotes the mean of a sample group.

The amount of glycerol, which was 30 wt% of BC bio-leather, was used to improve the processability of proteins. The resulting solutions were then ultrasonicated for 30 min at 25 °C to obtain uniform mixtures. Next, the solutions were subjected to denaturation. The pH levels of the solutions were adjusted to 10 (± 0.5) using 1 N NaOH solution and the solutions were shaken in a shaking water bath (BS-31; JEIO

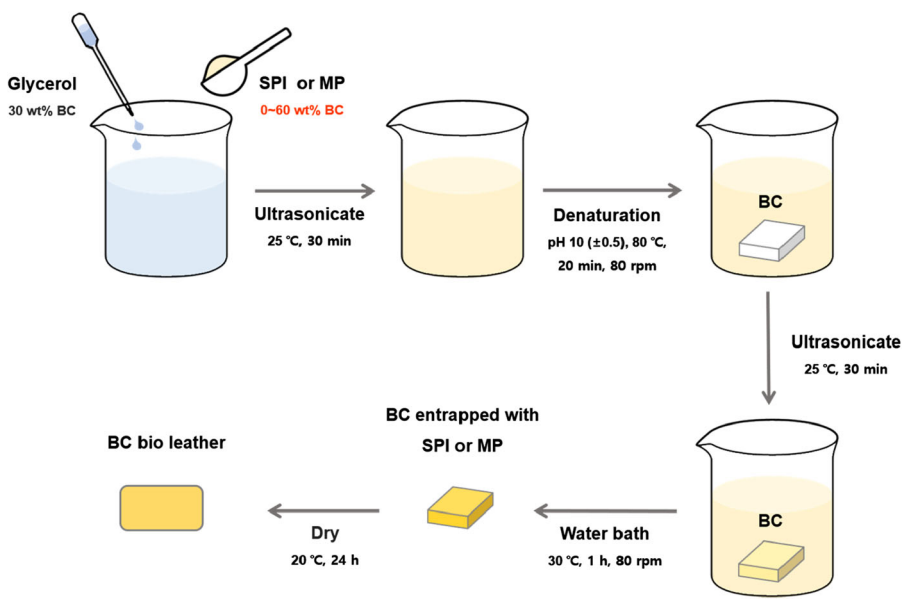

Fig. 1 Schematic illustration of the production method of BC bio-leathers

TECH Co., Daejeon, Korea) at 80 °C for 20 min at 80 rpm. The pretreated BC bio-leather was then immersed in the solutions, ultrasonicated for 30 min at 25 °C, and additionally treated at 30 °C in a shaking water bath for 1 h at 80 rpm. Finally, the obtained BC bio-leathers were dried in a drying oven (OF-22G; JEIO TECH Co., Daejeon, Korea) for 24 h at 20 °C.

Evaluation of the durability of BC bio-leather

The durability of BC bio-leather before and after physical entrapment of proteins was tested by the evaluation of parameters such as water resistance, tensile strength, flexibility, crease recovery, and dimensional stability.

Water resistance

The water resistance properties were examined by water contact angle (WCA) and water absorption time measurements. First, WCA was analyzed using a contact angle measurement system (DSA 25; KRUSS Inc., Hamburg, Germany) by the sessile drop method, in which a 2 μL droplet of deionized water was placed on the surface of each sample using a Hamilton 500 μL syringe at a suitable distance to the testing platform. The angle formed by the tangent of the droplet with the surface of each sample was recorded by ADVANCE software (KRUSS Inc., Hamburg, Germany). The average WCA value was obtained by measuring five different spots on the surface of each sample. Next, the water absorption time measurement was performed according to Song et al. (2019). A 0.01 % Methylene blue (C.I. 52,015) solution was used to visually confirm the complete absorption of droplets on the surface of samples. A 5 μL drop of this solution was placed onto the surface of each sample, and the water absorption time was measured until the specular reflectance of a droplet was completely disappeared.

Tensile strength

The tensile strength was evaluated according to ISO 13934-2:2014 (Tensile properties of fabrics—Determination of maximum force using the grab method) with a slight modification in the size of the tested sample. The size of the sample was modified to 5 × 10 cm. All measurements were performed five times for each sample, and the average values were obtained.

Flexibility

The flexibility was tested according to ASTM D1388-18 (Standard Test Method for Stiffness of Fabrics: The Heart Loop Test) with some modifications. The size of the sample was modified to 5 × 10 cm. Samples were shaped as loops, and after 1 min, the distance from the upper end to the lowest point of the loop was measured. The change in distance was calculated according to the following Eq. (2):

$$\Delta d(\%) = \frac{d_1 - d_0}{d_0} \times 100 \tag{2}$$

where Δd is the change in the distance, d_0 is the distance of the loop before the measurement, and d_1 is the distance of the loop after 1 min.

Crease recovery

The crease recovery angles were measured according to ISO 2313:1972 (Determination of the recovery from creasing of a horizontally folded specimen of fabric by measuring the angle of recovery). Crease recovery was calculated according to the following Eq. (3):

$$\text{Crease recovery}\,(\%) = \frac{\text{crease recovery angle}\,(^\circ)}{180^\circ} \times 100 \tag{3}$$

All measurements were performed five times for each sample and the results were averaged.

Dimensional stability

The dimensional stability was evaluated according to ISO 7771:1985 (Determination of dimensional changes of fabrics induced by cold-water immersion) with a slight modification. The size of the samples was modified to 5 × 10 cm, and the experiment time was varied from 60 to 180 min. Samples were marked at four points to measure the dimensional change. Samples were immersed in 0.5 g/L of a wetting agent (sodium dodecylbenzenesulfonate, $C_{18}N_{29}NaO_3S$). After immersion, BC bio-leathers were dried in a drying oven at 25 °C for 5 h, and then the dimensional

change was measured. The percentage of dimensional stability was calculated using the following Eq. (4):

$$\text{Dimensional stability}\,(\%) = \frac{A_{mm}}{B_{mm}} \times 100 \quad (4)$$

where B_{mm} is the size in millimeters of samples before immersion, and A_{mm} is the size in millimeters of samples after immersion. All samples were tested five times and the average value was measured.

Surface analysis of BC bio-leathers

A Fourier transform-infrared (FT-IR) spectrometer (Nicolet IS50; Thermo Fisher Scientific, MA, USA) was used to examine the chemical structures of BC bio-leathers. The FT-IR spectra of the samples were recorded in the wavenumber range of 650–4000 cm^{-1} at a resolution of 0.4 cm^{-1} with 32 scans. Baseline normalization was carried out for each spectrum using OMNIC software (Thermo Fisher Scientific, MA, USA).

The crystalline structures of BC bio-leathers were examined by X-ray diffraction (XRD) analysis using a D8 ADVANCE diffractometer (Bruker AXS Inc., WI, USA) in the 2θ range of 0°–40°. XRD measurements were carried out with a Cu-K_α radiation source (λ = 1.5406 nm) at 40 kV and 40 mA.

The surface morphologies of BC bio-leathers were characterized by a field emission scanning electron microscope (FE-SEM) (JSM-7600F; JEOL Ltd., Tokyo, Japan). All samples were sputter-coated with platinum using a magnetron sputter coater (108auto; Cressington Scientific Instruments, Watford, UK) and then observed at an acceleration voltage of 3 kV.

