AN ABSTRACT OF THE THESIS OF

Virginia P. Gouw for the degree of Master of Science in Food Science and Technology presented on March 11, 2016.

Title: Investigation of Bioactive Compounds in Different Types of Fruit Pomace and Their Applications as Bulk Materials for Creating Biocomposite

Abstract approved:

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Yanyun Zhao

The objectives of this study were to evaluate the physicochemical properties and bioactive compounds from four different types of fruit pomace, including apple, blueberry, raspberry, and cranberry, and further to investigate the feasibility of creating apple pomace based biocomposite boards using thermal compression molding and to optimize the biocomposite formulations possessing high mechanical strength, low water sensitivity, and slow biodegradation.

Fruit pomace were collected per batch at the end of juice processing, frozen at -18 °C, and further thawed for 30 min at room temperature for analysis. Apple pomace had pectin as high as 18.87% for acid extractable pectin and 8.66% for total soluble pectin. Blueberry pomace was significantly higher in anthocyanins among other pomace (256.18 mg cyanidin-3-glucoside/100 g dry weight). Raspberry pomace contained insoluble dietary fibers (73.30%) that was predominated by Klason lignin. The total phenolic content and radical scavenging activity in cranberry pomace were significantly higher than other pomace, being 6.77 mg gallic acid equivalent/g dry weight and 2.68 mg

ascorbic acid equivalent/g dry weight, respectively. Cranberry pomace also had high amount of acid extractable pectin (10.58%) following apple pomace. In addition, blueberry and cranberry pomace were also high in insoluble dietary fibers (63.85% and 67.20%, respectively).

Since apple pomace is rich in dietary fibers and the amount generated from apple juice industry is huge, apple pomace was chosen to create biocomposite boards through thermal compression molding at 30 MPa and 160 °C for 20 min. The biocomposite formulations were optimized through $L_9$ orthogonal array of Taguchi design aimed for high mechanical strength, low water sensitivity, and slow biodegradation. In the pomace biocomposite formulations, soy protein isolate (SPI) and poly(methyl methacrylate) (PMMA) were added as binders, stearic acid as hydrophobic agent, span 80 as surfactant, and 5% methylene diphenyl diisocyanate (MDI) as crosslinking agent. The ratio of SPI and PMMA and the concentration of span 80 did not affect any of the tested parameters significantly ($P > 0.05$). On the other hand, stearic acid significantly influenced breaking strength ($P < 0.05$), while pomace-to-binder (P/B) ratio gave significant effect on modulus of elasticity, water solubility, moisture content, and biodegradability ($P < 0.05$). The optimum formula to create biocomposite board from apple pomace was SPI:PMMA = 2:1 at P/B ratio of 7:3 with 5% MDI and without the addition of stearic acid and span 80.

The results from this study provided new information on the utilizations of different types of fruit pomace. Dietary fibers in apple and cranberry pomace have potential to create packaging materials, whereas bioactive compounds in blueberry and raspberry pomace are good candidates to fortify different types of food products. Moreover, the

developed biocomposite boards from apple pomace can be applied to make ecofriendly packaging materials.

# Investigation of Bioactive Compounds in Different Types of Fruit Pomace and Their Applications as Bulk Materials for Creating Biocomposite

by
Virginia P. Gouw

A THESIS

submitted to

Oregon State University

in partial fulfillment of
the requirements for the
degree of

Master of Science

Presented March 11, 2016
Commencement June 2016

Master of Science thesis of Virginia P. Gouw presented on March 11, 2016

APPROVED:

Major Professor, representing Food Science and Technology

Head of the Department of Food Science and Technology

Dean of the Graduate School

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# ACKNOWLEDGMENTS

First and foremost, I would like to dedicate my sincerest gratitude to my major advisor, Dr. Yanyun Zhao, for her continuous encouragement throughout my study at Oregon State University. Her invaluable advice, patience, and guidance were instrumental in the accomplishment of this master program. Through her and this experience, I gained skills and confidence that are and will continue to be beneficial to me in the future.

I would also like to recognize Dr. Melinda Manore, Dr. Mark Daeschel, and Dr. John Simonsen for taking time to serve as my graduate committees. Special to Dr. Daeschel, thank you for providing me valuable advice, forcing me to think out of the box, and encouraging me to apply the critical thinking skills I learned throughout this research. To Dr. Simonsen, thank you for imparting expertise on the use of machines and necessary instrumentations as well as the ability to use them in your laboratory.

Many thanks to Hood River Juice Co. and Kerr Concentrates, Inc. for donating the fruit pomace, Dr. Jooyeoun Jung for her patience and lending her knowledge to teach me basic laboratory skills, developing an effective experimental design, as well as giving me valuable advice in writing the manuscript, and Dr. George Cavender for designing the mold that helped carry out this experiment. I greatly appreciate Brian Jensen and Darin Kempton, who manufactured the mold and helped troubleshoot whenever issues arose.

Many thanks also go to Dr. Robert McGorrin, Ms. Linda Hoyser, Ms. Linda Dunn, Ms. Debby Yacas, Ms. Christina Hull, Ms. Iset Sevilla-Bazan, Jeff Clawson, and Brian Yorgey for providing assistance in every aspect, and thanks to my awesome lab mates:

Wenjie Wang, Zilong Deng, Hongcai Zhang, and Brenda Rojas for being my little family and sharing our success and failures together. Thanks to Myra Koesdjojo, Yolanda Tennico, Rina Permanasari, Yuanyuan Wu, and Sumate Pengpumkiat, who helped me make the transition when I arrived to the United States. Thanks to Lukas Suriyo Bintoro for his support and patience during throughout this journey.

Last but certainly not least, I would like to thank my parents, family, and friends in Indonesia for their remarkable encouragement. Their unconditional love was the driving force and motivation that got me through every obstacle faced every day. This accomplishment would not be possible without any of those mentioned.

# CONTRIBUTION OF AUTHORS

Dr. Jooyeoun Jung and Dr. Yanyun Zhao assisted with the experimental design, data analysis, and writing of each chapter. Dr. John Simonsen provided machines and instrumentations for Chapter 4.

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## CHAPTER 1

## Introduction

Fruit pomace is the by-product from fruit juice manufacture, consisting of skins, seeds, stems, and de-juiced pulps. It is susceptible to microbial attack due to high moisture and sugar contents. The bulky and perishable characteristics of fruit pomace make shipment and storage costly. The majority of the pomace ends up in the landfill for direct disposal or partially used as animal feed. As a result, more than $10 million has to be spent for the disposal of apple pomace in the United States (Shalini and Gupta, 2010), while the disposal of berry fruit pomace is further aggravated by legal restrictions (Zhao, 2007). Despite being a by-product, fruit pomace is rich in bioactive compounds, such as dietary fibers and polyphenols that have beneficial effects and may be converted into various value-added products.

Many studies have been conducted in analyzing the bioactive compounds in fruit pomace. Previously, Deng et al. (2011) evaluated the dietary fibers and polyphenols in different varieties of wine grape pomace, Grigoras et al. (2013) analyzed the antioxidant activity in different cultivars of apple pomace, and Reque et al. (2014) characterized the physicochemical properties and bioactive compounds of blueberry fruit and derived products. Although numerous fruit pomace have been examined, huge variations among studies sometimes occurred as a result of different cultivars of fruit, processing procedures, and methods of analysis. Therefore, it is necessary to study the characteristics

of different types of fruit pomace as a pool instead of individual cultivar to obtain comprehensive values. Apple, blueberry, raspberry, and cranberry represent predominant fruit in the northwest region of United States, and their pomace from the juice manufacture were analyzed for their physicochemical properties and bioactive compounds using the same methods of analysis. The results from this study can be used as a baseline to select suitable pomace for developing value-added applications in food and/or other fields.

Moreover, apple pomace was chosen to create value-added products owning to high quantity from apple juice and cider processing. In the United States, it is estimated that over 25,000 tons of apple pomace are produced each year (Bhushan et al., 2008; Roberts et al., 2004). Previous studies utilized apple pomace to extract the pectin (Canteri-Schemin et al., 2005), as a source of dietary fibers (Reis et al., 2014; Sudha et al., 2007), and to extract the antioxidant compounds, such as epicatechin, quercetin, and chlorogenic acid (Lu and Yeap Foo, 2000; Reis et al., 2014). Nonetheless, the utilizations of apple pomace to develop packaging material are scarce. Apple pomace is rich in dietary fibers that are good candidates to create biocomposite. Therefore, this study investigated the feasibility of creating apple pomace based biocomposite boards using thermal compression molding and optimized the biocomposite formulations possessing high mechanical strength, low water sensitivity, and slow biodegradation. This study would provide new insights about apple pomace as ecofriendly packaging material and further expand to create various value-added biodegradable packaging containers, such as nursery pots.

Overall, this project has two specific objectives: 1) evaluating the physicochemical properties and bioactive compounds from four different types of fruit pomace with the same methods of analysis, and 2) developing and optimizing the formulations of apple pomace based biocomposite boards through $L_9$ orthogonal array of Taguchi design. This study would supply information about the different characteristics of fruit pomace and their potential applications to create value-added products as well as help the juice manufacture reducing this biowaste stream.

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# CHAPTER 2

# Literature Review

## 2.1 Overview of fruit pomace

### 2.1.1 Industrial production and disposal of fruit pomace

The awareness of healthy lifestyle leads the food and beverage industries moving towards nutritious alternatives, including fruit juice or juice concentrate. National Agricultural Statistics Service (NASS) provided the information about the quantity of fruit processed into juice/cider and wine in the United States as shown in Table 2.1. High demand of these products significantly increased the output of pomace, a by-product consisting of skins, stems, seeds, and de-juiced pulps. Majority of the pomace ends up in the landfill for direct disposal to the soil or partially used as animal feed.

**Table 2.1 The amount of fruit processed into juice/cider and wine (NASS, 2014)**

| Types of fruit | Year | Quantities processed (Million tons) | Note |
|---|---|---|---|
| Oranges* | 2012/2013 | 8.268 | Include fruit used for juice, concentrates, grapefruit segments, and other citrus fruit. |
| Grapefruits** | 2012/2013 | 1.204 | |
| Lemons | 2012/2013 | 0.912 | |
| Apples | 2013 | 0.881 | Juice, cider, vinegar, wine, and slices for pie making. |
| Wine grapes | 2013 | 5.067 | Crushed for wine. |
| Table grapes | 2013 | 0.504 | Crushed for juice (includes some quantities used for jam, jelly, etc.). |
| Sweet cherries | 2013 | 0.029 | California canned utilization and other processed utilizations (frozen, juice, etc.) from all States. |
| Tart cherries | 2013 | 0.046 | Some quantities used for juice, wine, brined, and dried. |

* Includes small quantities of tangerines in Texas and Temples in Florida.
** Includes seedy grapefruit.

The disposal of this by-product poses considerable economic and environmental problems. Shalini and Gupta (2010) reported that more than $10 million has to be spent for the disposal of apple pomace in the United States, while Zhao (2007) mentioned that the disposal of berry fruit pomace is further aggravated by legal restrictions. Fruit pomace contain high moisture and sugar contents that provide suitable environment for spoilage microorganisms to grow.

### 2.1.2 Dehydration of fruit pomace

Fruit pomace contain high amount of water and carbohydrates with low amount of protein and fat. Along with the basic chemical compositions, pomace have functional compounds, such as phenolics and dietary fibers that have beneficial effects on human health (Zhao, 2007). Nonetheless, bulky and perishable characteristics of fruit pomace limit their applications. Different dehydration methods have been evaluated since they can reduce the volume and weight as well as to extend the shelf life of fruit pomace.

Tseng and Zhao (2012) studied the effect of different drying methods including conventional oven drying at 40 °C, vacuum oven drying at 40 °C, ambient air drying at 25 °C, and freeze drying at -55 °C on the bioactive compounds in wine grape pomace. They found that freeze drying retained higher total phenolic content initially compared to other methods, however, the differences in other bioactive compounds measurements were not statistically significant. Freeze drying removes the water through sublimation of ice on a frozen product under vacuum conditions. Due to the low temperature and the absence of liquid water in the process, the chemical and biological reactions are slowed down, thus maintaining excellent quality of the product (Ratti, 2001). However, this

method is the most expensive dehydration process, and it is necessary to have economical feasible drying techniques to preserve waste products. Therefore, conventional oven drying and ambient air drying are highly acceptable to be applied in commercial scale since they are much less cost and have similar quality in retaining the bioactive compounds of wine grape pomace compared to freeze drying (Tseng and Zhao, 2012). Another research has been conducted recently by Jung et al. (2014) on drying apple pomace using an impingement oven at 110 °C. The drying rates among different drying methods, including conventional oven drying at 40 °C for 48 h, freeze drying at -55 °C for 60 h, and impingement oven at 110 °C for 3 h were compared. The results showed that the impingement oven gave higher total phenolic content than conventional oven drying, freeze drying, and freshly thawed apple pomace, because high temperature in impingement oven could liberate the bound phenolics in the fiber matrix (Jung et al., 2014). Impingement oven reduced the drying time to 3 h by accelerating the heat transfer through high velocity hot air and impinging directly on the product surface (Xiao et al., 2015; Yemmireddy et al., 2013). Therefore, this drying method can be used in the commercial scale to reduce the processing time and cost as well as to retain the antioxidant activity of fruit pomace (Jung et al., 2014).

### 2.1.3 Value-added applications of fruit pomace

Different value-added applications of fruit pomace have been evaluated. Some of the researches used the fruit pomace in their wet form and others did some pretreatments, such as drying, grinding, and extracting to obtain certain properties from the pomace. The

examples of utilizations of fruit pomace to create value-added products are shown in Table 2.2.

**Table 2.2 Examples of value-added applications of fruit pomace**

| Types of application | Previous research | References |
|---|---|---|
| Source of dietary fibers | Fresh apple pomace was used to partially replace the meat in chicken patties and beef jerkies, while apple pomace flour was incorporated to partially substitute wheat flour in cookies and muffins. | Jung et al. (2014) |
| | Raspberry pomace in the form of crumbled and non-crumbled were used to partially substitute the flour in short-crust cookies. | Górecka et al. (2010) |
| Pectin extraction | Ultra-high pressure (UHP), microwave-assisted extraction, and traditional heating were used to extract pectin from navel orange peel. Pectin from UHP process had higher viscosity and stability. | Guo et al. (2012) |
| | Pectin from fresh and stored peach pomace were extracted in hot acidified solutions. Pectin from fresh pomace had higher gelling ability than stored pomace. | Pagán et al. (2001) |
| Phenolic extraction | Anthocyanin extraction from blueberry pomace has potential to be a good source of natural colorants. | Lee and Wrolstad (2004) |
| | Phenolic fractions of cranberry pomace showed antimicrobial activities against seven pathogenic bacteria | Caillet et al. (2012) |
| Essential fatty acids extraction | Black raspberry seed oil is an excellent source of omega-3 and omega-6 fatty acids that can reduce the risk of cancer and heart disease. | Parry and Yu (2004) |
| | Blackberry, blueberry, cranberry, kiwi, red raspberry, and strawberry seed oils provide interesting nutritional point of view. | Van Hoed et al. (2009) |
| Solid-state fermentations (SSFs) | SSFs of apple pomace using *Saccharomyces cerevisiae*, *Candida utilis*, and *Torula utilis* were evaluated. *Candida* exhibited three times higher in crude protein compared to unfermented apple pomace, which is necessary for the nutrition of livestock. | Joshi and Sandhu (1996) |
| Edible film and coating | Cranberry pomace extract was combined with pectin and plasticizer that have potential to create film for food wrapping or edible coatings on the surface of various food products. | Park and Zhao (2006) |
| | Extract from red wine grape pomace skin was added with different types of polysaccharides. This film is not only edible but also exhibiting antioxidant and antimicrobial properties. | Deng and Zhao (2011) |

**Table 2.2 Examples of value-added applications of fruit pomace (Continued)**

| | | |
|---|---|---|
| Packaging application | Blueberry, cranberry, and red wine grape pomace were added with biopolymers to create biodegradable packaging applications. Blueberry pomace showed the highest breaking strength and modulus of elasticity compared to other types of pomace. | Park et al. (2010) |
| | Red wine grape pomace (RWGP) and white wine grape pomace (WWGP) was developed to create biocomposite board. RWGP showed higher breaking strength and modulus of elasticity, while WWGP had higher flexibility and biodegradability. | Jiang et al. (2011) |

The growth of value-added products from fruit pomace is not limited in food applications merely. The following sections will elaborate more about the basic chemical compositions and functional compounds in fruit pomace as well as the examples from current research and development.

## 2.2 Fruit pomace as food ingredients and packaging materials

### 2.2.1 Bioactive compounds in fruit pomace as functional food ingredients

The definition of bioactive compounds is remained unclear, even though significant number of studies has been conducted. According to Guaadaoui et al. (2014), bioactive compound is "a compound which has the capability and the ability to interact with one or more component(s) of the living tissue by presenting a wide range of probable effects."

Fruit pomace contain abundant phytochemicals, especially polyphenols and dietary fibers, the bioactive compounds that have shown significant health benefits to humans. Many studies found that pomace have higher phytochemicals than the fruit itself. Lee and Wrolstad (2004) compared the anthocyanins and polyphenolics of whole blueberries and blueberry pomace and found that these bioactive compounds are much higher in the

pomace, where majority is contributed from the peels of berry fruit. They concluded that blueberry pomace might be a good source of natural pigments and nutraceuticals. Similar results were obtained by Fuentes et al. (2013) in the tomatoes, in which the peels contained higher antioxidant activities than that of pulp, and the pomace had higher crude fibers than the fruit. In addition, some of the berry fruit pomace have great amount of seeds that are rich in insoluble dietary fibers and essential fatty acids.

#### 2.2.1.1 Phenolic compounds in fruit pomace

Phenolic compounds comprise an aromatic ring with one or more hydroxyl groups, ranging from simple molecules to highly polymerized compounds (Bravo, 1998). Phenolics work as antioxidant with different mechanisms, such as scavenging free radicals, donating proton or electron, and chelating metal cations, and all of these mechanisms depend on the phenolic structures (Balasundram et al., 2006). Phenolic acids, flavonoids, and tannins are the main dietary phenolic compounds (Balasundram et al., 2006). Mostly, phenolic compounds are present as conjugates with monosaccharides or polysaccharides, linked to one or more of the phenolic groups, and may also occur as functional derivatives, such as esters and methyl esters (Balasundram et al., 2006).

Folin–Ciocalteu colorimetric method is widely used to analyze the total phenolic content in various food products (Singleton et al., 1999). Gallic acid is usually chosen as a standard because it has good solubility, adequate stability, and low cost (Singleton and Rossi, 1965). Table 2.3 provides the information about total phenolic content in different types of fruit pomace.

**Table 2.3 Total phenolic content in fruit pomace**

| Types of pomace | Total phenolic content (mg gallic acid equivalent/g dry weight) | Extraction solvent | References |
|---|---|---|---|
| Acerola | 6.81 | Methanol | de Oliveira et al. (2009) |
| Pineapple | 2.75 | | |
| Passion fruit | 1.03 | | |
| Apple | 46.00 | Water | Peschel et al. (2006) |
| | 52.18 | Methanol | |
| | 41.56 | Ethanol | |
| | 27.97 | Acetone | |
| | 31.93 | Hexane | |
| Strawberry | 39.39 | Water | |
| | 59.77 | Methanol | |
| | 38.74 | Ethanol | |
| | 34.55 | Acetone | |
| | 11.65 | Hexane | |
| Pear | 12.90 | Water | |
| | 18.41 | Methanol | |
| | 12.09 | Ethanol | |
| | 27.26 | Acetone | |
| | 13.38 | Hexane | |

Anthocyanins are the examples of flavonoid derivatives that give blue, purple, and red color to fruit, flower, and vegetables. Anthocyanins are water-soluble, and occur as glycosides or acylglycosides of their respective aglycone anthocyanidins (Wu et al., 2006). There are six major anthocyanidins found in nature, namely cyanidin, delphinidin, petunidin, peonidin, pelargonidin, and malvidin (Wu et al., 2006). Different anthocyanins compositions in fruit pomace are shown in Table 2.4.

**Table 2.4 Anthocyanins composition in fruit pomace**

| Compound | Types of pomace | | | | |
|---|---|---|---|---|---|
| | Black currant (% total anthocyanins) | Blueberry (% total anthocyanins) | Black raspberry (% total anthocyanins) | Cranberry (mg/100 g dry weight) | Grape (mg/g dry weight) |
| Cyanidin-3-arabinoside | - | 7.1 | - | 49.6 | - |
| Cyanidin-3-galactoside | - | 5.5 | - | 13.2 | - |
| Cyanidin-3-glucoside | 8.4[*]<br>8.4[**] | 8.9 | 7.1 | 4.5 | 0.30 |
| Cyanidin-3-rutinoside | 33.4[*]<br>36.2[**] | - | 68.8 | - | - |
| Delphinidin-3-galactoside | - | 5.4 | - | - | - |
| Delphinidin-3-glucoside | 12.6[*]<br>12.8[**] | - | - | - | 0.40 |
| Delphinidin-3-rutinoside | 31.4[*]<br>35.2[**] | - | - | - | - |
| Malvidin-3-arabinopyranoside | - | 19.3 | - | - | - |
| Malvidin-3-galactoside | - | 23.8 | - | - | - |
| Malvidin-3-glucoside | - | 14.5 | - | - | 2.06 |
| Pelargonidin-3-glucoside | - | - | 6.0 | - | - |
| Peonidin-3-arabinoside | - | - | - | 26.6 | - |
| Peonidin-3-galactoside | - | 4.9 | - | 20.1 | - |
| Peonidin-3-glucoside | - | - | - | 7.4 | 4.22 |
| Petunidin-3-glucoside | - | 10.7 | - | - | 0.48 |
| Other[+] | 6.8[*]<br>5.2[**] | - | - | - | - |
| References | Kapasakalidis et al. (2006) | Gil (2013) | Gil (2013) | White et al. (2010a) | Corrales et al. (2008) |

[+] Mostly refers to petunidin-3-rutinoside and peonidin-3-rutinoside

[*] Methanol/formic acid as extraction solvent; [**] Methanol/water/acetic acid as extraction solvent.

