

Development and preliminary field validation of water-resistant cellulose nanofiber based coatings with high surface adhesion and elasticity for reducing cherry rain-cracking

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ABSTRACT

This study was aimed to systematically develop and validate cellulose nanofiber (CNF)-based hydrophobic coatings (Innofresh™) for reducing cherry rain-cracking through a lab-scale optimization study and the preliminary field validation trials. The base coating formulation consist of 0.5% CNF (w/w) and 0.5% potassium sorbate (KSB) (w/w). For optimizing the coating formulations with desired water resistance, wettability and elasticity, three different types of plasticizer (glycerol, PEG 400, and sorbitol) and their concentrations (0, 0.05, and 0.1% (w/w)), as well as surfactant mixture (1:1 ratio of Tween 80 and Span 80) at 0.05, 0.1, and 0.2% (w/w) were evaluated as additional functional substances in the base coating formulation. It was found that 0.5% CNF/0.5% KSB based coatings containing 0.1% glycerol and 0.1% or 0.2% surfactant mixture provided high wettability and elasticity along with superior water resistance. The effectiveness of the optimized coating formulations on reducing cherry rain-cracking was validated through two field studies conducted in Chile and the United States during November–December, 2014 and May–June, 2015, respectively. The 0.5% CNF/0.5% KSB/0.1% glycerol coating containing 0.1% or 0.2% surfactant mixture resulted in significant reduction in cherry rain-cracking (~31.18–44.60%) ($P<0.05$), while no any detrimental effect on fruit firmness, size, soluble sugar, pedicel/fruit retention force, and color was observed in comparison with non-coated cherries. Therefore, the simple, but versatile CNF-based coatings incorporated with an appropriate amount of glycerol and surfactant was effective to reduce cherry rain-cracking without impacting fruit growth and quality.

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1. Introduction

Cherry rain-cracking mostly occurs at the late stage of cherry growth. Due to the high osmotic potential within the fruit, rainwater can be easily absorbed through cherry cuticles (Long, 2005). Increasing fruit internal pressure eventually bursts cherry skins (Koumanov, 2015; Measham et al., 2013). Cherry rain-cracking has led severe economic losses to the cherry industry. To cite some, 'Bing', the number one cherry variety grown in the U.S. for fresh market, is highly susceptible to cracking in the rain, and showed ~55% rain cracking in 2005 around Pacific Northwest, USA with two rain events (totaling 8.9 mm of precipitation) occurred 12 and 13 days prior to 'Bing' harvest (Long et al., 2008). In the US northwest region, rainfall in late June and early July during 2007–08 caused 10% and 27% cherries cracked, respectively (unpublished data).

Several technologies have been employed to prevent cherry rain-cracking, including physical protections (e.g., rain cover), chemical treatments (e.g., CaCl_2), and hydrophobic coatings (Blanke and Balmer, 2008; Børve et al., 2008; Sotiropoulos et al., 2014; Wermund et al., 2005; Meland et al., 2014). Among them, the hydrophobic coating technology has attracted great attention because it is easy to apply and relatively low cost. Two products, RainGard® based on carnauba wax (Pace international, LLC, WA, USA) and Parka™ using elastic co-polymer of cellulose and palm oil (Cultiva, NV, USA) are commercially available now (Hanrahan, 2013; Meland et al., 2014). Each product has its own unique functionality and limitation, such as requiring multiple applications to insure the coating integrity under field conditions (Meland et al., 2014). In this study, a cellulose nanofiber (CNF) based coating (Innofresh™, patent pending) was developed and validated with the goal to create a simple, but versatile coating system to reduce cherry rain-cracking without detrimental effect on fruit growth and quality (Zhao et al., 2014). Based on current knowledge, there is no evidence for serious influence or damage of nanocellulose at both

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cellular and genetic levels, and the inhalation of nanocellulose may induce pulmonary inflammation owing to the self-aggregation and non-degradation of nanocellulose (Lin and Dufresne, 2014; Shatkin and Kim, 2015). More studies are under the way to investigate the safety and toxicity of nanocellulose.

Cellulose nanofiber (CNF) prepared from bleached kraft pulp contains both crystalline and amorphous regions with dimension of 10–30 nm in width and aspect ratio greater than 50. CNF has been utilized as film forming matrix to produce film or coating with superior water and gas barrier properties (Azeredo et al., 2010, 2009; Jung et al., 2015; Luo et al., 2013; Österberg et al., 2013; Podsiadlo et al., 2005), in which the water barrier property is essential for protecting cherries from rainfalls. Other substances, such as silver or silver nanoparticles, caffeine, and polygalaturnoic acid, were incorporated into CNF film and coating to enhance gas barrier and antimicrobial properties (Lavoine et al., 2014; Martins et al., 2012; Mølgaard et al., 2014). In addition, CNF has been used as a filler for other polymers, such as gluten, polylactic acid (PLA), starch, chitosan, and edible mango puree films for improving their hydrophobicity, mechanical and/or gas barrier properties (Abdulkhani et al., 2014; Azeredo et al., 2010, 2009; Rafieian et al., 2014; Savadekar and Mhaske, 2012). In this study, it is hypothesized that by incorporating the appropriate type and amount of plasticizer and surfactant into CNF-based coatings, it would enhance coating integrity against water attack and improve coating wettability and elasticity, thus effectively reducing cherry rain-cracking without negative impact on fruit growth and quality (Zhao et al., 2014). To the best of our knowledge, no previous study has utilized CNF as a coating forming matrix for reducing cherry rain-cracking.