Along with the SEM analysis using FE-SEM, energy dispersive X-ray analysis (EDX) was performed to determine the existence of plant-based proteins inside BC bio-leathers. All samples were sputter-coated with platinum using a magnetron sputter coater (108auto; Cressington Scientific Instruments, Watford, UK).

Results and discussion

Physical entrapment of plant-based proteins on BC bio-leather

The physical entrapment of plant-based proteins on BC bio-leather was controlled by evaluating the amount of proteins from 0 to 60 wt% of BC. The amount of protein to be entrapped was determined by selecting the production conditions with the highest tensile strength. The conditions used in determining the amounts of SPI and MP, and tensile strength (N) with standard deviations were presented in Table 1. As shown in Fig. 2a, b, the tensile strength of BC bio-leather increased with an increase in the amount of entrapped proteins. In Fig. 2a, after entrapping SPI at an amount of 20 wt% of BC, the tensile strength of BC bio-leather increased approximately 3.73 times compared to that of the original BC. When the amount of SPI exceeded 20 wt% of BC, there was no significant change in the tensile strength of BC bio-leather, which is attributed to the lower availability of bonding sites in BC to react with functional groups of SPI (Behera et al. 2012). In Fig. 2b, the highest tensile strength value was obtained when MP at an amount of 50 wt% of BC was entrapped. However, the tensile strength of BC bio-leather decreased after entrapping MP at an amount of 60 wt% of BC. This may have occurred because there were fewer available hydroxyl groups in BC to react with functional groups of MP. Hence, the excess MP molecules agglomerated on the surface of BC bio-leather, disrupting the interaction between BC and MP (Xie et al. 2020).

The reason why the optimum amount of SPI and MP are different is that the amino acid composition, which can react with hydroxyl groups in BC (Liu et al. 2017), are different. Thus, the reactivity of SPI and MP with BC would be different. To be specific, SPI is composed of amino acids such as lysine, arginine, histidine, glutamate, aspartate, serine, threonine, and tyrosine (Liu et al. 2017), and MP is consisted of amino acids such as serine, threonine, alanine, proline, aspartic acid, glutamic acid, leucine, isoleucine, lysine, methionine, phenylalanine, and histidine (Finimundy et al. 2014; Park et al. 2017). We assumed that the differences in the amino acid compositions of SPI and MP had an influence on the tensile strength of BC bio-leathers, but we could not specify which element

Table 1 Conditions used in determining the amounts of SPI and MP, and tensile strength (N) with standard deviations

Sample #	Protein	Amount (wt% BC)	Glycerol (wt% BC)	Tensile strength (N)
1	–	–	30	63.6 ± 8.3
2	SPI	10	30	425.3 ± 96.9
3	SPI	20	30	589.1 ± 54.9
4	SPI	30	30	583.9 ± 66.2
5	SPI	40	30	542.5 ± 53.5
6	SPI	50	30	569.5 ± 40.7
7	SPI	60	30	536.3 ± 32.2
8	MP	10	30	308.2 ± 158.7
9	MP	20	30	307.4 ± 153.7
10	MP	30	30	430.7 ± 150.6
11	MP	40	30	531.5 ± 46.4
12	MP	50	30	647.3 ± 27.0
13	MP	60	30	462.6 ± 209.0

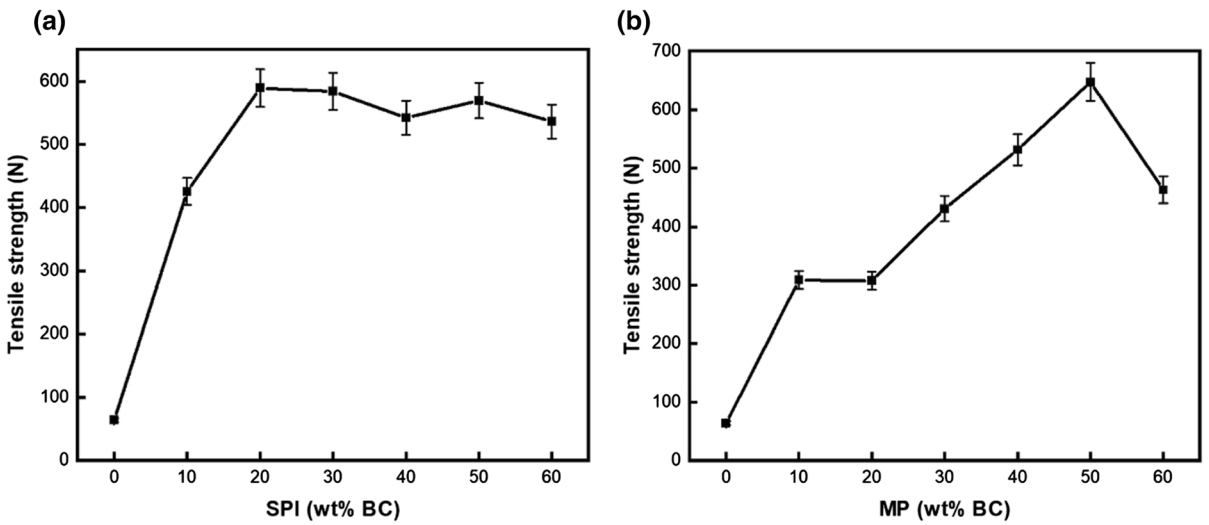

Fig. 2 The change in tensile strength (N) of different amounts of **a** SPI and **b** MP entrapped in BC with 95 % confidence interval bars

had improved the tensile strength. However, this study is mainly focused on the methods of improving the durability of BC to be used as a leather substitute. Thus, we found that when physically entrapping proteins inside BC, the amount of proteins had to be controlled due to the different amino acid composition of each protein.

Evaluation of the durability of BC bio-leather

To confirm the effect of only proteins in the durability of BC bio-leathers, samples entrapped with only SPI or MP and a sample entrapped with only glycerol were produced and analyzed. Samples were coded as follows. BC samples entrapped with both proteins and glycerol were named as BC-SPI (with glycerol) and BC-MP (with glycerol), respectively. BC samples entrapped with proteins only were named as BC-SPI (without glycerol) and BC-MP (without glycerol), respectively. In the case of BC entrapped with only glycerol, the sample was named as BC-glycerol.

Before the evaluation, the thickness and weight of each sample was measured ten times and the average values were provided in Table 2.