Moreover, cranberry pomace have procyanidins with degree of polymerization (DP) of 1-6, with A-type of DP2 being the most abundant (White et al., 2010a). Blueberry pomace only have 7% of DP1 and the rest is dominated by tetramers and higher oligomers, while grape pomace have more than 40% of DP1 and some amount of DP2 and DP3 (Khanal et al., 2010). Although procyanidins exhibit high antioxidant activity, only monomers, dimers, and trimers can be absorbed and maintain health benefits (White et al., 2010b).

#### 2.2.1.2 Dietary fibers in fruit pomace

According to the American Association of Cereal Chemists (AACC, 2001), "dietary fiber is the edible parts of plants or analogous carbohydrates that are resistant to digestion and absorption in the human small intestine with complete or partial fermentation in the large intestine." Dietary fiber includes all non-starch polysaccharides (cellulose, hemicellulose, polyfructose, galactooligosaccharide, gum, mucilage, and pectin), analogous carbohydrates (indigestible dextrin, synthesized carbohydrate compound, and resistant starch), lignin, and the plant substances associated with the non-starch polysaccharides and lignin complex (wax, phytate, cutin, saponin, suberin, and tannin) (AACC, 2001).

Dietary fibers can be determined by the Uppsala method using thermostable α-amylase and amyloglucosidase followed by ethanol precipitation of solubilized dietary fiber components. The obtained residue is subjected to acid hydrolysis generating neutral polysaccharides, uronic acids, and Klason lignin that are analyzed using gas-liquid chromatography, colorimetry, and gravimetrically, respectively (Theander et al., 1995).

Soluble dietary fibers consist of uronic acid and neutral sugar, while insoluble dietary fibers contain uronic acid, neutral sugar, and Klason lignin (Jung et al., 2014; Manthey et al., 1999). Soluble dietary fibers can lower the cholesterol, blood glucose, as well as insulin levels, while insoluble dietary fibers contribute to increase fecal bulk (Manthey et al., 1999). Different amount of dietary fibers in fruit pomace are shown in Table 2.5.

**Table 2.5 Dietary fibers composition in fruit pomace**

| Types of pomace | SDF (%) | IDF (%) | TDF (%) | References |
|---|---|---|---|---|
| Grapefruit (Ruby) | 4.57 | 56.0 | 62.6 | Figuerola et al. (2005) |
| Grapefruit (Marsh) | 6.43 | 37.8 | 44.2 | |
| Lemon (Eureka) | 9.20 | 50.9 | 60.1 | |
| Lemon (Fino 49) | 6.25 | 62.0 | 68.3 | |
| Orange (Valencia) | 10.28 | 54.0 | 64.3 | |
| Apple (Royal Gala) | 14.33 | 63.9 | 78.2 | |
| Apple (Granny Smith) | 4.14 | 56.5 | 60.7 | |
| Apple (Liberty) | 8.20 | 81.6 | 89.8 | |
| Wine grape (Muller Thurgau) | 0.72 | 27.29 | 28.01 | Deng et al. (2011) |
| Wine grape (Morio Muscat) | 0.84 | 16.44 | 17.28 | |
| Wine grape (Cabernet Sauvignon) | 0.81 | 52.40 | 53.21 | |
| Wine grape (Merlot) | 1.51 | 49.59 | 51.09 | |
| Wine grape (Pinot Noir) | 1.72 | 54.59 | 56.31 | |

SDF = Soluble dietary fibers; IDF = Insoluble dietary fibers; TDF = Total dietary fibers.

Some studies have analyzed the effects of dietary fibers *in vitro* and *in vivo* from different types of pomace. Chau et al. (2004) evaluated the hypoglycemic effects *in vitro* from different insoluble fiber fractions of carambola pomace, and found that carambola pomace exhibit mechanisms in lowering the rate of glucose absorption. Furthermore, Hsu et al. (2006) conducted *in vivo* study in investigating the effects of carrot pomace on the lipid and cholesterol absorption and excretion in male hamsters and observed that carrot pomace significantly reduced the levels of serum triglyceride and cholesterol, and

increased the levels of fecal lipids, cholesterol, and bile acids. These results suggested that pomace fibers could be incorporated in the diets to provide health benefits.

#### 2.2.1.3 Fatty acids in fruit pomace

Berry species within the genus *Rubus* have pretty high seed masses, varying from 8.5 to 12.2% fresh weight of fruit. However, the seed mass of *Vaccinium* and *Oxycoccus* are low, where 0.7% fresh fruit weight is the minimum value (Johansson et al., 1997). In the raspberry juice production, seed becomes a by-product that is currently underutilized, in which it contains high amount of oils (Oomah et al., 2000).

Fatty acids can be classified into saturated fatty acids and unsaturated fatty acids (monounsaturated and polyunsaturated). Unsaturated fatty acids have been associated with health benefits due to the presence of double bonds. Gotoh et al. (2010) mentioned that higher number of double bonds in the structure has higher ability to suppress the oxidation of other compounds.

Berry fruit pomace contain seeds that are rich in oils, providing essential fatty acids that cannot be synthesized in the human body (Van Hoed et al., 2009). In addition, berry seed oils have a favorable ratio of omega-3 and omega-6 fatty acids compared to some vegetable oils (Van Hoed et al., 2009), in which this ratio can reduce the risk of cancer and heart disease (Parry and Yu, 2004). Different amount of fatty acids in berry seeds are listed in Table 2.6.

**Table 2.6 Fatty acids composition of cold-pressed berry seeds**

| Fruit pomace | Fatty acid (g/100 g oil) | | | | | | | | References |
|---|---|---|---|---|---|---|---|---|---|
| | 12:0 | 14:0 | 16:0 | 18:0 | 18:1 | 18:2 | 18:3 | 20:0 | |
| Blackberry | 0.04 | 0.05 | 3.71 | 2.18 | 14.72 | 61.22 | 17.60 | 0.47 | Van Hoed et al. (2009) |
| Blueberry | 0.02 | 0.09 | 5.66 | 1.78 | 21.42 | 42.51 | 28.28 | 0.25 | |
| Cranberry | 0.14 | 0.08 | 5.38 | 1.25 | 25.30 | 37.68 | 30.09 | 0.07 | |
| Kiwi | 0.02 | 0.03 | 5.96 | 3.09 | 14.60 | 17.55 | 58.40 | 0.34 | |
| Red raspberry | - | 0.07 | 2.43 | 0.90 | 10.87 | 53.67 | 31.68 | 0.37 | |
| Strawberry | - | 0.05 | 4.32 | 1.68 | 14.55 | 42.22 | 36.48 | 0.71 | |
| Black raspberry | NA | ND | 1.22 | Trace | 7.70 | 55.85 | 35.22 | NA | Parry and Yu (2004) |
| Boysenberry | NA | NA | 4.2 | 4.5 | 18.0 | 53.8 | 19.5 | NA | Parry et al. (2005) |
| Pinot Noir | 0.8 | 0.4 | 35.0 | 2.7 | 32.2 | 13.0 | ND | 1.3 | Parry et al. (2006) |
| Chardonnay | ND | Trace | 7.8 | 4.3 | 19.2 | 65.9 | 1.8 | 0.2 | |

NA = Not available; ND = Not detected.

### 2.2.2 Current applications of fruit pomace as functional food ingredients

Many studies have investigated the potential utilizations of fruit pomace in food for the purpose of promoting human health. The pomace were used in either wet form or further processed through drying, grinding, and extracting to obtain specific properties. Some studies about the fortification of fruit pomace in food products are shown in Table 2.7.

Even though the incorporation of fruit pomace in food products has been done successfully, it is still necessary to develop applications in bulk amount to reduce this biowaste. The following sections discussed the potentials of using fruit pomace to develop biodegradable packaging materials.

**Table 2.7 Fortification of fruit pomace in food products**

| Types of pomace | Summary of the previous research | References |
|---|---|---|
| Apple | Apple pomace flour (15% and 20%) were used to partially substitute wheat flour in muffins and cookies, while fresh apple pomace (10% and 20%) replaced some amounts of meat in chicken patties and beef jerky. The incorporation of apple pomace flour did not give detrimental effect to the physicochemical and textural properties of the baked goods. Fresh apple pomace reduced the firmness of meat products, but increased the fiber content and radical scavenging activity. | Jung et al. (2014) |
| Orange | Orange peel and pulp were dried and ground (separately) to obtain citrus flour. Citrus flour (5%, 15%, and 25%) partially substituted the wheat flour in making sweet biscuits. The result demonstrated that 15% flour substitution was highly acceptable. The incorporation of citrus flour increased the dietary fiber and dough development time and stability, while reduced the fat, protein, as well as the dough mixing tolerance. | Nassar et al. (2008) |
| Pinot Noir | Whole pomace powder (skins and seeds) and pomace extracts (liquid and freeze-dried) were added in yogurt and salad dressings. The addition of fruit pomace in the products had similar physicochemical properties with the control. The results showed that wine grape pomace could fortify those products by increasing dietary fibers, total phenolic content, as well as delaying lipid oxidation during refrigeration storage. | Tseng and Zhao (2013) |
| Raspberry | Raspberry pomace in the form of crumbled and non-crumbled were used (25% and 50%) to replace flour partially in short-crust cookies. The authors figured that the incorporation of raspberry pomace influenced the organoleptic qualities of the cookies. However, the fortified cookies had higher dietary fiber, mainly insoluble dietary fiber. The cookies with non-crumbled pomace had the highest acceptance. | Górecka et al. (2010) |
| Tomato | Bleached tomato pomace powder was incorporated in beef frankfurter, beef ham, and meat-free sausage. Overall, the addition of pomace improved the textural and sensory characteristics in the products. The fortification of pomace increased the water holding capacity in sausages, but decreased the color and texture parameters in beef ham. | Savadkoohi et al. (2014) |

### 2.2.3 Compositional aspects of fruit pomace to create biodegradable packaging materials

This review focused on the discussion of using pomace as bulk materials for creating biocomposite and biodegradable packaging materials. Composite materials are material systems with one or more discontinuous phases embedded in a continuous phase (Santos Rosa and Lenz, 2013). The discontinuous phases are called reinforcing agent or filler, while the continuous phase is termed matrix. Composite materials are frequently added by some additives, such as plasticizers, pigments, and stabilizers to achieve certain properties (Santos Rosa and Lenz, 2013). Fruit pomace consist of lignocellulosic compounds that act as the composite materials and extractives that can be used as additives.

#### 2.2.3.1 Lignocellulosic compounds as the building blocks in packaging materials

Dietary fibers in fruit pomace can be divided into two major classes, *viz.* water-soluble (pectin and gums) and water-insoluble (cellulose, lignin, and some of the hemicellulose) (Nawirska and Kwaśniewska, 2005). Pectin, hemicellulose, lignin, and gum have thermoplastic properties, while cellulose is a non-thermoplastic material (Jiang et al., 2011; Park et al., 2010; Stokke et al., 2013), all are good candidates for creating biocomposites. Lignocellulosic compounds in fruit pomace are summarized in Table 2.8.

**Table 2.8 Lignocellulosic compounds in fruit pomace and their properties**

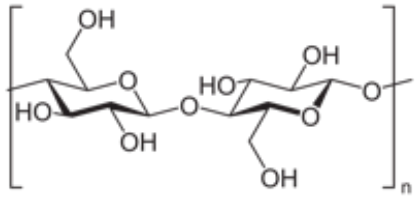
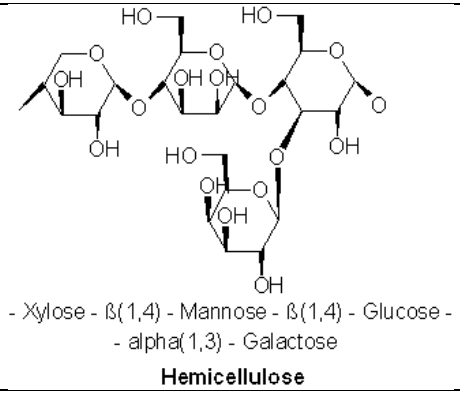
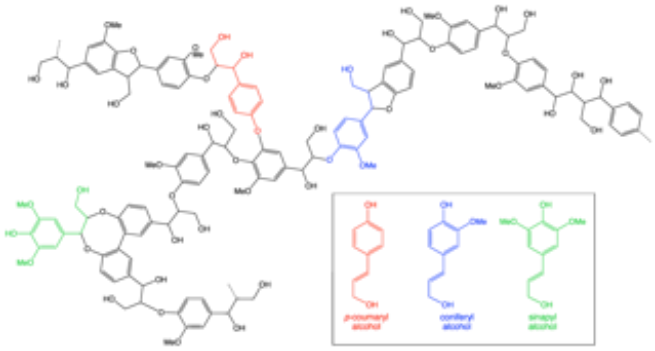
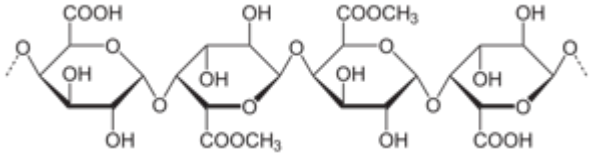
| Lignocellulosic compound | Chemical structure | Definition |
|---|---|---|
| Cellulose |  | Cellulose is the most abundant biopolymer, built by glucose anhydride residues that are linked end-to-end by β-1,4 glycosidic bonds. Intramolecular and intermolecular hydrogen bonds stabilize the cellulose structure, making it less hygroscopic (Stokke et al., 2013). |
| Hemicellulose |  | Hemicellulose has β-1,4 linked backbones of glucose, mannose, xylose, and may be substituted with sugars, uronic acids, and acetyl groups (McCann et al., 2013). Hemicellulose is more hygroscopic and more soluble in comparison to cellulose because it has more open structure than cellulose (Stokke et al., 2013). |
| Lignin |  | Lignin is an amorphous molecule containing the combination of aromatic structures and aliphatic chains. It was constructed from 3 precursors, namely *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol (Stokke et al., 2013). Lignin is hydrophobic due to the aromatic structures and high degree of crosslinking within a molecule. It gives rigidity to the cell wall as well as serves as the "glue" to hold cells together. However, it softens at high temperature like a plastic material (Stokke et al., 2013). |

**Table 2.8 Lignocellulosic compounds in fruit pomace and their properties (Continued)**

| | | |
|---|---|---|
| Pectin |  | Pectin is a major component of the plant cell wall. It is a polymer linked by α-1,4 glycosidic bonds of galacturonic acid ester and minor amount of galacturonic acid (Chen, 2014). It is hygroscopic and thermally labile (Stokke et al., 2013). |

#### 2.2.3.2 Extractives in fruit pomace as additives in biocomposite

Extractives are materials that do not form fundamental structure of the cell wall. They consist of proteins, tannins, waxes, aromatics, and low molecular weight carbohydrates (Stokke et al., 2013). They are classified as extractives due to their solubility in water and/or organic solvent, thus can be extracted from plant materials under mild chemical treatment. Extractives are important in determining the adhesive bonding on the surface of a composite (Stokke et al., 2013).

Fruit pomace contain high amount of soluble solids. It was reported that apple pomace have about 40% w/w soluble solids on a dry basis, consist of a mixture of monosaccharides (fructose, glucose, and sucrose) and organic acids (predominantly malic acid) (Queji et al., 2010). Jiang et al. (2011) stated that soluble sugars are good plasticizers by reducing the intermolecular forces of the polymers, thus increasing the mobility of the molecules and making the materials less stiff. Vieira et al. (2011) divided the plasticizers into water-soluble and water-insoluble. Hydrophilic plasticizers can lead the increment of water diffusion in the polymers, while hydrophobic plasticizers can cause phase separation, lose the flexibility, and create discontinuity zones during drying, thus increasing the water vapor permeability of a material (Vieira et al., 2011).

#### 2.2.3.3 Chemical interactions among cell wall components in fruit pomace

In the cell wall, fibers can interact within themselves or with other fibers through physical and chemical interactions. It is necessary to understand their interactions so that the fibers can associate with other components such as synthetic polymer, hydrophobic

agent, and crosslinking agent to create biocomposites. Some possible chemical interactions between cell wall components are shown in Table 2.9.

**Table 2.9 Possible chemical interactions between cell wall components (Adapted from (Harmsen et al., 2010) and (Grierson, 2012))**

| Types of interaction | | Polymers involved |
|---|---|---|
| Intra-polymer | Hydrogen bond | Cellulose, hemicellulose |
| | Ether bond | Cellulose, hemicellulose, lignin, pectin |
| | Ester bond | Hemicellulose |
| | Carbon-to-carbon | Lignin |
| Inter-polymer | Hydrogen bond | Cellulose-hemicellulose |
| | | Cellulose-lignin |
| | | Hemicellulose-lignin |
| | Ether bond | Cellulose-lignin |
| | | Hemicellulose-lignin |
| | Ester bond | Hemicellulose-lignin |
| | | Cellulose-pectin |
| | Ionic bond | Acidic pectin-protein |

Harmsen et al. (2010) explained in details about the types of functional groups that interact among the polymers. They mentioned that intra-polymer linkages in lignin that create ether and carbon-to-carbon bonds may appear from two aryl carbon atoms, two allylic carbon atoms, and between one aryl and one allylic carbon atom. In addition, they also predicted that around 70% of the total bonds in lignin come from ether type, while the rest is from carbon-to-carbon type. In hemicellulose, fructosic and glucosidic bonds are the main ether bonds contributing to the intra-polymer linkages (Harmsen et al., 2010).

Besides the chemical interactions described above, some other interactions may also occur. According to Chen (2014), cellulose and hemicellulose are mainly linked through hydrogen bonds. Hemicellulose can form covalent bonds (mainly α-benzyl ether linkages) with lignin and an ester linkage with acetyl units and hydroxycinnamic acids. In

addition, lignin can create a stable complex with carbohydrate due to strong hydrogen bonds internally in the lignin. Grierson (2012) elaborated that there is possibility that hemicellulose may be linked with the pectic polymers through covalent bonds. The glycosidic bond may appear on the $4^{th}$ position of rhamnose residue in pectin with terminal residues of galactan, arabinan, or arabinogalactan in hemicellulose (Grierson, 2012). Chen (2014) mentioned that the esterification in cellulose is highly reactive at C6, while etherification is highly possible at C2.

Chen (2014) explained further that cellulose makes a skeleton in the form of microfibrils in the cell wall, while hemicellulose and lignin are crosslinked to create three-dimensional structure to wrap the microfibrils. Moreover, the outside of the cell wall is mainly composed of lignin and pectin. Grierson (2012) stated that cell walls may be highly hydrated or highly lignified with hemicellulose surrounding the cellulose fibrils and being embedded in a matrix of pectin or galactomannans and protein. Both statements concluded that cellulose, hemicellulose, lignin, and pectin are entangled in the cell wall, and the presence of additives is important to enhance the interactions among fibers and other functional agents.

### 2.2.4 Examples of research and development in using fruit pomace to create biocomposites

The utilizations of fruit pomace as biocomposites for packaging applications have not been done widely. Most of the materials used are from non-wood fibers, such as wheat straw (Berthet et al., 2015), sugarcane bagasse (Boontima et al., 2014), kenaf (Pan et al., 2007), hemp (Hu and Lim, 2007), and bamboo (Tokoro et al., 2007). Drying, cutting,

grinding, or alkali treatment are some treatments that usually made before creating the biocomposites. Table 2.10 summarized the studies of using fruit pomace to create biocomposites.

**Table 2.10 Studies on the utilization of fruit pomace to create biocomposites**

| Types of pomace | Summary of the previous research | References |
|---|---|---|
| Blueberry, cranberry, and red wine grape | Blueberry, cranberry, and red wine grape pomace powder were combined with soy flour (SF) or combination of pectin and xanthan gum (P-XG). Glycerol was used as plasticizer. The used of P-XG was very sticky and difficult to handle. Therefore, SF was used for further development. Blueberry pomace gave the highest breaking strength and modulus of elasticity, thus it was chosen to optimize the formulations with modified SF (NaOH treated). The ratio of pomace-to-binder and the amount of glycerol were the factors that were optimized. The higher the amount of modified SF improved the adhesion and stiffness, while the addition of glycerol weakened the biocomposite board. | Park et al. (2010) |
| Coconut | Coconut shell powder (15%, 30%, 45% and 60%) was incorporated with poly(lactic acid). The authors used coupling agent to improve the interactions between filler and matrix. The results showed that the addition of coconut shell powder reduced the tensile strength and elongation at break, but increased the modulus of elasticity. | Chun et al. (2012) |
| Durian | Cellulose was extracted from ground durian peel. This cellulose was combined with poly(lactic acid) (PLA) and the optimization process was conducted (cellulose loading, mixing temperature, and mixing time). The results concluded that the addition of cellulose decreased the tensile strength in comparison to neat PLA due to irregular shape of the reinforcing agent. | Penjumras et al. (2015) |
| White and red wine grapes | White wine grape pomace (WWGP) and red wine grape pomace (RWGP) powder were optimized for their types of binder (soy flour, poly(vinyl alcohol), soy protein isolate, and their combinations), pomace-to-binder ratios, hydrophobic agent (stearic acid), and crosslinking agent (epichlorohydrin). Poly(ethylene glycol) 400 was added as plasticizer. The used of hydrophobic and crosslinking agents gave more cohesive fracture surfaces. RWGP had higher breaking strength and modulus of elasticity due to less soluble solid content, while WWGP had higher flexibility and biodegradability because of high amount of soluble solids. | Jiang et al. (2011) |

## 2.3 Biocomposites as biodegradable packaging materials

### 2.3.1 Concerns on petrochemical-based plastics waste

In 2013, Environmental Protection Agency (EPA) summarized the waste being disposed in the United States (Figure 2.1). Among them, 12.8% was plastic waste (33 million tons) that consists of 14 million tons of containers and packaging, 12 million tons of durable goods (appliances), and 7 million tons of nondurable goods (plates and cups) (EPA, 2016). In this review, focus is given to the plastic waste in the form of packaging containers.