For developing an effective coating to reduce cherry rain-cracking, the coating should not only provide good water resistance, but should also have desired wettability for uniform coverage onto fruit surface and sufficient elasticity to allow the continuous growth of fruit before harvest. Plasticizer provides the fluidity of coating formulation and also, homogeneity or elasticity of derived coatings. Glycerol, sorbitol, and polyethylene glycol (PEG) are among those commonly used plasticizers. The selection depends on their interactions with other substances in the coating matrix (Azeredo et al., 2010; Srinivasa et al., 2007). Meanwhile, non-ionic surfactant (polyethoxylated sorbitan esters or sorbitan esters) can reduce surface tension of coatings and improve the wettability of coatings along with the uniform coverage onto the product (Cisneros-Zevallos and Krochta, 2003). To improve the compatibility among the various substances in the coating formulations that possess different properties (i.e., hydrophilicity or chemical structures), two (or more) types of surfactants might be mixed by considering hydrophilic-lipophilic balance (HLB) (Casariego et al., 2008). Therefore, it is necessary to identify the most suitable type and concentration of plasticizer and surfactant(s) that can be incorporated into CNF-based coating formulations with the desired coating properties. In addition, potassium sorbate (KSB) as an antifungal agent might be able to reduce fungal diseases which might occur in cherries, and also preserve CNF coating dispersions for long-term storage at ambient conditions.

Therefore, the overall goal of this study was to develop water-resistant CNF-based coatings with high wettability and elasticity for reducing cherry rain-cracking without any harmful effect on fruit growth and quality. For achieving the goal, a systematic approach was applied through two studies: (1) lab-scale optimization study to identify optimal coating formulations through evaluating targeted coating performance using derived films, and (2) preliminary field validation study to test the effectiveness of the optimized coating formulations for reducing cherry rain-cracking. It was anticipated that this study would provide new insights into the correlations of the various functional substances in CNF-based coat-

ing formulations, and demonstrate the potentiality of CNF-based coating for reducing cherry rain-cracking.

2. Material and method

2.1. Materials

A 2.95% CNF slurry was obtained from the Process Development Center of the University of Maine (ME, USA). It was prepared from northern bleached softwood kraft pulp in dry lap form, and then slushed into aqueous slurry (Luo et al., 2013). Potassium sorbate and glycerol were purchased from Arcos (NJ, USA) and Fisher Scientific (NJ, USA), respectively. Sorbitol, polyethylene glycol 400 (PEG400), and acetic acid were purchased from J.T. Baker (NJ, USA). Tween 80 (polyoxyethylene (20) sorbitan monooleate) and Span 80 (sorbitan monooleate) were acquired from Amresco (OH, USA).

2.2. Experimental approaches to develop the optimal coating formulations

The CNF based coatings were aimed to possess high wettability and elasticity along with the superior resistance against water. To identify the optimal coating formulation meeting above criteria, three different coating formulation factors (type and concentration of plasticizer and concentration of surfactant mixture) at three different levels were tested through lab-scale performance evaluation of prepared coating dispersions and their derived films using Taguchi design and analysis. Wettability of the coating dispersions and water-resistance and elasticity of the derived films were determined at two different pH levels (4.8 or 6.5) of the coating dispersions.

The optimized coating formulations were then validated in the field studies by spray-coating cherries on the trees in two different locations, Coihueco and Angol (Chile) and The Dalles, Oregon (USA), during 2014–2015 as described in Section 2.5.

2.3. The lab-scale optimization study

2.3.1. Preparation of coating dispersions and derived films

Both CNF and KSB concentrations were set to 0.5% (w/w wet base) by considering coating forming ability and potential antifungal property based on our preliminary studies (data not shown). Nine different coating formulations and their derived films containing different plasticizers (glycerol, sorbitol or PEG400) at 0, 0.05, or 0.1% (w/w wet base) and surfactant mixture (1:1 of Tween and Span 80) at 0.05, 0.1, or 0.2% (w/w wet base) were prepared by following L9 (3^3) orthogonal array (Table 1). It should be noted that the surfactant mixture of Tween 80 and Span 80 at 1:1 ratio (w/w) was used to improve the homogenous and hydrophobic properties of the coatings. The prepared coating dispersions were thoroughly mixed by a blender (Intertek, USA) for 1 min at speed level 4 and adjusted to pH 4.8 using acetic acid to improve the antimicrobial effect of KSB. Prepared mixtures were blended for another 1 min at the same speed, and then degassed to remove air bubbles by using a self-build water flow vacuum system (Chen and Zhao, 2012).

For evaluating water resistance, water permeation, mechanical property, and morphology of the coatings, the coating dispersions were cast to form films. For preparing films, each coating dispersion was uniformly distributed onto a leveled Teflon-coated glass plate (170 × 170 mm), and dried at room temperature ($25 \pm 2^\circ\text{C}$) for 2 days (Chen and Zhao, 2012). Prepared films were conditioned at a 25°C and 50% relative humidity (RH) self-assembled chamber (Vesta, PA, USA) for 2 days prior to the measurement (Chen and Zhao, 2012).

Table 1

Orthogonal array using L₉ (3³) with measured quality characteristics and Taguchi analysis with signal-to-noise (S/N) ratios (dB) and the contribution (Δ) of the factor on each measurement.

No.	Treatment factors*			Coating solutions		Film properties				
	A	B	C	Contact angle (°)	Spreadability (mm)	EL** (%)	TS*** (MPa)	WS ⁺ (%)	WA ⁺⁺ (%)	WVP ⁺⁺⁺ (g mm/m ² d Pa)
1	Glycerol	0	0.05	63.31	22.23	2.53	31.15	63.00	149.15	0.10
2	Glycerol	0.05	0.10	61.25	25.92	3.53	21.14	61.77	191.55	0.11
3	Glycerol	0.10	0.20	56.89	27.34	4.83	11.64	61.80	235.64	0.12
4	Sorbitol	0	0.10	60.79	25.03	2.24	33.35	60.02	172.49	0.11
5	Sorbitol	0.05	0.20	58.28	25.22	3.67	17.16	62.93	245.87	0.11
6	Sorbitol	0.10	0.05	61.29	22.76	2.82	23.46	64.41	192.92	0.12
7	PEG400	0	0.20	56.88	26.30	2.98	16.63	53.45	228.17	0.10
8	PEG400	0.05	0.05	59.48	20.87	3.06	24.29	61.84	164.58	0.09
9	PEG400	0.10	0.10	58.92	22.79	3.47	16.94	58.04	216.48	0.10
Factor	A	Levels			Signal-to-noise ratio (dB)					
		Glycerol	+35.6 ^a	+7.7 ^a	+1.7 ^a	+26.2 ^a	+4.1 ^a	+5.5 ^a	+19.0 ^a	
		Sorbitol	-35.6 ^a	7.6 ^a	1.2 ^b	-27.8 ^b	4.1 ^a	-6.0 ^a	18.8 ^a	
		PEG400	-35.3 ^a	7.5 ^a	1.4 ^{ab}	-25.8 ^a	5.4 ^a	-6.1 ^a	20.0 ^a	
	B	Δ	0.3	0.1	0.5	2.0	1.3	0.6	1.2	
		0	-35.6 ^a	7.7 ^a	1.0 ^b	-28.5 ^c	4.6 ^a	-5.1 ^a	19.6 ^a	
		0.05	-35.5 ^a	7.6 ^a	1.5 ^a	-26.7 ^b	4.1 ^a	-6.0 ^a	19.4 ^a	
		0.10	-35.4 ^a	7.6 ^a	1.7 ^a	-24.7 ^a	4.8 ^a	-6.6 ^a	18.8 ^a	
	C	Δ	0.2	0.1	0.6	3.8	0.5	1.5	0.8	
		0.05	-35.8 ^b	7.3 ^a	1.2 ^b	-28.7 ^c	4.0 ^a	-4.5 ^a	19.4 ^a	
		0.10	-35.6 ^{ab}	7.7 ^a	1.1 ^b	-27.5 ^b	5.0 ^a	-5.7 ^{ab}	19.2 ^a	
		0.20	-35.2 ^a	7.9 ^a	1.9 ^a	-23.6 ^a	4.5 ^a	-7.5 ^b	19.1 ^a	
		Δ	0.6	0.2	0.8	5.1	1	3	0.3	

