Compression-Molded Biocomposite Boards from Red and White Wine Grape Pomaces

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ABSTRACT: Biocomposite boards from red wine grape pomace (WGP; Pinot Noir) or white WGP (Morio Muscat) were investigated on the basis of crosslinking and thermal compression mechanisms. We used an orthogonal experimental design to optimize the formulations by examining the effects of binder type, pomace-to-binder (P/B) ratio, and hydrophobic and crosslinking agents on the mechanical properties, water sensitivity, and biodegradability of the board. The optimized formulations were as follows: (1) for red WGP boards, soy flour (SF) or soy protein isolate (SPI) and poly(vinyl alcohol) (PVA; 1 : 1) as binders at a P/B ratio of 19 : 1 with 1% stearic acid (SA) and 1% epichlorohydrin and (2) for white WGP boards, SF or SPI–PVA (1 : 1) as binders, with a P/B ratio of 4 : 1, and 1% SA. The red WGP boards showed a high break strength and modulus of elasticity with a moderate percentage strain value, whereas the white WGP boards had a high flexibility and biodegradability. After burial in soil for 30 days, the red and white WGP boards degraded by about 50 and 80%, respectively. Microstructure studies indicated that the use of binders and other functional agents resulted in a compact fracture surface of the WGP biocomposite boards.
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Key words: biodegradable; biopolymers; crosslinking; strength

INTRODUCTION

Wine grape pomace (WGP), the solids (skins, seeds, and stems of the wine grapes) left after the grapes are pressed for juice in winemaking, can be a serious environmental disposal problem.[1,2] Attempts have been made to use WGP, including in the production of ethanol,[3] in the extraction of grape seed oil,[4] and as a source of functional food ingredients, such as dietary fiber,[5] antioxidants,[6–9] antimicrobial agents,[10] and dietary supplements.[11] However, only a small fraction of the pomace is used for these purposes, and thus, a large quantity of bulk solids remains as biowaste. Hence, there is a great need for research into the utilization of WGP, especially in the area of converting pomace into value-added products.

WGP contains a variety of polysaccharides, including celluloses, hemicelluloses, pectin, and sugars, and small amounts of proteins, lipid, and polyphenolics. Some of these components (pectin, proteins, organic acids, and sugars) have thermoplastic properties and are good candidates for thermoforming application to make biocomposites.[12,13] Biocomposites consist of biodegradable polymers as the matrix material and biofibers as the biodegradable filler.[13–15] The thermoplastic components in WGP can form the composite matrix, and the nonthermoplastic parts can act as dispersed fillers. WGP can, thus, be processed to create biocomposites through the incorporation of biopolymers, such as binding materials, plasticizers, and other functional additives, to achieve desired mechanical properties, water sorption, and biodegradability.[13]

Our previous study reported the development of biocomposite boards from berry fruit pomaces.[13] The study found that high-molecular-weight biodegradable polymers of soy flour (SF), pectin, and xanthan gum could be used as polymeric binders and glycerol could be used as a plasticizer to improve the mechanical properties, whereas the pomace-to-binder (P/B) ratio was a key factor in determining the water absorption (W_a) and water solubility (W_s) of the pomace boards.[13] However, the biocomposites developed from berry fruit pomaces and SF had lower mechanical properties compared to conventional plastics and were also brittle and susceptible to moisture because of their hydrophilic characteristics.[13] Therefore, further efforts are necessary to reduce the moisture sensitivity and to simultaneously improve the mechanical properties of pomace-based biocomposites by the

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incorporation of hydrophobic materials and crosslinking agents to enhance the interactions between the filler and matrix materials without detriment to their biodegradability.[16–18] Hydrophobic lipids, such as long-chain fatty acids, waxes, oils, and surfactants are known to exhibit hydrophobic properties and good structural properties.[19,20]

When WGP-based biocomposites are developed, different formulations should be considered for red and white WGPs because their chemical composition can be significantly different because of the different varieties of wine grapes used and the different winemaking processes they undergo.[11] White WGPs are obtained immediately after crushing without fermentation and are, thus, rich in sugars, nitrogen, and amino acids, whereas red WGPs are the residuals after fermentation, in which sugars and many other compounds have been removed.[11]

The objectives of this study were to investigate the use of different binding materials and functional modifiers, such as plasticizers, hydrophobic compounds, and crosslinking agents, to improve the mechanical properties, water resistance, and biodegradability of red and white WGP boards and to optimize the formulations to tailor specific systems for specific applications. SF and soy protein isolate (SPI)[21,22] were good candidates as binding materials because of their abundant availability and proven effectiveness, as shown in our previous study.[13] In addition, poly(vinyl alcohol) (PVA), a hydrophilic and low-cost polymer, has excellent mechanical strength and thermal and chemical stability and has been successfully used in other composite materials.[23,24] These biopolymers are all environmentally friendly and economical.[23] According to our preliminary studies, the combination of different binding materials together may provide better functionality than a single material alone. Hence, mixtures of SF and PVA (1 : 1) and SPI and PVA (1 : 1) were used as binders to augment the matrix in this study. Our preliminary studies also found that poly(ethylene glycol) (PEG), because of its less hydrophilic nature and higher molecular weight,[25–27] makes more rigid pomace boards than glycerol, and this was further evaluated in this study. Moreover, the incorporation of stearic acid (SA) as a hydrophobic compound[19,20] and epichlorohydrin (ECO) as a crosslinking agent[16–18,27] caused improvements in the strength, thermal properties, and water sorption of the biocomposites. They were, thus, used in the product formulation.

EXPERIMENTAL

Materials

Two white WGPs, Morio Muscat (MM) and Müller Thurgau (*Vitis vinifera*) were obtained from a private winery in Corvallis, Oregon. One red WGP, Cabernet Sauvignon (*V. vinifera*), was obtained from a commercial winery in Kennewick, Washington, and two other red WGPs, Pinot Noir (PN) and Merlot (*V. vinifera*), were obtained from Oregon State University Research Winery, Corvallis, Oregon. The pomaces were packaged in poly(ethylene terephthalate) containers and stored at −18°C until use. Defatted SF (industrial, 100/90) with about 7% water, 50% protein, and 2% oil and SPI with 90% protein were obtained from Cargill, Inc. (Minneapolis, MN) and were used without any further treatment. PVA (99% hydrolyzed, molecular weight = 89,000–98,000) was purchased from Sigma-Aldrich Co. (St. Louis, MO), PEG (PEG 400) was purchased from Merck KGaA (Darmstadt, Germany) as a plasticizer, ECO was purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan) as a crosslinking agent, and SA was purchased from Integra Chemical Co. (Renton, WA) as a hydrophobic agent.

Preparation of the WGP

Frozen pomace was thawed at room temperature, seeds and stems were discarded, and only the skin materials were used. The pomace was ground with a disintegrator (M8A-D, Corenco, Inc., Sebastopol, CA) equipped with a Cornider screen. To obtain a consistent moisture content (MC) in the pomace materials, they were dried overnight in a T10RS environmental chamber (Tenney Environmental, Williamsport, PA) set at 70°C and 10% relative humidity (RH) and then stored at room temperature until use. The MC and total soluble solid content (TSSC) of the wet pomace materials and the basic chemical composition of the dried pomace were measured with Association of Official Analytical Chemists standards[12,13] and are reported in Table I. No significant differences in the measured chemical composition among three red WGPs or the two white WGPs were detected; thus, only one white WGP (MM) and one red WGP (PN) were used for this study.

