Bio-poly(butylene succinate) and Its Composites with Grape Pomace: Mechanical Performance and Thermal Properties

Alison Gowman,†‡ Tao Wang,† Arturo Rodriguez-Uribe,† Amar K. Mohanty,*,†‡ and Manjusri Misra†‡

†Bioproducts Discovery and Development Centre, Department of Plant Agriculture, University of Guelph, Crop Science Building, 50 Stone Road E, N1G 2W1 Guelph, ON, Canada
‡School of Engineering, University of Guelph, Thornbrough Building, 50 Stone Road E, N1G 2W1 Guelph, ON, Canada

ABSTRACT: Biocomposites from bio-based poly(butylene succinate) (BioPBS) and grape pomace (GP) were made by melt extrusion— injection molding. Grape pomace is a low value byproduct from the wine industry that can be utilized as a filler to increase its value and to decrease the amount of polymer required in a composite blend. Experiments were performed with up to 50% grape pomace by weight. Composites were also compatibilized with in situ manufactured maleic anhydride-grafted BioPBS (MA-g-BioPBS). Flexural and impact strength were improved with the addition of GP up to the addition of 50 wt % GP, suggesting that at this loading the formulation reached threshold performance. The blend of (57:40:3) BioPBS/GP/MA-g-BioPBS showed the best overall performance in terms of a balance of both mechanical properties and thermal properties. The increase in impact resistance confirmed that the GP acted as a reinforcing phase. The addition of 3 wt % MA-g-BioPBS in samples containing 40 wt % of grape pomace resulted in improvements of 28.4 and 59% in flexural and impact strengths, respectively, compared to neat BioPBS. Heat distortion temperature increased with the addition of grape pomace by 14.3% in a blend combination of 57% BioPBS, 40% grape pomace, and 3% MA-g-BioPBS compared to neat BioPBS. Scanning electron microscopy results show improved interfacial adhesion with the addition of MA-g-BioPBS and thermogravimetric analysis results prove that the GP is thermally stable under the processing conditions. This study shows that GP can be successfully incorporated into a BioPBS matrix to create biocomposites with improved thermal and mechanical properties.

INTRODUCTION

A report from the United Nations Environmental Program in 2014 has estimated that the environmental cost of utilizing all synthetic plastics is more than $75 billion USD per year. Food packaging is the biggest contributor of plastic utilization at 23% of all costs. Soft drink packaging is the second biggest contributor at 12%. The total amount for both food packaging and soft drink packaging is 35% or $26.3 billion USD per year.1

The development of biodegradable and/or compostable materials among others is envisioned as one of the most reliable alternatives to reduce the environmental costs associated with traditionally used packaging. The ideal materials to be developed for these purposes are mainly composed of a biodegradable, compostable, or bio-based polymer matrix and a bio-based filler and/or natural fibers. These new materials, however, must comply with specific industrial quality requirements for their commercialization, which are mainly focused on their mechanical and thermal properties. In this scenario, a lot of research has been done on creating environment-friendly alternatives with optimized properties.2–4

Grape pomace (GP) is the main byproduct of the wine and grape juice industries. Current reports show that around 70–75% of the total world annual production of grapes (∼50–60 million tons) is used for the production of wine (∼27 billion liters a year).5 The manufacturing of wine results in approximately 20–25% of grape pomace.6 This byproduct contains mainly the skin, seeds, and stems of the wine grapes and it is composed of cellulose, hemicellulose, pectin, sugars, and small amounts of proteins, lipids, and polyphenolics.7 The improper disposal of GP results in a serious and negative environmental impact. The pomace lacks the high amounts of nitrogen required to be used as a suitable fertilizer, and it is only used in small quantities as animal feed.8 The skin under pressing still contains high quantities of phenolic compounds, antioxidants, and fiber, the stem contains tannins, while the seeds are a potential source for the production of oil as well as fiber.9 In general, most of the wine industries in the disposal of their wastes due to high disposal fees and transportation costs.