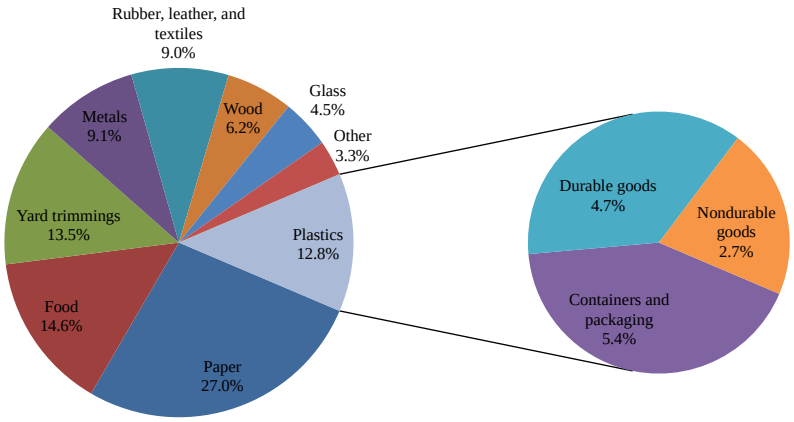



**Figure 2.1 Total municipal solid waste generation (by material) in 2013 before recycling (Adapted from EPA (2015))**

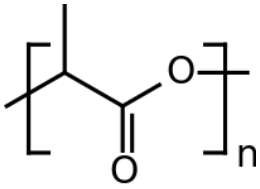
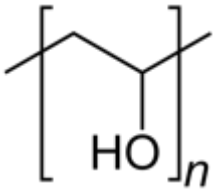
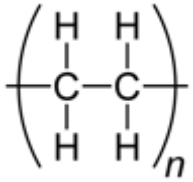
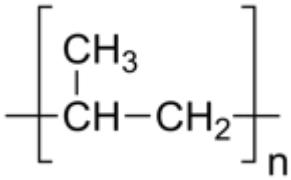
In general, commercial plastic containers and packaging materials are made from non-renewable (petrochemical-based) resources that have slow rate of degradation. Some studies have been conducted to make biodegradable plastics from renewable (bio-based) resources that have similar functionalities with the petrochemical-based (Song et al., 2009). In addition, studies about the development of packaging materials in a form of composite also have been done. The investigation from previous researches aimed to find

the alternatives to slow down the depletion of non-renewable resources. In 2013, only 9% of total plastic waste was recovered for recycling (EPA, 2016). This low amount of recycling process may be caused by two reasons: 1) the lack of continuous and reliable supply of bio-based waste in large quantity presently make recycling process less economically attractive; and 2) the addition of biofibers complicates the recycling procedures (Song et al., 2009). It is important to create packaging materials that can be degraded naturally in a short period of time, thus recycling process is not necessary.

### 2.3.2 Different types of polymers used to create biocomposites

The polymers that are utilized to create biocomposites should have ability to interact chemically with the biofibers. In general, biofibers have hydrophilic property, while polymers have hydrophobic characteristic that cannot be combined together. Therefore, some treatments need to be conducted either to make the biofibers more hydrophobic or make the polymers more hydrophilic. The level of wettability can be measured by contact angle that indicates the degree of wetting when a solid interacts with liquid. Small contact angle (< 90°) corresponds to high wettability, while large contact angle (> 90°) means low wettability (Yuan and Lee, 2013). The addition of crosslinking agents can also improve the interactions between polymers and biofibers. Different types of polymer utilized to create biocomposite are shown in Table 2.11.

**Table 2.11 Different types of polymer in biocomposites and their interactions with biofibers**

| Biocomposite polymer | Chemical structure | Definition |
|---|---|---|
| Poly(lactic acid) (PLA) |  | Wang et al. (2001) used methylene diphenyl diisocyanate (MDI) as a coupling agent in the PLA and starch biocomposites. The results exhibited that the addition of MDI improved the interfacial adhesion between PLA and starch by urethane linkages that can transfer the internal stress from the filler to the matrix. |
| Poly(vinyl alcohol) (PVA) |  | Cellulose was mechanochemically activated by Zhang et al. (2011) through high shearing and compressing forces generated by the pan-mill reactor. Cellulose with different cycle of pan-milling was combined with PVA. The results demonstrated that pan-milling could destroy the hydrogen bonds in the cellulose both intra- and inter-molecular, thus exposing the reactive hydroxyl groups that could establish new hydrogen bonds with PVA. |
| Polyethylene (PE) |  | Liu et al. (2010) studied the effect of plasma treatment to wood/PE composites. The results presented that air plasma treatment reduced the contact angle, introduced more polar functional groups, and increased the roughness on the surface of the composites, thus enhancing the wettability of the surface. |
| Polypropylene (PP) |  | Cantero et al. (2003) made biocomposites from PP and natural flax and flax pulp. The fibers were treated with different chemicals (maleic anhydride, maleic anhydride-polypropylene copolymer, and vinyl trimethoxy silane). The results showed that the wettability between PP and fibers was increased due to the reduction of the polar components of their surface energies. |

Biodegradable polymers can be made from bio-based as well as petrochemical-based polymers. Most of the bio-based polymers are from natural origins such as polysaccharides (starch and cellulose), proteins (gelatin and gluten), and lipids (plant oils and animal fats). In addition, microorganisms can produce natural rubbers and certain

polyesters (poly(hydroxyalkanoate) and poly(hydroxybutyrate)) and synthesized from bio-derived monomers can create poly(lactic acid) (Song et al., 2009). On the other hand, synthesizing monomers derived from petrochemical refining generates petrochemical-based polymers, such as aliphatic polyesters (poly(glycolic acid), poly(butylene succinate), and poly(caprolactone)), aromatic copolyesters (poly(butylene succinate terephthalate)) and poly(vinyl alcohol) (Song et al., 2009). It should be noted that not all bio-based polymers are biodegradable and the degraded polymer residues have to be assimilated completely by the microorganisms in a short time period to prevent harming the environment (Song et al., 2009).

### 2.3.3 Quality characteristics of biocomposites as packaging materials

In many literatures, the term biocomposites is often used to define the combination of natural fibers as the filler with polymeric material as the matrix. These natural fibers are intended to improve the mechanical properties of biocomposites. However, plant fibers are hydrophilic as their major components are cellulose, hemicellulose, lignin, and pectin. This hydrophilic behavior is a major problem for their use as reinforcement in biocomposites because the absorption of water will decrease the mechanical properties (Célino et al., 2014). In addition, the process temperature should not exceed 200 °C due to low temperature resistance of the plant fibers. Therefore, the biofiber integrity is not guaranteed if the process is conducted above 200 °C (Célino et al., 2014). The following sections describe the common parameters measured in biocomposite products.

#### 2.3.3.1 Mechanical properties of biocomposites

In general, mechanical properties describe the response from materials that occur under physical forces. This review section elaborates three different parameters, including strain, flexural strength, and flexural modulus. Stress is defined as the force on a material divided by the cross-sectional area over which it initially acts, while strain is defined as the deformation of a material divided by a corresponding un-deformed dimension (Rosato and Rosato, 2013). Flexural strength or cross-breaking strength is the maximum stress developed when a test specimen in a shaped of a bar is subjected to a bending force (Lampman, 2003). There are two methods that can be used to analyze flexural strength, namely three-point bending and four-point bending. Four-point bending test can be applied when the test specimens do not fail at the point of maximum stress in three-point bending test (Lampman, 2003). Flexural modulus of elasticity is usually reported as the initial modulus from the load-deflection curve. It is nominally the average of tension and compression moduli (Rosato and Rosato, 2013). Flexural modulus measures the stiffness of a material that is obtained by plotting the flexural stress versus strain to get the slope (Lampman, 2003).

Cellulose microfibrils provide good mechanical properties to plant fibers. They orient themselves at low microfibril angle that significantly increase the modulus (Célino et al., 2014). Poor adhesion between biofibers and polymer matrix also affects the mechanical properties. Many researches were conducted to improve the interactions between these two phases by physical and chemical treatments as mentioned previously in Table 2.11. Célino et al. (2014) explained that the matrix in a composite acts as a binder to transfer

fibers stiffness to the material. If the adhesion between phases is weak, the composite will not be durable in its application.

The presence of low molecular weight non-volatile compounds as plasticizers also influences the mechanical properties. Monosaccharides and water are the examples of plasticizers that occupy intermolecular spaces between polymer chains, thus reducing the degree of crystallinity of the composites. The addition of plasticizers improves the flexibility or reduces the elastic modulus of the materials (Vieira et al., 2011).

#### 2.3.3.2 Water sensitivities of biocomposites

Cellulose, hemicellulose, lignin, and pectin are rich in hydroxyl groups that are responsible to the water uptake. The water absorption by the plant fibers influences the modification of their physical and chemical properties. The presence of water can act in two different mechanisms: 1) as a plasticizer, by creating gap between polymers so they have more space to move, and 2) as an anti-plasticizer, by screening off the forces between polymers (Pittia and Sacchetti, 2008). The absorption of water during the life cycle of the plant fibers makes the fibers swollen, while the compounding process above 100 °C shrinks the fibers due to the vaporization of trapped water. These phenomena generate internal stresses at the interface of fibers and matrix, thus eventually diminishing the properties of the composites (Célino et al., 2014).

The incorporation of crosslinking agents can reduce the water sensitivities of biocomposites and improve the flexural strength and modulus. Chiellini et al. (2001) studied the effect of hexamethoxymethylmelamine (HMMM) on the film composites. They increased the amount of HMMM (3%, 4%, and 8%) in the samples and the results

showed that the degree of swelling in water was decreased as the amount of crosslinks increased. Also, samples with 8% HMMM had lower moisture uptake at 95% relative humidity compared to non-crosslinked samples. Similar results were obtained by Lee and Wang (2006), where the addition of lysine diisocyanate (LDI) as coupling agent in bamboo fiber and poly(lactic acid) or poly(butylene succinate) could reduce the water absorption of the biocomposites due to the reaction of LDI with the hydroxyl and carboxyl groups of polymers and bamboo fibers creating urethane bonds, thus reducing the hydrophilicity of plant fibers.

#### 2.3.3.3 Biodegradability of biocomposites

The term biodegradation has not been applied consistently. In medical fields, biodegradation indicates the hydrolysis, while for environmentally degradable plastic, biodegradation means fragmentation, loss of mechanical properties, or degradation through the action of living organisms (van der Zee, 2005). Sometimes, loss in physical integrity is often mistaken as biodegradation (van der Zee, 2005). Despite different definitions have been implemented, the internal workshop on biodegradability was conducted to achieve agreement on definitions, standards, and testing methodologies from experts around the world. It was concluded that specified periods of time, specific disposal pathways, and standard test methodologies need to be incorporated into definitions (van der Zee, 2005).

According to ASTM D883-12, degradable plastic is defined as “a plastic designed to undergo a significant change in its chemical structure under specific environmental conditions resulting in a loss of some properties that may vary as measured by standard

test methods appropriate to the plastic and the application in a period of time that determines its classification," while biodegradable plastic is "a degradable plastic in which the degradation results from the action of naturally-occurring microorganisms such as bacteria, fungi, and algae". Müller (2005) and Karak (2012) described polymer biodegradation as a surface erosion process because the enzymes cannot penetrate into the polymer materials. Even though enzymatic reaction is the primary process in biodegradation, chemical hydrolysis, thermal degradation, and photo-degradation also affect the polymer degradation either in parallel or at the initial stage of the process (Müller, 2005). Karak (2012) explained that the biodegradation occurs in two main steps. The first step is fragmentation of polymers into low molecular weight products by direct hydrolysis, oxidation followed by hydrolysis, or depolymerization in the presence or absence of enzymes. The second step is the assimilation of low molecular weight products in the cell walls of microorganisms for their nutrients, and then converts them into carbon dioxide, water, mineral, and biomass (or methane in the case of anaerobic degradation) by mineralization process (Karak, 2012). The activities of microorganisms are also influenced by humidity, temperature, pH, salinity, oxygen level, and nutrient supplied. In addition, the geometry and polymer structure (degree of crystallinity and types of bond) affect the biodegradation rate (Karak, 2012; Müller, 2005; van der Zee, 2005).

There are three different categories to conduct the biodegradation test, namely field test, simulation test, and laboratory test (Karak, 2012; Müller, 2005). In the field test, samples can be buried in soil, lake, river, or compost. This represents the ideal environmental conditions, however, external parameters such as temperature, pH, and

humidity cannot be controlled. The only possible analyses for this test are evaluating changes in the samples appearance and determining the weight loss of samples. Another drawback from this method is recovering the materials from the soil, lake, river, or compost if the samples disintegrate into small fragments (Müller, 2005). In the simulation test, samples can be buried in soil, water, compost, and are placed in a controlled reactor in a laboratory. Therefore, the external parameters can be controlled and adjusted as well as more analyses can be conducted (production of carbon dioxide or consumption of oxygen) (Müller, 2005). Müller (2005) and Karak (2012) agreed that laboratory test is the most reproducible, where sample is put in a well-defined man-made media that is inoculated with mixed microorganisms or selected strain. Although this method can only derive limited conclusions about the degradation in a natural environment, this can be used as an accelerated test to study the basic mechanisms of polymer degradation (Karak, 2012; Müller, 2005).

#### 2.3.3.4 Thermal properties of biocomposite materials

Thermal properties evaluate the change of properties in a material as a result of temperature and/or time alteration and are recorded as thermograms. Many methods may be used for determining thermal properties, depending on the objectives of the study. In this review, differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) are covered for analyzing thermal properties of biocomposites.

DSC can measure the glass transition temperature ($T_g$) and melting temperature ($T_m$) of a material as well as analyze the compatibility of polymer blends. Homogeneous blends will show single sharp $T_g$ between the blend components (Rao and Johns, 2008).

No polymer is 100% crystalline, but always having amorphous regions. Glass transition temperature ($T_g$) is the property of the amorphous regions in a polymer, where above $T_g$ polymer has rubbery property and below $T_g$ polymer has glassy property (Brazel and Rosen, 2012). All polymers have $T_g$, but they do not always have $T_m$ because they do not crystallize or some of them will degrade before melting (Brazel and Rosen, 2012).

The principle of DSC instrumentation is measuring the heat energy necessary to obtain a zero temperature difference between the sample and reference materials as a function of temperature or time (Kaur, 2010). In general, the rate of temperature ramp for running the DSC is 5-20 °C/min (Brazel and Rosen, 2012). Brazel and Rosen (2012) also mentioned that at $T_g$, the heat capacity of the sample is increased as shown by a drop in the thermogram since the sample need more energy (relative to the reference) to maintain the same temperatures. In regard to the $T_m$ (endothermic peak), a large amount of energy is needed to melt all crystals and maintain the temperature rising at the same rate with the reference. On the other hand, at crystallization temperature, a large amount of heat is given off as shown by the occurrence of exothermic peak (Brazel and Rosen, 2012).

TGA thermogram provides the information about the decomposition profile of a material (Rao and Johns, 2008). There are three types of thermogravimetry, namely static, quasistatic, and dynamic thermogravimetry (Kaur, 2010). Static thermogravimetry records the weight of sample as a function of time at a constant temperature, while quasistatic thermogravimetry heats the sample to constant weight at each step in a series of temperature increased (Kaur, 2010). The dynamic thermogravimetry heats the sample at a uniform rate, but the data cannot be used for precise constant determination due to

the effect of changing air buoyancy and convection. Nonetheless, these data are suitable for approximating quantitative thermal behavior of a system (Kaur, 2010).

### 2.4 Summary

Fruit pomace from juice industry are abundant natural resources that have many functionalities, but remained underutilized. Some studies have explored the polyphenols and dietary fibers in fruit pomace for potential food applications. However, different varieties and cultivars of fruit, processing procedures, and methods of analysis affected the results. Therefore, it is necessary to study the bioactive compounds and physicochemical properties from different types of fruit pomace as a pool instead of individual cultivar using the same method of analysis. This study evaluated physicochemical properties and bioactive compounds of four different types of fruit pomace, including apple, blueberry, raspberry, and cranberry. The obtained results can be used as a baseline to develop value-added applications in food and/or packaging fields.

Moreover, apple pomace was selected for creating biocomposite owning to high quantity from apple juice and cider processing, and rich in dietary fibers that are good candidates to create biocomposite. Nevertheless, the utilizations of apple pomace to develop biodegradable packaging material are scarce. Therefore, this study investigated the feasibility of creating apple pomace based biocomposite boards using thermal compression molding and optimized the biocomposite formulations possessing high mechanical strength, low water sensitivity, and slow biodegradation.

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# CHAPTER 3

## Quantification of Bioactive Compounds and Physicochemical Properties of Different Fruit Pomace

Virginia P. Gouw, Jooyeoun Jung, Yanyun Zhao*

Department of Food Science and Technology, 100 Wiegand Hall,
Oregon State University, Corvallis, OR 97331, USA
*Corresponding author: yanyun.zhao@oregonstate.edu

**Abstract**

Four different types of fruit pomace (apple, blueberry, raspberry, and cranberry) were evaluated for their physicochemical properties and bioactive compounds. Apple pomace contained 18.87% of acid extractable pectin and 8.66% of total soluble pectin. Blueberry pomace had 256.18 mg cyanidin-3-glucoside/100 g dry weight. Raspberry pomace was rich in insoluble dietary fibers (73.30%), mainly from Klason lignin. Cranberry pomace showed the highest total phenolic content and radical scavenging activity (6.77 mg gallic acid equivalent/g dry weight and 2.68 mg ascorbic acid equivalent/g dry weight) as well as abundant in acid extractable pectin (10.58%). In addition, blueberry and cranberry pomace also had great amount of insoluble dietary fiber, which were 63.85% and 67.20%, respectively. This study provided baseline data for the selection of suitable pomace for developing various value-added applications.

**Key words:** Fruit pomace, physicochemical properties, bioactive compounds

## Introduction

The amount of generated pomace has been significantly increased along with the increment amount of fruit juice and concentrate production. Fruit pomace consist of skins, seeds, stems, and de-juiced pulp, and contain valuable polyphenols and rich in dietary fibers that possess potential health benefits (Figuerola et al., 2005; Vulic et al., 2011). Unfortunately, most of them are ended up in the landfill for disposal or partially used as animal feed. Several previous studies have attempted to expand their utilizations, such as extracting the polyphenolics and anthocyanins from berry fruit pomace as antioxidant (Lee and Wrolstad, 2004), processing into dried pomace flour to partially substitute wheat flour in bakery goods (Walker et al., 2014), incorporating fresh pomace in meat products to improve product quality and increase bioactive compounds (Jung et al., 2014), creating edible films and coatings (Park and Zhao, 2006), and developing biocomposite boards as biodegradable packaging materials (Park et al., 2010).

Depending on the types of fruit, the generated pomace may have different physicochemical properties and contain different types and amounts of bioactive compounds, which could directly impact their potential applications. Previously, Van Hoed et al. (2009) evaluated the oils in the seeds of berry fruit pomace, Deng et al. (2011) characterized the antioxidant dietary fibers of different varieties of wine grape pomace, Caillet et al. (2012) analyzed the antimicrobial effect of cranberry pomace against the growth of pathogens, and Grigoras et al. (2013) investigated the antioxidant activity in different cultivars of apple pomace. Although various fruit pomace have been investigated, there could be huge variations among the studies due to the different process conditions applied from different fruit juice manufacture and methods of analysis. To the

best of our knowledge, the investigation of important physicochemical properties and bioactive compounds in different fruit pomace using the same treatment procedures and analytical methods has not been reported. Such information is essential to understand their compositions to further develop various value-added applications.

This study aimed to evaluate the physicochemical properties (moisture content, water activity, pH, titratable acidity, total soluble solid, and color), to examine the total lipid extraction, to analyze the total phenolic content, radical scavenging activity, and their total monomeric anthocyanins, and to quantify dietary fiber (soluble and insoluble dietary fibers) and pectin (acid extractable pectin and fractionated pectin compositions) of four different types of fruit pomace. The results from this study would provide baseline data for the selection of suitable pomace for developing value-added applications in food, packaging, and other fields, while helping the juice manufacture to reduce these unavoidable biowaste.

## Materials and Methods

### Materials

Four types of fruit pomace, including apple, blueberry, raspberry, and cranberry, were investigated in this study, by considering their high amount of production in the northwest region of United States and different compositional properties. Fresh apple pomace prepared without pectic enzyme treatment was donated by Hood River Juice Co. (Hood River, OR), while fresh blueberry, red raspberry, and cranberry pomace were provided by Kerr Concentrates, Inc. (Salem, OR). All berry fruit pomace were obtained

from berry juice process subjected to pectinase and/or cellulase treatment. Each fruit pomace was packed in a 5-gallon plastic bucket and stored at -18 °C until usage.