Experimental design

Two separate experiments were conducted. The first one was done to develop optimal formulations for the pomace boards for each WGP with an orthogonal experimental design.[28–30] Orthogonal experimental design is an optimization method for studying multiple factors with an orthogonal table to arrange the experiment scientifically and to evaluate multiple factors, so it requires a minimum number of experiments with symmetrical distribution of the data points. The corresponding range analysis, variance analysis, and regression analysis methods can be used

TABLE I
Basic Chemical Compositions of Five WGPs

	Wet pomace					Dried pomace powder (% dry matter)			
Variety of pomace	Skin (%)	Seed (%)	Stem (%)	MC (%)	TSSC (%)	Protein	Fat	Carbohydrate	Ash
MM	85.99	12.77	1.25	74.9 ± 0.75	83.9 ± 1.64	5.38	1.14	90.18	3.31
Muller Thurgau	90.67	7.84	1.49	72.4 ± 0.38	72.4 ± 1.52	6.54	2.64	88.29	2.53
Cabernet Sauvignon	77.41	20.91	1.68	73.9 ± 0.42	28.2 ± 1.67	12.34	6.33	73.73	7.59
PN	73.35	12.34	0.54	73.7 ± 0.56	27.7 ± 2.49	12.13	4.74	76.96	6.17
Merlot	83.18	14.98	1.84	75.1 ± 0.13	22.2 ± 1.67	11.26	3.35	77.60	7.79

The carbohydrate content was calculated as 100 −(Protein + Fat + Ash).

to analyze the testing results to obtain valuable conclusions. The properties optimized were the mechanical properties, water resistance, and biodegradability. The factors considered were the binding material, the P/B ratio, and the hydrophobic and crosslinking agents. On the basis of our preliminary tests, the following materials and their concentrations were evaluated: binder types [SF, PVA, SF–PVA (1 : 1), and SPI–PVA (1 : 1)], P/B ratios (19 : 1, 9 : 1, and 4 : 1), and concentrations of hydrophobic agent (1 or 3% SA) and crosslinking agent (0.5 or 1% ECO). An orthogonal experimental design L_8 (41×2^4) in triplicate was performed (Table II). In all formulations, 15% PEG 400 (total solid weight of pomace and binder) was added as a plasticizer to improve the flexibility and obtain moderate strength in the case of the red WGP boards. For white WGP boards, the plasticizer was not used because of the high sugar content of the white WGP, which could act as a plasticizer.[27] Instead, high concentrations of binder (P/B ratios = 9 : 1 and 4 : 1) were necessary to improve the stiffness of the white WGP boards (Table II). In addition, the addition of a crosslinking agent into white WGP board increased the water resistance but decreased the mechanical properties of the board (data not shown). We believed that the high P/B ratio in the white WGP boards provided enough strength and sufficient crosslinking between the pomace and binder. Hence, a crosslinking agent was unnecessary for the white WGP boards (Table II).

In the second experiment, the optimal formulations obtained from the first experiment were used to make WGP boards, and their mechanical properties, W_a and W_s, thermal properties, biodegradability, and microstructure were evaluated. The results were compared with those of pomace boards made without the use of any functional compounds.

Preparation of biocomposite boards from WGP

Pomace, binder, and other functional compounds, as described in Table II, were mixed together in a preheated Brabender counterrotating batch mixer (Intelli-Torque Plasticorder, C. W. Brabender Instruments, Inc., South Hackensack, NJ) with roller blades attached at 40 rpm and at 90°C for 10 min.[13] Each mixture was reground with a mill (Thomas Scientific, Swedesboro, NJ) with 20-mesh rack to control the particle size of the mixtures. A 38 ± 1 g aliquot of the mixture was molded in a 101.6 × 101.6 × 2 mm^3 steel mold with a Carver laboratory hot press (Carver, Inc., Wabash, IN) at 10 MPa for 10 min. The set temperature was 130°C. After it was cooled under pressure under ambient conditions for 2 h, the thermoformed biocomposite board was separated from the mold and stored at room temperature until testing.

Analysis of the mechanical properties

The mechanical properties of the developed biocomposite boards were measured by three-point bending tests in accordance with ASTM D 790-03 with a Sintech testing machine (MTS Systems Corp., Enumclaw, WA). Sample specimens 12.5 × 2.5 ×

TABLE II
Factors and Levels for the Orthogonal Design of the Pomace Board Study

	PN[a]					MM		
Label	A Binder	B P/B ratio	C SA (%)	D ECO (%)	Label	A Binder	B P/B ratio	C SA (%)
1	SF	19 : 1	1	0.5	1	SF	9 : 1	1
2	PVA	4 : 1	3	1.0	2	PVA	4 : 1	3
3	SF + PVA (1 : 1)	—	—	—	3	SF + PVA (1 : 1)	—	—
4	SPI + PVA (1 : 1)	—	—	—	4	SPI + PVA (1 : 1)	—	—

[a] PEG400 was added at 15% of total solids weight in red WGP boards.

60 mm were cut and conditioned at 30°C and 50% RH for 2 days. The support span was set at 50 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 three measurement replications is reported for each sample.

Thermal analysis

Differential thermogravimetric analysis (DTGA) was carried on thermogravimetric analysis (TGA) spectra with a TA Instruments 2920 instrument (TA Instruments, New Castle, DE). The samples were subjected to a heating rate of 20°C/min at a temperature range of 20–500°C in air at ambient MC.[13] About 10 mg of sample was used for each measurement. The original WGP material was included in all of the scans, and two measurement replications were conducted.

W_a and W_s

Water sensitivity (measured as W_a and W_s) was tested according to ASTM D 570-98 with some modifications.[13] Sample specimens (12.5 × 2.5 × 60 mm^3) were preconditioned by drying at 50°C and 10% RH for 24 h, weighed, submerged in distilled water at 23°C for 24 h, and reweighed after the removal of its surface excess water with a dry paper towel. The weight gain after immersion was calculated as the percentage ratio of the increase in the weight of the submerged specimen to the weight of the initial dry specimen.[13] After 24 h of water immersion, the sample residues were dried at 105°C for 24 h and weighed again. W_s was calculated as the percentage weight loss of the specimen after immersion in water to the initial weight of the dry specimen.[13]

Microstructure

The microstructures of the surface and fractured cross section of the biocomposite boards were evaluated with scanning electron microscopy (SEM; 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 a gold–palladium alloy with a sputter coater (Edwards model S150B sputter coater; BOC Edwards Vacuum, Ltd., West Sussex, United Kingdom) to improve their interfacial conductivity. Digital images of the board fractured surfaces were collected at an accelerating voltage of 5 kV.

