

# Feasibility of Creating Compression-Molded Biocomposite Boards from Berry Fruit Pomaces

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**ABSTRACT:** In this study, we investigated the feasibility of creating biocomposite boards from berry fruit pomaces on the basis of a crosslinking mechanism. Blueberry, cranberry, and wine grape pomaces were ground, dried, and mixed with soy flour (SF) or pectin and xanthan gum mixture at a ratio of 1 : 1 and with the addition of 15% glycerol (w/w of pomace and SF). Blueberry pomace (BP) was also blended with NaOH-modified soy flour (MSF) at pomace/MSF ratios of 1 : 1, 4 : 1, and 9 : 1 and with 5, 10, or 15% glycerol. The mixtures were compression-molded at 130–140°C into biocomposite boards to evaluate their mechanical and thermal properties, water absorption and solubility, and microstructure. Among the three pomaces, the BP board was the stiffest, whereas the wine grape pomace board was the most flexible. The breaking strength and modulus of elasticity of the BP/MSF boards increased with increasing MSF concentration but decreased with increased glycerol concentration. Mix-

ing the pomace and glycerol into SF shifted the endothermic peaks and initial degradation to lower temperatures compared to that of SF alone. Increasing the glycerol concentration decreased the water absorption but increased the water solubility of the BP/MSF board. The pomace/MSF ratio in the board did not affect ( $P > 0.05$ ) the water absorption, but the water solubility increased with increasing pomace concentration. Glycerol addition in the BP/MSF board smoothed the fracture surface, as shown by scanning electron microscopy images. This study may provide an approach to reducing fruit pomace disposal through the development of new value-added biodegradable products for industrial applications, such as nursery pots and egg cartons. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 127–136, 2010

**Key words:** biofibers; blending; mechanical properties; thermal properties; water-soluble polymers

## INTRODUCTION

Fruit pomaces are bioresiduals from the fruit juice industry and wineries. In 2006, about 5.0 million tons of noncitrus fruits were processed for juice and wine in the United States, which comprised about 52% of the total processed fruit and 30% of the total used fruit production.<sup>1</sup> As a result, large quantities of pomaces were produced annually. Fruit pomaces contain large amounts of insoluble carbohydrates, small amounts of proteins and minerals, and some remaining juices, which contain sugars, acids, and other soluble substances.<sup>2–4</sup> These bioresiduals have traditionally been used as animal feed and fertilizer.<sup>3</sup> However, because of their extremely low protein content, fruit pomaces are not good candidates for animal feed.<sup>4</sup> The disposal of pomaces may present

added cost to processors, and direct disposal into soil or landfills can contribute to serious economic losses and potential environmental problems.<sup>2,4</sup>

Several new applications for fruit pomaces have been recently developed. For example, citrus and apple pomaces are industrially used for pectin production.<sup>5,6</sup> Cranberry pomace (CP)<sup>7</sup> and blueberry pomace (BP)<sup>8</sup> are used for the extraction of pigments and phenolic compounds, such as anthocyanin,<sup>7–9</sup> carotene,<sup>10</sup> and polyphenolics.<sup>7,11</sup> However, the extraction of the functional substances only uses a small fraction of the pomace, and a large quantity of bulk solids still remains as biowaste. Hence, there is a great need for research into the utilization of fruit pomace, especially in the area of converting pomace into value-added products.

Fruit pomace consist of polysaccharides, including celluloses, hemicelluloses, pectin, and sugars, and a small amount of proteins and polyphenolics;<sup>12</sup> thus, they are good candidates for thermoforming applications to make biocomposites because some of these components (pectin, proteins, organic acids, and sugars) have thermoplastic properties. Biocomposites

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**TABLE I**  
**Approximate Compositions of the Selected Fruit Pomaces**

Source of pomace	Components (% dry matter)	References
Cranberry	Carbohydrate (89.4), <sup>a</sup> protein (8.5), fat (1.3), and ash (0.8)	Park and Zhao <sup>12</sup>
Raspberry	Dietary fiber (59.5), lignin (11.7), protein (10), fat (11.1), and ash (4.1)	McDougall and Beames <sup>31</sup>
Blueberry	Carbohydrate (83.6), <sup>a</sup> protein (9.8), fat (5.1), and ash (1.5)	This study
Grape	Carbohydrate (84.1), <sup>a</sup> protein (6.5), fat (3.3), and ash (6.1) Sugars (22.64), Klason lignin (53.64), protein (10.72), uronic acids (5.45), and ash (8.77)	This study Valiente et al. <sup>3</sup>

<sup>a</sup> The carbohydrate content was calculated as follows: 100 – (Protein + Fat + Ash).

consist of biodegradable polymers as the matrix materials and biofibers as the biodegradable fillers.<sup>13</sup> The thermoplastic components in fruit pomaces can form the composite matrix, and the nonthermoplastic parts may act as dispersed fillers. Fruit pomaces can thus be processed to create biocomposites through the incorporation of other biopolymers.