Table 2 Fabric characterizations of original BC, cowhide leather, BC-glycerol, BC-SPI (with glycerol), BC-SPI (without glycerol), BC-MP (with glycerol), and BC-MP (without glycerol) (production conditions for BC-SPI (with glycerol): fabric to liquor ratio of 1:10, SPI at an amount of 20 wt% of BC, 30 wt% of BC of glycerol; production conditions for BC-SPI (without glycerol): fabric to liquor ratio of 1:10, SPI at an amount of 20 wt% of BC; production conditions for BC-MP (with glycerol): fabric to liquor ratio of 1:10, MP at an amount of 50 wt% of BC, 30 wt% of BC of glycerol; production conditions for BC-MP (without glycerol): fabric to liquor ratio of 1:10, MP at an amount of 50 wt% of BC)

Sample	Thickness (mm)	Weight (g/m^2)
Original BC	0.9 ± 0.1	186.7 ± 12.5
Cowhide leather	0.7 ± 0.1	466.7 ± 18.3
BC-glycerol	0.5 ± 0.2	190.0 ± 37.2
BC-SPI (with glycerol)	0.7 ± 0.2	466.0 ± 34.5
BC-SPI (without glycerol)	0.5 ± 0.1	104.0 ± 25.3
BC-MP (with glycerol)	0.5 ± 0.1	364.0 ± 32.8
BC-MP (without glycerol)	0.5 ± 0.1	173.3 ± 19.0

Water resistance

The water resistance of BC bio-leather was measured by WCA and the water absorption time. As shown in Fig. 3, the original BC had the lowest WCA. This is due to the free hydroxyl groups in BC, which exhibit hydrophilic properties (Wen et al. 2015). BC-glycerol also had a low WCA, which was related to the hydrophilic behavior of glycerol (Epure et al. 2011). After physical entrapment of plant-based proteins inside BC, WCAs were increased significantly. The increased WCAs could be attributed to the formation of hydrogen bonding between BC fibers and plant-based proteins, reducing the number of free hydroxyl groups, and thus increasing the hydrophobicity of BC bio-leather (Lima et al. 2018). It was also found that BC entrapped with both protein and glycerol had improved WCA than BC entrapped with protein only. This could be explained by the rearrangement of hydrophobic moieties of protein molecules: Glycerol may strengthen the interactions with protein molecules by forming hydrogen bonds, resulting in the reorientation of hydrophobic moieties of proteins on the surface of BC bio-leathers (Yin et al. 2007). Moreover, both BC-SPI (with glycerol) and BC-MP (with glycerol) were found to have better WCAs when

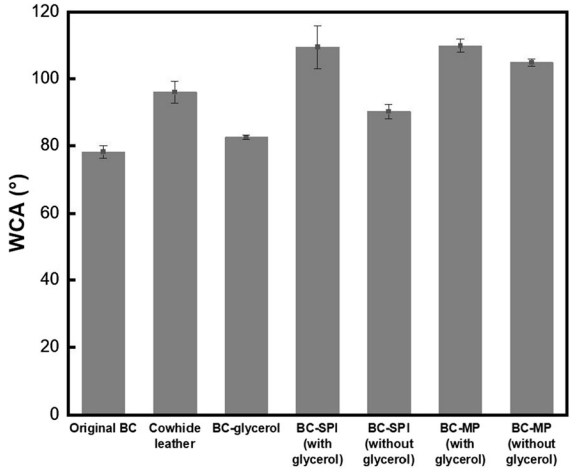

Fig. 3 Average WCA of original BC, cowhide leather, BC-glycerol, BC-SPI (with glycerol), BC-SPI (without glycerol), BC-MP (with glycerol), and BC-MP (without glycerol) (production conditions for BC-SPI (with glycerol): fabric to liquor ratio of 1:10, SPI at an amount of 20 wt% of BC, 30 wt% of BC of glycerol; production conditions for BC-SPI (without glycerol): fabric to liquor ratio of 1:10, SPI at an amount of 20 wt% of BC; production conditions for BC-MP (with glycerol): fabric to liquor ratio of 1:10, MP at an amount of 50 wt% of BC, 30 wt% of BC of glycerol; production conditions for BC-MP (without glycerol): fabric to liquor ratio of 1:10, MP at an amount of 50 wt% of BC)

glycerol was added. Those WCAs were higher than cowhide leather of similar thickness.

Figure 4 describes the water absorption behaviors of BC bio-leather. When the water droplet was dropped on the surface of the original BC, it quickly spread sideways and was completely absorbed within 10 min. Since BC has high water retention capability and hydrophilicity (Li et al. 2014), BC can absorb water quickly. BC-glycerol also absorbed the water droplet completely within 10 min due to the water sensitivity and hydrophilicity of glycerol (Tian et al. 2018). After BC was entrapped with plant-based proteins such as SPI and MP, the water absorption time of BC was increased. Moreover, it took a longer time for BC entrapped with both proteins and glycerol, compared to BC entrapped with only proteins. This phenomenon was in accordance with the WCA result, which could be attributed to the reorientation of hydrophobic functional groups of proteins on the surface of BC by the addition of glycerol (Yin et al. 2007).

Based on these results, it was confirmed that the water resistance of BC bio-leather could be improved

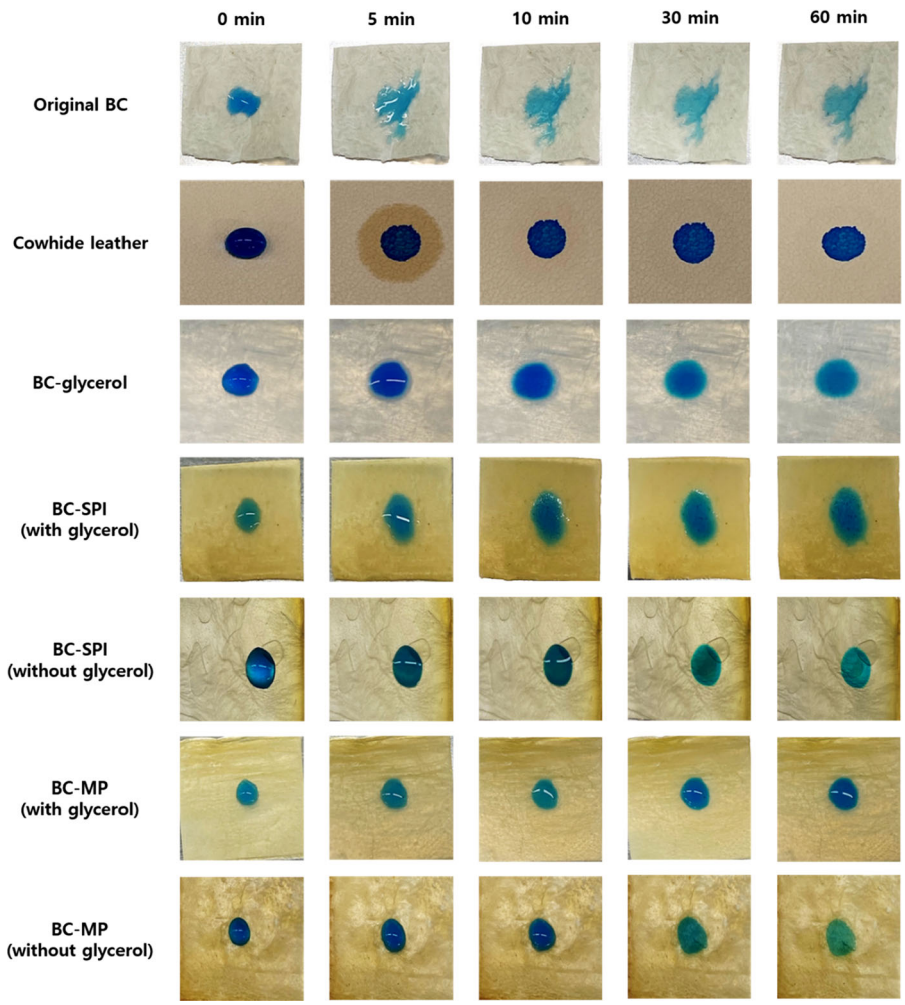

Fig. 4 Water absorption behaviors of original BC, cowhide leather, BC-glycerol, BC-SPI (with glycerol), BC-SPI (without glycerol), BC-MP (with glycerol), and BC-MP (without glycerol) (production conditions for BC-SPI (with glycerol): fabric to liquor ratio of 1:10, SPI at an amount of 20 wt% of BC, 30 wt% of BC of glycerol; production conditions for BC-SPI (without glycerol): fabric to liquor ratio of 1:10, SPI at an amount of 20 wt% of BC; production conditions for BC-MP (with glycerol): fabric to liquor ratio of 1:10, MP at an amount of 50 wt% of BC, 30 wt% of BC of glycerol; production conditions for BC-MP (without glycerol): fabric to liquor ratio of 1:10, MP at an amount of 50 wt% of BC)

by entrapping proteins such as SPI and MP, and that BC-SPI (with glycerol) and BC-MP (with glycerol) had better water resistance compared to cowhide leather of similar thickness.