Soil burial degradation test

Soil burial degradation tests were carried out at ambient temperature under moisture-controlled conditions.[31,32] Duplicate specimens (15 × 2.5 × 30 mm^3) of each board were buried in a series of glass vessels containing moisturized potting soil (MC ≈ 40%). The samples were dug out from the soil at predetermined time points, carefully washed under a gentle water stream to remove surface soil particles, and then dried at 105°C to a constant weight. The biodegradation was expressed as the percentage ratio of the weight loss of the buried sample to the weight of the initial sample.

Data analysis

First, PROC GLM for analysis of variance was performed for all of the treatments with the SAS program (SAS 9.2, SAS institute, Inc., Cary, NC) to determine the significance of each factor on each functional property. The least squares difference (LSD) test was used for the comparisons of multiple means on the basis of a 95% confidence level.

Second, an orthogonal range analysis (ORA) was conducted to optimize the formulations of the WGP boards studied in the orthogonal experimental design. In ORA, two parameters were calculated as criteria for the selection of the optimal formulations. The first one, K_{ij} was the average value of each measured functional parameter for each factor i (i = A, B, C, or D) under each level j (j = 1, 2, 3, or 4), K_{ij}, and was expressed as

$$K_{ij} = \frac{1}{N_i}\sum_{u=1}^{N_i} y_{i,j,u} \quad (1)$$

where N_i is the number of trials for each factor i (N_i = 2 when i = A and N_i = 4 when i = B, C, or D) and $y_{i,j}$ is the objective function value of factor i at level j.

The second parameter was the extreme deviation for each measured functional parameter, that is, the range between the maximum and the minimum K_{ij} (R_i) and was calculated as

$$R_i = \left(K_{ij}\right)_{\max} - \left(K_{ij}\right)_{\min} \quad (2)$$

The K_{ij} and R_i values for the red and white WGP boards are reported in Tables III and IV, respectively. A large R_i value indicates a large effect of a factor on a given parameter, whereas the best treatment level for each factor can be chosen on the basis of the designable functionalities for that factor and K_{ij} values. The following targeted material functionalities were used to optimize the formulations of the WGP biocomposite boards: (1) high BS and moderate MOE and percentage strain, (2) low water sensitivity, (3) high thermal degradation temperature, and (4) high soil burial

TABLE III
Optimization of the Formulations for the PN Pomace Board

No.		Factor (i)[a] A	B	C	D	BS (MPa)	MOE (MPa)	Strain (%)	W_a at 24 h (%)	W_s at 24 h (%)	Biodegradation (%)
1		1	1	1	1	4.33	155.06	2.4	40.16	19.04	39.3
2		1	2	2	2	4.96	260.12	1.87	38.31	18.84	46.9
3		2	1	1	2	4.27	182.04	2.3	40.37	17.79	43.2
4		2	2	2	1	3.41	358.93	1.33	44.54	16.26	40.2
5		3	1	2	1	4.28	292.08	1.77	41.01	17.84	39.4
6		3	2	1	2	3.7	138.87	2.57	41.59	18.38	40.5
7		4	1	2	2	5.53	395.46	1.33	39.58	17.07	37.4
8		4	2	1	1	3.06	320.18	1.10	39.36	15.73	41.8
BS (MPa)	K_{i1}	4.65	4.60	3.84	3.77			D > B > A > C $A_1B_1C_2D_2$			
	K_{i2}	3.84	3.78	4.545	4.62						
	K_{i3}	3.99	—	—	—						
	K_{i4}	4.30	—	—	—						
	R_i	0.81	0.82	0.71	0.85						
MOE (MPa)	K_{i1}	207.59	256.16	199.04	281.56			A > C > D > B $A_4B_2C_2D_1$			
	K_{i2}	270.49	269.53	326.65	244.12						
	K_{i3}	215.48	—	—	—						
	K_{i4}	357.82	—	—	—						
	R_i	150.23	13.37	127.61	37.44						
Strain (%)	K_{i1}	2.14	1.95	2.09	1.65			A > C > D > B $A_3B_1C_1D_2$			
	K_{i2}	1.82	1.72	1.58	2.02						
	K_{i3}	2.17	—	—	—						
	K_{i4}	1.22	—	—	—						
	R_i	0.96	0.23	0.52	0.37						
W_a at 24 h (%)	K_{i1}	39.25	40.28	40.37	41.27			A > D > B > C $A_1B_1C_1D_2$			
	K_{i2}	42.46	40.95	40.86	39.96						
	K_{i3}	41.3	—	—	—						
	K_{i4}	39.47	—	—	—						
	R_i	3.22	0.67	0.49	1.31						
W_s at 24 h (%)	K_{i1}	18.94	17.94	17.74	17.22			A > D > B > C $A_4B_2C_2D_1$			
	K_{i2}	17.03	17.30	17.50	18.02						
	K_{i3}	18.11	—	—	—						
	K_{i4}	16.4	—	—	—						
	R_i	2.54	0.63	0.23	0.80						
Biodegradation (%)	K_{i1}	43.09	39.83	41.18	40.16			A > B > D > C $A_1B_2C_1D_2$			
	K_{i2}	41.71	42.32	40.97	41.99						
	K_{i3}	39.92	—	—	—						
	K_{i4}	39.58	—	—	—						
	R_i	3.51	2.49	0.22	1.83						

Strain = percentage strain at peak load (%); biodegradation = weight loss of the samples after burial in soil for 60 days (%).
[a] See Table II for the factors A, B, C, D, and their levels.

biodegradability. Hence, the treatment levels corresponding to high K_{ij} values were chosen with respect to the mechanical properties and biodegradability, whereas low values on W_a were desirable; therefore, treatment levels corresponding to low K_{ij} values were selected with regard to water sensitivity. With ORA, the orders of the factors influencing the performance, the significance levels of the different factors, and the optimized formulations were determined.

RESULTS AND DISCUSSION

Optimization of the pomace board formulations with an orthogonal experimental design

The significance of each factor for each measured functional property was determined on the basis of the analysis of variance results. For the red WGP boards, factor A (binder type) significantly ($p < 0.05$) affected all of the measured properties except biodegradability. Factor B (P/B ratio) had a significant ($p < 0.05$) effect on BS and percentage strain but not on water sensitivity ($p > 0.05$). Factor C (hydrophobic agent concentration) and factor D (crosslinking agent concentration) only affected the mechanical properties ($p < 0.05$). For the white WGP boards, factor A (binder type) was a significant factor that affected all of the functional properties. Factor B (P/B ratio) had a significant ($p < 0.05$) effect on BS, MOE, and W_a. Factor C (hydrophobic agent concentration) only significantly ($p < 0.05$) affected the percentage strain.