Received: July 16, 2018
Accepted: October 10, 2018
Published: November 9, 2018

DOI: 10.1021/acsomega.8b01675
ACS Omega 2018, 3, 15205−15216
While research activities aimed at finding economically viable and safe routes of extraction of fine chemicals and materials must be encouraged, alternative uses of industrial pomaces should also be examined. GP can also be considered for the derivatization of energy which can be obtained through thermo-chemical processing or pyrolysis—yielding gaseous, liquid, as well as solid fuels, and/or novel materials including bio-based plastics.10 This study is focused on the development of biocomposites based on a biodegradable matrix and GP as a reinforcing filler.

There are several biodegradable polymers that are currently being used for composite production, such as polybutylene adipate terephthalate (PBAT), poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), polyactic acid (PLA), and poly-(butylene succinate) (PBS), among others. PBS is an aliphatic, biodegradable, and sometimes bio-based polyester that shows promise due to its good melt processability and biodegradability when exposed to compositing conditions.10 It is a white thermoplastic polymer with a density of 1.25 g/cm³, a glass transition temperature of −45 to −10 °C, a melting temperature of 90–120 °C, it can be processed similarly to polyolefin at a range of 160–200 °C under controlled conditions.11 Its tensile strength is between polyethylene and polypropylene, and its stiffness is between high and low density polyethylene.11 PBS is advantageous over polyolefins because of its good biodegradability, which can make it an attractive alternative to other nonrenewable polymers.12 PBS can be made from either petroleum-based chemicals or it can be partially biobased with the succinic acid portion coming from biomass. Current production of bio-based poly(butylene succinate) (BioPBS) has a bio content of around 54% but there is potential to produce 100% bio-based PBS in the future when bio-based 1,4-butanediol becomes commercially available.13

PBS has a higher cost compared to traditionally used petroleum polymers that are nonbiodegradable.14 In the particular case of composite formulations, the higher cost of the polymers can be lowered with the addition of inexpensive fillers. In addition to lowering costs, fillers also allow the modification or enhancement of thermal properties and mechanical properties of the polymer matrices. Furthermore, the addition of bio-based fillers results in the production of bio-based or totally compostable materials. Due to these advantages, a variety of different natural fillers have been used to create green composites.15 Natural fillers have added advantages of being renewable, sustainable, abundant, biodegradable, and low density, and they have satisfactory specific properties when compared to mineral fillers like talc or glass fiber.13 Although, there has been a huge impact on research related to the use of wood fibers and/or grass derived fibers,14,15 there has been little work done on the use of fillers sourced from post-industrial food processing; such as tomato, grape, or apple pomace.

Bio-based fillers face basic challenges that can be overcome by choosing the materials and processing methods wisely, the most common include relatively low thermal stability, lack of filler–matrix interaction, and higher water absorption when compared with synthetic plastics.16 The thermal stability can be an issue if the filler decomposes below the processing temperature of the matrix, which was not the case in the composites made. Usually, there are compatibility problems between the natural filler and matrix because of their different polarities. This incompatibility between the filler and matrix causes inferior properties when compared to a neat polymer. There are two different ways to enhance the filler and matrix. The first way is using chemical, physical, or biological methods to modify the surface of the filler.17 The other method is to add a reactive compatibilizer into the system to enhance the interfacial adhesion between the polymer matrix and the biofiller.18 In natural filler composites, maleic anhydride (MA) is grafted to functional polymers and is commonly used as a reactive compatibilizer.19 MA can form a chemical bond with free hydroxyl groups on the surface of the filler in the composite.18 In addition to improving the interfacial adhesion, water absorption decreases because of the strong interfacial bonding between the filler and the polymer matrix, therefore improving the dimensional stability.20

To date, there has been no research done on grape pomace BioPBS composites, and no research done on utilizing all the components of pomace. Spiridon et al. (2016)21,22 have used grape seeds in different amounts in a polyactic acid (PLA) matrix, but no work has been done with grape pomace in a PBS matrix. Jiang et al. (2010) and Park et al. (2009) utilized grape skins in a soy flour matrix and found that biodegradable composites could be created with the incorporation of the grape skins. Both groups performed flexural tests on such materials and showed good breaking strength results, however, no other mechanical properties were tested.7,23 Due to the lack of literature available on incorporation of all components of grape pomace, we believe that there is an opportunity to create a compostable grape pomace/BioPBS-based composite with good mechanical properties for possible food packaging applications. In this study, we investigate the mechanical, physical, morphological, and thermal properties of composites manufactured with bio-based poly(butylene succinate) (PBS) and GP. GP is used as an inexpensive filler and as a source of reinforcing filler. We also provide a general analysis of the chemical composition of the grape pomace used, compared to the current published data.