*Treatment factors includes the type of plasticizer (A), concentration of plasticizer (B), and concentration of surfactant mixture (Tween 80 and Span 80 at a ratio of 1:1) (C). PEG400 = polyethylene glycol 400.

*EL: elongation at break.

***TS: tensile strength.

*WS: water solubility of films while soaking for 2 h at the ambient temperature.

**WA: water absorption ability of films while soaking for 2 h at the ambient temperature.

***WVP: water vapor permeability.

$$^{+}S/N \text{ ratio was analyzed by using smaller-the-better, } SN_S = -10 \log \left(\frac{1}{n} \sum_{i=1}^n \frac{1}{y_i^2} \right).$$

$$^{+}S/N \text{ ratio was analyzed by using larger-the-better, } SN_L = -10 \log \left(\frac{1}{n} \sum_{i=1}^n y_i^2 \right).$$

*Largest difference (Δ) of S/N ratios between levels indicates the most contributed factor on each measurement.

**Means preceded by the same small letter in the same row within each factor were not significantly different ($P > 0.05$).

2.3.2. Properties of developed coating dispersions

Contact angle (°) of the coating dispersions was measured using a video contact angle system (FTA 32, First Ten Angstroms, Inc., USA) with a face contact angle meter by dropping 10 μL sample from 10 mm height to a horizontal silicon board surface. To control experimental error, all data were collected after 60 s (Zhong et al., 2012). The spreadability of the coating dispersions was determined through 'drop absorbency' by measuring the spread of a drop (0.25 mL) above the cardboard from a fixed height (20 mm). The extended diameter of the wet 'ring' around the drop after 60 s was measured (Duncan et al., 2005).

One of the key criteria for coatings applied on cherry fruit on the trees (before harvesting) is to have sufficient elasticity and less physical tension (stress) so that fruit can continuously grow to reach desired size and maturity. The coating stress onto the fruit was estimated through a self-assembled device shown in Fig. 1. A U-shape glass tube filled with water was tightly connected to a blown balloon that was spray-coated using the controlled amount of coating dispersion to uniformly cover the whole surface of the balloon. The water level increase inside the U-shape tube connected to the balloon was used to estimate any stress perceived from the applied coating. Hence, this simulated system allowed assessment of coating stress onto fruit, and could possibly reveal any harmful effect of the coatings on continuous fruit growth (increase in fruit size) before fruit harvesting.

2.3.3. Mechanical property of derived films

Elongation at break (EL, %) and tensile strength (TS, MPa) of the films were determined using a texture analyzer (TA-XT2 Texture Analyzer, Texture Technologies Corp., NY, USA) according to ASTM D882 standard (ASTM, 2001), in which the initial grip separation and crosshead speed were set at 50 mm and 0.4 mm/s, respectively. Film piece (25 cm wide and 86 cm long) was mounted on a sample grip (TA 96). TS was calculated using maximum load (N) divided by film cross-sectional area (mm^2), and EL (%) was calculated as distance at break divided by the initial length of the specimen and multiplied by 100% (Zhong et al., 2012).

2.3.4. Water absorption, water solubility, and water vapor permeability (WVP) of the derived films

For testing water absorption ability (WA) and water solubility (WS), film sample piece (3 × 3 mm) was individually placed in a petri dish with 30 mL of distilled water. Samples were collected after 2 h, placed on a paper tissue flatwise to absorb water from the film surface, and then weighed. WA was measured as the percentage weight gain of films after suspending in water for 2 h. WS was determined by the percentage weight loss of films after suspending in water for 2 h and drying at 40 °C for 24 h (Zhong et al., 2012).

A cup method following ASTM Standard E96-87 (ASTM, 2000) was applied to measure WVP of the films (Park and Zhao, 2004). Film sample (75 × 75 mm) was sealed by vacuum grease on the top