Tensile strength

The tensile strength of BC bio-leather was tested after physical entrapment of SPI and MP. In Fig. 5, the original BC had poor tensile strength due to the brittle property of BC (Feng et al. 2012; Muller et al. 2013). BC entrapped with only SPI had the lowest tensile strength because of the stiff and brittle nature of SPI (Kokoszka et al. 2010). After the physical entrapment of proteins with glycerol, the tensile strength of BC remarkably increased. It is explained that the addition of glycerol improved the processability of plant-based proteins, and thus proteins could be effectively entrapped in BC (Wang et al. 2017; Tian et al. 2018). Moreover, BC-MP (with glycerol) had better tensile strength than cowhide leather of similar thickness. These results showed that the mechanical properties of BC were successfully enhanced by physical entrapment of plant-based proteins, and that

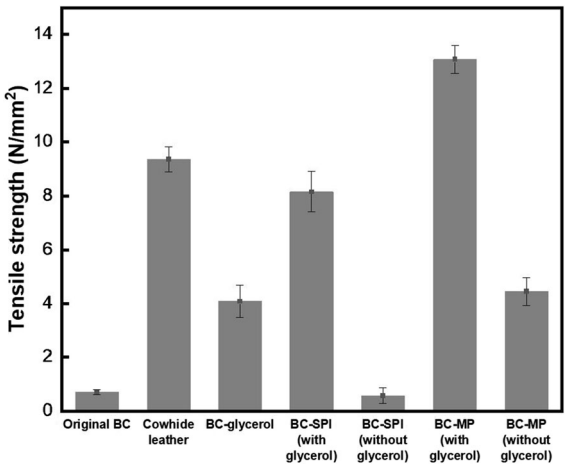

Fig. 5 Tensile strength of original BC, cowhide leather, BC-glycerol, BC-SPI (with glycerol), BC-SPI (without glycerol), BC-MP (with glycerol), and BC-MP (without glycerol) (production conditions for BC-SPI (with glycerol): fabric to liquor ratio of 1:10, SPI at an amount of 20 wt% of BC, 30 wt% of BC of glycerol; production conditions for BC-SPI (without glycerol): fabric to liquor ratio of 1:10, SPI at an amount of 20 wt% of BC; production conditions for BC-MP (with glycerol): fabric to liquor ratio of 1:10, MP at an amount of 50 wt% of BC, 30 wt% of BC of glycerol; production conditions for BC-MP (without glycerol): fabric to liquor ratio of 1:10, MP at an amount of 50 wt% of BC)

glycerol was essential to control the processability of proteins.

Flexibility

The flexibility test results of BC bio-leather according to the modified heart-loop method are shown in Figs. 6 and 7a. When the sample shows better flexibility, the change in the distance between the upper and lower ends of the loop increases (Abbott 1951). BC-glycerol had the highest change in the distance of the loop among all samples. This is because glycerol itself could act as a plasticizer that improves the flexibility of BC (Cielecka et al. 2019). The original BC had some cracks when it was bent into a loop, and it had very low change in the distance of the loop. This might be due to the stiff and brittle nature of BC (Feng et al. 2012; Muller et al. 2013). When BC entrapped with SPI only, it was impossible to measure the flexibility of BC. This could be explained that the strong polar interactions between SPI molecules and hydroxyl groups of BC decreased molecular mobility, resulting in the increased brittleness of BC (Kokoszka et al. 2010). Meanwhile, BC entrapped with MP only was found to have a certain level of flexibility even in the absence of glycerol because some fungal biomass included in MP might have influenced the flexibility of BC (Silverman 2018). When BC was entrapped with both proteins and glycerol, the flexibility was improved. This is consistent with the previous studies that glycerol was needed to improve the processability of proteins by reducing the intermolecular forces between protein chains (Kokoszka et al. 2010; Tian et al. 2012; Chhavi et al. 2017; Rhim et al. 2006). Moreover, the flexibility of BC-SPI (with glycerol) and BC-MP (with glycerol) was improved than that of cowhide leather of similar thickness by the addition of glycerol. Thus, it was confirmed that the flexibility of BC could be improved by entrapping both proteins and glycerol, and MP itself can impart the flexibility to BC.

Crease recovery

Generally, a sample with good crease recovery can return to its original state without being damaged (Kim et al. 2020a). Thus, it can be assumed that a sample with a high crease recovery value has good durability (Kim et al. 2020a). According to Fig. 7b, the crease recovery of original BC was 27.8 %. After the entrapment of SPI only, the crease recovery of BC bio-leather could not be measured because the sample was broken due to the highly brittle property (Kokoszka et al. 2010). After entrapping both plant-based proteins and glycerol, the crease recovery of BC bio-leather was highly improved. This could be explained that glycerol improved the processability of proteins by weakening the intermolecular forces between protein chains (Chhavi et al. 2017; Rhim et al. 2006). However, entrapping glycerol itself could not improve the crease recovery of BC. Although the flexibility of BC-glycerol was good due to the reduced rigidity of BC (Indrarti et al. 2016; Cielecka et al. 2019), the crease recovery of BC-glycerol was poor than the original BC because the sample was too soft to retain its shape. In addition, the highest value of crease recovery was observed for BC-MP (with glycerol), showing that it has the best ability to return to its original shape among other samples. From the crease recovery analysis, it was confirmed that glycerol is essential to improve the processability of plant-based proteins, and that it was difficult to produce BC bio-