Gallic acid, D-galacturonic acid monohydrate, 3,5-dimethylphenol, Folin & Ciocalteu's phenol reagent, and protease from *Bacillus licheniformis* were obtained from Sigma-Aldrich, Inc. (St. Louis, MO). L-ascorbic acid and D-glucose anhydrous were purchased from Amresco (Solon, OH), 2,2-diphenyl-1-picrylhydrazyl and anthrone from Alfa Aesar (Ward Hill, MA), 0.1*N* sodium hydroxide and sodium phosphate monobasic monohydrate from J.T. Baker Chemical Co. (Phillipsburg, NJ), sodium carbonate from BDH (West Chester, PA), sodium chloride, sodium acetate anhydrous, hydrochloric acid, and sulfuric acid from EMD Chemicals Inc. (Gibbstown, NJ), potassium chloride, sodium hydroxide pellet, citric acid monohydrate, chloroform, acetone, and methanol from Macron Fine Chemicals (Center Valley, PA), boric acid from Mallinckrodt (Paris, KY), disodium ethylenediaminetetraacetate (EDTA) dihydrate from Mallinckrodt Chemicals (Phillipsburg, NJ), sodium phosphate dibasic anhydrous from EM Science (Gibbstown, NJ), acetic acid glacial from EMD Millipore Corporation (Billerica, MA), and ethanol from Oregon State University Chemistry Store (Corvallis, OR).

**Preparation of fruit pomace**

Freshly collected pomace were frozen at -18 °C, and further thawed for 30 min at room temperature before further analysis.

**Analysis of physicochemical properties**

**Moisture content (MC) and water activity (Aw).** Briefly, 5 g of fruit pomace was weighed and dried in an oven (Isotemp® Oven Forced Draft, Fisher Scientific, Waltham, MA) at 105 °C for 24 h. MC was calculated on wet basis as the weight loss after drying divided by the weight of initial sample and multiplied by 100. MC was reported as mean of three replications. Aw was determined using a water activity meter (AquaLab®, Model Series 3, Pullman, WA), and was reported as mean of three replications.

**pH, titratable acidity (TA), and total soluble solids (TSS).** Fruit pomace samples were tested for their pH, TA, and TSS based on our previous studies (Cavender et al., 2014; Fisk et al., 2008). Briefly, 10 g of pomace was diluted 9 times with distilled water, and blended for 1 min using a blender (Osterizer®, Jarden Corporation, Mexico). The obtained slurry was filtered through Whatman #1 filter paper (Whatman™, Buckinghamshire, UK) to remove the residual solid. Thirty mL of the resultant filtrate was used to measure the pH with an electrolytic pH meter (Orion 9102BNWP, Thermo Scientific, Waltham, MA), and then continued measuring the TA by titration using 0.1*N* sodium hydroxide to the endpoint of 8.2. TA for each type of pomace was calculated using malic acid as the predominant organic acid for apple pomace, while citric acid as the predominant organic acid for blueberry, raspberry, and cranberry pomace. The resultant filtrate was also used to determine TSS using an electronic refractometer (Model RA-250HE, Kyoto Electronics Manufacturing Co., Ltd., Japan). Three replications were performed for each measurement.

**Color measurement.** The color of fruit pomace samples were analyzed using a colorimeter (LabScan XE, Hunterlab, Reston, VA) by putting the pomace sample in a

plastic petri dish and randomly measured 6 zones from the bottom of petri dish. The color parameters, L* (lightness), a* (redness), and b* (yellowness) were recorded. Hue angle [arctangent (b*/a*)] and Chroma $[(a^{*2} + b^{*2})]^{1/2}$ were calculated as the mean value of six replications.

**Total lipid extraction**

Pomace contain significant amount of seeds, thus total lipid was extracted and analyzed. Briefly, 1 g of pomace was added to 18 mL of chloroform/methanol (2:1, v/v), then homogenized using a homogenizer at setting 3 (Polytron® PT 10-35 and Power Control Unit PCU 11, Kinematica, Switzerland) for 30 s, and filtered through Whatman #1 filter paper. The obtained filtrate was mixed with 4 mL of 0.88% NaCl solution gently, and left overnight for phase separation. The top layer of the sample was siphoned off and the volume of lipid on the bottom layer was recorded. Total lipid was determined gravimetrically as the mean value of three replications (Duan et al., 2010).

**Extraction and analysis of phenolic compounds**

For extracting the phenolic compounds in fruit pomace, 3 g of pomace was extracted by 30 mL of 60% methanol acidified with 1% acetic acid glacial in the ultrasonic water bath (Branson B-220H, SmithKline Co., Shelton, CT) for 20 min. The mixture was filtered through Whatman #1 filter paper, and the obtained filtrate was evaporated using a vacuum rotary evaporator (Brinkmann Instruments, Westbury, NY) to remove the volatile solvent. The concentrated filtrate was diluted to 25 mL using distilled water to

evaluate the total phenolic content, radical scavenging activity, and total monomeric anthocyanins. Three replications were conducted for each test.

**Total phenolic content (TPC).** TPC was determined using Folin–Ciocalteu (FC) colorimetric method (Cavender et al., 2014; Singleton and Rossi, 1965). In a test tube, 0.5 mL of aqueous extract was combined with 0.5 mL of FC reagent and 7.5 mL of distilled water, and then vortexed. After 10 min, 3 mL of 20% sodium carbonate solution was added into a test tube and vortexed again. The test tube was incubated in a water bath (Precision, Model Shallow Form Bath, LabCare America, Winchester, VA) at 40 °C for 20 min, and then quenched in an ice bath to room temperature. The solution was transferred into cuvette and measured the absorbance at 765 nm using a spectrophotometer (Model UV-3100PC, VWR International, LLC, Radnor, PA). The obtained absorbance was reported as mg gallic acid equivalents (GAE)/g dry weight (DW).

**Total monomeric anthocyanins (TMA).** TMA was measured using pH differential method (Cavender et al., 2014; Lee et al., 2005). In a test tube, 0.5 mL of aqueous extract was diluted with either 2.5 mL of sodium acetate buffer (pH 4.5) or 2.5 mL of potassium chloride buffer (pH 1.0), followed by incubation for 15 min at room temperature. The solution was transferred into cuvette and measured the absorbance at 520 nm and 700 nm using a spectrophotometer. The obtained absorbance was calculated as cyanidin-3-glucoside (Eq. (1)) as the most common anthocyanin pigment found in nature (Francis, 1989; Lee et al., 2005), and expressed as mg cyanidin-3-glucoside equivalent (cy-3-glu)/100 g dry weight (DW) as follows:

$$\text{TMA (mg cy-3-glu/100 g DW)} = \frac{A \; x \; MW \; x \; 6}{\varepsilon \text{ x } 1} x \frac{25 \; x \; 100}{g \; dry \; weight} \qquad (1)$$

where $A = (A_{520nm} - A_{700nm})pH\ 1.0 - (A_{520nm} - A_{700nm})pH\ 4.5$; *MW* (molecular weight) = 449.2 g/mol for cy-3-glu; *6* = dilution factor established from the procedure; $\varepsilon$ (molar extinction coefficient) = 26,900 L x $mol^{-1}$ x $cm^{-1}$ for cy-3-glu, *1* = pathlength in cm; *25* = dilution factor of initial aqueous extract; and *100* = factor conversion from per g to per 100 g.

**Radical scavenging activity (RSA).** RSA was evaluated based on the colorimetric assay method using a stable free radical 2,2-diphenyl-1-picrylhydrazyl (DPPH) with a slight modification (Brand-Williams et al., 1995). In a test tube, 0.5 mL of aqueous extract was reacted with 2 mL of DPPH solution (9 mg of DPPH in 100 mL of methanol), followed by vortexing and incubating at dark place for 15 min. The solution was transferred into cuvette and measured the absorbance at 517 nm using a spectrophotometer. The obtained absorbance was reported as mg ascorbic acid equivalents (AAE)/g dry weight (DW).

## Dietary fiber profiling

The preparation of dietary fiber samples was done by following our previous studies with some modifications (Deng et al., 2011; Jung et al., 2014). Briefly, 0.5 g of pomace was defatted twice with 25 mL of chloroform using an ultrasonic water bath for 10 min, and then separated the filtrate and residue with Whatman #1 filter paper. The lower molecular weight saccharides in the residue were removed by extracting the residue three times using 20 mL of 80% ethanol. The residue was dried in a fume hood overnight, treated with 0.03 mL of protease in 25 mL of 0.05*M* phosphate buffer (pH 7.5), and then placed in a water bath at 60 °C for 30 min. The suspension was filtered through Whatman

#1 filter paper and the supernatant was saved for soluble dietary fibers (SDF) analysis. The resulting residue was washed twice with 10 mL of distilled water using an ultrasonic water bath and the supernatants were combined with the supernatant obtained from the protease treatment for determining the SDF. The residue was washed again with 20 mL of 96% ethanol once, followed by 20 mL of acetone twice using an ultrasonic water bath as explained formerly, and finally the residue was dried in an oven at 40 °C for 24 h for insoluble dietary fibers (IDF) analysis.

**Analysis of SDF.** The SDF samples were dialyzed in dialysis membranes (Spectrum Laboratories, Inc., Rancho Dominguez, CA) with molecular weight cut off of 12,000–14,000 in 1.5 L of distilled water. The distilled water was changed after 12 h of dialysis and the process was finished at 48 h. The dialyzed SDF samples were freeze-dried (Consol 4.5, The Virtis Co., Inc., Gardiner, NY) for 3 days, followed by hydrolysis using 36 mL of 6% sulfuric acid, and then autoclaved at 121 °C for 1 h. The obtained solutions were used for determining the uronic acid (UA) and neutral sugar (NS) (Deng et al., 2011).

**Analysis of IDF.** The IDF samples were hydrolyzed using 3 mL of 72% sulfuric acid at room temperature for 1 h, followed by the addition of 86 mL of distilled water and autoclaved at 121 °C for 1 h. The hydrolyzed samples were filtered through crucibles and the clear solutions were kept for UA and NS analyses, while the residues were used for Klason lignin (KL) determination (Deng et al., 2011).

**Analysis of uronic acid (UA).** In a test tube, 250 µL of sample was added with 250 µL of boric acid–sodium chloride solution (0.3 g of boric acid and 0.2 g of sodium chloride in 10 mL of distilled water) and 4 mL of 96% sulfuric acid, vortexed to mix, and

incubated in a water bath at 70 °C for 40 min. The test tube was cooled down to room temperature and 200 µL of dimethylphenol solution (10 mg of 3,5-dimethylphenol in 10 mL of acetic acid glacial) was added, vortexed to mix, transferred into cuvette, and measured the absorbance at 400 nm and 450 nm using a spectrophotometer. The obtained absorbance was quantified as galacturonic acid equivalent (GAE) and the result was expressed as a percentage of dry weight (Deng et al., 2011; Jung et al., 2014). Three replications were conducted for each fruit pomace.

**Analysis of neutral sugar (NS).** In a test tube, 1 mL of sample was mixed with 2 mL of 75% sulfuric acid and 4 mL of anthrone solution (0.5 g of anthrone in 250 mL of 75% sulfuric acid), vortexed to mix, and incubated in a water bath at 100 °C for 15 min. The test tube was cooled down to room temperature, transferred into cuvette, and measured the absorbance at 578 nm using a spectrophotometer. The obtained absorbance was quantified as glucose equivalent and the result was expressed as a percentage of dry weight (Jung et al., 2014). Three replications were conducted for each fruit pomace.

**Analysis of Klason lignin (KL).** KL was determined gravimetrically by drying the residue in the crucible in an oven at 100 °C for 24 h and then recorded its weight. Furthermore, the crucible with residue was subjected to the ashing process using a furnace (Thermolyne, Model F-A1730, Sybron Corp., Dubuque, IA) at 525 °C for 5 h and reweighed. The oven-dried weight sample was subtracted with the ash weight to get the KL value that was expressed as a percentage of dry matter (Jung et al., 2014). Three replications were conducted for each fruit pomace.

**Pectin analysis**

Pectin analysis in this study was conducted in two different methods, *viz.* 1) acid extractable pectin and 2) total soluble pectin, including water soluble pectin (WSP), chelator soluble pectin (CSP), and hydroxide soluble pectin (HSP).

**Analysis of acid extractable pectin.** Acid extractable pectin was performed by extracting the fruit pomace with hot acid, following Canteri-Schemin et al. (2005) with a slight modification. Briefly, 5 g of pomace was added with 250 mL of citric acid solution (pH 2.5), and then incubated in a water bath at 95 °C for 30 min. The mixture was filtered through Whatman #1 filter paper to obtain the filtrate, and then left the filtrate in a refrigerator at 4 °C overnight. Furthermore, the cold filtrate was added with 125 mL of 96% ethanol, stirred for 10 min, and left at room temperature overnight to precipitate the pectin. The precipitated pectin was filtered through Whatman #1 filter paper and dried in an oven at 55 °C for 24 h. Total acid extractable pectin was determined gravimetrically as the mean value of three replications.

**Analysis of total soluble pectin.** Total soluble pectin was determined following the method described by Silacci and Morrison (1990) with some modifications. Briefly, 1 g of pomace was added with 20 mL of distilled water, sonicated for 10 min, and filtered through Whatman #1 filter paper to obtain the filtrate, defined as water soluble pectin (WSP). The WSP residue was treated with 20 mL of 96% ethanol in a water bath at 100 °C for 10 min, followed by filtration as mentioned above and saved the filtrate for determining the chelator soluble pectin (CSP). The obtained residue was extracted three times with 40 mL of 20*mM* $Na_2EDTA$ (pH 8.0) in an ultrasonic water bath, filtered following each extraction to obtain the filtrates as described formerly, and combined with

filtrate obtained from the ethanol treatment for CSP. Lastly, the CSP residue was reacted with 50 mL of 50*mM* NaOH, sonicated for 15 min, and then filtered to obtain the filtrate, defined as hydroxide soluble pectin (HSP). WSP, CSP, and HSP were quantified as mg galacturonic acid equivalent as explained previously and each result was expressed as a percentage of dry weight. The total soluble pectin was described as the sum of fractionized WSP, CSP, and HSP. Three replications were conducted for each fruit pomace.

**Experimental design and statistical analysis**

A completely randomized design was applied for each parameter in this study. Data analysis was conducted using SAS (SAS 9.3, SAS institute, Inc., Cary, NC) program with PROC GLM to determine the significance of each parameter on different types of fruit pomace. The *post hoc* least significant difference (LSD) test was used for the comparisons of multiple means on the basis of a 95% confidence level.

**Results and Discussions**

**Physicochemical properties of fruit pomace**

Apple pomace (AP) had the highest MC (81.50%) followed by cranberry pomace (CB) (68.92%), blueberry pomace (BB) (65.08%), and lastly raspberry pomace (RB) (36.12%) (Table 3.1). Based on the appearance of fruit pomace, it can be explained that pulp is the predominant material in AP, where it contains significant amount of dietary fibers holding more water. The MC value of our AP was similar to Ćetković et al. (2008), while it was slightly higher for CB in comparison to Park and Zhao (2006) that might be

caused by the grinding process in their study degrading and/or modifying fibers in cranberry pomace. BB has similar constituents to CB, but it was observed that the skin of BB is softer than CB in terms of different compositions in lignocellulosic structures. RB is unique in comparison to other pomace since it predominantly consists of seeds that have less ability to hold the water. The studies from Reque et al. (2014) and Dimic et al. (2012) showed that MC for BB and RB were 81.45% and 48.38%, respectively, which were higher than our results. These might be caused by our samples were obtained from the juice manufacturers, where enzymatic treatment was utilized, thus causing degradations and/or modification of fibers and lowering the water holding ability in our samples.

**Table 3.1** Physicochemical properties of fruit pomace

| Fruit pomace | MC (%) | Aw | pH | TA (%) | TSS (%) | Lightness (L*) | Hue (°) | Chroma |
|---|---|---|---|---|---|---|---|---|
| Apple | 81.50$^{a*}$ | 0.98$^{c}$ | 4.28$^{a}$ | 1.83$^{a}$ | 11.00$^{a}$ | 29.42$^{b*}$ | 66.26$^{a}$ | 27.68$^{a}$ |
| Blueberry | 65.08$^{c}$ | 1.00$^{a}$ | 3.88$^{b}$ | 0.50$^{c}$ | 2.00$^{b}$ | 15.50$^{d}$ | 19.44$^{d}$ | 11.84$^{d}$ |
| Raspberry | 36.12$^{d}$ | 0.99$^{b}$ | 4.27$^{a}$ | 0.43$^{c}$ | 2.00$^{b}$ | 37.98$^{a}$ | 53.26$^{b}$ | 24.74$^{b}$ |
| Cranberry | 68.92$^{b}$ | 1.00$^{a}$ | 3.44$^{c}$ | 0.92$^{b}$ | 1.67$^{b}$ | 22.92$^{c}$ | 22.84$^{c}$ | 22.72$^{c}$ |

MC = Moisture content; Aw = Water activity; TA = Titratable acidity; TSS = Total soluble solids.

$^{*}$ Means with different lowercase superscripts in the same column indicated significant difference ($P < 0.05$) among fruit pomace.

In regard to the Aw (Table 3.1), BB and CB had the highest Aw (1.00), followed by RB (0.99) and AP (0.98). These high values of Aw are suitable for the chemical and biological activities as well as the growth of pathogens (Zhao, 2012). It is necessary to keep the fruit pomace frozen (-80 °C) to slow down the biochemical activities and to maintain product quality and safety.

The pH data among the pomace can be seen in Table 3.1. AP and RB had similar pH, which were 4.28 and 4.27, respectively. Moreover, the pH of BB was significantly higher than the pH of CB. The pH of our BB was 3.88, and it was slightly higher than the one obtained by Reque et al. (2014), probably due to different cultivars of blueberry fruit. In addition, the pH of our CB was 3.44, higher than the result from Park and Zhao (2006) because they treated the pomace using hot water, in which more acids could be extracted. All pH values of fruit pomace were below 4.6, that could prevent the growth of deadly *Clostridium botulinum* (Zhao, 2012).

TA evaluates the total acid concentration in a product and is a parameter for predicting the impact of acid on flavor (Sadler and Murphy, 2003). AP had the highest TA value among other pomace (Table 3.1), which was 1.83 and this number represented the malic acid. In comparison to other fruit pomace that have citric acid as the predominant organic acid, CB (0.92%) was significantly higher than BB (0.50%) and RB (0.43%). According to Forney et al. (2012), ripe cranberry fruit had 75% greater total acid content than that of blueberry, explaining higher TA values in cranberry pomace than blueberry pomace. However, it is obvious that CB has higher TA value than RB because RB is dominated by seeds that have very limited amount of organic acids, but they have abundant oil contents. Interestingly, there was no significant difference between the TA values of BB and RB. This can be explained that the grinding step using blender for the TA measurement, the water used as solvent could interact with oils and other compounds that behaved as surfactant or emulsifier from the RB, creating colloid and brought this colloid down through the filter paper. It was reported that red raspberry seeds had 12.2% protein (Bushman et al., 2004) and 3.5% phospholipids (Oomah et al.,

2000) that are useful as surfactant or emulsifier. Therefore, the titration using sodium hydroxide did not only react with the organic acids, but also saponified the fatty acids.

In regard to the TSS results (Table 3.1), TSS in AP (11.00%) was significantly higher than other pomace, showing AP is rich in sugar and other soluble materials. There was no significant difference among BB, RB, and CB (2.00%, 2.00%, and 1.67%, respectively). Our TSS value for BB was only one fifth than the one obtained by Reque et al. (2014). However, our TSS value for CB was similar than the result from Park and Zhao (2006).

Different colors of fruit pomace can be seen in Table 3.1. RB showed the lightest color (L* of 37.98), while BB gave the darkest color (L* of 15.50) among fruit pomace. It could be said that AP was vivid brown (hue of 66.26° and Chroma of 27.68), BB was dull dark purple (hue of 19.44° and Chroma of 11.84), RB was vivid orange-brown (hue of 53.26° and Chroma of 24.74), and CB was vivid red (hue of 22.84° and Chroma of 22.72). The vividness intensity of AP was the highest, followed by RB, and CB was the least. These color differences might be related to the chemical constituents in each pomace, such as sugar and anthocyanins. Brown color in AP was contributed by enzymatic reaction, while brown color in RB represented the color of the seeds. Purple and red colors in BB and CB, respectively, indicated the presence of anthocyanins.

**Total lipid content of fruit pomace**

The total lipid contents in different fruit pomace are reported in Fig. 3.1. AP had the lowest lipid content among other pomace, which was 11.29%, because AP is dominated by pulp. This total lipid value could be contributed from the skins and seeds of apple. Apple skin naturally has wax layer and majority of its constituent is nonacosane (Verardo

et al., 2003; Veraverbeke et al., 2001), while apple seed predominantly contains linoleic acid (Yu et al., 2007; Yukui et al., 2009). There was no significant difference among BB, RB, and CB regarding the lipid content (14.27%, 15.98%, and 15.62%, respectively). Cranberry seeds had the highest oleic acid compared to blueberry and raspberry seeds. However, raspberry seeds had the highest linoleic acid compared to blueberry and cranberry seeds. Blueberry, raspberry, and cranberry seeds had similar amount of linolenic acid (Van Hoed et al., 2009). The ratios of omega 6 and omega 3 of blueberry, raspberry, and cranberry seeds were 1.50, 1.69, and 1.25, respectively (Van Hoed et al., 2009).