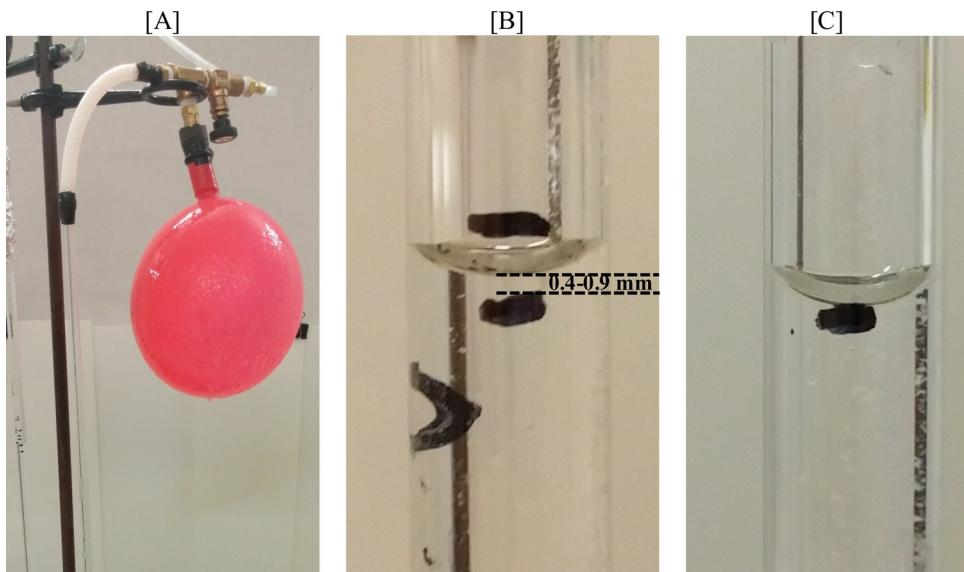


Fig. 1. Illustration of coating elasticity by measuring the change of water level in U-shape glass tube connecting to balloon; [A] increase of water level indicated the pressure from dried coating materials; [B] result from applied coating containing 0.5% (w/w wet base) cellulose nanofiber, 0.5% (w/w wet base) potassium sorbate, and 0.1% (w/w wet base) surfactant mixture (Tween 80 and Span 80 at a ratio of 1:1) without plasticizer (treatment no. 4 in Table 1); [C] represented treatments showing no increase of water level among different coating formulations, and was taken for the coating formulations containing 0.1% glycerol and 0.2% surfactant (no. 3 in Table 1).

of a Plexiglas test cup with 11 mL of distilled water, and four rubber bands were used to tighten the cup with lid. The testing cups were placed in the same temperature and humidity chamber at 25 °C and 50% RH. The weight loss of each cup was measured hourly for up to 6 h.

2.3.5. Surface microstructure of the derived films

The surface microstructures of the derived films from the two optimized coating formulations prepared at pH 4.8 and 6.5 were evaluated by using a scanning electron microscopy (SEM) (FEI Quanta 600F, OR, USA). For investigating the effect of moisture on the surface microstructure modifications and/or degradation of CNF-based films, film samples were soaked in distilled water for 2 h followed with drying at 50 °C for 16 h. Dried film pieces were placed on aluminum mounts with double sided adhesive tape, and coated by a gold–palladium alloy sputter coater (Edwards Model S150B sputter coater; BOC Edwards Vacuum, Ltd., West Sussex, UK) to improve the interface conductivity. Digital images were collected at an accelerating voltage of 5 kV.

2.4. Field studies to validate the effectiveness of developed coatings for reducing cherry rain-cracking

Two field studies were conducted in Chile and USA, respectively by taking advantage of extended fruit production times at different geographical locations. For the Chile trial during November–December, 2014, the 0.5% CNF/0.5% KSB/0.1% glycerol based coating dispersions containing different concentrations (0, 0.05%, 0.1%, and 0.2%) of surfactant mixture were applied to 'Sweetheart' cherry variety. The pH of the prepared coating dispersion was 8.5, and not further adjusted since pH did not show significant effect on the physicochemical and mechanical properties of the derived films. Two different locations in Chile, Coihueco and Angol, were chosen by considering the geographic and climatic effects (e.g., temperature, humidity, or rainfall). The standard foliar program for the orchards where the trials were carried out was as follows: for mineral nutrients and plant growth regulator to insure fruit size with 1 SETTM (calcium and boron) four times from fruit set until yellow straw color and 2 PROGIB® (gibberellic acid) one time at yellow straw color, and for fungicides to prevent diseases (Monilinia

and Botrytis) with 1COMET® (pyraclostrobin) two times during the bloom and 2 TACORA® (tebuconazole) one time during the bloom. Each treatment consisted of six replications laid out in randomized pattern with one tree per replication protected by buffer trees on each side of the treatment, thus 6 replications were considered for each treatment and control (non-sprayed) at two different locations. Each tree was sprayed at two different times with 2 L of coating dispersion applied each time ($2 \times 2\text{ L} = 4\text{ L}$ total for each tree). The first spraying was conducted at the yellow straw color stage in November 25, 2014 at Coihueco, Chile and in November 26, 2014 at Angol, Chile, and the second spraying was done ten days later, December 5, 2014 and December 6, 2014 at each location, respectively. The first rainfall event occurred four days after the first spray and reached up 6 mm at Coihueco and 2 mm at Angol. The second event of rainfall occurred two days before harvest and reached up 15 mm at Coihueco and 3.5 mm at Angol. At harvest, fruit were randomly collected, and evaluated for rain cracking percentage and fruit quality. Rain cracking percentage was evaluated for 100 fruits per tree (replicate) by considering three different cracking types on fruit: around stem, side, or stylar end (Fig. 3C). Twenty-five cherries per tree (replication) were also picked from each treatment to evaluate fruit size by measurement fruit diameter (mm) using an electronic digital caliper (Altraco, Inc., CA, USA).

For the Oregon trial during May–June, 2015, two coating formulations (0.5% CNF/0.5% KSB/0.1% glycerol/0.1% surfactant mixture and 0.5% CNF/0.5% KSB/0.1% glycerol/0.2% surfactant mixture) that showed the least rain-cracking in Chile trial were applied to 'Skeena' cherries. In addition, the latter coating formulation without 0.5% KSB was also applied to evaluate the effect of KSB absence on rain-cracking and fruit quality. Hence, total 3 coating formulations were studied. 'Skeena' cherries were treated at a cherry orchard in The Dalles, Oregon, USA. Each tree was sprayed at two different times with 2 L coating formulation per spray ($2 \times 2\text{ L} = 4\text{ L}$ total for each tree). Similar to the Chile trial, the first spraying was applied at the straw color stage on May 20, 2015, and the second spray (post-straw spray) was 14 days later on June 4, 2015. Each treatment consisted of 6 tree replications laid out in a randomized pattern. Each treatment was protected by buffer rows (non-coated trees) on each side. Samples (75–150 cherries) from each tree were collected on June 24, 2015 to evaluate fruit quality, including

firmness (g/mm) and size (mm) by a Firm Tech 2 (BioWorks, KS, USA), soluble solid content by a refractometer (Atago Co., Ltd., PAL-1, Tokyo, Japan), pedicel/fruit retention force (g) by a Digital Force Gauge (Imada Inc., DS2-4, IL, USA), and color (mesophyll and epidermis) by a CIEL scale (Afcotel, France). Unfortunately, the cherry rain-cracking (%) data were unable to be collected since there was no sufficient rain fall during the Oregon trial period.