Because of ecological concerns and resource availability,<sup>14–16</sup> biodegradable polymers from renewable resources such as starch,<sup>5,17,18</sup> cellulose,<sup>19</sup> pectin,<sup>20,21</sup> and soy protein<sup>15,22–24</sup> have been studied and developed. Soy protein has been successfully used as an alternative to petroleum polymers in the manufacture of adhesives, plastics, and various binders.<sup>15,25</sup> Plastics made from soy protein have high strengths and good biodegradable performances.<sup>25</sup> Defatted soy flour (SF) is an abundant renewable material and is economically more favorable than soy protein concentrate and soy protein isolate (SPI) for many applications.<sup>26–28</sup> SF contains both soy protein aggregate and soy carbohydrate, in which the protein aggregates are embedded in a filmlike soy–carbohydrate matrix.<sup>29</sup> According to a previous study,<sup>30</sup> SF improved the shear elastic modulus in composites compared to SPI; thus, they are suitable as the reinforcement phase in elastomers. A variety of soy-based plastic systems have been reported in the scientific literature.<sup>26–30</sup> However, a literature search showed no reports combining soy-based plastics with pomaces of any kind. A soy–pomace system has the potential to provide mechanical properties appropriate for a variety of nonstructural applications where biodegradability is a key factor.

The objectives of this study were to evaluate the feasibility of creating fruit-pomace- and SF-based biocomposites by thermoforming and to investigate the mechanical, thermal, water absorption, solubility, and binding properties of the produced biocomposites. Pomaces from berry fruits were investigated in this study as they are currently less used than other fruit pomaces. SF was used to augment the matrix for the fruit pomaces, and glycerol was added as a plasticizer to reduce the brittleness of the formed composites. The development of biodegradable materials, especially from renewable agricultural

feed stocks, is environmentally and economically significant. Knowledge developed from this study can be transferred to other fruit pomaces and would be a good precursor for the development of biodegradable composites with other forming methods, such as extrusion and injection molding for industrial-scale applications. Furthermore, the development of pomace-based biocomposites may be suitable for many agricultural and food applications, such as nursery pots, egg cartons, and condiment cups.

## EXPERIMENTAL

### Materials

Fresh blueberry (*Vaccinium* sp.) and cranberry (*Vaccinium macrocarpon* Aiton) pomaces were donated by a local juice concentrate processor (Kerr Concentrates, Inc., Salem, OR) and were used without further treatment. Wine grape pomace (GP; *Petit Verdot*) was obtained from the Oregon State University research winery (Corvallis, OR); the seeds and stems were discarded, and only the skin materials were used. The pomaces were packaged in poly(ethylene terephthalate) containers and stored at  $-18^{\circ}\text{C}$  until use. The approximate compositions of the pomaces were analyzed by the Food Products Laboratory, Inc., a certified analytical laboratory in Portland, Oregon, and are reported in Table I, along with data on the composition of carbohydrates in the pomaces, as published in previous studies.<sup>12,31</sup> Carbohydrate contents, such as the cellulose, lignin, and hemicellulose contents, are important for the production and functionality of biocomposites. A comprehensive study to investigate the specific carbohydrate composition of berry fruit pomace is under the way in our laboratory. Defatted SF (industrial 100/90) was obtained from Cargill, Inc. (Minneapolis, MN) with about 7.35% water, 50% protein, and 2% oil. High-methoxyl pectin (71–75% of degree of esterification, Grindsted RS 400) extracted from citrus peels was obtained from Danisco (New Century, KS), and xanthan gum was obtained from Rhodia, Inc. (Washington, PA).

Glycerol (Fisher Scientific, Inc., Fair Lawn, NJ) was used as a plasticizer.

### Preparation of biocomposite boards from the fruit pomaces

Each frozen pomace was ground with a disintegrator (M8A-D, Corenco, Inc., Sebastopol, CA) equipped with a Cornider screen. To obtain consistent moisture contents in the pomaces, they were dried overnight in an environmental chamber (T10RS, Tenney Environmental, Williamsport, PA) set at 70°C and 10% relative humidity (RH) and then stored at room temperature to equilibrate to ambient conditions. The moisture contents of the dried pomaces were 5.8, 7.2, and 8.2% for blueberry, cranberry, and grape, respectively. SF or a mixture of pectin and xanthan gum (P-XG) was added to each ground pomace as a binder, and glycerol was added as a plasticizer. The mixing ratio of pomace to binder was 1 : 1 by weight, and glycerol was added at 15% total solid weight of the pomace and binder. Preliminary studies in our laboratory showed that 15% was the maximum concentration of glycerol for producing pomace boards with useful mechanical strengths. Hence, this glycerol concentration was used as an upper limit in this study. The mixture was mixed in a preheated Brabender counter-rotating batch mixer with roller blades attached (Intelli-Torque plasticorder, C. W. Brabender Instruments, Inc., South Hackensack, NJ) at 30 rpm and 80°C for 10 min, as described by Saputra et al.<sup>32</sup> Each mixture was then reground with a mill (Thomas Scientific, Swedesboro, NJ) with 20-mesh rack to control the particle size of the mixtures.

In this initial study, compression molding was used to create biocomposite boards to determine the effect of the material formulations on the mechanical properties and internal bonding of the produced biocomposites. The pomace/binder mixture ( $36 \pm 2$  g) was molded into a  $101.6 \times 101.6 \times 2$  mm<sup>3</sup> steel mold with a Carver laboratory hot press (Carver, Inc., Wabash, IN) at 10 MPa for 5 min. The set temperatures were 130 and 140°C for the pomace/P-XG and pomace/SF mixtures, respectively. These temperatures were chosen on the basis of the suggested curing temperature for SPI from a previous study<sup>15</sup> and our preliminary results on the quality of the boards processed at a temperature range of 120–150°C (data not shown). After cooling under pressure under ambient conditions for 10 min, the thermoformed biocomposite board was separated from the mold and stored at room temperature until testing.