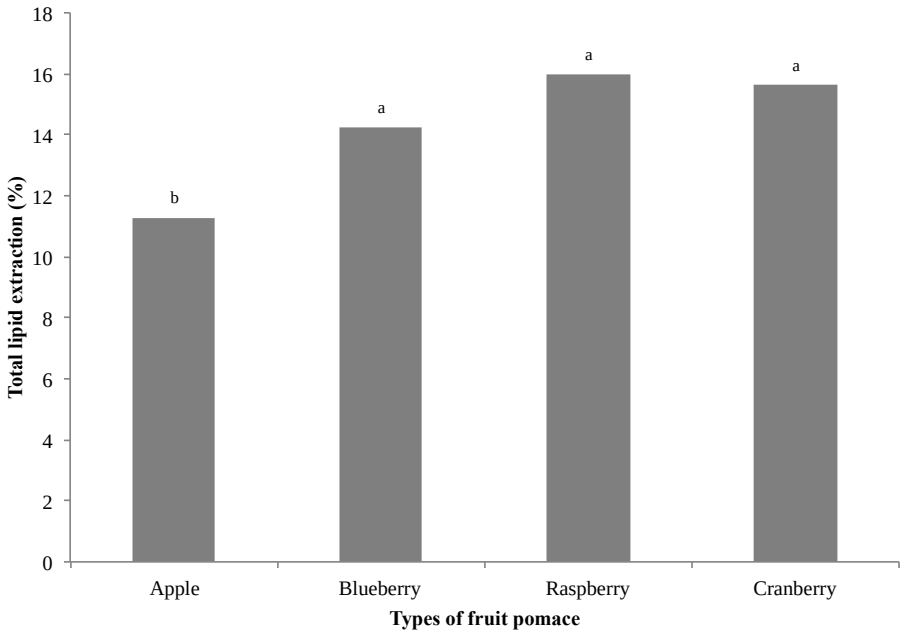



**Fig. 3.1** Total lipid extraction of fruit pomace. Means with different lowercase above the histogram indicated significant difference ($P < 0.05$) among fruit pomace.

**TPC, RSA, and TMA of fruit pomace**

From the data in Fig. 3.2, TPC of CB was the highest (6.77 mg GAE/g DW), followed by BB (6.14 mg GAE/g DW), RB (4.19 mg GAE/g DW), and AP (0.79 mg GAE/g DW). All TPC results were significantly different among fruit pomace. Laroze et al. (2010) mentioned that different results may be attributed by several factors, such as polarity of solvent and phenolic compounds, time and temperature during extraction, as well as raw materials. Higher TPC value in CB compared to BB might be related to the structure-activity relationship, where the phenolic compounds in CB have more available free hydroxyl groups and less steric hindrance (Singleton et al., 1999). The TPC in RB was lower than BB due to hard seed coats of raspberry seeds could protect the phenolic compounds inside the seeds. Moreover, AP had the lowest amount of TPC probably due to the phenolics complexed with other compounds through ester, ether, and acetal bonds (Jung et al., 2014), making them difficult to be extracted from structures for characterization.

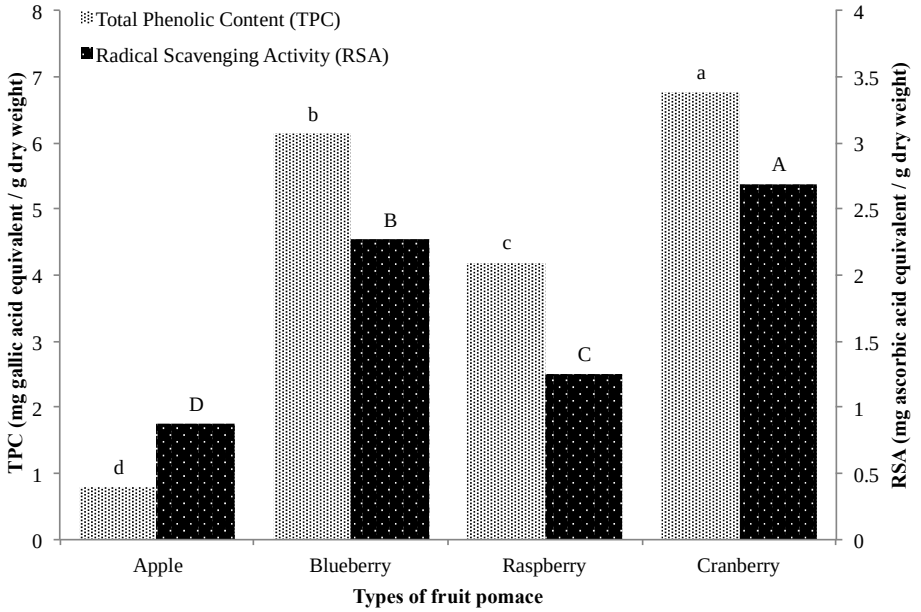



**Fig. 3.2** Total phenolic content (TPC) and radical scavenging activity (RSA) of fruit pomace. Means with different lowercase above the TPC histogram indicated significant difference ($P < 0.05$) among fruit pomace. Means with different uppercase above the RSA histogram indicated significant difference ($P < 0.05$) among fruit pomace.

RSA analysis measured the absorbance of reduced DPPH as a result of antiradical compounds as shown in Fig. 3.2. RSA from all fruit pomace had similar trend with TPC results, where CB was the highest (2.68 mg AAE/g DW), followed by BB (2.27 mg AAE/g DW), RB (1.25 mg AAE/g DW), and AP (0.88 mg AAE/g DW). All RSA results were significantly different among fruit pomace. Fruit pomace have different antiradical compounds, that might react with DPPH radicals at different kinetic types and different mechanisms (Brand-Williams et al., 1995). Polyphenols have higher antioxidant activity than that of monophenols. Brand-Williams et al. (1995) explained that polyphenols with second hydroxyl group in the ortho or para position have higher activity than in the meta position, while monophenols react with three possible mechanisms, i.e., donation of a second hydrogen, dimerization, and complexation.

The TMA results reported in Fig. 3.3 clearly showed that BB had the highest value among all pomace. Our TMA data for BB was similar to Reque et al. (2014), which was 256.18 mg cy-3-glu/100 g DW. Our TMA value for CB was 84.29 mg cy-3-glu/100 g DW, significantly lower than BB because cranberry fruit had more procyanidins and less total anthocyanins compared to blueberry fruit (Prior et al., 2001). Both AP (0.2 mg cy-3-glu/100 g DW) and RB (2.38 mg cy-3-glu/100 g DW) had very low cyanidin-3-glucoside and they were not statistically significant. Our result for AP was in agreement with Wijngaard and Brunton (2009), where they could not detect the presence of anthocyanins in apple pomace. Anthocyanins only present in the red apple skins. Since our AP was a blend from different types of apple cultivar, thus very low amount of anthocyanins could be obtained. Moreover, Parry et al. (2006) also could not detect the presence of anthocyanins in RB with their experimental condition.

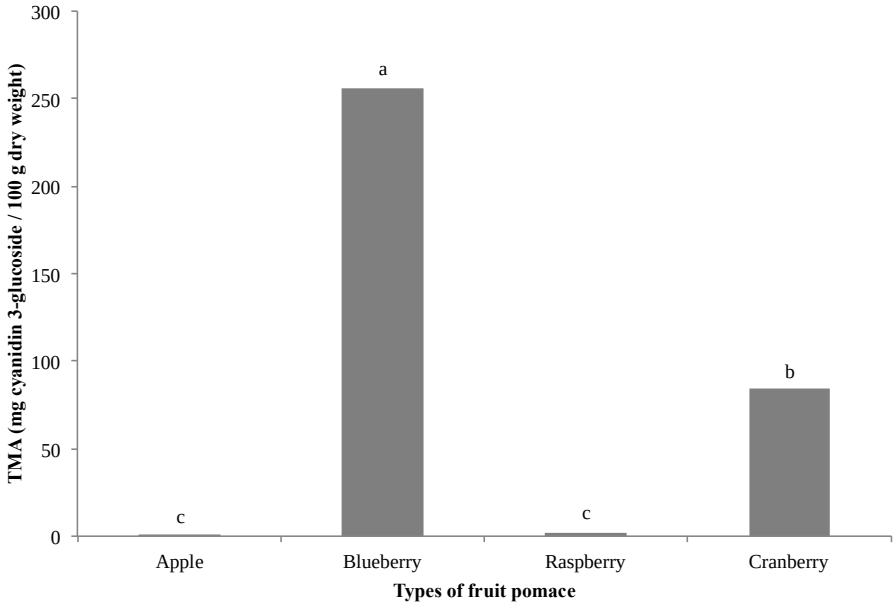



**Fig. 3.3** Total monomeric anthocyanins (TMA) of fruit pomace. Means with different lowercase above the histogram indicated significant difference ($P < 0.05$) among fruit pomace.

**Dietary fiber profile of fruit pomace**

The dietary fiber contents are presented in Table 3.2. UA residues represent pectin (D-galacturonic acid) and hemicellulose (D-glucuronic acid) (Theander et al., 1995). NS residues indicate pectin (rhamnose, arabinose, galactose, xylose) (Sriamornsak, 2003), hemicellulose (xylose, glucose, galactose, mannose, arabinose) and cellulose (glucose). KL is defined as pulp material that is insoluble in 72% sulfuric acid. Overall, the SDF had lower values than the IDF, explaining very limited amount of loosely bound fibers and most of them were intermeshed in the matrix network. Different amounts of each component in fruit pomace could be beneficial for their further applications.

**Table 3.2** Dietary fibers profile of fruit pomace

| Fruit | SDF (%) | | | IDF (%) | | | |
|---|---|---|---|---|---|---|---|
| pomace | UA | NS | Total | UA | NS | KL | Total |
| Apple | $1.90^{a*}$ | $1.04^{a}$ | $2.93^{a}$ | $5.65^{a}$ | $16.20^{c}$ | $4.78^{d}$ | $26.63^{c}$ |
| Blueberry | $1.18^{b}$ | $1.14^{a}$ | $2.32^{ab}$ | $3.02^{c}$ | $21.05^{b}$ | $39.77^{b}$ | $63.85^{b}$ |
| Raspberry | $0.30^{c}$ | $0.37^{b}$ | $0.67^{c}$ | $3.65^{b}$ | $11.96^{d}$ | $57.69^{a}$ | $73.30^{a}$ |
| Cranberry | $0.78^{b}$ | $0.86^{a}$ | $1.64^{b}$ | $3.85^{b}$ | $31.79^{a}$ | $31.55^{c}$ | $67.20^{b}$ |

SDF = Soluble dietary fibers; IDF = Insoluble dietary fibers; UA = Uronic acid; NS = Neutral sugar; KL = Klason lignin.

* Means with different lowercase superscripts in the same column indicated significant difference ($P < 0.05$) among fruit pomace.

It was hypothesized that SDF could be dominated by pectin (Table 3.2). AP contained the highest SDF (2.93%) because it did not receive any enzymatic treatments during the juice processing, however its value was not significantly different with BB (2.32%). Rhamnose creates kink in pectin (Van Buren, 2012), thus increasing the amorphous structure of pectin and making it easier to solubilize in water. Moreover, CB had 1.64% of SDF that was significantly different with AP, but not with BB, and RB had the least

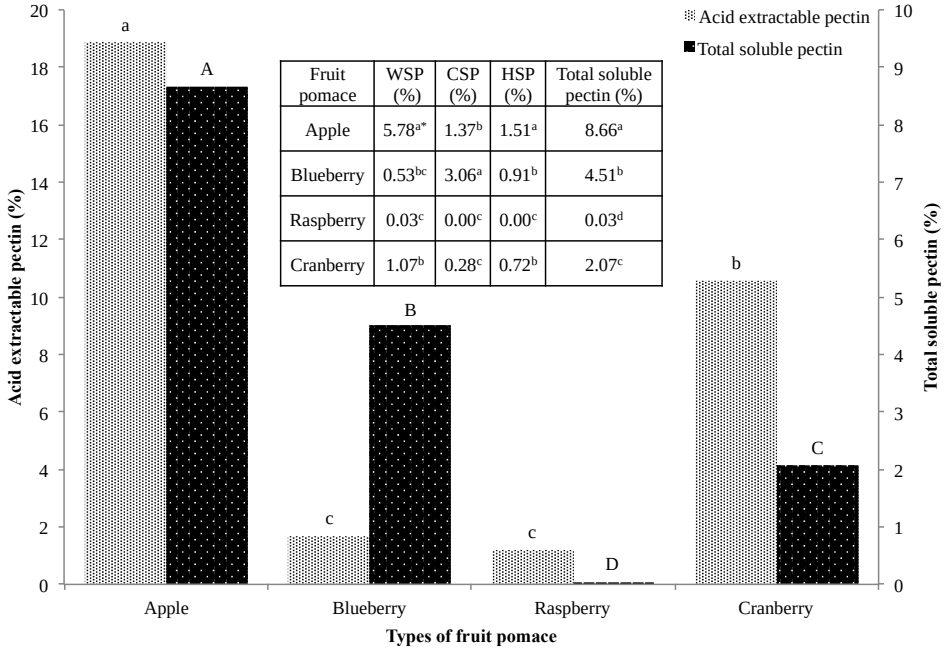
SDF (0.67%). From the UA and NS results of all pomace, it could be predicted that rhamnogalacturonan was the predominant structure of pectin.

Pectin, hemicellulose, cellulose, and lignin are intermeshed in the cell wall and acid hydrolysis is frequently used to hydrolyze the fiber polymers to obtain the monomers. In contrast to SDF data, RB had the highest IDF value (73.30%) among other pomace that was predominated by KL (Table 3.2). This could be explained that the strong seed coat was able to protect the compounds inside seeds from being hydrolyzed. This result was supported by Mccobb et al. (2001) that analyzed the blackberry seed coat with flash pyrolysis showing lignin was the predominant composition in the seed coat. The IDF values of BB (63.85%) and CB (67.20%) were not statistically significant. Similar with RB, IDF of BB was also dominated by KL. However, IDF of CB was contributed by equal amount of NS and KL. The NS value of CB was higher than BB probably due to higher carbohydrate content in cranberry pomace (Park et al., 2010). AP had the lowest IDF value (26.63%) and it was predominated by NS. It can be seen that UA in AP was still the highest among other fruit pomaces and AP had the lowest content of KL. Low amount of IDF in AP could be explained because AP is rich in soluble solids and pectin that were washed away during the extraction process using 80% ethanol and degraded during the treatment with 72% sulfuric acid (Garna et al., 2004, 2006), respectively.

**Pectin composition in fruit pomace**

The acid extractable pectin data showed that AP had the highest value (18.87%) compared to other pomace (Fig. 3.4). One of the reasons was that apple pomace analyzed in this study did not receive enzymatic treatment as discussed above. Canteri-Schemin et

al. (2005) also stated that pectin in apple pomace is mainly present in the form of protopectin. CB (10.58%) was also rich in protopectin (Pappas and Schaich, 2009), however it was significantly lower in comparison to AP. Acid extractable pectin in BB (1.69%) was not significantly different with RB (1.21%). This could be explained by the drawback of the method, where the precipitation of pectin with ethanol was not specific, since ethanol could also precipitate with the degradation of hemicellulose or other compounds in the cell wall, thus increasing the yields as reported by Garna et al. (2007) in apple pomace.




| Fruit pomace | WSP (%) | CSP (%) | HSP (%) | Total soluble pectin (%) |
|---|---|---|---|---|
| Apple | 5.78$^{a*}$ | 1.37$^{b}$ | 1.51$^{a}$ | 8.66$^{a}$ |
| Blueberry | 0.53$^{bc}$ | 3.06$^{a}$ | 0.91$^{b}$ | 4.51$^{b}$ |
| Raspberry | 0.03$^{c}$ | 0.00$^{c}$ | 0.00$^{c}$ | 0.03$^{d}$ |
| Cranberry | 1.07$^{b}$ | 0.28$^{c}$ | 0.72$^{b}$ | 2.07$^{c}$ |

**Fig. 3.4** Acid extractable pectin and total soluble pectin of fruit pomace. Means with different lowercase above the acid extractable pectin histogram indicated significant difference ($P < 0.05$) among fruit pomace. Means with different uppercase above the total soluble pectin histogram indicated significant difference ($P < 0.05$) among fruit pomace. WSP = Water soluble pectin; CSP = Chelator soluble pectin; HSP = Hydroxide soluble pectin; Total soluble pectin = WSP + CSP + HSP. Means with different lowercase superscripts in the same column indicated significant difference ($P < 0.05$) among fruit pomace.

Total soluble pectin was calculated as the sum of fractionized pectin, including water soluble pectin (WSP), chelator soluble pectin (CSP), and hydroxide soluble pectin (HSP) (Fig. 3.4). According to Christiaens et al. (2012), WSP was defined as pectic polymers that bound weakly to the cell wall through non-covalent and non-ionic bonds, CSP was dominated by ionically cross linked pectin, and HSP was mainly pectic polymers that link to the cell wall through ester bonds. The total soluble pectin of AP was still the highest (8.66%) that was dominated by WSP. Interestingly, the total soluble pectin of BB (4.51%) was significantly higher than CB (2.07%), predominantly from CSP. Blueberry fruit contain higher percentage of calcium than cranberry fruit (Nile and Park, 2014) that possibly interacts with free carboxyl groups or other functional groups (Van Buren, 2012). Total soluble pectin in RB was very low (0.03%), indicating the lack of pectin, as seeds were mainly presented in the pomace.

The different values between acid extractable pectin and total soluble pectin were affected by different mechanisms from each chemical used in the pectin extractions. Acid extractable pectin is mainly used in industrial extraction (Garna et al., 2007), while total soluble pectin is usually used in analyzing fruit development and ripening (Van Buren, 2012).

## Conclusions

This study suggested that fruit pomace are high in pectin, dietary fiber, and phenolic contents, but the exact amount varied depending on the types of fruit source. Apple pomace was rich in soluble solid materials and pectin. Blueberry pomace had abundant anthocyanins, while cranberry pomace showed strong antioxidant ability. Both pomace

contained great amount of dietary fibers. Raspberry pomace exhibited high insoluble dietary fiber, mainly from Klason lignin. The results showed that apple and cranberry pomace have potential to create packaging materials, while blueberry and raspberry pomace are suitable to fortify food products.

**Acknowledgments**

The authors thank Hood River Juice Co. for donating the apple pomace and Kerr Concentrates Inc. for providing the blueberry, red raspberry, and cranberry pomace.

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# CHAPTER 4

## Optimization of Formulations to Create Apple Pomace Based Biocomposite Boards Using Thermal Compression Molding

Virginia P. Gouw, Jooyeoun Jung, John Simonsen, and Yanyun Zhao*

Department of Food Science and Technology, 100 Wiegand Hall,
Oregon State University, Corvallis, OR 97331, USA
*Corresponding author: yanyun.zhao@oregonstate.edu

**Abstract**

Apple pomace biocomposite boards (APBs) through thermal compression molding at 30 MPa and 160 °C for 20 min were created. APB formulations were optimized via $L_9$ orthogonal array of Taguchi design aimed for high mechanical strength, low water sensitivity, and slow biodegradation. Pomace-to-binder ratio (P/B) gave significant effects on modulus of elasticity, water solubility, moisture content, and biodegradability ($P < 0.05$). Stearic acid (SA) as hydrophobic agent significantly influenced breaking strength ($P < 0.05$). The ratio of two binders (soy protein isolate (SPI) and poly(methyl methacrylate) (PMMA)) and concentration of surfactant (span 80) did not significantly affect any of the tested parameters ($P > 0.05$). The optimum formula for APB was identified as SPI:PMMA = 2:1 and P/B ratio = 7:3 without the need of using SA and span 80. This study provided valuable information in the development of biocomposites using apple pomace for various potential value-added applications.

**Key words:** apple pomace; biocomposite boards; mechanical properties; water sensitivity; biodegradability

**Practical Applications**

Apple pomace is an abundant by-product resulting from the production of apple juice and apple cider. It contains compounds that have thermoplastic and non-thermoplastic properties that are good candidates to create biocomposites. In this study, thermal compression molding technology was applied to apple pomace combined with soy protein isolate (SPI) and poly(methyl methacrylate) (PMMA) as binders and methylene

diphenyl diisocyanate (MDI) as a crosslinking agent. The objectives of this investigation were to improve mechanical properties, water sensitivity, as well as the biodegradation rate of biocomposite boards. This formulation could serve as a prototype for nursery pots. Currently, commercial pots available are produced from polyethylene, which is a non-renewable resource on the brink of depletion. Apple pomace could provide an alternative material to replace polyethylene. This study will supply novel information about the utilization of apple pomace in bulk amount while simultaneously reducing biowaste streams.

## Introduction

Apple pomace is a by-product from apple juice or cider processes. It consists of skins, seeds, stems, and de-juiced pulp. Typically for apple juice manufacture, every 100 pounds of fruit will result in approximately 25 pounds of pomace (Shalini and Gupta, 2010). In the United States, it is estimated that over 25,000 tons of apple pomace are produced each year (Bhushan et al., 2008; Roberts et al., 2004). High moisture and sugar content of wet pomace make it susceptible to microbial attack. Storage and shipment of this by-product are costly. Majority of apple pomace generally ends up being placed into the landfill for direct disposal to soil or as animal feed by combining with proteins for the growth and reproduction of animals (Azizi et al., 2014). Although several attempts have been made to develop more value-added utilization of apple pomace, including extracting pectin (Canteri-Schemin et al., 2005; Sharma et al., 2014), as a source of dietary fibers (Reis et al., 2014; Sudha et al., 2007), extracting bioactive compounds, such as epicatechin, quercetin, and chlorogenic acid (Lu and Yeap Foo, 2000; Reis et al., 2014), and producing L-lactic acid (Gullón et al., 2008), it is still necessary to develop more applications in a vast amount to reduce this biowaste and simultaneously create highly value-added products.