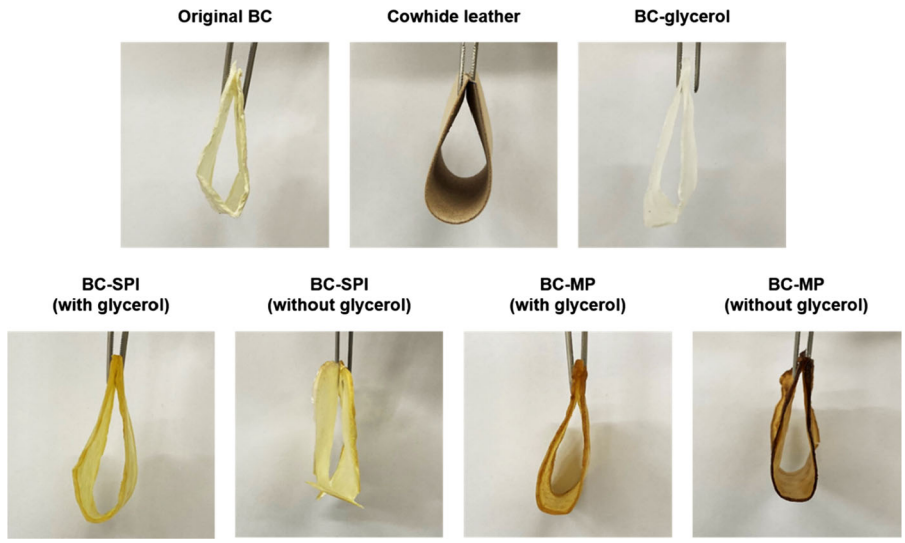

Fig. 6 The appearance of loops of original BC, cowhide leather, BC-glycerol, BC-SPI (with glycerol), BC-SPI (without glycerol), BC-MP (with glycerol), and BC-MP (without glycerol) (production conditions for BC-SPI (with glycerol): fabric to liquor ratio of 1:10, SPI at an amount of 20 wt% of BC, 30 wt% of BC of glycerol; production conditions for BC-SPI (without glycerol): fabric to liquor ratio of 1:10, SPI at an amount of 20 wt% of BC; production conditions for BC-MP (with glycerol): fabric to liquor ratio of 1:10, MP at an amount of 50 wt% of BC, 30 wt% of BC of glycerol; production conditions for BC-MP (without glycerol): fabric to liquor ratio of 1:10, MP at an amount of 50 wt% of BC)

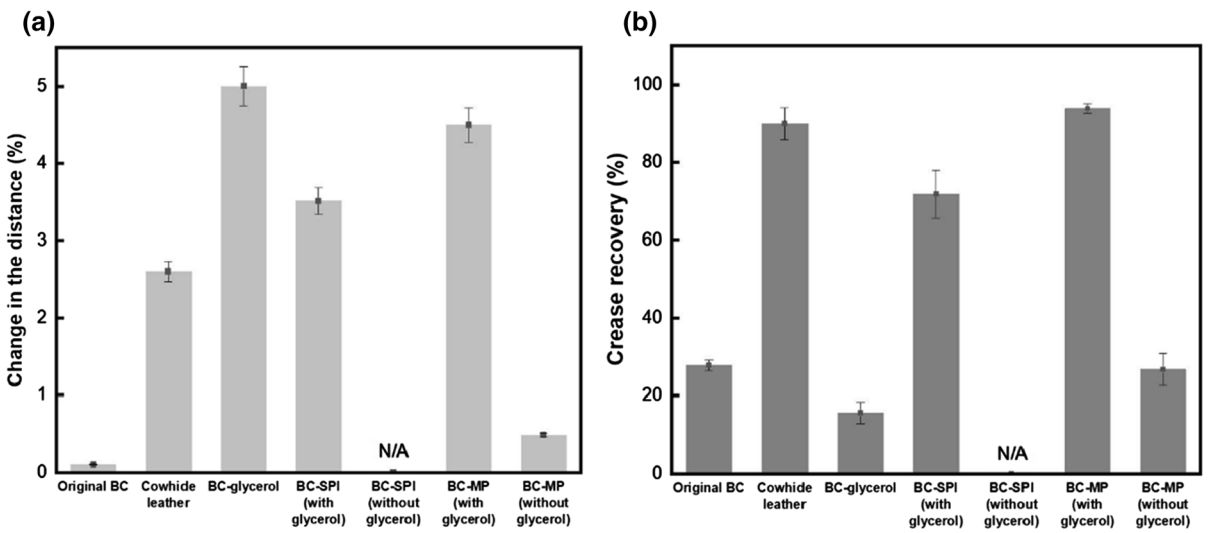

Fig. 7 **a** The change in the distance of loops (%); **b** the crease recovery (%) of original BC, cowhide leather, BC-glycerol, BC-SPI (with glycerol), BC-SPI (without glycerol), BC-MP (with glycerol), and BC-MP (without glycerol) (production conditions for BC-SPI (with glycerol): fabric to liquor ratio of 1:10, SPI at an amount of 20 wt% of BC, 30 wt% of BC of glycerol; production conditions for BC-SPI (without glycerol): fabric to liquor ratio of 1:10, SPI at an amount of 20 wt% of BC; production conditions for BC-MP (with glycerol): fabric to liquor ratio of 1:10, MP at an amount of 50 wt% of BC, 30 wt% of BC of glycerol; production conditions for BC-MP (without glycerol): fabric to liquor ratio of 1:10, MP at an amount of 50 wt% of BC)

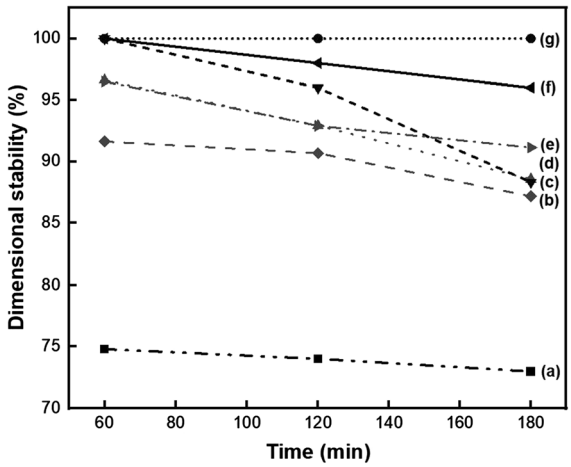

Fig. 8 The dimensional stability (%) of **a** original BC, **b** BC-SPI (without glycerol), **c** BC-SPI (with glycerol), **d** BC-glycerol, **e** BC-MP (without glycerol), **f** BC-MP (with glycerol), and **g** cowhide leather (production conditions for BC-SPI (with glycerol): fabric to liquor ratio of 1:10, SPI at an amount of 20 wt% of BC, 30 wt% of BC of glycerol; production conditions for BC-SPI (without glycerol): fabric to liquor ratio of 1:10, SPI at an amount of 20 wt% of BC; production conditions for BC-MP (with glycerol): fabric to liquor ratio of 1:10, MP at an amount of 50 wt% of BC, 30 wt% of BC of glycerol; production conditions for BC-MP (without glycerol): fabric to liquor ratio of 1:10, MP at an amount of 50 wt% of BC)

leather with good crease recovery by entrapping proteins only.

Dimensional stability

Figure 8 demonstrates the dimensional stability of BC bio-leather. In Fig. 8a, the dimensional stability of the original BC decreased from 74.5 to 73.0 % after immersion in the wetting solution for 180 min. BC shrank remarkably after drying due to the high water absorption property of BC (Li et al. 2014). After entrapping SPI and MP only, the dimensional stability of BC was improved about 20% and 31%, respectively. By the addition of glycerol, the dimensional stability of BC-SPI (with glycerol) (Fig. 8c) and BC-MP (with glycerol) (Fig. 8f) was further increased. This could be due to the strong adhesion between BC nanofibers and proteins which decreased the water absorption, as evidenced in the water resistance analysis (Song et al. 2019), and the enhanced processability of proteins by the addition of glycerol (Wang et al. 2017). On the other hand, entrapping glycerol only was not sufficient to improve the dimensional stability of BC (Fig. 8d). As confirmed in the water resistance analysis (Fig. 3), glycerol is a hydrophilic material so that it absorbs the wetting agent well, resulting in a low dimensional stability. Moreover, the dimensional stability of BC-MP (with glycerol) was comparable to that of cowhide leather (Fig. 8g), confirming that BC-MP (with glycerol) could be a suitable leather substitute.