Effect of the binder type (factor A)

The R_i value was the largest for factor A on all of the measured properties, except BS of the red WGP

TABLE IV
Optimization of the Formulations for the MM Pomace Board

No.		Factor (*i*) A	B	C	BS (MPa)	MOE (MPa)	Strain (%)	W_a at 24 h (%)	W_s at 24 h (%)
1		1	1	1	0.62	13.98	3.93	3.65	53.21
2		1	2	2	1.41	39.21	3.9	3.6	47.07
3		2	1	1	0.34	8.09	3.83	5.66	51.96
4		2	2	2	0.62	27.62	3.2	8.67	46.59
5		3	1	2	0.57	16.08	3.6	3.51	51.44
6		3	2	1	0.94	27.86	4.27	4.45	47.48
7		4	1	2	0.44	13.01	3.9	5.82	51.09
8		4	2	1	1.13	35.91	3.97	2.21	44.81
BS (MPa)	K_{i1}	1.02	0.49	0.76			$A = B > C$ $A_1B_2C_2$		
	K_{i2}	0.48	1.03	0.76					
	K_{i3}	0.76	—	—					
	K_{i4}	0.79	—	—					
	R_i	0.54	0.54	0.00					
MOE (MPa)	K_{i1}	26.60	12.79	21.46			$B > A > C$ $A_1B_2C_2$		
	K_{i2}	17.86	32.65	23.98					
	K_{i3}	21.97	—	—					
	K_{i4}	24.46	—	—					
	R_i	8.74	19.86	2.52					
Strain (%)	K_{i1}	3.92	3.82	4.00			$A > C > B$ $A_{34}B_2C_1$		
	K_{i2}	3.52	3.84	3.65					
	K_{i3}	3.94	—	—					
	K_{i4}	3.94	—	—					
	R_i	0.42	0.02	0.35					
W_a at 24 h (%)	K_{i1}	13.91	10.60	9.82			$A > C > B$ $A_2B_2C_1$		
	K_{i2}	7.85	9.85	10.62					
	K_{i3}	9.56	—	—					
	K_{i4}	9.57	—	—					
	R_i	6.07	0.75	0.80					
W_s at 24 h (%)	K_{i1}	3.63	4.66	3.99			$A > C > B$ $A_1B_1C_1$		
	K_{i2}	7.17	4.73	5.40					
	K_{i3}	3.98	—	—					
	K_{i4}	4.02	—	—					
	R_i	3.54	0.07	1.41					

See Table II for factors A, B, C, and their levels. Strain = percentage strain at peak load (%).

boards (Table III) and MOE of the white WGP boards (Table IV). The tested polymer binders showed different effects on the measured mechanical properties and water sensitivity of both the red and white WGP boards. For the red WGP boards, those containing SF had higher BS, percentage strain, W_s, and biodegradation values but lower MOE values, whereas the boards with SPI and PVA had lower W_s and percentage strain values. For the white WGP boards, those containing SF had higher BS, MOE, and W_a values, whereas the boards containing PVA had lower mechanical properties and higher W_s values.

SF contains about 55% protein and about 32% carbohydrate. Soy protein is a globular protein. Its aggregates are similar to colloidal aggregates, which are rigid and suitable as a reinforcement phase in the biocomposite to improve the elastic modulus in the biocomposite. Soy carbohydrate is a nonglobular and film-forming material and improves the flexibility and water sensitivity of the biocomposite.[33] WGP fibers and soy protein macromolecules interacted to form carbohydrate–protein network structures, which contributed to a higher BS and lower W_a. This result was in agreement with our previous findings for berry-fruit-pomace-based biocomposites.[13] The boards containing PVA showed a high flexibility and water sensitivity, which may have been because PVA is a water-soluble polymer and contains highly hydrophilic groups, which tend to increase the water sensitivity.[23] A study by Lee et al.[22] on red clay composites reinforced with fully hydrolyzed PVA also showed the highest flexural strength.

Greater reinforcement (high MOE value) was observed when SPI was used as a binder in the red WGP boards. Among all of the polymer binders evaluated in this study, SPI–PVA resulted in a maximum improvement in MOE and water resistance in the red WGP boards. SPI contains about 90% protein, which consists of polar and nonpolar side chains and leads to hydrogen bonding, dipole–dipole interactions that restrict the mobility of chain segment rotation, and molecular mobility.[34] The use

of two binding materials may allow increased interactions between a broader array of components in a composite mixture.[35] Increasing the protein and/or carbohydrate interactions in a multicomponent systems may form continuous and cohesive networks, which in turn, may increase the coherence between the pomace and polymeric binders.[36]

According to the K_{ij} values (Table III), K_{A1} and K_{A4} on BS and W_a and K_{A1} and K_{A3} on percentage strain were almost equal. That is, SF (A_1) and SPI–PVA (1 : 1; A_4) had a similar influence on BS and W_a, and A_1 and SF–PVA (1 : 1; A_3) had a similar influence on the percentage strain. However, A_4 resulted in the highest MOE and the lowest W_s, whereas A_1 resulted in the highest level of biodegradation in the red WGP boards. With all of these results in mind, A_1 and A_4 were chosen as the binders in the red WGP boards for further study. For white WGP boards, the binder type showed a similar effect as that in the red WGP boards on the basis of the ORA results (Table IV); thus, A_1 and A_4 were also selected as the binders in the white WGP boards.

Effect of the P/B ratio (factor B)

According to the R_i values, factor B had the least effect on MOE and the percentage strain in the red WGP boards but the largest effect on MOE and the least effect on the percentage strain, W_a, and W_s in the white WGP boards. The low P/B ratio led to a low BS and high biodegradability in the red WGP boards (Table III) but a high BS and MOE and low W_a in the white WGP boards (Table IV).

The effect of the P/B ratio on BS in the red WGP boards was inconsistent with our previous findings, in which a decrease in the P/B ratio increased BS of blueberry pomace and modified SF boards.[13] This different result may have been a decreasing effect of the binder level on the properties as additional functional compounds were included in the composite. As shown in Table III, the R_i value of factor D (concentration of the crosslinking agent) was higher than that of factor B. The low P/B ratio also resulted in a low percentage strain, which was also observed in our previous results.[13] The P/B ratio had no significant ($p > 0.05$) effect on the water sensitivity, although the board with a P/B ratio of 19 : 1 contained more hydrophilic compound than that the board with a P/B ratio of 4 : 1. This result was probably due to the addition of hydrophobic and crosslinking agents in the formulation. A high P/B ratio led to low biodegradation after soil burial for 60 days (Table III). Pomace contains mainly cell-wall polysaccharides, which are mostly fibers that serve as the filler in a matrix of the binders in these biodegradable composites.[27] As microorganisms consumed the material, the composites lost their structural integrity, which led to further degradation.[32] Compared to the polymeric binders, the pomace fibers showed a much higher crystallinity, and this rendered them relatively resistant to degradation by microorganisms compared to the binders.[31]

For the white WGP boards, the effect of the P/B ratio was different from the red WGP boards. The white WGP alone could be thermally pressed into a board without the addition of any other functional compounds, but the board was very soft and, thus, not very useful. On the basis of our preliminary work, a high concentration of binding material was necessary to improve the stiffness and other mechanical properties of the pomace-based composites. As shown in Table I, TSSC of MM pomace was significantly higher than that of PN pomace, 83.9% versus 27.7% dry base (db); this suggested a high soluble sugar content. Soluble sugar is an efficient plasticizer because it tends to reduce the intermolecular forces along polymer chains and to increase the polymer chain mobility and, thereby, improve the flexibility and extensibility, but this makes the material weaker and not as stiff.[27,37,38] A high P/B ratio in the white WGP boards meant a high amount of water-soluble sugars; this, in turn, resulted in an increased W_s in the white WGP boards. After 60 days of soil burial, the white WGP boards had completely vanished; that is, they experienced complete degradation. This was probably because of the high sugar content and the lack of crosslinking agents. A similar result was reported by Domenek et al.[32] in wheat gluten-based bioplastics, which were fully degraded within 50 days in farmland soil.