**RESULTS AND DISCUSSION**

**Fourier Transform Infrared (FTIR) Spectroscopy.** The FTIR curve of neat BioPBS and MA-g-BioPBS were examined, as shown in Figure 1. At 1716 cm⁻¹, the ester carbonyl (C=O) group was seen as a stretching vibration.24 At 1045 cm⁻¹ there was a band corresponding to the stretching vibrations of the −O−C−C=O in BioPBS.25 The peaks at 2945 and 1330 cm⁻¹ corresponded to symmetric and asymmetric deformational vibrations from the −CH₂− groups in the main chains of PBS.26 The peaks at 918, 806, and 654 cm⁻¹ can be associated with the −C−OH bending in the carboxylic acid group of PBS,25 the in-plane bending of the CH₂ in OC(CH₂)₂CO, and the −COO− bending bands, respectively.27 There is one new small peak present at 1781 cm⁻¹ which can be attributed to the maleic anhydride grafting onto the BioPBS.28 These peaks correspond to the succinic anhydride group.28,29 The presence of these peaks further confirms that the MA has been grafted onto the BioPBS backbone and has been reported within the specialized literature.29 A strong −C−O−C stretching peak is seen at 1151 cm⁻¹, representing an ester linkage. At 955 cm⁻¹, the peak corresponds to C=O stretching, 806 cm⁻¹ to the in-plane bending of the CH₂ in OC(CH₂)₂Cl, and 644 cm⁻¹ to the −COO− bending as seen in both BioPBS and MA-g-BioPBS.

**Thermogravimetric Analysis (TGA).** The TGA curve for the grape pomace is smooth, without any peaks or dips (Figure...
This indicates that the sample experienced decomposition with the formation of gaseous reaction products. The onset temperature for thermal degradation was lower for the composites than that of BioPBS due to the grape pomace having lower thermal stability. The maximum degradation point occurred at 343°C for the grape pomace and 400°C for the BioPBS. In composites, these values are intermediate between grape pomace and the matrix. The thermal profile shows higher amounts of carbonaceous residues also containing the ash, as shown at the end of the curve for samples containing the grape pomace. These results are similar to rice husk flour and wood flour-filled PBS composites. In general, grape pomace can be safely incorporated with a polymer with a relatively low melting point. Table 1 shows the temperature weight loss values and 5 and 50% weight loss. It can be seen that the GP is the first to lose 5% of its weight.

Dynamic Mechanical Analysis (DMA). DMA was utilized to determine the heat deflection temperature (HDT) of the blends, as well as the viscoelastic properties of the composites. Storage modulus (E’) is the ratio of oscillating
stress to applied strain, related to the elastic portion of a material. It is measured in energy stored per cycle. Loss modulus ($E''$) is the shifted phase component relating to the viscous portion of a material. The ratio of $E''$ to $E'$ yields the mechanical damping factor (tan $\delta$).

Storage modulus values of green composites are influenced by the dispersion of the filler in the matrix and by interfacial bonding between phases. Figure 3a shows the $E'$ of BioPBS and the composites between temperatures of −60 and 100 °C. $E'$ for the composites increased, comparatively to neat BioPBS in all cases. This improvement could be due to the reinforcing effect of the pomace. The compatibilized samples performed better than their uncompatibilized counterparts. At $E'$ −30 °C, the samples showed a drastic reduction which can be related to the $T_g$ of BioPBS. The $E'$ continued to decrease when the temperature was increased up to a temperature of 100 °C, when the test was stopped. The decrease in $E'$ can be related to the molecular motion/relaxation with increasing temperatures. The degree of loss in the composite system was very similar to the neat polymer. With increasing temperature, the composites went through the glass transition zone of BioPBS and softened which can be seen in the decrease in storage modulus. The highest $E'$ was seen in the 55:40:5 blend of BioPBS/GP/MA-g-BioPBS.