Surface analyses of BC bio-leathers

After evaluating the physical properties of BC bio-leather by comparison with cowhide leather, it was confirmed that the durability of BC bio-leather could be improved by physical entrapment of both proteins and glycerol. Thus, the surface analyses, such as FT-IR, XRD, SEM, and EDX, were performed with original BC, BC-SPI (with glycerol), and BC-MP (with glycerol). Here in, BC-SPI (with glycerol) and BC-MP (with glycerol) were coded as BC-SPI(G) and BC-MP(G), respectively.

FT-IR was used to evaluate the physically entrapped plant-based proteins inside BC bio-leathers. As indicated in Fig. 9, all FT-IR spectra displayed peaks around 3350 cm^{-1} to 3400 cm^{-1}, and around 2900 cm^{-1}, indicating the presence of hydrogen-bonded –OH groups of cellulose and the presence of amorphous cellulose, respectively (Fu and Liu 2011; Vigentini et al. 2019) (Table 3). These peaks confirmed that the chemical structure of BC remained unchanged after entrapping proteins such as SPI and MP. In addition, the FT-IR spectrum of proteins usually has nine characteristic absorption bands, among which amide I ($\sim$ 1650 cm^{-1}) and amide II ($\sim$ 1550 cm^{-1}) bands are the two major bands (Qi et al. 2016; Yang et al. 2015; Gu et al. 2019). In the FT-IR spectra of BC-SPI(G) and BC-MP(G), amide I and amide II peaks were clearly observed. These peaks were ascribed to the presence of SPI and MP inside BC-SPI(G) and BC-MP(G), respectively.

XRD was used to examine the crystalline structures of BC bio-leathers. In Fig. 10, three peaks at 2θ = 14.5°, 16.8°, and 22.7° were observed in the diffraction patterns of original BC, BC-SPI(G), and BC-MP(G), respectively. These peaks were attributed to the cellulose structure of BC (Bekatorou et al. 2019), implying that it was retained after the entrapment of SPI or MP. This was consistent with the FT-IR results discussed previously. In the XRD patterns of

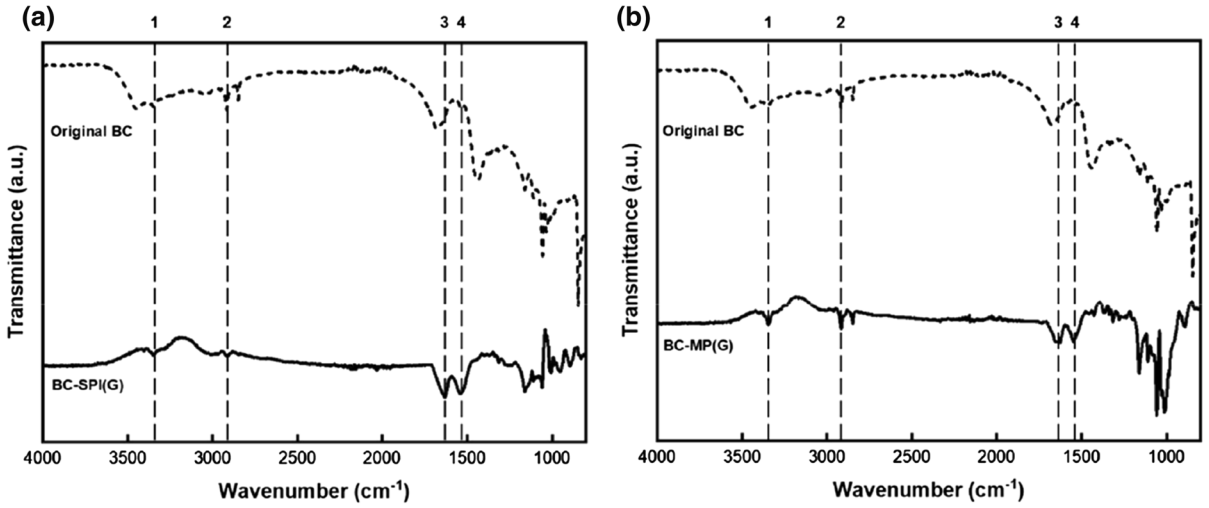

Fig. 9 FT-IR spectra of **a** original BC and BC-SPI(G); **b** original BC and BC-MP(G) (production conditions for BC-SPI(G): fabric to liquor ratio of 1:10, SPI at an amount of 20 wt% of BC, 30 wt% of BC of glycerol; production conditions for BC-MP(G): fabric to liquor ratio of 1:10, MP at an amount of 50 wt% of BC, 30 wt% of BC of glycerol)

Table 3 Characteristic peaks of original BC, BC-SPI(G), and BC-MP(G) (production conditions for BC-SPI(G): fabric to liquor ratio of 1:10, SPI at an amount of 20 wt% of BC, 30 wt% of BC of glycerol; production conditions for BC-MP(G): fabric to liquor ratio of 1:10, MP at an amount of 50 wt% of BC, 30 wt% of BC of glycerol)

Wavenumber (cm^{-1})				Peak assignment
Peak no.	Original BC	BC-SPI(G)	BC-MP(G)	
1	3448	3350	3346	–OH stretching (Fu and Liu 2011; Vigentini et al. 2019)
2	2916	3010	2915	C–H stretching (Vigentini et al. 2019)
3	–	1630	1627	C=O stretching (Qi et al. 2016; Yang et al. 2015)
4	–	1543	1548	N–H bending (Yang et al. 2015; Gu et al. 2019)

SPI and MP powders, two characteristic peaks at $2\theta = 9.1°$ and 20.2°, were observed. These peaks corresponded to the α-helix and β-sheet structures of the protein secondary conformations, respectively (Pang et al. 2019). These peaks were also observed in the XRD patterns of BC-SPI(G) and BC-MP(G), thus confirming the successful entrapment of proteins inside the BC nanostructure.

Table 4 shows the crystallinity degrees of BC bio-leathers. In comparison with the original BC, the crystallinity degrees of BC-SPI(G) and BC-MP(G) decreased because protein chains could not move freely after being cross-linked with BC fibers (Wu et al. 2018). In most cases, when the crystallinity degree decreases, the tensile strength also decreases. However, the experimental results in this study showed the opposite tendency. According to Liu et al. (2013), the reason of this opposite tendency is that crystallinity is not a major factor that affects the tensile strength. It is known that the tensile strength of BC is more affected by the drying condition than crystallinity. Thus, factors other than the crystallinity might influence the improvement of the tensile strength of BC bio-leather. Also, the decrease in the crystallinity could prove the successful cross-linking between BC fibers and protein chains.