On the basis of the previous discussions, the boards with high P/B ratios exhibited better mechanical properties without a significant reduction in the water resistance and biodegradability in the red WGP boards. Because the purpose of this study was to fully use pomaces as a source for biocomposites, a P/B ratio of 19 : 1 (B_1) was selected as the optimal P/B ratio for the red WGP boards. Although for white WGP boards, a low P/B ratio led to high mechanical properties and low W_s without affecting the biodegradation, a P/B ratio of 4 : 1 (B_2) was chosen for the white WGP boards.

Effect of the hydrophobic agent concentration (factor C)

On the basis of the R_i values, factor C showed lesser effects on the BS, W_a, W_s, and biodegradation of the red WGP boards and on the BS and MOE of the white WGP boards compared with factors A and B. Our preliminary studies showed that the addition of less than 1% SA decreased W_a and W_s for both the red and white WGP boards (this was also confirmed in a later study, as reported in Table V). This was

likely because the carboxylic groups of SA reacted with the amine, imine, and hydroxyl groups of soy protein to anchor SA to the structure, and then, the long hydrocarbon chain of SA increased the hydrophobicity of the resulting composite.[19] However, the addition of greater than 1% SA (3%, as shown in Tables III and IV) did not improve the water resistance but decreased the percentage strain in this study, which may have been because high concentrations of SA reduced the interfacial adhesion between the binders and pomace and led to decreased internal bond strength.[20] This result was in agreement with those of Lodha and Netravali[20] for SA-modified SPI plastic, in which MOE was increased and the percentage strain was decreased when the SA concentration was increased to 30%. A higher SA concentration did not significantly ($p > 0.05$) affect W_a and W_s. Therefore, 1% SA (C_2) was chosen as the optimal concentration in both the red and white WGP boards.

Effect of the crosslinking agent (factor D)

Factor D had the largest R_i value for BS and the second largest value for W_a and W_s of the red WGP boards (Table III). Increasing the ECO concentration increased BS and the percentage strain of the red WGP boards, probably because ECO could form covalent bonds with the amino groups of soy protein and the hydroxyl groups of pomace polysaccharide.[34] High concentrations of ECO also increased the number of intermolecular crosslinks in the composite, which may have stabilized the structure and reduced the effect of the plasticizers.[17,18] Zhang et al.[34] studied the covalent crosslinking of ECO with soy protein molecules and found that the interactions stiffened the soy protein molecules; this led to an increase in the Young's modulus.

An increased ECO concentration also significantly ($p < 0.05$) reduced W_a of the red WGP board (Table III). No crumbling or disintegration of the board was observed throughout the experiment. With increased concentration of crosslinking agent, interactions between the ECO, pomace, and binders became a predominant factor affecting W_a.[39] Therefore, 1% ECO (D_2) was chosen in the red WGP board.

Another consideration was the different applications of the white WGP boards from the red ones. Red WGP biocomposites that are high in BS and low in water sensitivity may be used to make containers, such as nursery pots, that require good mechanical strength and water resistance, whereas white WGP biocomposites with moderate mechanical properties and water resistance are more appropriate for other applications, such as nursery pot covers to prevent weed growth. Also, without the use of a crosslinking agent, materials can degrade much faster (as confirmed in a later experiment, see Fig. 3, shown later)

TABLE V
Validation of the Optimal Formulations

WGP	Optimum formulation						Property					
	Treat	Binder	P/B	SA (%)	ECO (%)	PEG (%)	Density (g/mm^3)	MC (%)	BS (MPa)	MOE (MPa)	Strain (%)	W_a (%)	W_s (%)
Red (PN)	Control	SF	19 : 1	—	—	15	$1.07 \pm 0.01^{a,A}$	$6.14 \pm 0.03^{a,A}$	$3.49 \pm 0.30^{a,A}$	$144.41 \pm 32.96^{a,A}$	$1.50 \pm 0.10^{a,A}$	$46.32 \pm 1.61^{a,A}$	$21.94 \pm 0.22^{a,A}$
	1	SF	19 : 1	1	1	15	$1.07 \pm 0.01^{a,A}$	$6.42 \pm 0.01^{a,A}$	$4.22 \pm 0.28^{b,B}$	$248.21 \pm 29.61^{b,B}$	$1.43 \pm 0.06^{a,A}$	$33.69 \pm 0.96^{b,B}$	$16.70 \pm 0.26^{b,B}$
	2	SPI–PVA (1 : 1)	19 : 1	1	1	15	$1.06 \pm 0.01^{a,A}$	$6.09 \pm 0.24^{a,A}$	$4.60 \pm 0.03^{c,B}$	$428.83 \pm 18.36^{c,C}$	$1.53 \pm 0.21^{a,A}$	$33.37 \pm 1.78^{b,B}$	$16.21 \pm 0.91^{b,B}$
White (MM)	Control	SF	4 : 1	—	—	—	$1.15 \pm 0.01^{b,A}$	$13.05 \pm 0.18^{b,A}$	$0.96 \pm 0.06^{d,A}$	$30.58 \pm 0.71^{d,A}$	$4.57 \pm 0.32^{b,A}$	$6.87 \pm 0.41^{c,A}$	$55.30 \pm 0.94^{c,A}$
	1	SF	4 : 1	1	—	—	$1.16 \pm 0.01^{b,A}$	$13.45 \pm 0.19^{b,A}$	$1.32 \pm 0.01^{e,B}$	$44.62 \pm 3.74^{e,B}$	$4.07 \pm 0.12^{c,B}$	$2.46 \pm 0.45^{d,B}$	$46.31 \pm 0.26^{d,B}$
	2	SPI–PVA (1 : 1)	4 : 1	1	—	—	$1.16 \pm 0.01^{b,A}$	$13.86 \pm 0.92^{b,A}$	$1.27 \pm 0.05^{e,B}$	$45.61 \pm 5.50^{e,B}$	$4.03 \pm 0.06^{c,B}$	$2.11 \pm 0.12^{e,B}$	$43.52 \pm 0.78^{e,C}$

Means with different lowercase superscripts indicate that the difference among six WGP boards were significantly different by the LSD test ($p < 0.05$). Means with different uppercase superscripts indicate that the difference among three red or three white WGP boards were significantly different by the LSD test ($p < 0.05$).

