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

Jooyeoun Jung[a], Zilong Deng[a], John Simonsen[b], Richard M. Bastías[c], Yanyun Zhao[a,*]

[a] *Department of Food Science & Technology, Oregon State University, Corvallis, OR 97331-6602, USA*
[b] *Department of Wood Science & Engineering, Oregon State University, Corvallis, OR 97331, USA*
[c] *Universidad de Concepción, Facultad de Agronomía, Av. Vicente Méndez 595, Chillán, Chile*

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A B S T R A C T

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.

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

* Corresponding author.
E-mail address: yanyun.zhao@oregonstate.edu (Y. Zhao).

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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 coating 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 ± 2 °C) for 2 days (Chen and Zhao, 2012). Prepared films were conditioned at a 25 °C and 50% relative humidity (RH) self-assembled chamber (Versa, PA, USA) for 2 days prior to the measurement (Chen and Zhao, 2012).