The surface morphologies of BC bio-leathers are shown in Fig. 11. The SEM image of the original BC showed the fine cellulose nanostructure of BC. Different morphologies were observed after the entrapment of SPI and MP. In the SEM image of BC-SPI(G), the SPI particles agglomerated inside the

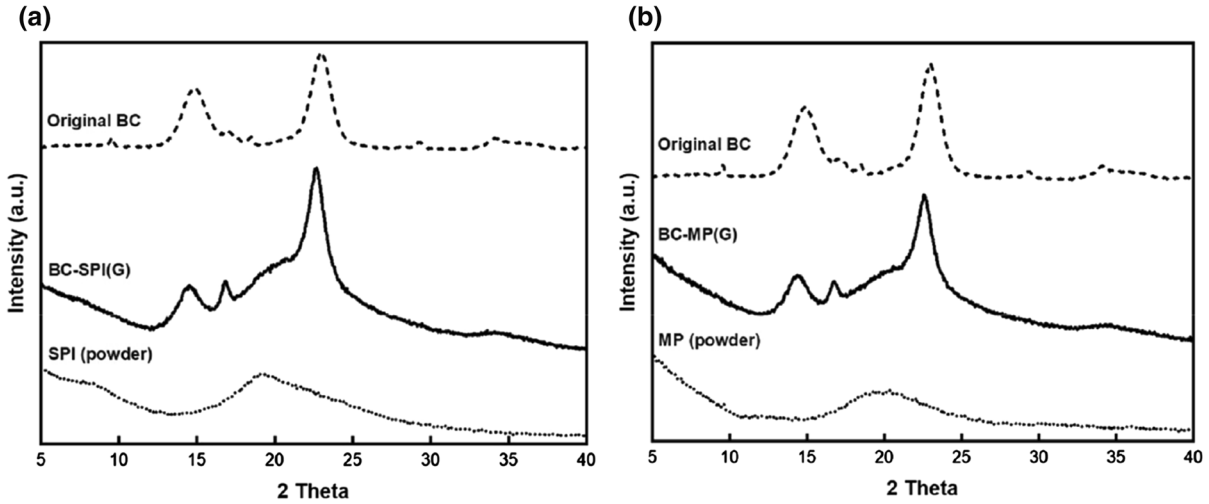

Fig. 10 XRD spectra of **a** original BC, BC-SPI(G), and SPI (powder); **b** original BC, BC-MP(G), and MP (powder) (production conditions for BC-SPI(G): fabric to liquor ratio of 1:10, SPI at an amount of 20 wt% of BC, 30 wt% of BC of glycerol; production conditions for BC-MP(G): fabric to liquor ratio of 1:10, MP at an amount of 50 wt% of BC, 30 wt% of BC of glycerol)

Table 4 Crystallinity degree of original BC, BC-SPI(G), and BC-MP(G) (production conditions for BC-SPI(G): fabric to liquor ratio of 1:10, SPI at an amount of 20 wt% of BC, 30 wt% of BC of glycerol; production conditions for BC-MP(G): fabric to liquor ratio of 1:10, MP at an amount of 50 wt% of BC, 30 wt% of BC of glycerol)

Sample	Crystallinity (%)
Original BC	82.6 ± 3.6
BC-SPI(G)	68.3 ± 2.4
BC-MP(G)	71.6 ± 5.8

BC nanostructure, possibly due to the crosslinking between SPI and BC, filling the fibrous structure of BC (Arfa et al. 2007). The BC fiber structure was not seen in the SEM image of BC-MP(G), though a densely coated surface was observed. This is attributed to the strong interaction between BC and MP (Liu et al. 2017). Moreover, the surface of BC-MP(G) was relatively smoother than that of BC-SPI(G). This might be related to the higher concentration of MP than that of BC-SPI(G). The surface smoothness is an important factor because the user feels comfortable when using the BC bio-leather (Ramnath et al. 2011). From the results, it was confirmed that BC-MP(G) would be more suitable than BC-SPI(G) as a leather substitute.

EDX was used to provide both quantitative and qualitative information regarding the amount of proteins on the surface and inside BC bio-leathers. In Fig. 12, all three samples exhibit peaks of C and O elements, which were attributed to the BC component (Janpetch et al. 2016; Gutierrez et al. 2013), thus confirming the presence of the cellulose structure of BC. In the EDX spectrum of the original BC, a negligible peak of Na element was observed due to the use of sodium hydroxide in the purification and swelling of BC (DeMello 2012). As shown in Table 5, the weight percentages of Na and P elements in BC-SPI(G) were higher than those of BC-MP(G). This was in accordance with a previous study in which Na and P were the distinctive markers of SPI (Sett et al. 2015). In addition, the equivalent wt% of S element was detected in the EDX spectra of both BC-SPI(G) and BC-MP(G) due to the presence of sulphureted amino acids in the protein (Porras-Saavedra et al. 2015). Based on the FT-IR, XRD, surface morphology, and EDX results, it was confirmed that the SPI and MP were successfully entrapped inside the BC bio-leather without significantly changing the chemical and crystalline structures of the original BC.