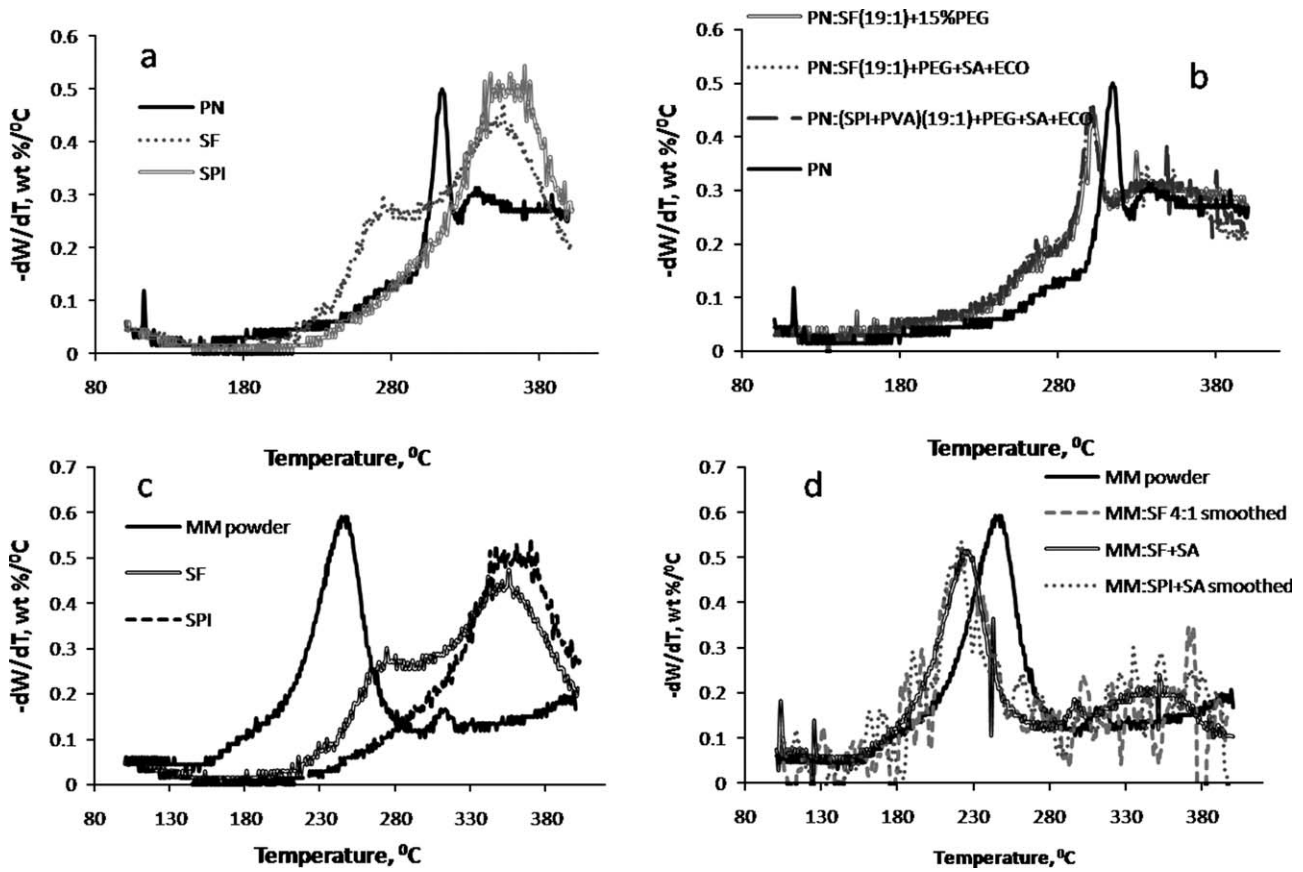

Figure 1 DTGA scans of the (a) starting materials for the red WGP composites, (b) composite products incorporating the red WGP, (c) starting materials for the white WGP composites, and (d) composite products incorporating the white WGP. The original WGP material was included in all scans. All of the samples were run in air at ambient MC (see Table V). dW/dT is the first derivative of weight change with respect to temperature.

and should, thus, be targeted for applications requiring fast degradation.

In conclusion, when all levels of the factors were considered, the optimal formulations were determined as $A_{1,4}B_1C_1D_2$ for the red WGP board and $A_{1,4}B_2C_1$ for the white WGP board. That is, the optimal combinations of all of the factors and their levels were (1) SF or SPI–PVA (1 : 1) as binders, a P/B ratio of 19 : 1, 1% SA, and 1% ECO for the red WGP boards and (2) SF or SPI–PVA (1 : 1) as binders, a P/B ratio of 4 : 1, and 1% SA for the white WGP boards.

Validation of the optimal formulations

WGP boards developed with the optimized formulations were analyzed for their density, MC, mechanical properties, water sensitivity (Table V), thermal properties (Fig. 1), biodegradability (Fig. 2), and microstructure (Figs. 3 and 4). These functional properties are essential for the development of their potential applications.

Density and MC

Overall, the density and MC of the white WGP boards were significantly ($p < 0.05$) higher than those of the red ones (Table V). The low P/B ratio in the white WGP board may have contributed to its high density because binders are higher density materials compared to pomace.[40] The higher sugar content in the white WGP also helped it retain more water during thermal pressing because sugar is a humectant. No significant difference in the density

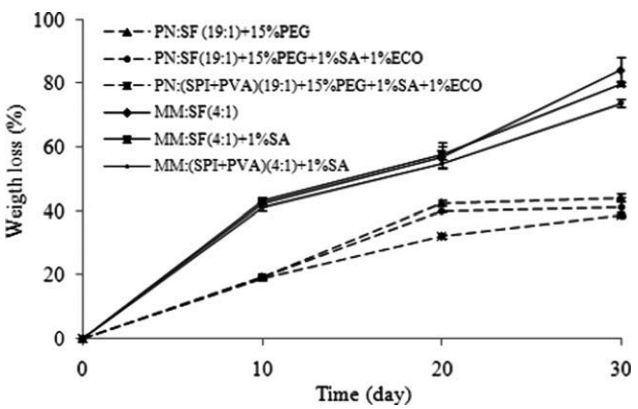

Figure 2 Degradation curves of the red (PN) and white (MM) WGP biocomposites as a function of the soil burial time.