2.5. Experimental design and statistical analysis

Taguchi design was employed to identify the optimal coating formulations by considering three treatment factors: type of plasticizer (factor A: glycerol, sorbitol, and PEG400), concentration of plasticizer (factor B: 0, 0.05, and 0.10% w/w wet base), and concentration of surfactant mixture (factor C: 1:1 of Tween 80:Span 80 at 0.05, 0.10, and 0.20% w/w wet base). These ranges of plasticizer and surfactant concentrations were selected based on our preliminary studies (data not shown). Nine different coating formulations shown in Table 1 were developed based upon the Orthogonal array using L₉ (3³). This design statistically increased the efficiency of experiments by decreasing the total numbers of workloads (Jung and Zhao, 2011). In Taguchi design, the variation of the response was examined using S/N ratio, the ratio of the mean (signal) to the standard deviation (noise) (Chaulia and Das, 2008). Generally, three standard S/N equations are used to classify the objective function as: 'larger the better', 'smaller the better', or 'nominal the best'. In the present study, wettability of coating formulation and EL of derived films were considered as 'larger the better (S_{NL})' type, while contact angle of coating formulation and WS, WA, TS, and WVP of derived films were all analyzed by using a 'smaller the better (S_{NS})' (Dimou et al., 2009).

S/N ratios at each level of three treatment factors and the difference between the highest and lowest S/N ratios are reported in Table 1. Taguchi analysis provided the optimal level corresponding to the highest S/N ratio, and the largest difference (Δ) between the highest and the lowest S/N ratio indicated the most contributing factor on each quality measurement. The combined level of each treatment factor was optimized to employ high wettability of coating formulation and superior elasticity of film along with low water solubility, water absorption ability, and strength of films.

For the confirmation study, the quality parameters of the coating formulations and derived films prepared based on the optimized formulations were compared with the predicted values using the following equation from Taguchi analysis:

$$\text{The predicted value} = Y + (A_{\text{highest}} - Y) + (B_{\text{highest}} - Y) \\ + (C_{\text{highest}} - Y)$$

where Y is the grand average of quality character, and A_{highest}, B_{highest}, and C_{highest} are the average values of responses at their optimal levels, respectively (Chaulia and Das, 2008).

Experiments for coating formulation and derived film studies were conducted in triplicate. Results were analyzed for statistical significance via post hoc testing using least significant difference (LSD) by means of statistical software (SAS v 9.2, The SAS Institute, USA). Results were considered to be significantly different at $P < 0.05$.

3. Result and discussion

3.1. Optimization of CNF-based coating formulations

For providing sufficient wettability of a coating dispersion, a lower contact angle (<90°) and a higher spreadability (tested as 'drop absorbency' on the cardboard) are required (Duncan et al., 2005; Seo and Lee, 2006). Based on the Taguchi analysis (Table 1), the

concentration of surfactant mixture had significant ($P < 0.05$) effect on contact angle, with higher S/N ratio at 0.2% surfactant mixture, but no effect on the spreadability. This might be because the surfactant containing both hydrophilic head and hydrophobic tail was able to interact with both the liquid–solid and the liquid–vapor interfaces, thus reducing interfacial tensions of the coating dispersions (Seo and Lee, 2006). In addition, the surfactant mixture of 1:1 of Tween 80:Span 80 had a hydrophilic–hydrophobic balance (HLB) of 7–9, which was capable of acting as the wetting agent (Jin et al., 2008). Therefore, it was revealed that the concentration of surfactant mixture was the most important substance in the CNF-based coating formulations for improving the wettability of the coatings.

For obtaining high water resistant coatings, it was desired to have lower WS, WA, and WVP of derived films (Table 1). For WS and WVP, no significant treatment effect was observed, whereas the concentration of surfactant mixture had significant effect on WA, in which 0.05% surfactant mixture resulted in significantly ($P < 0.05$) lower WA value than that of 0.20% surfactant mixture. This was probably due to the hydrophilic nature of Tween 80 (Tsai et al., 2001). Within 0.05–0.20% surfactant mixture in the coating formulations, however, CNF-based coatings retained superior resistance against water, showing no significant increase in water solubility. Consistently, Österberg et al. (2013) reported that CNF film absorbed a substantial amount of solvent, but its original structure remained after 24 h of solvent soaking. This special characteristic of CNF based coatings would be excellent for preventing cherry rain-cracking since it can prevent water penetration into fruit by absorbing water onto the fruit surface, meanwhile, the coating would not be dissolved by rainwater neither. Hence, 0.5% CNF-based coating containing 0.2% surfactant mixture met the need for being water resistant and having high wettability.

To have high elasticity for allowing continuous fruit growth before harvest, higher EL and low TS of coatings are necessary. All treatment factors showed significant ($P < 0.05$) effect on EL and TS (Table 1). Coating formulation with 0.05% and 0.1% of glycerol or 0.2% surfactant mixture offered the highest EL, while the formulation with 0.1% glycerol, 0.1% PEG400, or 0.2% surfactant mixture provided the lowest TS. Overall, the addition of 0.1% glycerol and 0.2% surfactant mixture generated high elastic CNF based films. Previous study reported that adding plasticizer improved film elasticity since plasticizer can penetrate into polymeric matrix, thus increasing the mobility of polymer chains (Cagri et al., 2001). In addition, glycerol might be more compatible with nanoporous and hydrophilic CNF than PEG or sorbitol since PEG has larger molecule weight and sorbitol is more hydrophobic in comparison with glycerol. Hydrophilic Tween surfactant could also act as the plasticizer (Tsai et al., 2001).