### Preparation of the blueberry biocomposite boards with NaOH-modified soy flour (MSF)

On the basis of the results obtained from the first experiment on the three types of pomaces, BP was selected for further evaluation to make biocomposite boards with different concentrations of MSF and glycerol. BP was chosen on the basis of its high stiffness and moderate flexibility among the three tested pomace boards. SF was modified with NaOH solution to improve its adhesive properties.

Frozen BP was ground with the same disintegrator described previously and then thawed. The moisture content of the thawed ground pomace was about 78%. SF (20 wt %) was dispersed into a 0.05N NaOH distilled water solution and stirred at room temperature for 2 h to unfold the protein structure of SF. The ground BP was then added to the MSF solution at a pomace/SF ratio of 9 : 1, 4 : 1, or 1 : 1 on the basis of the dry weight of pomace and SF. Each mixture was mechanically mixed with a food processing mixer (Hobart, Jorgensen Bros., Inc., Eugene, OR) for 15 min and was then dried at 70°C for 16 h with occasional stirring. The dried mixtures were ground with a mill with a 20-mesh rack. Designated amounts of glycerol (5, 10, and 15% of the total solid weight of the pomace and binder) were added to each pomace/MSF mixture and blended with the Brabender counter-rotating batch mixer at 30 rpm and 80°C for 10 min. The biocomposite mixtures were then molded into boards with the same procedures described previously.

### Mechanical analysis

The mechanical properties of the developed biocomposite boards were measured by three-point bending tests in accordance with ASTM D 790-03 with some modifications with a Sintech testing machine (MTS Systems Corp., Enumclaw, WA). Sample specimens  $12.5 \times 2.5 \times 50$  mm<sup>3</sup> were cut and conditioned at 23°C and 65% RH for 2 days. The support span was set at 40 mm, and the crosshead speed was set at 1.4 mm/min. The breaking strength (BS), modulus of elasticity (MOE), and percentage strain at peak load (% 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. The mean value of five measurement replications is reported for each sample.

### Thermal analysis

Differential scanning calorimetry (DSC) measurements of the SF and developed BP and MSF

biocomposites were performed with a Pyris 6 DSC system (PerkinElmer Instruments, Shelton, CT) with a temperature range of  $-25$  to  $250^{\circ}\text{C}$  at a heating rate of  $10^{\circ}\text{C}/\text{min}$  under a nitrogen atmosphere. Before the test, the specimens were heated from room temperature to  $100^{\circ}\text{C}$ , held at that temperature for 10 min, and then cooled to  $-25^{\circ}\text{C}$ . About 5 mg of sample was used for each measurement.

In addition, thermogravimetric analysis (TGA) was carried out on the same samples with a TA Instruments 2920 (TA Instruments, New Castle, DE). The samples were subjected to a heating rate of  $20^{\circ}\text{C}/\text{min}$  over a temperature range of  $20$ – $600^{\circ}\text{C}$  under a nitrogen atmosphere. About 5 mg of sample was used for the analysis.

### Water absorption and solubility

We tested the water absorption and solubility of the BP/MSF biocomposite boards following ASTM D 570-98 with some modifications. Sample specimens ( $76 \times 25 \times 2.5 \text{ mm}^3$ ) were preconditioned by drying at  $50^{\circ}\text{C}$  and 10% RH for 24 h. Each specimen was weighed and submerged in distilled water at  $23^{\circ}\text{C}$  and weighed again after 2 and 24 h of submergence. At each sampling time, the excess surface water was wiped off with a dry paper towel, and the sample was weighed. The percentage weight gain during 2 and 24 h of immersion was calculated as follows:

$$\text{Absorption at 2 or 24 h (\%)} = \left( \frac{W_{2\text{h or } 24\text{h}} - W_0}{W_0} \right) \times 100 \quad (1)$$

where  $W_0$  is the initial dry weight of the sample and  $W_{2\text{h}}$  and  $W_{24\text{h}}$  are the weights of the sample after immersion in water for 2 and 24 h, respectively.

After 24 h of water immersion, the specimen was dried again at  $50^{\circ}\text{C}$  for 24 h and weighed. The solubility was calculated as follows:

$$\text{Solubility (\%)} = \left( \frac{W_0 - W}{W_0} \right) \times 100 \quad (2)$$

where  $W$  is the dry weight of the sample after immersion in water for 24 h.

### Microstructure

The internal structures of the fracture surfaces of the pomace biocomposite boards were evaluated with an AmRay 3300FE field emission scanning electron microscope (AmRay, Bedford, MA). The fractured surfaces from the three-point bending test were mounted on aluminum stubs with the cross section oriented up and coated with 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 board fractured surfaces were collected at an accelerating voltage of 5 kV.

### Statistical analysis

A completely randomized factorial design was used in this study with the types of pomace and binder as two factors in the first experiment and the concentrations of BP and glycerol as two factors in the second experiment. PROC GLM for analysis of variance (ANOVA) was performed for all treatments with SAS software (SAS 9.2, SAS Institute, Inc., Cary, NC). The Tukey test was used for the comparisons of multiple means on the basis of a 95% confidence level.