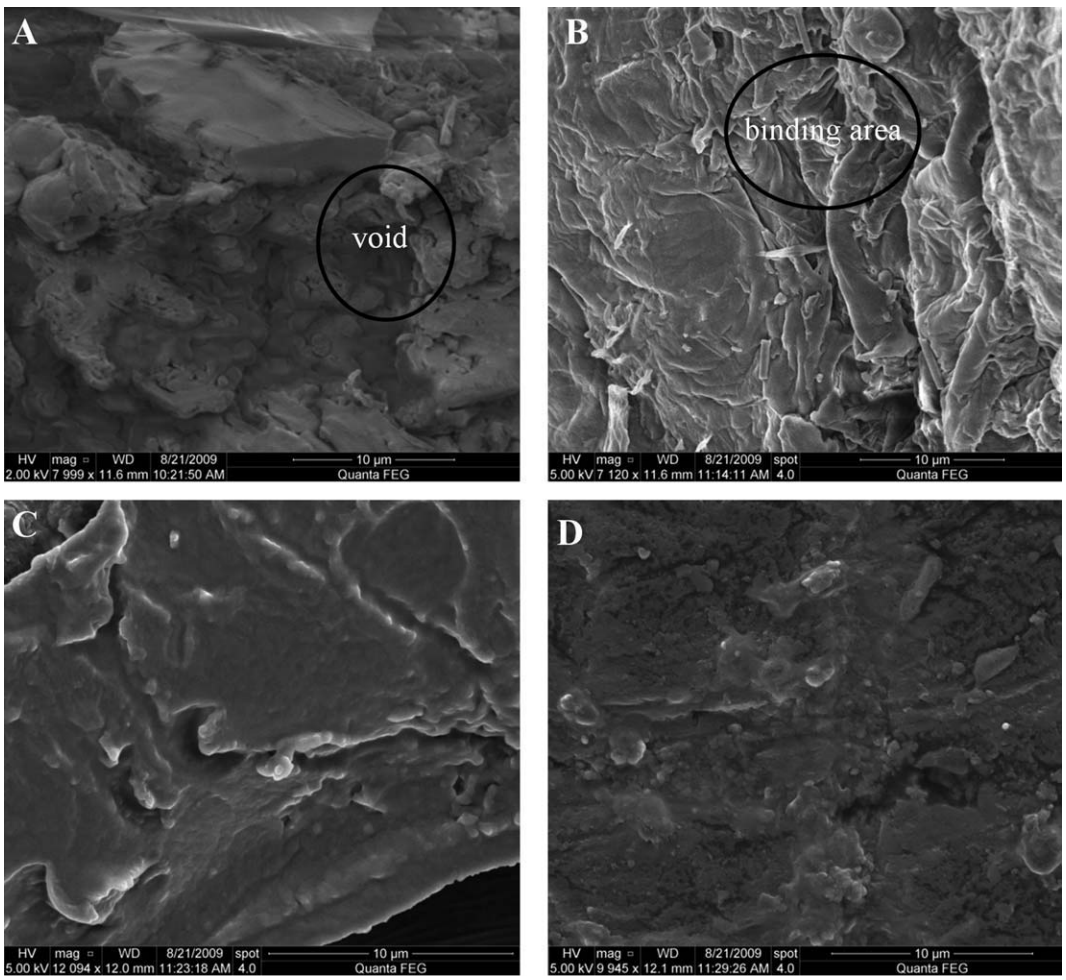

Figure 3 SEM images of the surfaces of the red and white WGP biocomposites: (A) red WGP–SF (19 : 1) without SA and ECO, (B) red WGP–SF (19 : 1) plus 1% SA and 1% ECO, (C) white WGP–SF (4 : 1) without SA, and (D) white WGP–SF (4 : 1) plus 1% SA. The PEG 400 content was 15% on the basis of the total solids weight of the red WGP and SF. Red WGP = PN pomace; white WGP = MM pomace.

and MC among the red and white WGP boards was observed (Table V).

Mechanical properties

With the optimized formulations, the red WGP boards showed a higher MOE and medium BS and percentage strain, whereas the white WGP boards had significantly improved mechanical properties (Tables III–V). The BS and MOE of the red WGP boards were significantly ($p < 0.05$) higher, but the percentage strain was lower than those of the white WGP boards (Table V). The higher percentage strain observed in the white WGP boards indicated that sugar was an effective plasticizer for increasing the material flexibility.[27] However, the plasticizing effect may have been responsible for the low strength, which explained the decrease in BS of the white WGP boards.[37,38] The addition of SA and ECO in the red WGP boards increased BS and MOE without a loss of flexibility (percentage strain). For the white WGP board, the addition of SA also increased BS and MOE but decreased the percentage strain.

W_a and W_s

Both the red and white WGP boards with the optimized formulations had improved water resistance, that is, lower W_a and W_s (Table V), in comparison with those from the orthogonal results (Table III and IV). The W_s values of the white WGP boards were higher than those of the red ones, probably because of the higher soluble sugar content in the white WGP, as described previously. The addition of SA and/or ECO in the red and white WGP boards reduced W_a and W_s significantly ($p < 0.05$) compared to the control. Surface cracking, crumbling, and disintegration were also observed in the control samples after immersion in water for 24 h, which was also reported by Lee et al.[22] for red clay composites reinforced with polymeric binders.

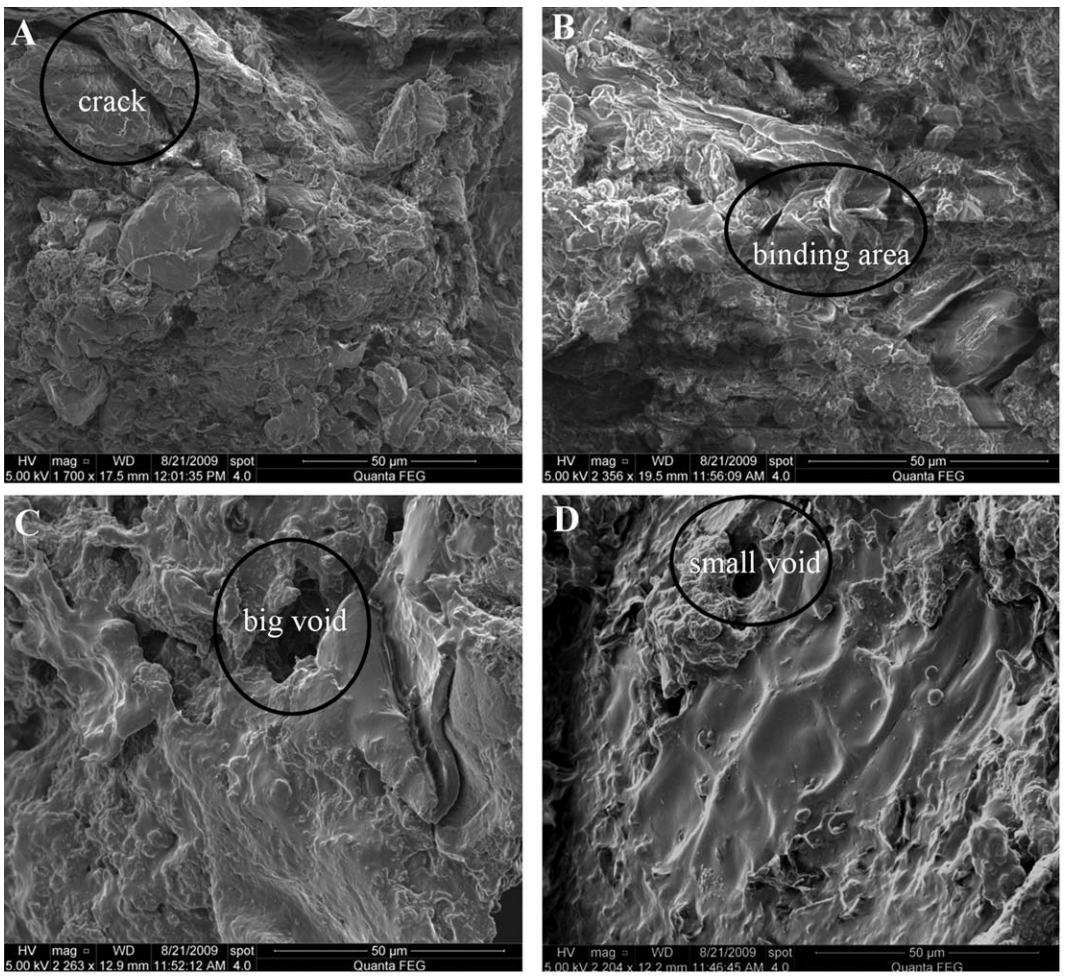

Figure 4 SEM images of the cross sections of the red and white WGP biocomposites: (A) red WGP–SF (19 : 1) without SA and ECO, (B) red WGP–SF (19 : 1) plus 1% SA and 1% ECO, (C) white WGP–SF (4 : 1) without SA, and (D) white WGP–SF (4 : 1) plus 1% SA. The PEG 400 content was 15% on the basis of the total solids weight of the red WGP and SF. Red WGP = PN pomace; white WGP = MM pomace.