Apple pomace contains high amount of thermoplastic compounds (pectin, hemicellulose, lignin, and gums) and non-thermoplastic compound (cellulose) (Jiang et al., 2011; Park et al., 2010; Stokke et al., 2013). The thermoplastic compounds can act as the matrix or continuous phase and the non-thermoplastic compound as the reinforcing agent, filler or discontinuous phase to be embedded in the continuous phase to make biocomposites (Jiang et al., 2011; Park et al., 2010; Santos Rosa and Lenz, 2013).

We have previously developed biocomposite boards from berry fruit pomace (BP) (Park et al., 2010) and wine grape pomace (WGP) (Jiang et al., 2011). Soy products were used as biodegradable binders to enhance mechanical property of the biocomposite boards (Jiang et al., 2011; Park et al., 2010), poly(vinyl alcohol) (PVA) was incorporated to improve the mechanical property and biodegradability of WGP boards (Jiang et al., 2011), and hydrophobic and crosslinking agents were also added to reinforce the mechanical property as well as water sensitivity characteristics (Jiang et al., 2011). Those previous studies showed that the types of binder and pomace-to-binder ratio (P/B ratio) are important factors significantly affecting the mechanical property and water sensitivity of biocomposite boards (Jiang et al., 2011; Park et al., 2010). The developed WGP boards had high rate of biodegradation in soil, a 50% and 80% of weight loss after 30 d of burial in soil for red wine grape pomace (RWGP) and white wine grape pomace (WWGP) boards, respectively (Jiang et al., 2011).

The utilization of apple pomace to create biocomposite boards had not been reported yet. In this study, we aimed to investigate the feasibility of creating apple pomace based biocomposite using thermal compression molding and to optimize the biocomposite formulations for creating a board with high mechanical strength, low water sensitivity, and slow bio-decomposition. Different types of binder, crosslinking agent, and surfactant as well as their ratios were evaluated. Specifically, soy protein isolate (SPI) and poly(methyl methacrylate) (PMMA) were used as binders and combined at different ratios of 1:2, 1:1, and 2:1 to determine their effect on water sensitivity and biodegradability. Different P/B ratio at 9:1, 8:2, and 7:3 were also studied on their effects on mechanical property, water sensitivity, and biodegradability. Moreover, stearic acid

(SA) was used as a hydrophobic agent to improve water absorption and water solubility of the boards, and span 80 was applied as a surfactant because it gave more spontaneous adsorption to longer hydrocarbon chain length compared to other sorbitan surfactants (Peltonen et al., 2001). Lastly, methylene diphenyl diisocyanate (MDI) was employed as a crosslinking agent instead of epichlorohydrin (ECH) used in our previous study (Jiang et al., 2011). In order to use ECH, pH needs to be adjusted to 10.5 to activate the polysaccharides so that they can react with ECH (Jyothi et al., 2006). On the other hand, the isocyanate groups of MDI could react with water in the mixture, creating cross-linked polyureas for better mechanical bonding (Mo et al., 2003). It is expected that the results generated from this study would provide new insights about the technology for creating apple pomace based biocomposite for various value-added applications and further expand the utilization of apple pomace in bulk amount.

## Materials and Methods

### Materials

Fresh apple pomace was donated by a local apple juice company (Hood River, OR) and used without further treatment to save the cost. Fresh pomace was packed in Ziploc® bags and stored at -18 °C until usage. SPI was obtained from Cargill, Inc. (Minneapolis, MN), PMMA (MW 75,000) from Scientific Polymer Products, Inc. (Ontario, NY), SA from Integra Chemical Co. (Renton, WA), span 80 and MDI from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan) and Acros Organics (Bridgewater, NJ), respectively.

**Preparation of apple pomace**

Frozen pomace was thawed in a refrigerator at 4 °C overnight, and then dried in an impingement oven (Lincoln® Impinger®, Fort Wayne, IN) set at 110 °C for 3 h to obtain a final moisture content of ~2.2%. The dried pomace was ground using a laboratory miller (Model No. 4, Thomas-Wiley, Philadelphia, PA) equipped with a steel screen 0.5 mm for further usage. The dried apple pomace contained 6.60% pectin, 1.79% of soluble dietary fibers (0.15% uronic acid and 1.64% neutral sugar) and 59.92% of insoluble dietary fibers (12.38% uronic acid, 23.50% neutral sugar, and 24.04% Klason lignin) (Jung et al., 2014).

**Development and optimization of apple pomace biocomposite formulations**

Different treatment factors in the biocomposite formulations were evaluated to create apple pomace boards (APBs) with high breaking strength (BS) and modulus of elasticity (MOE), low strain, water absorption ($W_a$), water solubility ($W_s$), and moisture content (MC), as well as slow biodegradability using an orthogonal array from Taguchi design.

The treatment factors included ratio of the two binders (SPI:PMMA), pomace-to-binder ratio (P/B ratio), concentration of SA as a hydrophobic agent, and amount of span 80 as a surfactant. Our preliminary work showed that combination of soy flour with PMMA gave better characteristic than soy flour alone. The ratio of the two binders was considered because a higher ratio of synthetic polymer (PMMA) could provide better water sensitivity and biodegradability than the natural polymer (SPI). P/B ratio was tested as it showed significant effects on the mechanical property and water sensitivity of WGP boards (Jiang et al., 2011; Park et al., 2010). SA was applied to improve the water

sensitivity characteristic (Jiang et al., 2011), and span 80 for reducing the surface tension between the hydrophilic and hydrophobic materials. In addition, 5% methylene diphenyl diisocyanate (based on the total weight of pomace with binders) was added into all biocomposite formulations with the goal of enhancing the rigidity of the boards by creating crosslinks through covalent bonds between the compounds. Mechanical property, water sensitivity, and biodegradability of the board were evaluated as quality indicators to identify optimal formulations.

Taguchi design was employed to test the pairs of the treatment combination. By using this design, data could be collected to determine which factors are predominant with less number of experimental runs for saving time and resources (Nguyen et al., 2014). The selection of suitable orthogonal array depends on the number of control factors and their levels (Zirehpour et al., 2014). In this study, four treatment factors with three levels for each factor were tested, and an $L_9$ orthogonal array was chosen (Table 4.1).

In the Taguchi design, signal-to-noise (S/N) ratio was used instead of the average value of each response since this ratio reflected the level of precision for each response in each single experiment in the total set of replications (Santra et al., 2014). Signal is the response corresponding to the change of each factor, and noise is any feature affecting the precision, mostly random and inherent for the operation (Santra et al., 2014). There are three static characteristics for S/N ratio, namely nominal-the-best, larger-the-better, and smaller-the-better (Mori, 2011). Since BS and MOE were expected to be high, the larger-the-better character was chosen. On the other hand, strain, $W_a$, $W_s$, MC, and biodegradability were expected to be low, thus the smaller-the-better character was selected for the S/N ratio calculation. The larger-the-better was calculated as:

$$\frac{S}{N} = -10 \log \frac{1}{n} \left( \Sigma \frac{1}{y^2} \right) \quad (1)$$

and the smaller-the-better was expressed as:

$$\frac{S}{N} = -10 \log \frac{1}{n} \left( \Sigma y^2 \right) \quad (2)$$

where *n* was the number of observations, and *y* was the observed response.

In the optimization study, the factors with significant effects on S/N ratio were chosen and the level with maximum S/N value was desired, because a larger S/N ratio had less variation (Mori, 2011). For the factors that had no significant effect, the level was determined based on "Quality first" or "Cost first" (Mori, 2011).

**Preparation of biocomposite boards from apple pomace**

Pomace and other ingredients as listed in Table 4.1 were mixed together in a torque rheometer (Intelli-Torque Plasti-Corder®, C.W. Brabender® Instruments, Inc., South Hackensack, NJ) at 40 rpm and 105 °C for 20 min based on our preliminary studies. The rheometer was equipped with a three-piece mixer with two roller blades attached. The mixture was reground by a mini mill (Thomas Scientific, Swedesboro, NJ) with 20-mesh rack to control the particle size of the mixtures less than 0.85 mm. An 8.5 g of the mixture was molded in a 68 x 41 x 2 $mm^3$ aluminum mold using a hot presser (Carver Auto Series Hydraulic Presses, Carver Inc., Wabash, IN) operated at 30 MPa and 160 °C for 20 min to form compactible biocomposite board. Our preliminary studies observed that temperature below 160 ºC gave higher water absorption and above 160 ºC created a charred board, and pressed time for 10 min was not sufficient to melt the board completely and 30 min did not give any improvement to water sensitivity compared to 20

min pressing. After thermal press, the mold was cooled down under pressure using a manual press (Carver Laboratory Press, Carver Inc., Summit, NJ) at room temperature for 1 h. The formed biocomposite board was then removed from the mold and stored in Ziploc® bags at ambient conditions until testing.

**Sample characterization**

**Mechanical property.** The mechanical property of APB was measured using a three-point bending test following ASTM D790-10 standard with some modifications on the TA-XT2 Texture Analyzer (Texture Technologies Corp., Scarsdale, NY). The samples (12.7 x 2 x 68 $mm^3$) were conditioned following ASTM D618-13 at 23 °C and 50% RH for 40 h in a chamber (Versa Tenn III, Tenney Environmental, Williamsport, PA). The support span and crosshead speed were set at 37.5 mm and 1.4 mm/min, respectively. Breaking strength (BS), modulus of elasticity (MOE), and strain were calculated from the load-deflection curve. BS was defined as the first point on the load-deflection curve to show a slope of zero, MOE was determined from the slope in the initial elastic region of the load-deflection curve (Jiang et al., 2011; Park et al., 2010), and strain was a deformation of sample due to stress. Three replications were performed for each measurement.

**Thermal property analysis.** Differential scanning calorimetry (DSC) measurements of APB powder were performed with DSC Q2000 (TA Instruments, New Castle, DE). About 10 mg of sample was tested from 0 to 250 °C with a heating rate of 20 °C/min under a nitrogen atmosphere.

**Water absorption ($W_a$) and water solubility ($W_s$).** Water sensitivity of APB was measured as water absorption ($W_a$) and water solubility ($W_s$) by following ASTM D570-98 with some modifications (Jiang et al., 2011; Park et al., 2010). Briefly, sample specimen (68 x 41 x 2 $mm^3$) was preconditioned in a chamber set at 50 °C and 10% RH for 24 h. Sample was weighed and submerged in distilled water at 23 °C for 24 h. Afterwards, the surface of the sample was wiped off using a paper towel to remove the excess of water and the sample was reweighed. $W_a$ was calculated as the percentage of weight increase in submerged sample to the initial weight of dry specimen (Jiang et al., 2011; Park et al., 2010). After 24 h of immersion, the sample was dried in an oven (Isotemp® Oven Forced Draft, Fisher Scientific, Waltham, MA) at 50 °C for 24 h, and then reweighed for the calculation of $W_s$ as the percentage of weight loss in dried sample to the initial weight of dry specimen (Jiang et al., 2011; Park et al., 2010). Three replications were performed for each parameter.

**Moisture content (MC).** APB was ground into powder and about 5 g of the powder was weighed and dried in an oven at 105 °C for 24 h. MC was calculated on wet basis as the weight loss after drying divided by the weight of initial sample and multiplied by 100. MC was reported as mean of three replications.

**Fourier transform infrared (FTIR) spectroscopy.** APB powder was mixed with KBr powder (FTIR Spectrograde, International Crystal Labs, Garfield, NJ) at a ratio of 1:100. The mixture was compressed into thin film flake. An FTIR spectrometer (Nicolet iS50 FT-IR, Thermo Scientific, Madison, WI) was used to analyze the functional groups in each sample.

**Microstructures.** The surface characteristics of APB were evaluated using a stereomicroscope (Leica Microsystems (Schweiz) AG, Heerbrugg, Switzerland) equipped with an extended digital camera (Q imaging, Surrey, British Columbia, Canada). The internal (cross-section) microstructure of APB was tested using AmRay 3300FE field emission scanning electron microscope (SEM) (AmRay, Bedford, MA). The fractured surfaces from the three-point bending test were placed on aluminum stubs with the cross-section oriented up and coated by gold–palladium alloy with a sputter coater (Edwards model S150B sputter coater; BOC Edwards Vacuum, Ltd., West Sussex, UK) to improve their interface conductivity. Digital images of the fractured surfaces were collected at an accelerating voltage of 5 kV (Jiang et al., 2011; Park et al., 2010).

**Soil burial degradation test.** Soil burial degradation test was conducted in triplicate at ambient temperature under moisture-controlled conditions (Jiang et al., 2011; Wan et al., 2009). Each sample (34 x 41 x 2 $mm^3$) was buried 100 mm underneath the surface of soil (All Purpose Top Soil, Mountain West, L.L.C., Rexburg, ID) in a plastic cup and moistened everyday by distilled water (Jiang et al., 2011; Wan et al., 2009) to maintain the moisture content of the soil ~40% (Jiang et al., 2011). The samples were dug out from the soil at day 15, 30, 45, and 60, washed gently with distilled water to remove soil particles from the surface, and dried in an oven at 50 °C for 24 h. The percentage of weight loss was obtained from the weight loss of the buried sample to the initial weight of dried sample (Jiang et al., 2011; Wan et al., 2009).

**Verification of the optimized formula**

The optimized formula obtained from Taguchi design was used to make APB. Mechanical and thermal properties, water sensitivity, FTIR spectroscopy, and microstructure of the APB were analyzed using the methods described above.

**Statistical analysis**

Data analysis was conducted using SAS (SAS 9.3, SAS institute, Inc., Cary, NC) program with PROC GLM to determine the significance of each treatment factor on measured properties. The least significant difference (LSD) test was used for the comparisons of multiple means on the basis of a 95% confidence level. In the orthogonal array of Taguchi design, $K_{ij}$ was calculated as the average value of S/N ratio for each parameter measured on each factor *i* (*i* = A, B, C, or D) under each level *j* (*j* = 1, 2, or 3). The extreme deviation for each factor, $R_i$, was also calculated by subtracting $K_{ij}$ maximum with $K_{ij}$ minimum. Higher number of $R_i$ indicated a dominant effect from the factor on a given parameter measured (Jiang et al., 2011). However, the best treatment level of each factor was chosen from the highest $K_{ij}$ values that gave significant difference among the levels in each parameter measured (Mori, 2011). Significant $K_{ij}$ values for each parameter measured were combined as the optimum formula for further verification study.

The S/N ratio from the verification study was compared to the predicted S/N value for each tested parameter from the optimization study to confirm the Taguchi design (Santra et al., 2014). The predicted S/N value $\eta_{opt}$ was calculated as:

$$\eta_{opt} = m_t + \sum_{i=1}^{n}(\eta_i - m_t) \quad (3)$$

where $m_t$ and $\eta_i$ was the overall mean and individual S/N ratio at the highest level, respectively, and $n$ was the number of the treatment factor (Santra et al., 2014). Confidence interval (CI) is required to provide the range of the predicted values, and was calculated as:

$$CI = \pm\sqrt{\frac{F_{0.05}(1,f_e)V_e}{N_e}} \quad (4)$$

where $F_{0.05}$ (1, $f_e$ ) was the $F$-value at a confidence level of 95% against degree of freedom (df) 1, $f_e$ was the df of error term, and $V_e$ was the mean square error from analysis of variance (ANOVA) (Santra et al., 2014). $N_e$ was expressed as:

$$N_e = \frac{N}{1+df_{opt}} \quad (5)$$

where $N$ was the number of experimental run required for $L_9$ orthogonal array and $df_{opt}$ was the total df of the factors with their levels (Santra et al., 2014).

## Results and Discussions

### Optimization of apple pomace board formulations

Table 4.1 reports the results of mechanical property, water sensitivity, and biodegradability of APB from different formulations. Based on LSD test (Table 4.2), while the ratios of binders (factor A) and concentration of surfactant (factor D) did not affect any of the parameters measured ($P > 0.05$), pomace-to-binder ratio (factor B) showed significant effects on MOE, $W_s$, MC, and biodegradability ($P < 0.05$), and the concentration of hydrophobic agent (factor C) affected BS ($P < 0.05$).

**Table 4.1** $L_9$ orthogonal array for mechanical property, water sensitivity, and biodegradability of apple pomace biocomposites*

| Experiment | Factor** | | | | BS | MOE | Strain | $W_a$ | $W_s$ | MC | Biodegradability |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | A | B | C | D | (MPa) | (MPa) | (%) | (%) | (%) | (%) | (%) |
| 1 | SPI:PMMA = 1:2 | 9:1 | 0% | 0% | 7.10 | 448.6 | 2.97 | 21.21 | 35.7 | 8.96 | 47.18 |
| 2 | SPI:PMMA = 1:2 | 8:2 | 2.5% | 1% | 8.45 | 651.1 | 2.19 | 23.1 | 28.0 | 7.42 | 39.66 |
| 3 | SPI:PMMA = 1:2 | 7:3 | 5% | 2% | 7.23 | 665.6 | 1.56 | 19.6 | 23.7 | 6.89 | 34.73 |
| 4 | SPI:PMMA = 1:1 | 9:1 | 2.5% | 2% | 6.87 | 436.8 | 2.94 | 24.7 | 32.5 | 8.52 | 45.39 |
| 5 | SPI:PMMA = 1:1 | 8:2 | 5% | 0% | 6.28 | 599.7 | 1.77 | 20.95 | 29.0 | 8.38 | 41.03 |
| 6 | SPI:PMMA = 1:1 | 7:3 | 0% | 1% | 10.00 | 948.7 | 1.52 | 21.7 | 24.7 | 7.22 | 35.22 |
| 7 | SPI:PMMA = 2:1 | 9:1 | 5% | 1% | 4.49 | 550.5 | 1.29 | 25.8 | 31.9 | 8.98 | 45.92 |
| 8 | SPI:PMMA = 2:1 | 8:2 | 0% | 2% | 9.71 | 729.6 | 2.33 | 24.2 | 28.1 | 7.75 | 40.95 |
| 9 | SPI:PMMA = 2:1 | 7:3 | 2.5% | 0% | 7.61 | 855.9 | 1.40 | 22.6 | 25.3 | 7.48 | 37.54 |

* For all experiments, 5% MDI was added based on the total weight of pomace and binder.

** A: ratio of SPI and PMMA; B: ratio of pomace-to-binder; C: concentration of stearic acid; D: concentration of span 80.

SPI: soy protein isolate; PMMA: poly(methyl methacrylate); MDI: methylene diphenyl diisocyanate; BS: breaking strength; MOE: modulus of elasticity; $W_a$: water absorption after soaking in the water for 24 h; $W_s$: water solubility after drying at 50 °C for 24 h; MC: moisture content; Biodegradability: weight loss of the samples after burial in soil for 60 d.

**Effect of the ratios of binders (factor A).** For the mechanical property, $R_A$ value had the lowest rank in BS and strain, but it was ranked the second highest in MOE (Table 4.2). SPI contains about 90% of protein and has both polar and non-polar side chains that lead to intramolecular and intermolecular interactions by hydrogen bonds, dipole-dipole, and hydrophobic interactions (Jiang et al., 2011). Unmodified SPI could provide poor mechanical properties in the biocomposite boards due to their hydrophilicity (Fang et al., 2009). PMMA was incorporated with SPI to enhance the hydrophobicity and structures of APB because PMMA has less hydrophilicity in comparison to PVA (Adoor et al., 2006). Both SPI and PMMA could interact with cellulose in apple pomace through hydrogen bonds between hydroxyl groups (proton donor) and carbonyl groups (proton acceptor) (Bhat and Kumar, 2006; Wu et al., 2009). Although PMMA could interact with cellulose through hydrogen bonds, in general, synthetic polymers are poorly dispersed onto natural fibers due to interfacial tension between two compounds that creates phase separation (Gironès et al., 2008). MDI as a crosslinking agent was added to induce polymer interactions and to reduce the interfacial tension by transferring internal stresses from the filler to the matrix (Wang et al., 2001). There are two possible mechanisms from MDI to reduce the interfacial tension. First, MDI can form covalent bonds between the filler (fibers) and matrix (PMMA) because it has isocyanate functional groups (–N=C=O) that are highly reactive toward nucleophile, such as hydroxyl, carboxyl, primary, and secondary amines across the C=N double bond of the NCO group (Mekonnen et al., 2014). Secondly, PMMA chains might penetrate into the fiber holes during the mixing process and by the addition of MDI, the cross-linked between MDI with a single fiber entrapped the PMMA chains, reduced the activity of PMMA and consequently

diminished the crystallization kinetics of PMMA (Gironès et al., 2008). Compared to our previously developed blueberry pomace (BP) boards (Park et al., 2010), APB had lower BS and MOE, but higher strain value, which might be due to the higher concentration of protein in BP that could function as a binder and make the board less flexible. However, compared to our previously developed wine grape pomace (WGP) boards (Jiang et al., 2011). APB had higher BS and MOE since less hydrophilic PMMA was incorporated in comparison to PVA in WGP boards, where PVA absorbed more water acting as plasticizer, thus weakening the boards. The strain of APB was lower than WWGP due to high sugar content in WWGP acting as a plasticizer (Jiang et al., 2011; Veiga-Santos et al., 2007), whereas that of APB was similar to RWGP boards (Jiang et al., 2011) because the utilization of PMMA overcame the plasticizing effect from the sugar in apple pomace.