## RESULTS AND DISCUSSION

### Appearance

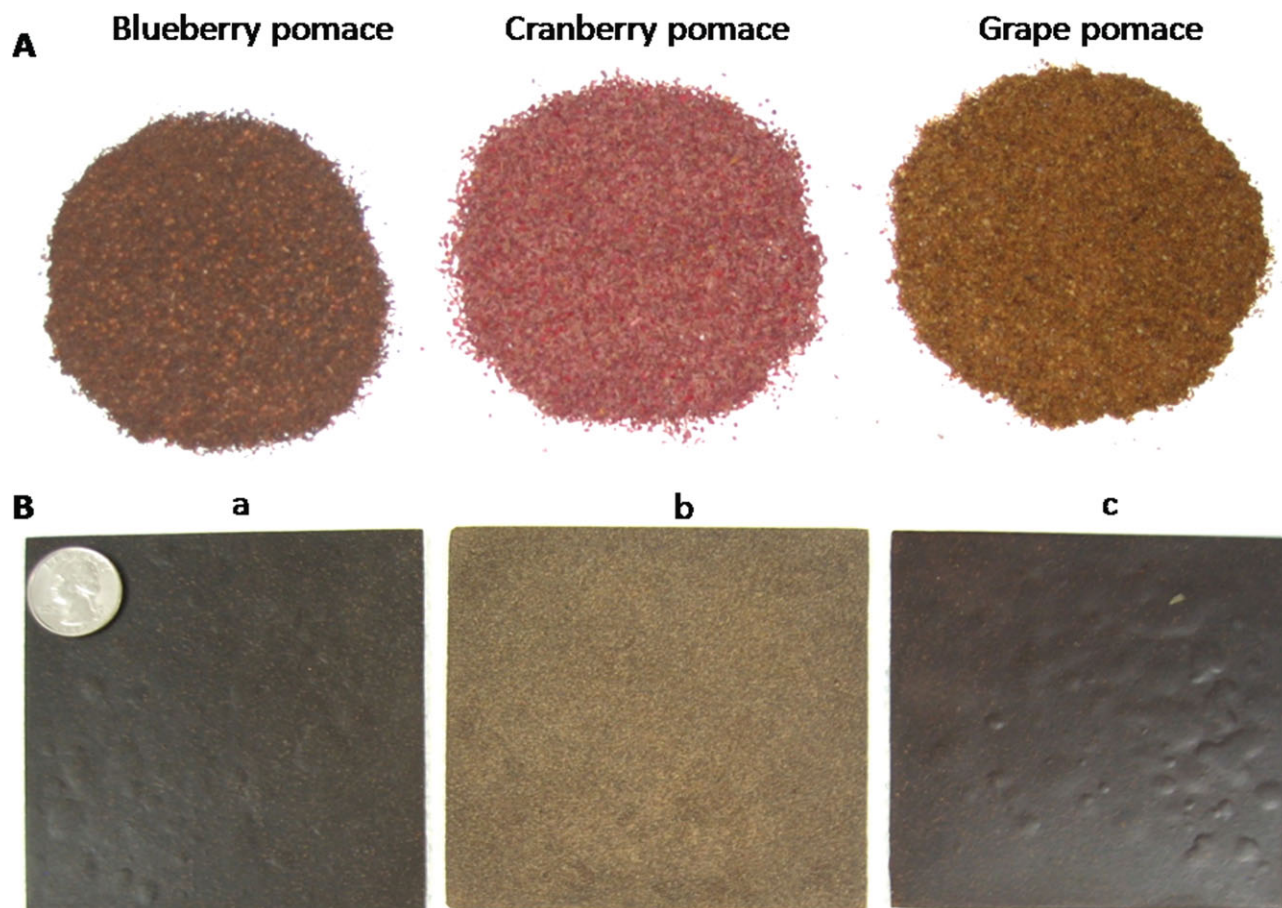
The pomace/SF biocomposite boards from different types of pomace had different and distinguishing appearances. The BP-based boards had the darkest color followed by the GP boards, probably because of the original dark color of the raw pomace materials [Fig. 1(A,Ba,Bb)]. The CP boards were yellowish, which may be explained by the degradation of the red pigments in CP by the high molding temperature of  $140^{\circ}\text{C}$  [Fig. 1(Bb)]. The GP boards had more uniform surfaces than those of blueberry or cranberry because seeds were removed from the GP and only the skin materials were used to form the boards [Fig. 1(Bc)], whereas for the other pomaces, seeds were retained in the raw pomace materials.

### Mechanical analysis

On the basis of the ANOVA results, the type of pomace and binder were significant factors affecting the measured mechanical properties, and there were significant ( $P < 0.05$ ) interactions between these two factors. Among all of the tested pomace boards, BP bound with P-XG had the highest BS and MOE values; the CP board had the lowest percentage strain values, whereas the GP board had the lowest MOE and highest percentage strain values (Table II). The BP board bound with P-XG had significantly ( $P < 0.05$ ) higher BS, MOE, and percentage strain values than those bound with SF. However, the binder type did not show different effects on the measured mechanical properties of the CP boards and only affected the MOE and percentage strain values of the GP boards.

BS, MOE, and percentage strain represent the flexural strength, stiffness, and flexibility of a material,





**Figure 1** (A) Pomace powders and (B) pomace/SF biocomposite boards formed by compression molding with a pomace/SF ratio of 1 : 1 plus 15% glycerol with respect to the total solid weight: (a) BP, (b) CP, and (c) GP. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