Thermal properties

The slope of the weight loss versus temperature curve (DTGA) showed a marked difference between the PN powder and the soy-based materials [Fig. 1(a)]. When combined in a composite, the separate peaks were retained, but the PN peak was shifted to about 13°C lower [Fig. 1(b)]. This downward shift was consistent, regardless of the additives used, in contrast with the mechanical properties data. It was also counter to an additive TGA response because both SF and SPI showed a higher maximum (peak) rate of thermal degradation (MRTD). This suggested that in the composite, the WGP either had more access to the atmosphere or that there were some chemical interactions that lowered its activation energy for degradation in air or that the composite-forming process affected the WGP. The decrease of the peak degradation temperature, even with the ECO crosslinking agent present, suggested that the amount of crosslinking was small because, typically, crosslinking increases the TGA scan in composite materials.[38,41] In addition to ECO, the presence of the other additives had little or no influence on the DTGA response. Both SF and SPI showed similar spectra. This suggested that the effect of the additives on the composite thermal degradation was small.

The white WGP showed similar behavior, with MRTD occurring at about 245°C for the MM powder alone. However, this value dropped to about 220–222°C in the composite. The lower MRTD for white WGP compared to that of the red WGP may have been due to the higher sugar content in the white WGP. The fact that both peaks moved to lower temperatures in the composite suggested that either the processing or some material common to both SF and SPI caused the change in MRTD. Because the MRTDs for both SF and SPI composites were very close (220 vs 222°C) for the white WGP, although their composition was quite different, we speculated

that the process of compounding the materials to make the composite was responsible for the drop in MRTD.

The shift in MRTD was larger for the white WGP (~ 25°C) than for the red WGP (~ 13°C). This may have been because the higher sugar content in the white WGP was more susceptible to thermal degradation, both during testing and during processing. Also, MRTD for the white WGP (245°C) was lower than that of the red WGP (313°C).

Biodegradation

All of the boards showed a rapid biodegradation rate in soil, and the weight loss of the red WGP boards was lower than that of the white ones at any given point in time (Fig. 2). The average degradation rate was about 1.3%/day and 2.8%/day for the red and white WGP boards, respectively.

After 10 days, the tested specimens appeared brittle and fragile and decreased in size; this indicated the natural biodegradation of the boards in soil as a result of the presence of bacteria and the high MC of the soil.[31,42] The red and white WGP boards had about 20 and 40% degradation, respectively, whereas there was no significant ($p < 0.05$) difference among the red and white WGP boards within their own respective groups, regardless of composition. After 20 days, the boards containing SA and/or ECO showed lower weight losses compared to the control, and the board with SPI–PVA as binders had delayed biodegradation as well. The addition of SA and/or ECO or SPI–PVA as binders led to higher mechanical strengths in the boards. However, this may have decreased the rate of biodegradation because of the consequent covalent crosslinking.[42,43] After 30 days, the weight loss of the white WGP boards exceeded 80%. These results were in concordance with the results from Domenek et al.,[32] who reported a weight loss of about 80% of glucten–glycerol–soy protein films after 30 days. Kumar and Zhang[44] also observed the biodegradation of soy protein film from SEM images and indicated that microorganisms in the soil directly attacked the soy protein films, which led to its degradation.[31]

Microstructure

We evaluated the morphology of the boards by observing the surface (Fig. 3) and the cross section of fracture surfaces (Fig. 4) using SEM. Larger holes and a coarser surface were observed on the surfaces of the red and white WGP boards without SA and/or ECO [Fig. 3(a,c)]; this suggested that the interaction between the matrix (binder) and the filler (pomace) was weak, which resulted in less interfacial adhesion.[45] After the addition of SA and/or ECO [Figs. 3(b,d)], more homogeneous and denser surfaces were observed, probably because of the crosslinking between the pomace and the binder.[45] This feature was more prominent for the red WGP boards, as shown in Figure 3(b). The white WGP boards [Fig. 3(c,d)] had a relatively plain surface compared to the red WGP samples [Fig. 3(a,b)], probably because of the high sugar content in the white WGP.

A similar observation was obtained in the SEM micrographs of the fractured cross sections of the biocomposites (Fig. 4). The white WGP boards [Fig. 4(c,d)] had relatively smoother fracture surfaces and more ductile failure compared to the red WGP samples [Fig. 4(a,b)]; this led to better material flexibility.[40] The red and white WGP boards without SA and/or ECO showed rough and heterogeneous fracture surfaces with large voids, as shown in Figure 4(a,c); this may have indicated poor interactions between the pomace matrix and the binders.[46] The addition of SA and/or ECO showed a more interlocked surface [Fig. 4(b,d), as marked]. This improved interfacial adhesion may have been due to the coupling effect of the crosslinking agent.[47] The morphology results supported the mechanical property and water sensitivity results. All showed improved properties because of the addition of SA and/or ECO into the WGP boards.

CONCLUSIONS

According to the orthogonal design and analysis, the formulations for making red and white WGP biocomposite boards were optimized as follows: (1) SF or SPI–PVA (1 : 1) as binders, a P/B ratio of 19 : 1, 1% SA, and 1% ECO for the red WGP boards and (2) SF or SPI–PVA (1 : 1) as binders, a P/B ratio of 4 : 1, and 1% SA for the white WGP boards. Between the red and white WGP boards, the red ones had higher BS and MOE values with a moderate percentage strain, whereas the white ones showed a higher flexibility and biodegradability. After soil burial for 30 days, the weight loss reached about 50 and 80% for the red and white WGP boards, respectively. The addition of the binders and hydrophobic and crosslinking agents resulted in more cohesive fracture surfaces compared to the samples without these functional agents. This study successfully demonstrated the feasibility of creating biodegradable composites from both red and white WGPs with desired functionality. The red and white WGP boards had different performances and could be targeted for different applications in the agricultural and food industries. For example, red WGP biocomposites may be used to make biodegradable containers, such as nursery pots, which require relatively high mechanical strengths, more stability in water, and

better thermal properties during use, whereas the white WGP biocomposites may be targeted for applications that require less water resistance and more rapid biodegradation. The knowledge developed from this study will hopefully contribute to a better understanding of biocomposite technology and lead to commercial applications for these highly value-added materials.

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