The tan $\delta$ plot of BioPBS and the composites with 40−50% grape pomace filler can be seen in Figure 3b. The damping peak, near glass transition is associated with partial relaxation of polymer chains which allows small groups and chain segments to move. The tan $\delta$ height of all the composites was lower than that of BioPBS and the peaks were widened. The decrease with filler incorporation has been observed by many researchers, incorporating natural fillers into biodegradable polymers. The height of the tan $\delta$ loss factor $d$ with the addition of the grape pomace filler corresponds to the higher stiffness from the filler. This is also seen with the increase in $E'$. The filler component of the composite controls the strain and can reduce the strain on the interface. This could explain the behavior of the composites mentioned above. Also, the incorporation of the pomace can reduce the amount of movement from the polymer molecules, as shown in the decrease in the peak height. The increase in the storage modulus with the addition of a biofilleer, decrease in tan $\delta$ peak height, and the shift in the glass transition temperature to higher temperatures have all been recognized by many researchers. The shift in $T_g$ is shown in Table 2 and Figure 3c.

Table 1. Temperature Weight Loss Values for BioPBS, GP, and BioPBS/GP Composites and Residue Weights Taken at 800 °C

| Sample                  | Temperature at 5% weight loss ($T_{5\%}$) (°C) | Temperature at 50% weight loss ($T_{50\%}$) (°C) | Residue weight at Td (%) |
|-------------------------|-----------------------------------------------|-----------------------------------------------|--------------------------|
| Neat BioPBS             | 344                                           | 388                                           | 3                        |
| GP                      | 171                                           | 396                                           | 31                       |
| BioPBS/GP (60:40)       | 265                                           | 381                                           | 16                       |
| BioPBS/GP/MA-g-BioPBS (57:40:3) | 250                                           | 384                                           | 15                       |

Figure 3. (a) $E'$ of BioPBS, BioPBS/GP, and BioPBS/GP/MA-g-BioPBS (b) tan $\delta$ (c) loss modulus (A) neat BioPBS, (B) BioPBS/GP (60:40 wt %), (C) BioPBS/GP/MA-g-BioPBS (57:40:3 wt %).

Table 2. DMA Results for BioPBS and BioPBS/GP Composite Blends

| Sample                  | $T_g$ maximum loss factor (°C) |
|-------------------------|--------------------------------|
| BioPBS                  | −17.0                          |
| BioPBS/GP (60:40)       | −13.9                          |
| BioPBS/GP/MA-g-BioPBS (57:40:3) | −14.7                          |

HDT is the temperature where a material deflects at least 0.25 mm under a load of either 0.455 or 1.82 MPa. It is an important measure for the design of products and for practical applications. High values typically are desired for composite applications. The HDT values of neat BioPBS along with uncompatibilized and compatibilized samples are shown in Table 1. The HDT of neat BioPBS was around 87 °C. The compositions increase in HDT values with higher filler percentages. The values remained almost similar from 40 to
50% load of grape pomace showing that the matrix reached a threshold (where additional loading would not benefit the system and properties would start to decrease). This is confirmed by the crystallinity values obtained for these samples showing lower values in composites loaded with 50% pomace. The observed improvements in HDT are attributed to the improved reinforcing/stiffness effect that composites experience, as reported in the literature. The improved stiffness of the composites is also shown in relation to the flexural and tensile modulus. The HDT values of other BioPBS composites also increased such as PBS/Basalt fibers (85:15 wt %) increasing from 82 to 114 °C,42 PBS/switchgrass (50:50 wt %) increased from 78 to 106 °C,34 and PBS/miscanthus (50:50 wt %) increased from 90 to 116 °C. The compatibilized samples increased the HDT values slightly. The improvement can be attributed to the increased interaction between the matrix and the filler with the addition of compatibilizer. The increase in storage modulus of the composites is also shown in relation to the mechanical properties.