**Table 4.2** Investigation of signal-to-noise (S/N) ratios (dB) and the contribution of each treatment factor for different properties of apple pomace biocomposites

| Experiment | | S/N Ratio (dB) | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | BS | MOE | Strain | $W_a$ | $W_s$ | MC | Biodegradability |
| 1 | | 17.00 | 52.98 | -9.45 | -26.53 | -31.06 | -19.04 | -33.47 |
| 2 | | 18.46 | 56.24 | -6.92 | -27.29 | -28.95 | -16.77 | -31.97 |
| 3 | | 17.09 | 56.45 | -3.88 | -25.88 | -27.52 | -17.42 | -30.81 |
| 4 | | 16.72 | 52.73 | -9.39 | -27.86 | -30.26 | -16.77 | -33.14 |
| 5 | | 15.80 | 55.56 | -5.02 | -26.43 | -29.28 | -18.61 | -32.26 |
| 6 | | 19.93 | 59.54 | -3.66 | -26.74 | -27.87 | -18.48 | -30.93 |
| 7 | | 13.04 | 54.72 | -2.20 | -28.25 | -30.09 | -17.18 | -33.24 |
| 8 | | 19.72 | 57.23 | -7.40 | -27.69 | -28.98 | -19.07 | -32.25 |
| 9 | | 17.56 | 58.63 | -2.96 | -27.11 | -28.09 | -17.79 | -31.49 |
| Factor* | Level* | | | | | | | |
| A | $K_{A1}$ | 17.52[a**] | 55.23[a] | -6.75[a] | -26.57[a] | -29.18[a] | -17.75[a] | -32.09[a] |
| | $K_{A2}$ | 17.48[a] | 55.94[a] | -6.02[a] | -27.01[a] | -29.13[a] | -18.09[a] | -32.11[a] |
| | $K_{A3}$ | 16.77[a] | 56.86[a] | -4.19[a] | -27.68[a] | -29.05[a] | -18.11[a] | -32.33[a] |
| | $R_A$ | 0.75 | 1.63 | 2.56 | 1.12 | 0.12 | 0.37 | 0.24 |
| B | $K_{B1}$ | 15.59[a] | 53.48[b] | -7.01[a] | -27.55[a] | -30.47[c] | -18.91[b] | -33.28[c] |
| | $K_{B2}$ | 17.99[a] | 56.34[a] | -6.44[a] | -27.14[a] | -29.07[b] | -17.90[a] | -32.16[b] |
| | $K_{B3}$ | 18.19[a] | 58.21[a] | -3.50[a] | -26.58[a] | -27.83[a] | -17.14[a] | -31.08[a] |
| | $R_B$ | 2.61 | 4.73 | 3.51 | 0.97 | 2.65 | 1.76 | 2.21 |
| C | $K_{C1}$ | 18.88[a] | 56.58[a] | -6.84[a] | -26.99[a] | -29.30[a] | -18.00[a] | -32.22[a] |
| | $K_{C2}$ | 17.58[ab] | 55.86[a] | -6.42[a] | -27.42[a] | -29.10[a] | -17.84[a] | -32.20[a] |
| | $K_{C3}$ | 15.31[b] | 55.58[a] | -3.70[a] | -26.85[a] | -28.96[a] | -18.11[a] | -32.11[a] |
| | $R_C$ | 3.57 | 1.01 | 3.14 | 0.57 | 0.34 | 0.27 | 0.11 |

**Table 4.2** Investigation of signal-to-noise (S/N) ratios (dB) and the contribution of each treatment factor for different properties of apple pomace biocomposites (Continued)

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| D | $K_{D1}$ | 16.79[a] | 55.72[a] | -5.81[a] | -26.69[a] | -29.48[a] | -18.33[a] | -32.41[a] |
| | $K_{D2}$ | 17.14[a] | 56.83[a] | -4.26[a] | -27.43[a] | -28.97[a] | -17.89[a] | -32.05[a] |
| | $K_{D3}$ | 17.84[a] | 55.47[a] | -6.89[a] | -27.15[a] | -28.92[a] | -17.72 [a] | -32.07[a] |
| | $R_D$ | 1.06 | 1.36 | 2.63 | 0.74 | 0.56 | 0.61 | 0.36 |
| Rank | | C(*)>B>D>A | B(*)>A>D>C | B>C>D>A | A>B>D>C | B(*)>D>C>A | B(*)>D>A>C | B(*)>D>A>C |

[*] A: ratio of SPI and PMMA; B: ratio of pomace-to-binder; C: concentration of stearic acid; D: concentration of span 80.
[**] Means with different lowercase superscripts in the same column within each factor indicated the significant ($P < 0.05$) difference among the levels.
Asterisk (*) in the rank shows the significant ($P < 0.05$) factor affecting each measurement.
BS: breaking strength; MOE: modulus of elasticity; $W_a$: water absorption after soaking in the water for 24 h; $W_s$: water solubility after drying at 50 °C for 24 h; MC: moisture content; Biodegradability: weight loss of the samples after burial in soil for 60 d.

Based on the $R_A$ values for water sensitivity test (Table 4.2), factor A had the highest rank in $W_a$, but the second lowest rank in MC and the lowest rank in $W_s$. Even though factor A had the highest rank on $W_a$, it did not give significant difference among the levels. APB showed lower $W_a$ values in comparison to BP boards (Park et al., 2010) and RWGP boards (Jiang et al., 2011), even though apple pomace contained higher amount of dietary fiber (Jung et al., 2014; Kitchen, 2013; Deng et al., 2011), probably because the incorporation of PMMA and MDI reduced the available hydroxyl groups for interacting with water through hydrogen bonds and covalent bonds, respectively. In comparison to WWGP boards (Jiang et al., 2011), APB exerted 5 times higher $W_a$ values due to very small amount of dietary fiber in WWGP (Deng et al., 2011). The $W_s$ values of APB were similar to that of BP boards probably due to the presence of sugar and organic acids as plasticizers (Jiang et al., 2011; Park et al., 2010; Veiga-Santos et al., 2007), which could weaken the intermolecular forces between the polymers, causing the loss of soluble materials from biocomposite boards. However, APB had higher $W_s$ than RWGP board because of less sugar content in RWGP (Jiang et al., 2011). The $W_s$ values of APB were lower than that of WWGP board since the sugar contents in WWGP were much higher than that of apple pomace (Deng et al., 2011; Gullón et al., 2008). The highest MC was observed in WWGP boards followed by APBs and RWGP boards. These results were in accordance with the amount of hygroscopic sugar contents in different types of pomace (Jaya and Das, 2004).

In respect to biodegradability (Fig. 4.1), $R_A$ showed the second lowest rank on day 60 (Table 4.2), but from day 15 to 45, $R_A$ values were the lowest rank (data not shown). SPI and PMMA are considered as natural and synthetic polymers, respectively, in which the

natural polymer degraded faster than the synthetic one (Bhat and Kumar, 2006). Even though apple pomace contains higher sugar than RWGP (Jiang et al., 2011), the biodegradability of APB and RWGP board were similar, probably related with applied binders and cross-linker. The incorporation of PMMA and MDI into APB improved interactions between polymer phases in comparison to PVA and ECH in WGP boards. In addition, more hydrophilic PVA could accelerate microbial growth than PMMA.

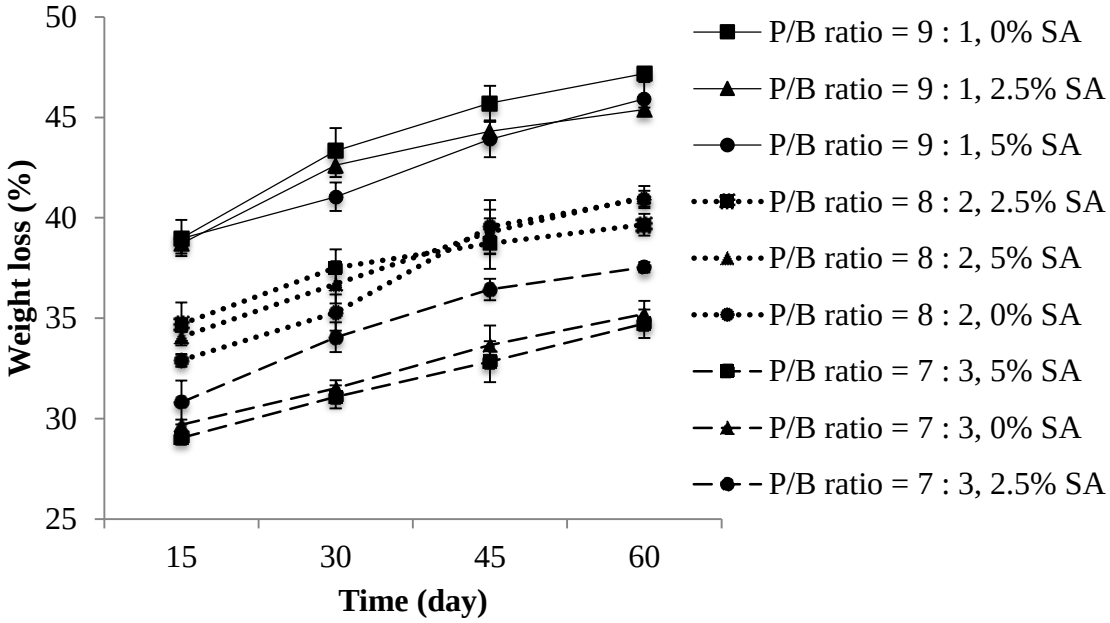



**Fig. 4.1** Biodegradation curves of apple pomace biocomposites as a function of soil burial time. P/B ratio: ratio of pomace-to-binder; SA: concentration of stearic acid.

Based on the results above, factor A did not significantly affect any of the parameters measured. Since the goal was to create economically and environmentally friendly biocomposite boards and SPI is cheaper and more sustainable, SPI to PMMA ratio at 2:1 was chosen as the optimal level for the verification study.

**Effect of P/B ratio (factor B).** For the mechanical property, $R_B$ values occupied the second highest rank in BS and the highest rank in MOE and strain (Table 4.2), and P/B ratio significantly affected MOE. MOE indicates the stiffness of a board, where higher value gives a stiffer board. SPI could provide moderate strength of polymeric resin as cysteine were strongly cross-linked through covalent disulfide bonds (Lodha and Netravali, 2005). The lowest P/B ratio resulted in the highest MOE because less sugar from apple pomace and more rigid binders that synergistically created stiffer APB due to physical and chemical interactions among the polymers. Compared to our previously developed BP boards (Park et al., 2010), APB had lower BS and MOE, but higher in strain. Similar to the previous discussions, this might be due to the lower protein content in apple pomace (Sudha et al., 2007) that made the biocomposites less stiff. In comparison to WGP boards (Jiang et al., 2011), APB had higher BS and MOE due to different type of binder, PMMA, was incorporated into APB instead of PVA in WGP. PMMA is more water resistant than PVA (Adoor et al., 2006), thus maintaining the rigidity of the boards. Also, the strain values showed a trend of WWGP boards > APBs > RWGP boards, probably due to the sugar content in WWGP > apple pomace > RWGP, since sugar in pomace behaved as plasticizers and made the biocomposites more flexible (Jiang et al., 2011; Veiga-Santos et al., 2007).

In respect to $R_B$ values for water sensitivity test (Table 4.2), P/B ratio did not give significant effect on $W_a$, but showed significant effects on $W_s$ and MC. The lowest P/B ratio contributed to more water resistance of the boards, which might be because higher ratio of binders including SPI and PMMA were more and strongly associated with other polymer phases, thus resulted in less available hydroxyl groups for interacting with water

through hydrogen bonds. The increment of $W_s$ values in APB along with increased apple pomace content were similar to the BP boards and WWGP boards, but not RWGP boards (Jiang et al., 2011; Park et al., 2010), possibly due to the presence of more sugar and organic acids that act as plasticizers, which give more voids in the biocomposite. For MC, lower MC was desired due to higher MC would promote the growth of microorganisms. APB had lower MC than WWGP board, but higher MC than RWGP board due to higher amount of hygroscopic sugar existed in APB (Jaya and Das, 2004).

For the biodegradability, factor B occupied the first rank and its level showed significant effect (Table 4.2). The biodegradability results were in accordance with $W_s$ and MC, where the more water resistance boards performed slower biodegradation because more water sensitive boards provided a better environment for the microbial growth. APBs had similar biodegradation trend to RWGP boards, which remained the shape after 60 d burial in soil unlike WWGP boards degraded much faster (Jiang et al., 2011). APB was more resistant against microorganisms due to strongly entangled fibrous structures than WWGP board. In addition, MDI incorporated into APB generated strong interactions through covalent bonds with nucleophile functional groups in the polymers. According to Bhat and Kumar (2006), microorganisms degraded the natural polymers first, then the presence of oxygen attacked the newly generated surface with the formation of peroxides, hydro peroxides, or oxides for promoting the scission of polymeric chains into small fragments that were susceptible to the attack of microorganisms. Hence, the binder of PMMA and crosslinking agent of MDI enhanced chemical and/or physical associations between polymer phases, thus extending the biodegradability of APB.

Based on the discussions above, factor B gave significant effects on MOE, $W_s$, MC, and biodegradability. A P/B ratio of 7:3 was selected as the optimal level because at this level, P/B ratio provided higher MOE and lower $W_s$, MC, and biodegradability, which are desirable for creating durable biocomposite boards.

**Effect of hydrophobic agent (factor C).** Stearic acid (SA) was used as a hydrophobic agent in this study. Based on $R_C$ results (Table 4.2), concentration of SA occupied the first rank in BS, the last rank in MOE, and the second highest rank in strain. SA levels only showed significant effect on BS, where the presence of SA reduced the BS since hydrophobic fatty acid was less able to interact with hydrophilic polysaccharides or proteins (Péroval et al., 2002). Hence, SA disrupted cohesive and continuous matrix in APBs (Colla et al., 2006; Péroval et al., 2002). In WGP boards, however, the addition of SA increased BS and MOE because the reaction between carboxylic acid of SA and hydroxyl groups of SPI increased the average molecular weight and promoted further entanglements with other protein molecules (Jiang et al., 2011; Lodha and Netravali, 2005). For APB, SPI cross-linked with apple pomace through reactive MDI causing less available functional groups in SPI for reacting with SA, thus resulted in the disruptions and breaking zones in APB (Phan The et al., 2002).

For water sensitivity, factor C had the last rank in $W_a$ and MC and the second last rank in $W_s$ (Table 4.2). There were no significant differences among the SA levels for $W_a$, $W_s$, and MC, although fibrous structures and soluble compounds could be highly reactive with water through the breaking zones in APBs incorporated with SA (Phan The et al., 2002). It could be attributed to the hydrophobic nature of SA presented in APBs,

causing less interaction with water. The same results were found in WGP boards, where SA did not affect the water sensitivity of the boards (Jiang et al., 2011).

For the biodegradability, $R_C$ gave the lowest value after 60 d burial in soil (Table 4.2). Similar to the water sensitivity, SA levels did not show significant effect because SA (C18:0) is a fatty acid that could be used by microorganisms as carbon source, and degraded sequentially through β-oxidation mechanism into palmitic (C16:0), myristic (C14:0), lauric (C12:0), capric (C10:0) acids, etc., until complete conversion to acetic acid (Lalman and Bagley, 2000). The previously developed RWGP boards also did not show any significant differences in biodegradability between 1% and 3% of SA (Jiang et al., 2011).

Therefore, factor C only affected BS. Since 0% of SA gave the highest BS, this condition was used in the verification study. It would also save cost without the use of SA.

**Effect of surfactant (factor D).** Span 80 was used as a surfactant in this study. $R_D$ values for mechanical properties always occupied the second lowest rank, and the surfactant level did not give significant differences (Table 4.2). The addition of span 80 was intended to reduce the surface tension between polymer phases consisting of the hydrophilic and hydrophobic compounds through hydrogen bonds and hydrophobic interactions for creating stronger boards. Apple pomace and SPI tend to be more hydrophilic than PMMA and SA. No significant difference in the mechanical property was observed between APB with and without span 80 due to two possible mechanisms. First, span 80 was less able to be distributed into strongly entangled fibrous structure in

APB. Secondly, MDI worked more spontaneous and creating stronger covalent bonds than hydrogen bonds or hydrophobic interactions with span 80.

From the water sensitivity standpoint (Table 4.2), factor D occupied the second lowest rank in $W_a$ and the second highest rank in $W_s$ and MC, and its level did not show significant difference. Similar with previously discussed, span 80 might not be distributed well in APB due to the fibers entanglement. In order to obtain good interactions between hydrophilic and hydrophobic compounds using surfactant, it is necessary to know the amount of each compound in the mixture, and to select the proper surfactant. Otherwise, the surfactant would be less effective.

For the biodegradability (Table 4.2), in general, $R_D$ occupied the second rank (data not shown). Span 80 is a sorbitan monooleate that contains both hydrophilic and hydrophobic characters. The hydrophilic part, sorbitan, is a derivative of sorbitol that is rich in hydroxyl groups. The hydrophobic part, monooleate, is an unsaturated lipid. The microorganisms could degrade these reactive functional groups during the soil burial study.

Based on the results above, factor D did not give any significant effects on the functional properties of the APB. Therefore, for the verification study, span 80 was not added for reducing the cost.

**Verification study**

The verification study tested the APB made from the optimum formulation developed from the Taguchi design, in which SPI/PMMA ratio of 2:1, P/B ratio of 7:3, and 5% MDI were employed and SA and span 80 were not used based on the reasons stated above.

APB was analyzed for mechanical property and water sensitivity. The results were compared with the predicted values obtained from the Taguchi design to confirm the optimized conditions.

As shown in Table 4.3, BS and MOE, as well as $W_s$ and MC values from the verification study were all in the range of 95% confidence interval prediction from the optimization study, which confirmed that the optimized formulation obtained from Taguchi design is valid for making desirable APB.

**Table 4.3** Verification study for optimal formula from apple pomace biocomposite using signal-to-noise (S/N) ratios (dB)*

| Parameter | Overall mean | Predicted mean | MSE | CI | Lower | Upper | Experimental result |
|---|---|---|---|---|---|---|---|
| BS | 17.26 | 20.67 | 0.53 | 2.76 | 17.91 | 23.43 | 22.96 |
| MOE | 56.01 | 60.46 | 0.81 | 3.41 | 57.05 | 63.86 | 60.58 |
| $W_s$ | -29.12 | -27.40 | 0.01 | 0.41 | -27.81 | -26.98 | -27.80 |
| MC | -17.98 | -16.51 | 0.06 | 0.90 | -17.40 | -15.61 | -17.38 |

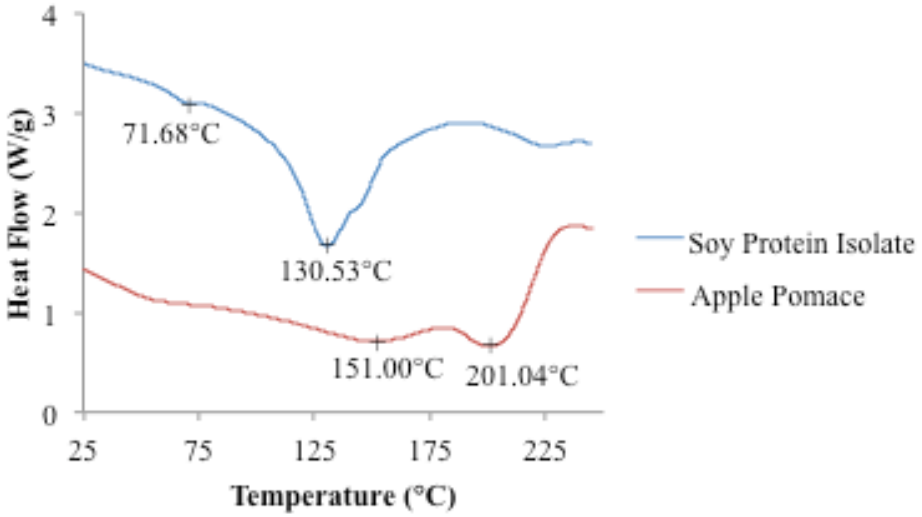
* Strain and water absorption were not included due to no treatment factor gave significant effect on these parameters.
Overall mean: the average of S/N ratio from each testing parameter; Predicted mean: overall mean + the difference of the highest S/N ratio for each factor with the overall mean; MSE: mean square error; CI: confidence interval at 95%; Lower: the minimum limit of CI; Upper: the maximum limit of CI; Experimental result: the result obtained from actual test.
BS: breaking strength; MOE: modulus of elasticity; $W_s$: water solubility after drying at 50 °C for 24 h; MC: moisture content.

Thermal property, FTIR spectroscopy, surface characteristic, and microstructure of the APB were further investigated to analyze their physicochemical property based upon the molecular and/or polymeric structures of raw materials and APB.

**Thermal property.** Fig. 4.2A shows the DSC profile of the raw materials, in which both SPI and apple pomace had two endothermic peaks. The two endothermic peaks of SPI contributed to the presence of conglycinin (7S) at 71.68 ºC and glycinin (11S) at

130.53 ºC, and were affected by the extraction process and the drying method of SPI (Bainy et al., 2008). The variation in the subunit composition of 11S strongly affected the melting point, but not the subunit composition of 7S (Bainy et al., 2008). In this study, apple pomace had two endothermic peaks at 151.00 ºC and 201.04 ºC, which might represent the monosaccharide and polysaccharide, respectively. Similarly, it was previously reported that glass transition of cellulose, hemicellulose, and lignin were 200 ºC to 205 ºC, 150 ºC to 220 ºC, and 130 ºC to 190 ºC, respectively (Stokke et al., 2013).