The possible stress from applied coatings onto fruit was assessed using the self-assembled equipment as stated previously. This equipment was designed to estimate the pressure of coatings applied onto a blown balloon connected to a U-shape tube filled with water. The water level increase resulting from the increased pressure of applied coating onto the balloon surface was only observed in the coating formulation containing 0.1% surfactant mixture without glycerol. This result indicated that glycerol addition improved the coating elasticity as well as providing the least stress onto the fruit surfaces. However, coating formulations without or with lower concentration (<0.1%) of plasticizer and/or with lower concentration (<0.1%) of surfactant mixture did not increase water level of U-shape tube. This was probably due to insufficient coverage of coating dispersion onto the balloon surfaces as a result of high surface tension of the coating formulations. Hence, CNF-based coating containing 0.1% glycerol and 0.2% surfactant mixture met the requirement of high elasticity and minimal stress onto fruit that otherwise would prevent the continuous fruit growth.

Table 2

Confirmation study for the optimized coating formulations and derived films by comparing predicted values with actually measured data.

Target properties of films or solution	Optimized levels of treatment factors			Confirmation study		
	Type of plasticizer	Concentration of plasticizer	Concentration of wetting agent	Predicted value ^a	95% confidence interval (CI ⁺⁺)	Confirmation (actual value)
Contact angle (°) ^a	Glycerol	0.10%	0.20%	55.72	2.68	56.88
Elongation (%) ^b	Glycerol	0.10%	0.20%	4.69	0.63	4.14
Tensile strength (MPa) ^a	Glycerol	0.10%	0.20%	8.28	6.33	11.35
Water absorption ability (%) ^a	Glycerol	0	0.05%	144.96	35.73	147.97

^a Predicted value = $Y + (A_{\text{highest}} - Y) + (B_{\text{highest}} - Y) + (C_{\text{highest}} - Y)$, where Y is the grand average of performance characteristic and A_{highest} , B_{highest} , and C_{highest} are the average values of responses at their respective optimal levels.

⁺⁺ CI = $\sqrt{F(0.05, 1, f_e)V_e[1/N_{\text{eff}} + 1/R]}$, $N_{\text{eff}} = N/1 + T_{\text{DOF}}$, where f_e was the degree of freedom for error, V_e was the error variance, R was the number of replications for confirmation experiment, N was the total number of experiments, T_{DOF} was the total degree of freedom associated with the estimation of mean optimum.

^a It was targeted to obtain lower values.

^b It was targeted to obtain higher values.

The optimal coating formulations were identified based on the quantified quality characteristics of coatings and derived films, including contact angle of coating dispersion, and WA, TS, and EL of derived films. To have lower WA, 0.5% CNF and 0.5% KSB should be combined with 0.05% surfactant mixture, whereas to have lower contact angle and TS with higher EL, 0.5% CNF and 0.5% KSB with 0.1% glycerol and 0.2% surfactant mixture should be used (Table 2). These two optimized coating formulations were further confirmed by comparing the predicted values with the experimental data within a 95% confidence interval. As shown in Table 2, the experimental values of contact angle, WA, TS, and EL were all within the predicted range of 95% confidence interval, thus successfully confirming the lab-scale optimization results. These coating formulations were further validated for ability to prevent cherry rain-cracking in the field studies reported in Section 3.3 below.

3.2. Effect of pH on the physicochemical, mechanical, and microstructural properties of the coatings

Since the association status of sorbic acids in the aqueous system of KSB is pH dependent (Shen et al., 2010), coating matrix could be affected by the pH of the coating formulations containing KSB, possibly due to the electrostatic forces, hydrogen bonds, and hydrophobic interactions between sorbic acids and other components dissolved in the aqueous coating system (Osaki and Werner, 2003). Hence, WS, WA, TS, and EL and the microstructure of the derived films were compared between films prepared at pH 4.8 and pH 6.4 for the two optimized coating formulations. It was observed that pH had no significant effect on WS, WA, TS, and EL in the optimized coating system (Table 3). In SEM images (Fig. 2), all derived films had well dispersed and entangled networks. It was found that KSB crystals were more assimilated onto CNF-based film surface at higher pH (6.5) (Fig. 2B and F) than at lower pH (4.8) (Fig. 2A and C). This might be because the dissociated sorbic acids had less available hydroxyl groups for interacting with CNF, thus depositing KSB crystals onto the film surface. Similarly, Bierhalz et al. (2012) reported that the incorporation of natamycin caused dramatic changes on the film surface structure with non-uniform distribution of the antimicrobial crystals due to its low solubility in the solution. The coating formulation containing 0.5% CNF/0.5% KSB/0.1% glycerol/0.2% surfactant mixture showed more homogeneous film structure (Fig. 2A, B, E and F) than that with 0.5% CNF/0.5% KSB/0.05% surfactant mixture (Fig. 2C, D, G and H). The homogeneous film matrix indicates good film structural integrity, and consequently provides good mechanical properties (Mali et al., 2002). Also, it was previously reported that a reasonable amount of plasticizer could induce smoother and more homogenous topography for the films (Pang et al., 2013). Water resistant film structure was observed by comparing the surface microstructures of films before and after soaked in water for 2 h. It

was found that KSB crystals were washed away from the film surfaces (Fig. 2E–H), indicating the fast release of the active compound at direct water contact and/or high moisture (relative humidity) atmosphere. In addition, fibrous matrix was strongly entangled and the film integrity was retained against water even after water soaking for 2 h. Therefore, it was observed that while glycerol, surfactant mixture, and KSB crystals altered the surface microstructures of CNF-based films (coatings), they did not change the strong fibrous entangled structures of the films (coatings).