Differential Scanning Calorimetry (DSC). DSC was used to determine the effects of grape pomace on crystalline temperature ($T_c$), crystalline enthalpy ($\Delta H_c$), melting temperature ($T_m$), melting enthalpy ($\Delta H_m$), and percentage crystallinity of BioPBS. The glass transition temperature ($T_g$) of neat BioPBS and the composites from the DSC curves could not be determined. Other literature on BioPBS composites have used DMA to report $T_g$ values, not DSC, possibly for the same reason. The melting temperature, melting enthalphy, crystallization temperature, crystallization enthalphy, and percentage crystallinity of BioPBS as a neat polymer and composites can be seen in Table 3. The melting temperature of BioPBS was around 115 °C (in terms of the second melting peak) since BioPBS has a double melting behavior of melting, recrystallization, and remelting. The melting temperature remained very similar among all the composites as well, suggesting that the presence of the grape pomace filler does not affect it. The crystallization temperature of neat BioPBS was 91 °C. The crystallization temperature decreased slightly for uncompatibilized samples, but compatibilized samples had crystallization similar to neat BioPBS. The crystallinity of the samples was also very similar to that of BioPBS. Neat BioPBS had a bimodal melting peak which can be attributed to melt crystallization phenomena. The bimodal peak became less distinct with the addition of grape pomace. The addition of compatibilizer resulted in a slight melting peak after the cold crystallization peak and endothermic melting peak which was not present in uncompatibilized samples.

BioPBS and the composites prepared showed two distinct endothermic peaks which could be a result of the presence of different lamellar thicknesses present in BioPBS and the composites. Double melting peaks can be observed in semi-crystalline polymers and polymer blends and can be explained by melt recrystallization. The melting peaks shifted to slightly lower temperatures with the addition of MA-g-PBS (Figure 4), although this change is very subtle. This could be due to the presence of the MA group. The presence of the MA group could prevent lamella growth and nucleation leading to a more imperfect crystal structure compared to uncompatibilized samples and neat BioPBS.6 The composites’ crystallinity was not substantially altered after the addition of grape pomace from 40 to 50 wt %, therefore, the degradation of the green composites is expected to be similar to neat BioPBS. Crystallization behavior increased with the addition of the coupling agent at 40% pomace load and it remained close to 35% even in composites manufactured at 50% filler. Thus, the increase of crystallization and on the mechanical properties can be clearly associated with the effects of the MA-g-BioPBS on and the matrix-filler interactions. In general, the grape pomace particles act as nucleating agents, whose behavior is promoted by the use of MA-g-BioPBS.

### Table 3. HDT and DSC Results of Neat BioPBS, BioPBS/GP, and BioPBS/GP/MA-g-BioPBS

| Sample | HDT (°C) | $T_c$ (°C) | $\Delta H_c$ (J/g) | $T_m$ (°C) | $\Delta H_m$ (J/g) | Crystallinity (%) |
|--------|----------|------------|------------------|------------|------------------|-----------------|
| Neat BioPBS | 89.0 ± 0.7 | 91.0 | 69.1 | 115.4 | 65.4 | 34.5 |
| BioPBS/GP (60:40 wt %) | 89.7 ± 1.4 | 82.6 | 44.7 | 114.2 | 41.2 | 37.3 |
| BioPBS/GP (50:50 wt %) | 90.7 ± 1.2 | 82.1 | 38.0 | 114.0 | 34.9 | 38.0 |
| BioPBS/GP/MA-g-BioPBS (59:40:1 wt %) | 96.0 ± 2.2 | 85.2 | 43.0 | 114.1 | 40.2 | 35.8 |
| BioPBS/GP/MA-g-BioPBS (57:40:3 wt %) | 94.7 ± 1.2 | 87.4 | 41.9 | 114.0 | 36.8 | 34.9 |
| BioPBS/GP/MA-g-BioPBS (55:40:5 wt %) | 99.4 ± 1.2 | 86.3 | 41.7 | 113.8 | 35.5 | 34.7 |
| BioPBS/GP/MA-g-BioPBS (47:50:3 wt %) | 98.6 ± 1.9 | 86.7 | 38.0 | 113.8 | 32.4 | 38.0 |
| BioPBS/GP/MA-g-BioPBS (45:50:5 wt %) | 97.6 ± 1.5 | 87.2 | 37.0 | 113.4 | 33.0 | 37.0 |