(A)




(B)

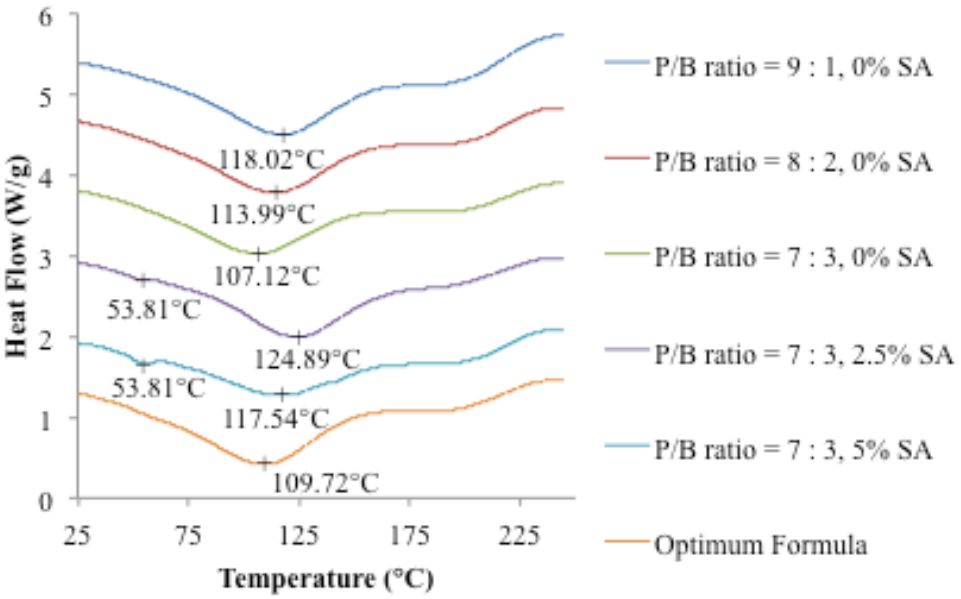



**Fig. 4.2** DSC thermograms: (A) Raw materials and (B) Apple pomace biocomposites. P/B ratio: ratio of pomace-to-binder; SA: concentration of stearic acid.

Fig. 4.2B represents the DSC profiles of APB made from different formulations as studied in the optimization and verification studies. APBs in the absence of SA showed a wide endothermic peak, representing that SPI, PMMA, span 80, and apple pomace were well associated by crosslinking with MDI. Moreover, the endothermic peak at lower P/B ratio in the absence of SA shifted to lower temperature than that at higher P/B ratio. Apple pomace contains cellulose, hemicellulose, and lignin that strongly intermeshed and chemically bonded through covalent and non-covalent bonds was less able to interact with binders (Pérez et al., 2002), thus shifting the endothermic peak to higher temperature. The presence of SA at the same P/B ratio generated two peaks (Fig. 4.2B), a new peak at 53.81 ºC attributed to the endothermic peak of SA because SA was not well associated with other compounds due to less affinity with polysaccharides, protein (Péroval et al., 2002), and PMMA. In addition, no linear trend was observed between the increment of SA and endothermic peak, probably owning to the presence of other compounds in APB (binders and/or span 80). DSC profile of APB from the verification study showed one endothermic peak (Fig. 4.2B), demonstrating that the optimized level of SPI, PMMA, and apple pomace with the use of MDI were well interacted with each other.

**Fourier transform infrared (FTIR) spectroscopy.** The structural properties of raw materials and developed APB analyzed by FTIR are illustrated in Fig. 4.3. For SPI spectra (Fig. 4.3A), the peaks from 3600 – 3000 $cm^{-1}$ were attributed to free and bound O–H and N–H groups, and the band at 2980 – 2850 $cm^{-1}$ was related to the C–H stretching from the saturated groups of $CH_2$ and $CH_3$ (Soares et al., 2005). The peaks at 1655 $cm^{-1}$ and 1540 $cm^{-1}$ were related with amide I (C=O stretching) and amide II (N-H

bending), respectively (Li et al., 2006; Wu et al., 2009). Similar peaks were observed in apple pomace spectra (Fig. 4.3A), but the peaks at 1655 $cm^{-1}$ and 1540 $cm^{-1}$ showed lower intensities than that of SPI, probably due to small amount of protein. However, an intense peak at 1060 $cm^{-1}$ was observed, which may be related to the presence of C–O–C glycosidic linkage from cellulosic compounds (Khan et al., 2010).

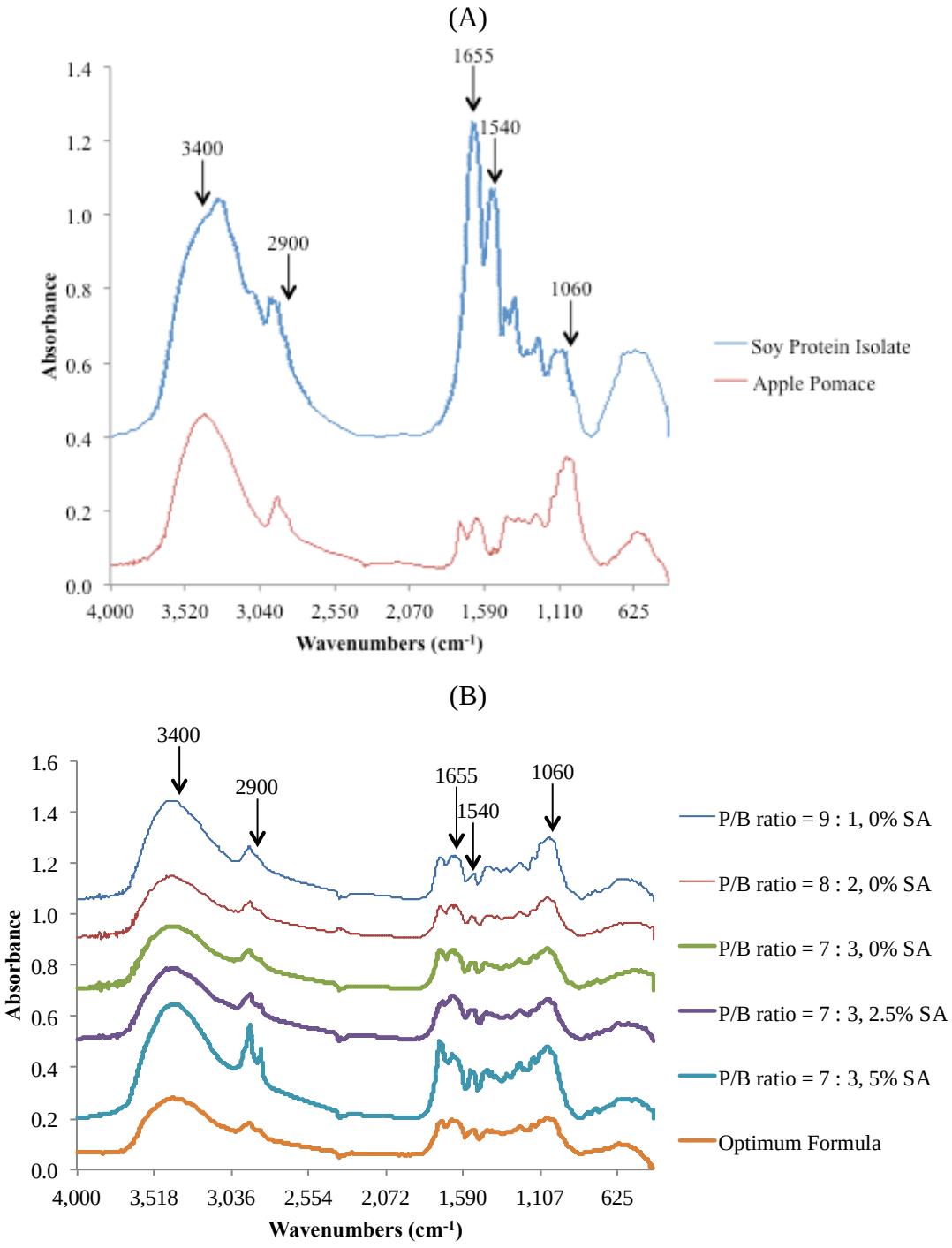



**Fig. 4.3** FTIR spectroscopy spectra: (A) Raw materials and (B) Apple pomace biocomposites. P/B ratio: ratio of pomace-to-binder; SA: concentration of stearic acid.

In the FTIR spectra of APB, no new peak and shifts were observed in comparison to the raw materials. Different intensities of FTIR spectra between APB and apple pomace was observed near amide II band at 1540 $cm^{-1}$, probably derived from SPI as a binder. The intensity level of the peaks indicated the degree of chemical interactions among various compounds, which could be different depending on the P/B ratio and SA concentration. In the absence of SA, P/B ratio affected the intensity of the absorption peaks at 1060 $cm^{-1}$ (Fig. 4.3B) since C–O–C glycosidic linkage became more intense with the increment of cellulosic compounds in apple pomace. At the same P/B ratio, the presence of SA further influenced the intensity of the peaks at 2980 – 2850 $cm^{-1}$ corresponding to the C–H stretching of the saturated groups in $CH_2$ and $CH_3$ of SA (C18:0), especially showing very intensive peak at 5% SA. No peak was observed at 2285 $cm^{-1}$ indicating isocyanates (Jiang et al., 2007), because the isocyanate functional groups of MDI were cross-linked with other compounds through covalent bonds. FTIR analysis confirmed that APB made from the verification study had similar structure to the APB from the optimization study.

**Microstructure of the APB.** To investigate the effect of SA on durability of the APB against water, stereomicroscopic images of APB incorporated with different amount of SA were studied and are illustrated in Fig. 4.4A (before soaking in water) and Fig. 4.4B (after soaking in water). SA particles were captured in the stereomicroscope showing white substances over APB. The increment of SA in the formulation and soaking in water both made the APB lighter in color, which were probably due to the lack of interaction of SA with other polymeric compounds, and once the boards were soaked in water, some compounds (sugar and organic acids) were washed out.

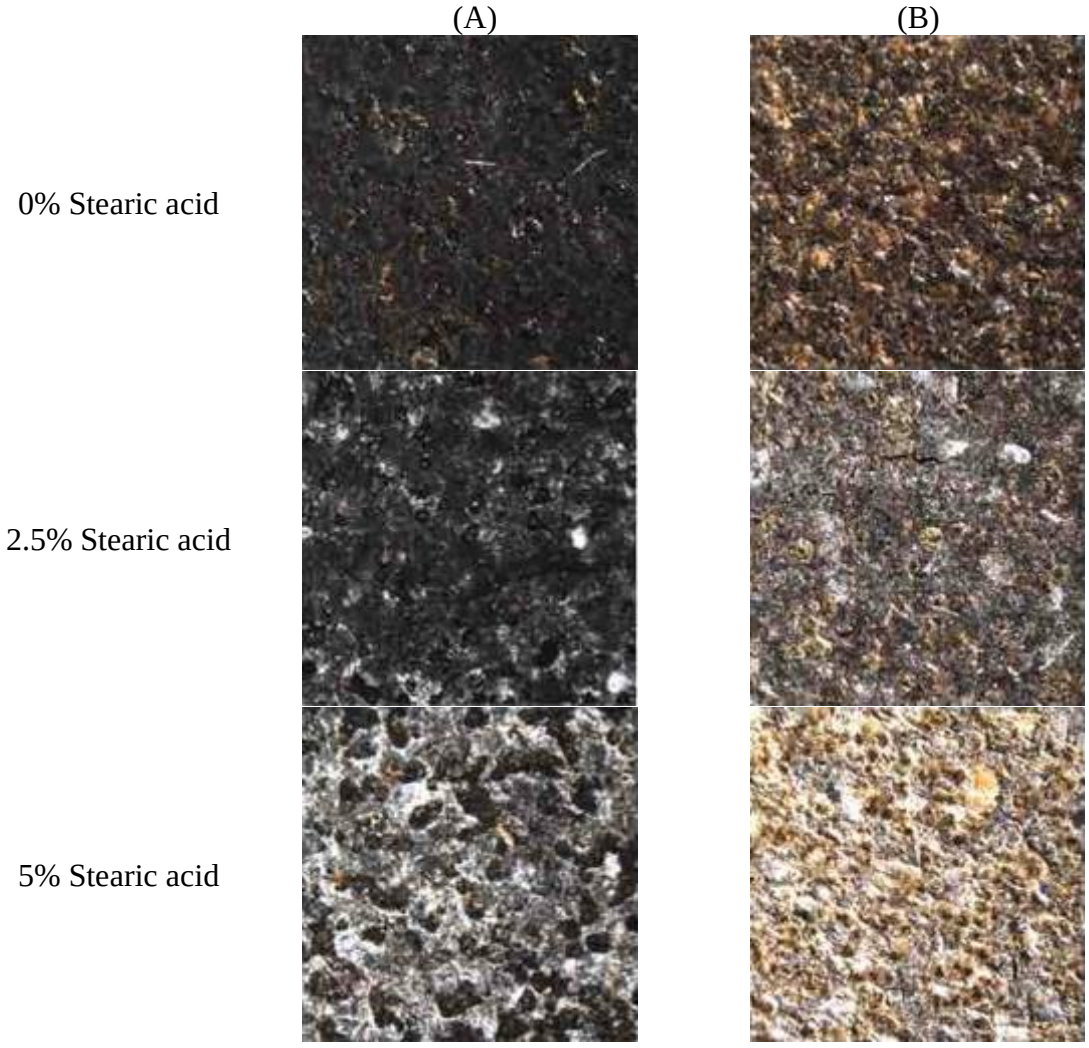



**Fig. 4.4** Microscope images of surfaces of apple pomace biocomposite with pomace-to-binder ratio of 7:3: (A) Before soaking in water and (B) After soaking in water for 24 h and then drying in the oven at 50 °C for 24 h.

The cross-section from the fracture surface of APB observed by SEM is exhibited in Fig. 4.5. Large voids were observed in APB (Fig. 4.5A) since the apple pomace fibers tended to aggregate by themselves with less available functional groups interacting with binders at high P/B ratio. With the presence of SA in APB, the number of large voids was reduced (Fig. 4.5B). Competing with the reactive MDI, SA would be less reactive with other functional groups in the biocomposites. These non-interacted SA particles

entrapped in the fibrous structures and induced the disruptions and breaking zones, as shown by many smaller voids. For optimized APB from the verification study (Fig. 4.5C), the aggregation of fibers was reduced as more binders were interacted with other compounds through covalent bonds, hydrogen bonds, and hydrophobic interactions. This SEM analysis could also support the results showing higher MOE at the lowest P/B ratio and the higher BS in the absence of SA as reported above.

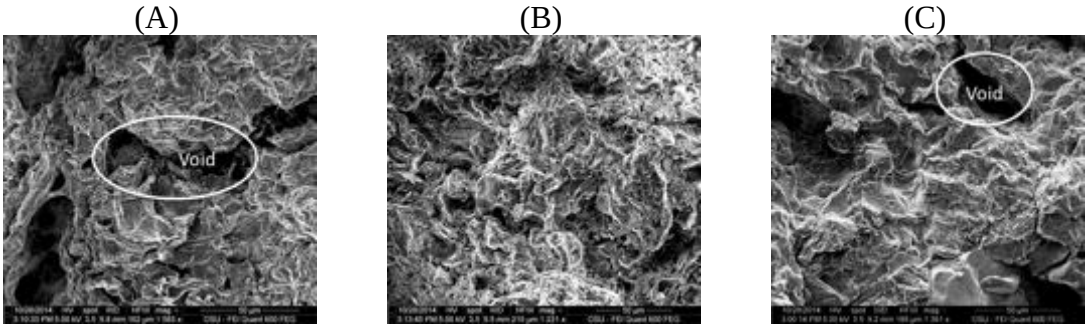
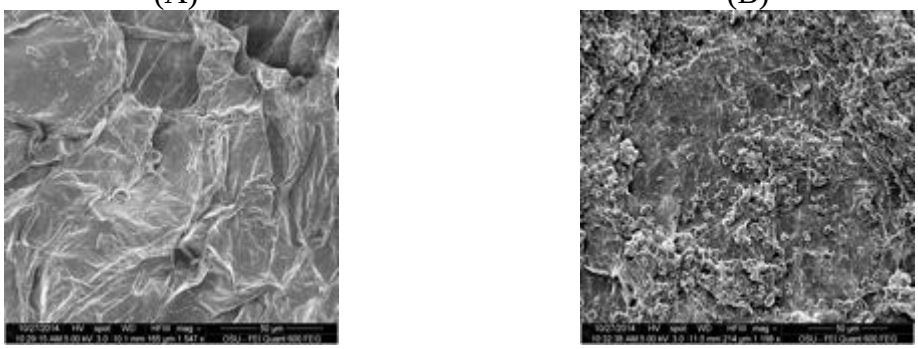



**Fig. 4.5** SEM images of fracture surfaces of apple pomace biocomposite: (A) SPI:PMMA = 1:2, P/B ratio = 9:1, 0% SA, 0% span 80, (B) SPI:PMMA = 2:1, P/B ratio = 9:1, 5% SA, 1% span 80, and (C) SPI:PMMA = 2:1, P/B ratio = 7:3, 0% SA, 0% span 80. P/B ratio: ratio of pomace-to-binder; SA: concentration of stearic acid.

The SEM images for dried apple pomace and RWGP are illustrated to characterize the fiber properties (Fig. 4.6). It was appeared that apple pomace contains strongly entangled fibrous structures (Fig. 4.6A), and has a high water holding ability of 546.72%, whereas RWGP had relatively less entangled fibers with less water holding ability of 419.74% (Fig. 4.6B). The round colonies in RWGP were found and assumed as the residue of yeasts due to the fermentation process in winemaking. For developing more water resistant APB, it is necessary to modify the fiber characteristics in apple pomace to make the fibrous structures more available from steric hindrance, thus could associate with other polymeric compounds.

(A) (B)



$W_a$ = 546.72% $W_a$ = 419.74%

**Fig. 4.6** SEM images of fiber characteristics from apple pomace and red wine grape pomace and water absorption ($W_a$) ability of their dried powders: (A) Apple pomace and (B) Red wine grape pomace.

## Conclusions

This study demonstrated that apple pomace could be utilized to create biocomposite boards through thermal compression molding. The developed boards have compatible functionalities with previously developed wine grape pomace and blueberry pomace boards. To obtain an apple pomace board with high BS, MOE, but low strain, $W_a$, $W_s$, MC, and biodegradability, the incorporation of SPI and PMMA at ratio of 2:1, P/B ratio of 7:3, and 5% MDI were desirable. The boards remained intact in structure after 60 days of soil burial. It was clear that the huge structures of the apple pomace fibers less interacted with other compounds due to steric hindrance. Therefore, it is necessary to treat the apple pomace either physically, chemically, biologically, or their combinations to make the fibers lengths shorter, thus more areas available for better interactions.

**Acknowledgments**

The authors thank Hood River Juice Company for donating the apple pomace, Steph Walker at Department of Chemical Engineering at Oregon State University for DSC, Jian Huang and Shaun Freitas at Department of Wood Science and Engineering at Oregon State University for FTIR spectroscopy.

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# CHAPTER 5

## General Conclusion

This project was the first study that analyzed the physicochemical properties and bioactive compounds from four different types of fruit pomace as well as developed apple pomace based biocomposite boards through thermal compression molding.

Depending on the types of fruit, the generated pomace may have very different physicochemical properties and contain different bioactive compounds, which may be utilized for different applications. Blueberry pomace had great amount of anthocyanins, while raspberry pomace exhibited high contents in insoluble dietary fiber. Those data suggested that both blueberry and raspberry pomace are excellent candidates to be utilized as fortifying agents in food products, such as meat or bakery goods, to increase human health. Analogous to blueberry and raspberry pomace, apple and cranberry pomace were rich in pectin. Moreover, cranberry pomace was also high in phenolic compounds. Both pomace can be used not only in food applications, but also they are promising materials to create biodegradable packaging.

The utilization of apple pomace to create biocomposite boards through thermal compression molding was successfully conducted. Five percent of methylene diphenyl diisocyanate (MDI) was added in all formulations. The ratio of pomace-to-binder (P/B) and concentration of stearic acid as hydrophobic agent significantly affected the tested parameters, including breaking strength, modulus of elasticity, moisture content, water solubility, and biodegradability. In contrast, the ratio of soy protein isolate (SPI) and poly(methyl methacrylate) (PMMA) as binders and the presence of span 80 as surfactant

did not influence any of the tested parameters. The optimum formula to create biocomposite boards from apple pomace was SPI:PMMA = 2:1 with P/B ratio of 7:3 and 5% MDI, without the use of stearic acid and span 80. These results showed that apple pomace could be used to create "green" packaging materials.

This study would provide new information in selecting the fruit pomace to develop different types of value-added product as well as help the juice manufacture reducing this unavoidable biowaste. Furthermore, it is necessary to analyze more fruit pomace from the juice industry to explore their characteristics, so that there will be more options to develop various applications. More specific development of fruit pomace can be classified into two categories, namely food applications and packaging applications. In food applications, *in vitro* test is recommended to see the antioxidant activity as well as the digestibility of bioactive compounds from fruit pomace. Furthermore, the pomace or their extract with the highest positive effect from *in vitro* test can be incorporated into various food products. In packaging applications, specific testing parameters for lignocellulosic compounds, including cellulose, hemicellulose, lignin, and ash are essential to develop packaging materials. Also, the microstructure analysis of fruit pomace is important to see the entanglement of fibers for the possibility partially substituting wood pulp materials. Finally, some treatments to reduce the entanglement of fibers by making them shorter can be done physically, chemically, biologically, or their combinations, thus more areas are available for better interactions.

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