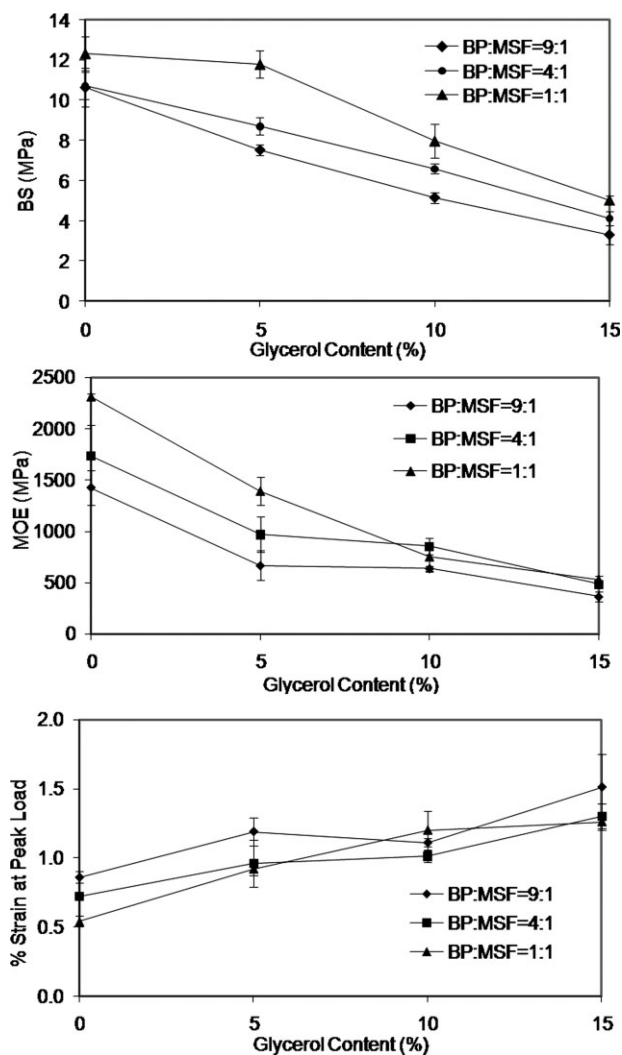
respectively. Hence, the BP/P-XG board was the stiffest, and the GP board was the most flexible and ductile material, no matter which type of binding material was used. BP had the strongest adhesion with P-XG, probably because of its high protein content (Table I), which functioned as a binder. The low MOE value of the GP board may be explained by its high ash content (Table I), which made it difficult for GP to be processed and adhere with the binders.<sup>29</sup> Although binding with P-XG provided the

highest BS and MOE values shown in this study, the material was very sticky and difficult to handle. SF was much more user friendly, thus it was chosen as the binder for further experiments. Among the three types of pomace bound with SF, the BP/SF board showed the highest BS and MOE values with a moderate percentage strain to break. Hence, BP was selected for further experiments in the formation of the biocomposite boards with different levels of MSF and plasticizer.

**TABLE II**  
Flexural Properties of the Biocomposite Boards Based on BP, CP, and GP

Pomace	Mechanical properties					
	BS (MPa)		MOE (MPa)		Strain at peak load (%)	
	SF	P-XG	SF	P-XG	SF	P-XG
BP	5.10 ± 0.55 <sup>a,A</sup>	10.25 ± 0.88 <sup>a,B</sup>	601 ± 58 <sup>a,A</sup>	884 ± 96 <sup>a,B</sup>	1.07 ± 0.06 <sup>a,A</sup>	1.26 ± 0.05 <sup>a,B</sup>
CP	4.07 ± 0.66 <sup>b,A</sup>	4.12 ± 0.57 <sup>b,A</sup>	664 ± 83 <sup>a,A</sup>	722 ± 120 <sup>b,A</sup>	0.74 ± 0.13 <sup>b,A</sup>	0.72 ± 0.07 <sup>b,A</sup>
GP	4.62 ± 0.51 <sup>a,b,A</sup>	4.38 ± 0.19 <sup>b,A</sup>	301 ± 42 <sup>b,A</sup>	215 ± 12 <sup>c,B</sup>	2.25 ± 0.36 <sup>c,A</sup>	4.20 ± 0.26 <sup>c,B</sup>

The pomace and binder were mixed in a 1 : 1 ratio, and 15% glycerol was added with respect to the total solid weight. P-XG was a mixture of pectin and xanthan gum with a 1 : 1 ratio. Means with different lowercase superscripts in the same column were significantly different by the Tukey test ( $P < 0.05$ ); means with different uppercase superscripts in the same row were significantly different by the Tukey test ( $P < 0.05$ ).



**Figure 2** Mechanical properties of the BP-based composites formed with MSF at different ratios and with different levels of added glycerol.

Overall, the BS and MOE values of the BP/MSF board increased and percentage strain decreased with increased MSF concentration (Fig. 2); this indicated that increased MSF level enhanced the material strength and stiffness but decreased the material flexibility. NaOH breaks internal hydrogen bonds that exist in coiled protein molecules and exposes the hydrogen bonds to available polar groups for stronger adhesion.<sup>28</sup> Previous studies have shown that protein molecules hydrolyzed in alkaline conditions produce peptide chains with high molecular weights, which can further enhance bonding strength.<sup>33</sup> The strong charge and polar interactions between the side chains of the soy protein molecules restricted segment rotation and molecular mobility, which led to increases in BS, MOE, and brittleness (a decrease in percentage strain) of the BP/MSF board. According to Cheng et al.,<sup>28</sup> SF is a rigid material and suitable as a reinforcement phase in biocompo-

sites as it improves the shear elastic modulus in composites compared to SPI. However, the effect of the MSF level on MOE and percentage strain values became less significant when the glycerol concentration was over 10% (Fig. 2); this means that the effect of glycerol became predominant.<sup>33</sup>