3.3. Cherry rain-cracking field study

Based on the results from lab-scale optimization study, three different coating formulations were prepared with different surfactant mixture concentrations (0.05%, 0.1%, and 0.2% incorporated into 0.5% CNF/0.5% KSB/0.1% glycerol based coating matrix), and applied to 'Sweetheart' cherries in Coihueco and Angol (Chile). The photos showing fruit before and after applying coatings are illustrated in Fig. 3A and B, where the coatings were well dispersed and attached on the fruit surfaces (Fig. 3B). Total cherry rain-cracking including side, around stem, and sylar end are reported in Fig. 3C and D. The application of coating dispersion containing 0.1% surfactant mixture resulted in significant reduction in total cherry cracking, 39.20% and 44.60% reduction in comparison with non-coated ones, in Coihueco and Angol, respectively (Fig. 3D and E). Likewise, coating formulations with 0.2% surfactant mixture reported 31.18% and 40.85% total cherry-rain cracking reductions in both locations, respectively (Fig. 3D and E). It has been well known that cherry rain-cracking "around stem" is the most common splitting due to water accumulation at that area (Jedlow and Schrader, 2005). In the Coihueco trial, the fruit cracking in the "around stem" was reduced 40.91% and 51.55% by applying coatings containing 0.1% and 0.2% surfactant mixtures, respectively in comparison with non-coated fruit (Fig. 3D). In the Angol trial, much greater reductions, 68.07%, 91.60%, and 55.70% when applying coatings containing 0.05%, 0.1%, and 0.2% surfactant mixture were observed compared with non-coated ones, respectively (Fig. 3E). These results indicated that cherry rain-cracking can be reduced significantly by applying coating against water. In addition, there was no significant difference in fruit growth (fruit size) between coated and non-coated fruit (Fig. 3D and E). The Chile trials, therefore, validated that CNF-based coatings containing an appropriate type and amount of plasticizer and surfactant provided superior water barrier along with the great wettability and elasticity for allowing fruit continuous growth before harvest.

Based on the results from the Chile trials, two coating formulations (0.5% CNF/0.5% KSB/0.1% glycerol containing 0.1% or 0.2% surfactant mixture) showing the significant reduction of fruit rain-cracking were selected and applied to 'Skeena' cherries for further validation of the coating in The Dalles, Oregon (USA) dur-

Table 3

The effect of pH on the physicochemical and mechanical properties of optimized coating formulations or derived films.

Different levels of factors				Physicochemical properties of coating formulations		Mechanical properties of derived films	
pH	Types of plasticizer	Con. of plasticizer	Con. of surfactant	Water solubility (WS, %)	Water absorption ability (WA, %)	Tensile strength (TS, MPa)	Elongation at break (EL, %)
4.8	Glycerol	0.10	0.20	66.24 ^a	283.88 ^{ab}	2.38 ^a	5.88 ^{ab}
6.5	Glycerol	0.10	0.20	64.79 ^a	428.38 ^a	4.01 ^a	7.36 ^a
4.8	Glycerol	0	0.05	65.89 ^a	147.97 ^b	5.27 ^{ab}	3.68 ^{ab}
6.5	Glycerol	0	0.05	61.71 ^a	229.64 ^b	9.19 ^b	3.43 ^b

* Means preceded by the same small letter in the same column were not significantly different ($P > 0.05$).

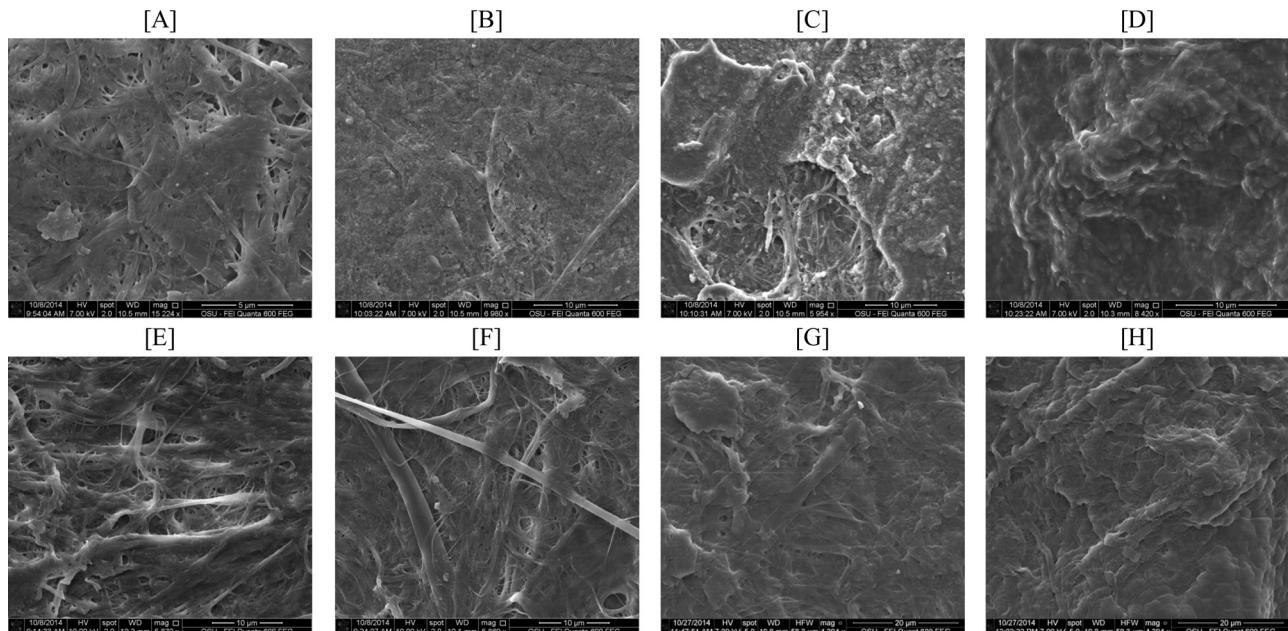


Fig. 2. Scanning electron microscope (SEM) images of derived films from coating formulations containing 0.50% (w/w wet base) cellulose nanofiber (CNF), 0.50% (w/w wet base) potassium sorbate (KSB), 0.05% or 0.20% (w/w wet base) surfactant mixture (Tween 80 and Span 80 at a ratio of 1:1), and with or without 0.1% (w/w wet base) glycerol; (A) 0.50%CNF/0.5% KSB/0.20% surfactant/0.10% glycerol at pH 4.8, (B) 0.50%CNF/0.5% KSB/0.20% surfactant/0.10% glycerol at pH 6.5, (C) 0.50%CNF/0.5% KSB/0.05% surfactant/0.10% glycerol at pH 4.8, (D) 0.50%CNF/0.5% KSB/0.05% surfactant/0.10% glycerol at pH 6.5; and (E, F, G, and H) A, B, C, and D films soaked in distilled water for 2 h at the ambient temperature, and dried at 50 °C for 24 h, respectively.