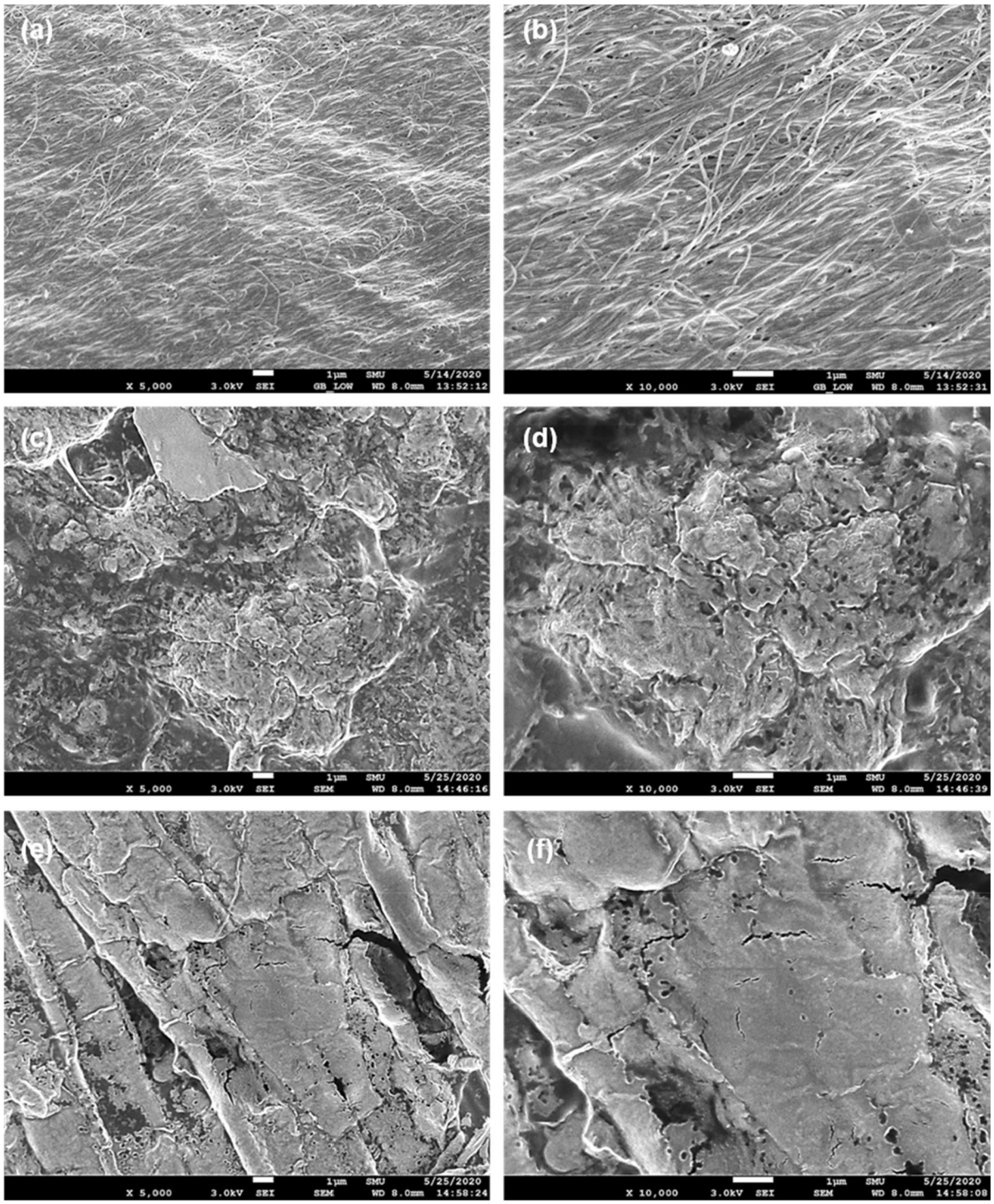

Fig. 11 SEM images of **a**, **b** original BC; **c**, **d** BC-SPI(G); **e**, **f** BC-MP(G) at 5000 and 10,000× magnification, respectively, with a scale bar of 1 μm (production conditions for BC-SPI(G): fabric to liquor ratio of 1:10, SPI at an amount of 20 wt% of BC, 30 wt% of BC of glycerol; production conditions for BC-MP(G): fabric to liquor ratio of 1:10, MP at an amount of 50 wt% of BC, 30 wt% of BC of glycerol)

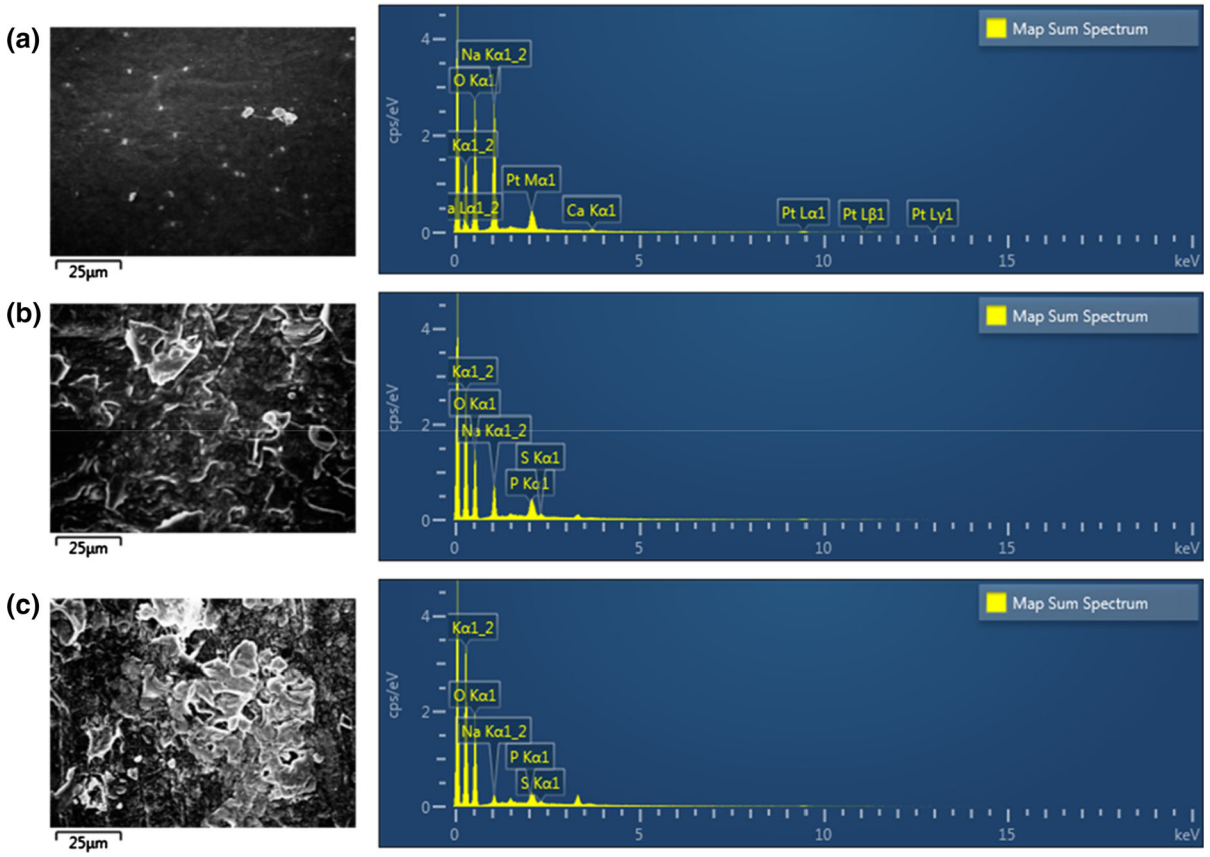

Fig. 12 EDX spectra of **a** original BC; **b** BC-SPI(G); **c** BC-MP(G) (production conditions for BC-SPI(G): fabric to liquor ratio of 1:10, SPI at an amount of 20 wt% of BC, 30 wt% of BC of glycerol; production conditions for BC-MP(G): fabric to liquor ratio of 1:10, MP at an amount of 50 wt% of BC, 30 wt% of BC of glycerol)

Table 5 Weight % of elements of original BC, BC-SPI(G), and BC-MP(G) (production conditions for BC-SPI(G): fabric to liquor ratio of 1:10, SPI at an amount of 20 wt% of BC, 30 wt% of BC of glycerol; production conditions for BC-MP(G): fabric to liquor ratio of 1:10, MP at an amount of 50 wt% of BC, 30 wt% of BC of glycerol)

Sample	Elements (wt%)				
	C	O	Na	P	S
Original BC	5.76	5.18	1.36	–	–
BC-SPI(G)	6.27	3.71	0.48	0.03	0.03
BC-MP(G)	7.01	4.74	0.14	0.01	0.03

Conclusions

This study aimed to develop eco-friendly BC bio-leather and improve its durability by physical entrapment of plant-based proteins as reinforcing additive materials. For this purpose, SPI and MP were selected, and their amounts for BC bio-leather were determined to be 20 and 50 wt% of BC, respectively. The durability of BC bio-leather remarkably increased after the entrapment of two types of plant-based proteins. The WCAs of BC entrapped with both plant-based proteins and glycerol were improved by 40 % compared to that of the original BC. The highest tensile strength of approximately 13 N/mm^2 was obtained from BC-MP(G), which was better than that of cowhide leather. The flexibility and crease recovery of BC bio-leathers were also improved after the entrapment of plant-based proteins. After immersed in the wetting solution for 180 min, the dimensional stability of BC-SPI(G) and BC-MP(G) was improved by 14 % and 22 %, respectively, compared to that of the original BC. The SPI and MP entrapped in BC bio-leather were chemically detected by FT-IR, XRD, and

EDX analyses, and the surface morphology of BC-SPI(G) and BC-MP(G) was evaluated by SEM. These results confirmed successful entrapment of plant-based proteins inside BC without changing the chemical and crystalline structure of the original BC.

Therefore, this study demonstrated that the durability of BC bio-leather can be enhanced by physical entrapment of plant-based proteins such as SPI and MP. In particular, MP was effective in improving the durability of BC bio-leather. Moreover, BC-MP(G) had lesser thickness, lighter weight, and higher strength compared to those of cowhide leather. It is expected that BC bio-leather, with its improved durability, can be a competitive bio-leather material for wide applications.

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Compliance with ethical standards

Conflict of interest The authors declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

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