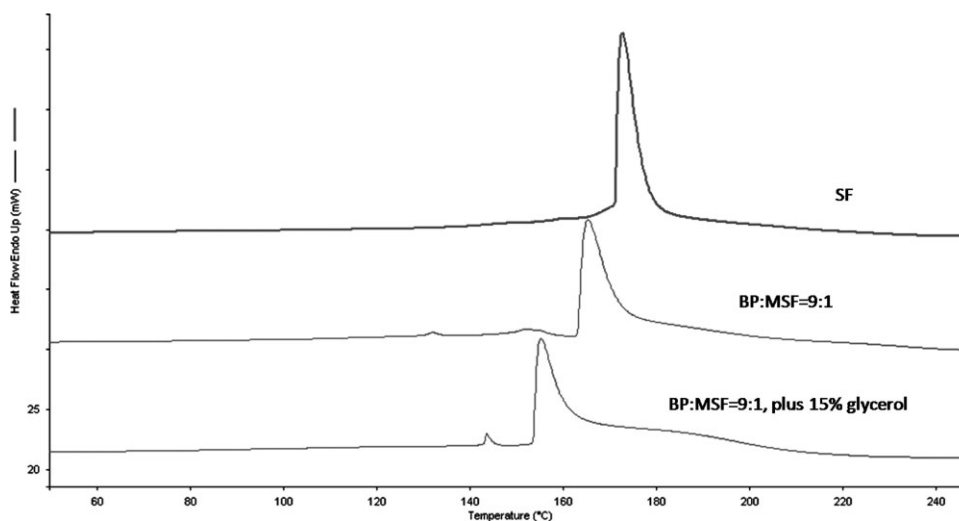
As expected, the addition of glycerol in the pomace board increased the percentage strain and decreased the BS and MOE values (Fig. 2); this made the material more flexible, weaker, and less stiff. As a plasticizer, glycerol decreased the interactions between the protein molecules and increased the flexibility, extensibility, and processability of the BP/MSF board.<sup>34,35</sup>

### Thermal analysis

The DSC results show a strong transition peak in the temperature range 150–190°C (Fig. 3). A major thermal transition at about 180°C was observed on the SF sample, which was believed to be associated with protein denaturation, as observed and discussed by Mo and Sun.<sup>36</sup> Soy protein consists of polar and non-polar side chains, and there are strong intramolecular and intermolecular interactions, such as hydrogen bonding and dipole–dipole, charge–charge, and hydrophobic interactions.<sup>29</sup> After binding with BP at a MSF/BP ratio of 1 : 9, the peak in the thermogram shifted to a lower temperature of about 168°C, which could be explained as some small molecular components in the pomace, including organic acids and sugars, reacting with the amino groups of the soy protein, improving the molecular mobility of the soy protein, and reducing the endothermic peak temperature.<sup>37–39</sup> Furthermore, the addition of pomace decreased the SF content in the biocomposite, which meant that the decreased amount of stiff chains and bonds could not easily coil and fold and needed more thermal energy for their denaturation.<sup>25</sup>

The addition of 15% glycerol into the BP/MSF mixture further decreased the endothermic peak temperature to about 158°C. As a plasticizer, glycerol can insert and position itself within the biopolymer network, reduce interactions between protein chains, and improve the segmental mobility of polypeptide chains,<sup>40</sup> thus decreasing the denaturation temperature of SF.<sup>25,36</sup>

Mo and Sun<sup>36</sup> observed the typical denaturation of SPI at two peaks, one at 139.7°C and one at 169.9°C, which corresponded to low-molecular-weight 7S globulins and high-molecular-weight 11S globulins, respectively.<sup>36</sup> Mo et al.<sup>15</sup> also pointed out that commercial soy protein products were denatured by various pretreatments and modifications, which resulted in no crystal melting transitions (no peak at DSC thermograms) that may have been caused by protein aggregation.



**Figure 3** DSC thermograms for the SF powder and BP/MSF biocomposites. The glycerol content was based on the total solid weight of BP and MSF.

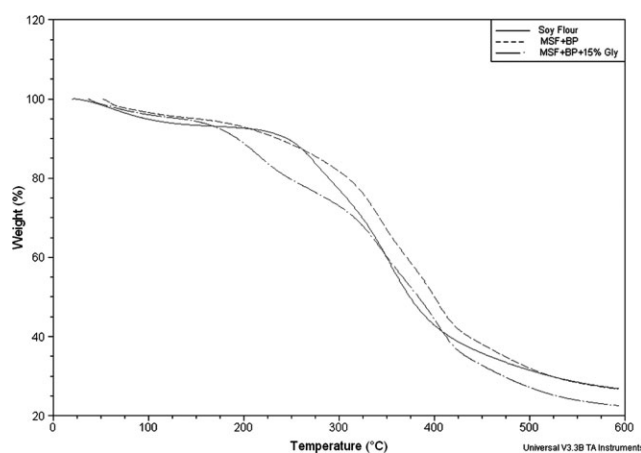
The TGA curves showed that as the temperature increased from 25 to 150°C, the weight (%) slightly decreased; this was probably due to the water evaporation of the samples (Fig. 4). Significant weight (%) drops occurred at about 227°C for the SF sample, 190°C for the BP/MSF = 9 : 1 biocomposite, and 156°C for the BP/MSF = 9 : 1 plus 15% glycerol sample. These temperatures corresponded to the beginning of thermal degradation. A pure SF sample underwent thermal decomposition with an initial degradation temperature of 227°C in a single-stage decomposition. For the BP/MSF blended sample, a slightly lower degradation temperature was observed, probably because of the relatively poor thermal stability of BP compared with SF. The addition of glycerol into the BP/MSF blend showed two-stage degradation, in which the first stage was

probably due to the thermal decomposition of the glycerol plasticizer.<sup>41</sup>

### Water absorption and solubility

On the basis of the ANOVA results, the glycerol level significantly ( $P < 0.05$ ) affected all of the measured water absorption properties, the MSF level affected water absorption at 2 h and water solubility but not water absorption at 24 h, and there was an interaction between the pomace and glycerol levels and water absorption at 2 and 24 h but not between the pomace and glycerol levels and water solubility.