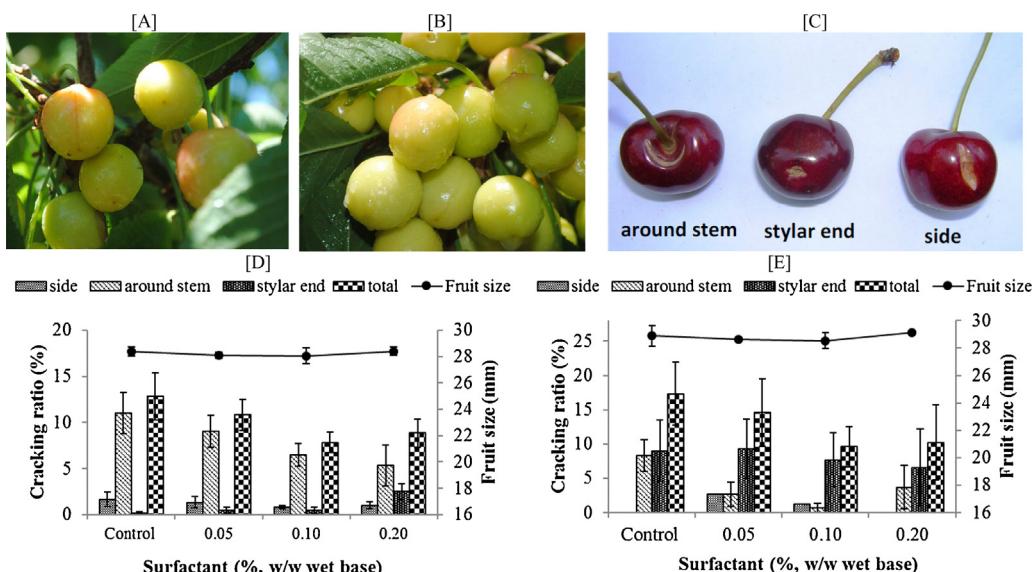


Fig. 3. Visual aspect of 'Sweetheart' cherries at the yellow straw stage before [A] and after [B] spray, types of cherry rain-cracking evaluated [C], and the effect of surfactant level (% w/w wet base) on cherry cracking (%) and fruit growth (mm) grown in two different locations of Coihueco [D] and Angol [E] in Chile; all formulations included 0.5% (w/w wet base) of cellulose nanofiber, 0.5% (w/w wet base) of potassium sorbate, and 0.1% (w/w wet base) of glycerol; surfactant was the mixture of Tween 80 and Span 80 at a ratio of 1:1. Each data point in the graphs represents the mean \pm SE ($n = 6$).

Table 4

The effect of coating formulations on fruit quality of "Skeena" cherries grown in The Dalles, Oregon (USA) during May–June, 2015.

Coating formulations	Firmness (g/mm)	Size (mm)	Soluble sugar (%)	Pedicel/fruit retention force (g)	Color (epidermis)	Color (mesophyll)
Control*	366.20 ^a	29.45 ^a	21.13 ^a	903.30 ^a	5.88 ^a	5.25 ^a
0.1% surfactant**	373.41 ^a	29.10 ^a	22.39 ^a	952.37 ^a	6.04 ^a	5.43 ^a
0.2% surfactant**	395.33 ^a	28.80 ^a	23.17 ^a	925.37 ^a	5.96 ^a	5.40 ^a
0.2% surfactant without potassium sorbate**	363.81 ^a	29.13 ^a	21.89 ^a	977.92 ^a	5.80 ^a	5.41 ^a

Surfactant contains the mixture of Tween 80 and Span 80 at a ratio of 1:1.

* Non-coated.

** All formulations included 0.5% (w/w wet base) cellulose nanofiber, 0.1% (w/w wet base) glycerol, and 0.5% (w/w wet base) potassium sorbate.

ing May–June, 2015. Unfortunately, the fruit cracking was unable to be evaluated since there was no rainfall during the period of fruit development in the trial site. However, fruit firmness, size (mm), soluble sugar (%), pedicel/fruit retention forces (g), and color (epidermis and mesophyll) were tested and showed no significant differences between coated and non-coated fruit ($P > 0.05$) (Table 4). Phytotoxic symptoms were visually observed in fruit and leaves at harvest time, and no indication of phytotoxicity was found (data not shown). Although the coating effect on cherry rain-cracking was unable to be evaluated from the Oregon trial, the developed coatings showed no detrimental effect on fruit growth and quality. Therefore, this systematic study was successful to develop and validate the CNF-based water resistant coatings with great wettability and elasticity for reducing cherry rain-cracking without detrimental impact on fruit growth and quality.

4. Conclusion

Cellulose nanofiber (CNF)-based coatings for reducing cherry rain-cracking were developed by using a two-step systematic approach: (1) lab-scale optimization study using Taguchi design and analysis, and (2) preliminary field validation study. This systematic approach led to develop CNF-based coatings possessing high wettability and elasticity with superior water resistance. Surfactant mixture (Tween 80 and Span 80 at a 1:1 ratio) was appeared as the most critical factor affecting wettability, hydrophilicity, and elasticity of the coatings. The 0.5% CNF/0.5% KSB-based coating containing 0.1% glycerol showed more homogenous matrix with high elasticity. Hence, the optimized coating formulations (0.5% CNF/0.5% KSB/0.1% glycerol with 0.05%, 0.1% or 0.2% concentrations of surfactant mixtures) were applied on 'Sweetheart' and 'Skeena' in Chile and USA, and results showed that the developed coatings significantly reduced cherry cracking in comparison with non-coated fruit and coatings did not have detrimental effect on fruit growth and quality. For the future studies, the developed CNF-based water resistant coatings may be applied in other cherry varieties and tested in other locations to further demonstrate its effectiveness as a physical protection for reducing cherry rain-cracking. In addition, fungicide or pesticide that is compatible with CNF may also be incorporated into the developed coatings to further expand its functionalities and applications.

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