Water absorption decreased, and water solubility increased with increased glycerol concentration in the boards (Table III). After 24 h of water immersion, the BP/MSF = 9 : 1 board with 15% glycerol had the lowest water absorption of 21%, compared to 52% for the nonglycerol board. A similar trend was observed for the 2-h water absorption test. These results were consistent with Sun et al.,<sup>23</sup> in which the molecular aggregate and the amount of glycerol in the molded boards both affected the water absorption. Glycerol increased the interactions between the fibers and protein, which could reduce the number of hydrophilic groups;<sup>42</sup> thus, the addition of more glycerol decreased the water absorption.<sup>38</sup> When the glycerol concentration increased from 0 to 15%, the water solubility increased from 28 to 38% and from 23 to 33% for the BP/MSF = 9 : 1 and BP/MSF = 1 : 1 board, respectively, after 24 h water immersion (Table III). In the plasticized boards, glycerol could be the main contributor to the loss of soluble materials, which likely consisted of plasticizer and some low-molecular-weight proteins.<sup>42,43</sup>



**Figure 4** TGA curves for the SF powder and BP/MSF biocomposites. The glycerol content was based on the total solid weight of BP and MSF.



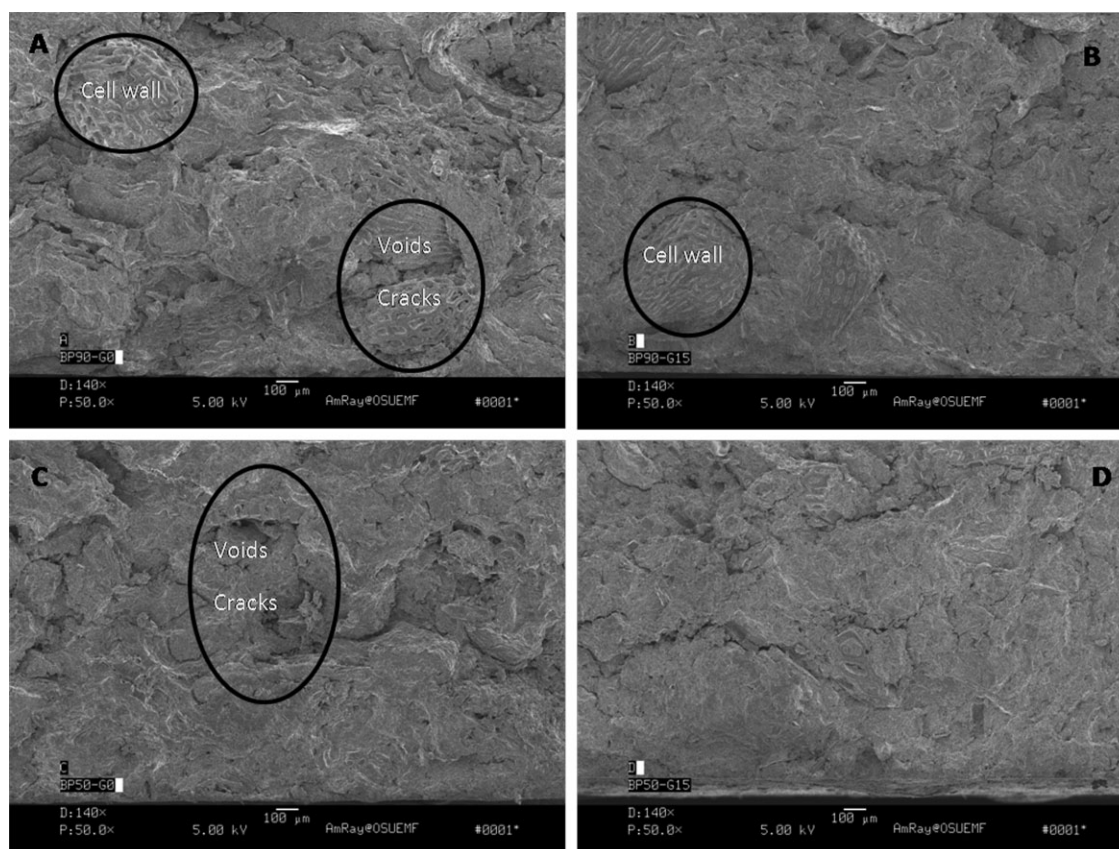
**TABLE III**  
**Water Absorption and Solubility of the BP-Based Biocomposite Boards**

Glycerol (%)	Absorption at 2 h (%)		Absorption at 24 h (%)		Solubility (%)	
	9 : 1 BP/MSF	1 : 1 BP/MSF	9 : 1 BP/MSF	1 : 1 BP/MSF	9 : 1 BP/MSF	1 : 1 BP/MSF
0	28.0 ± 1.6 <sup>a,A</sup>	20.1 ± 1.8 <sup>a,B</sup>	51.7 ± 3.8 <sup>a,A</sup>	43.9 ± 1.5 <sup>a,A</sup>	28.4 ± 0.5 <sup>a,A</sup>	23.4 ± 0.4 <sup>a,B</sup>
5	20.5 ± 0.6 <sup>b,A</sup>	19.7 ± 0.9 <sup>a,A</sup>	35.0 ± 1.3 <sup>b,A</sup>	38.0 ± 1.9 <sup>b,A</sup>	32.3 ± 0.3 <sup>b,A</sup>	27.3 ± 0.4 <sup>b,B</sup>
15	18.6 ± 1.7 <sup>b,A</sup>	19.2 ± 1.9 <sup>a,A</sup>	21.1 ± 0.3 <sup>c,A</sup>	25.5 ± 0.2 <sup>c,B</sup>	37.6 ± 0.3 <sup>c,A</sup>	33.1 ± 0.5 <sup>c,B</sup>

The amount of glycerol was based on the total solid weight of pomace and SF. The ratios are dry weight ratios of BP to MSF in the developed biocomposite boards. Means with different lowercase superscripts in the same column were significantly different by the Tukey test ( $P < 0.05$ ); means with different uppercase superscripts in the same row were significantly different by the Tukey test ( $P < 0.05$ ).

The ratio of BP to MSF did not affect the water absorption significantly ( $P > 0.05$ ) except for the water absorption at 2 h for the 0% glycerol board and the water absorption at 24 h for the 15% glycerol board (Table III). For the nonplasticized (0% glycerol) board, the BP/MSF = 9 : 1 board contained more hydrophilic compounds than the BP/MSF = 1 : 1 board;<sup>36,43</sup> thus, it absorbed water faster in the water absorption test. With added glycerol and a long period of water immersion, interactions between the glycerol and soy protein became the predominant factor affecting water absorption. According to Chen et al.,<sup>32</sup> there are glycerol-rich

and protein-rich domains in SPI sheets. The protein-rich domains, composed of the protein aggregates with relatively low compatibility to glycerol, were dispersed in the glycerol-rich domains, which were highly compatible with glycerol.<sup>32</sup> When the glycerol content reached 15%, the loose glycerol-rich domains occurred in the BP/MSF board, which led to higher water absorption. Mo et al.<sup>15</sup> reported water absorptions of 78 and 338% in the 2- and 24-h tests, respectively, for SPI plasticized with glycerol (25%). These numbers were significantly higher than our results. SF employment in multicomponent systems induces protein and/or carbohydrate interactions and forms



**Figure 5** SEM images of fracture surfaces of the BP and MSF biocomposite boards: (A) 9 : 1 BP/MSF without glycerol, (B) 9 : 1 BP/MSF plus 15% glycerol, (C) 1 : 1 BP/MSF without glycerol, and (D) 1 : 1 BP/MSF plus 15% glycerol. The glycerol content was based on the total solid weight of BP and MSF.



continuous and cohesive networks.<sup>44</sup> In the BP/MSF board, carbohydrate and soy protein macromolecules interacted to form carbohydrate–protein network structures that contributed to the lower water absorption of BP/MSF than of SPI as a matrix alone.<sup>15,45</sup> Water solubility increased with increasing BP content because SF had a poor solubility, whereas the small molecular weight components in the pomace were more soluble than SF.<sup>46,47</sup>

### Microstructure

The scanning electron microscopy (SEM) images of the BP/MSF board are presented in Figure 5. SEM images are often difficult to interpret, and those obtained in this project were no exception. Our general, and speculative, conclusions follow, and the areas of interest are marked in the corresponding figures. The cell wall in the pomace (as marked) in Figure 5(A,B) (BP/MSF = 9 : 1) were clearly observed, but with increasing binder concentrations, BP/MSF = 1 : 1 as shown in Figure 5(C,D), the cell wall was rarely seen and the surface of the samples were more compact. The addition of glycerol [Fig. 5(B,D)] appeared to result in relatively smoother fracture surfaces and more ductile failure compared to the nonplasticized samples [0% glycerol; Fig. 5(A,C), note some cracks as marked]. The nonplasticized samples showed a rough and heterogeneous fracture surface with large voids and clusters of various sizes. These voids and cracks in the BP/MSF = 1 : 1 boards [Fig. 5(C,D)] were perpendicular to the direction of the applied stress. These results suggest that the pomace-based boards showed increased ductility with added glycerol, which was consistent with the mechanical properties test results. A wide distribution of fragment sizes meant that there were fewer interactions among the protein molecules and thus more separation between phases.

### CONCLUSIONS

Among biocomposite boards made of three different types of pomaces with SF as a binder, BP-based boards showed the highest BS and MOE values with a moderate percentage strain value. The binding of BP with MSF further improved the adhesion and stiffness of the developed biocomposite board. Plasticizing with glycerol increased the flexibility while decreasing the stiffness of the boards. The addition of pomace and glycerol into SF shifted the endothermic peak temperature and degradation temperature of the materials to a lower temperature. Water absorption of the BP- and MSF-based biocomposites decreased and water solubility increased with increasing glycerol concentration. The ratio of pomace to MSF did not affect the water absorption, but

the water solubility increased with increasing pomace concentration. The addition of glycerol resulted in a smoother fracture surface of the composite board compared to the nonplasticized samples. In this study, we successfully demonstrated the feasibility of creating biodegradable composites from small fruit pomaces with the aid of SF as a binding material and glycerol as a plasticizer to achieve desired functionality. Hence, compression-molded fruit pomaces hold the potential to be good precursors for the development of biodegradable composites for industrial-scale applications, such as nursery pots, egg cartons, and condiment cups.

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