![Figure 4](image_url)

**Figure 4.** DSC of second heat cycles of BioPBS, BioPBS/GP, and BioPBS/GP/MA-g-BioPBS with example integration line for enthalpy of crystallization calculations: (A) neat BioPBS, (B) BioPBS/GP (60:40 wt %), (C) BioPBS/GP (50:50 wt %), (D) BioPBS/GP/MA-g-BioPBS (59:40:1 wt %), (E) BioPBS/GP/MA-g-BioPBS (57:40:3 wt %), (F) BioPBS/GP/MA-g-BioPBS (55:40:5 wt %), (G) BioPBS/GP/MA-g-BioPBS (47:50:3 wt %), and (H) BioPBS/GP/MA-g-BioPBS (45:50:5 wt %).
tensile strength of BioPBS/GP composites with different filler loadings, with and without compatibilizer. Neat BioPBS had a tensile strength of 40.7 MPa and a tensile modulus of 0.74 GPa. The incorporation of grape pomace into the BioPBS matrix decreased the tensile strength substantially. This can be explained by the lack of interfacial interaction and incompatibility between the grape pomace and BioPBS. The addition of 50% grape pomace in the BioPBS matrix showed the biggest decrease in tensile strength with a reduction of 60%. The tensile modulus depends on the amount of filler added into the system. The tensile modulus increased with increasing amounts of fillers up to a filler content of 50%. For example, the blend of BioPBS/grape pomace/compatibilizer (45:50:5) had a tensile modulus of 1.84 GPa, a value which is 246% higher than neat BioPBS. Both tensile modulus and strength were improved with the addition of MA-g-BioPBS (compatibilizer). Compatibilized samples had a higher tensile strength than their uncompatibilized counterparts which can be attributed to the improved interfacial interaction between the composites. The enhanced filler–matrix is thought to be from the grafted MA groups of the MA-g-BioPBS interacting with the hydroxyl groups of the grape pomace; the BioPBS parts are miscible with the BioPBS in the matrix through co-crystallization.\(^4\) The expected reaction between MA-g-BioPBS and grape pomace is shown in Figure 6, as proposed in refs 49, 50. The tensile modulus did not show any dramatic improvement between the compatibilized and uncompatibilized samples. This is consistent with PBS/miscanthus green composites and with PLA/wood composites.\(^3\)\(^,\)\(^5\) The tensile strength of PBS/grape pomace/MA was not significantly different between the 40 and 50% grape pomace filler. The tensile strength also did not change with different amounts of MA. The elongation at break percentage for neat BioPBS was found to be around 119% (Figure 5a,c). With the addition of grape pomace into the BioPBS matrix, the elongation at break dropped to 3.5–7%. The reduction in elongation is a common occurrence in green composites because the addition of filler reduces the molecular mobility of the polymer chains.\(^4\)

The flexural properties of BioPBS grape pomace composites with different amounts of fillers, with and without compatibilizer can be seen in Figure 7a. The flexural strength of neat BioPBS was 33.65 MPa and the flexural modulus was 0.779

Figure 5. (a) Tensile stress–strain curves (A) neat BioPBS, (B) BioPBS/GP (60:40 wt %), and (E) BioPBS/GP/MA-g-BioPBS (57:40:3 wt %). (b) Tensile properties of BioPBS and BioPBS/GP composites. (c) Elongation at the break of BioPBS and BioPBS/GP composites (A) neat BioPBS, (B) BioPBS/GP (60:40 wt %), (C) BioPBS/GP (50:50 wt %), (D) BioPBS/GP/MA-g-BioPBS (59:40:1 wt %), (E) BioPBS/GP/MA-g-BioPBS (57:40:3 wt %), (F) BioPBS/GP/MA-g-BioPBS (55:40:5 wt %), (G) BioPBS/GP/MA-g-BioPBS (47:50:3 wt %), and (H) BioPBS/GP/MA-g-BioPBS (45:50:5 wt %).
GPa. The flexural strength of all the composites, comparatively to neat BioPBS, except for the blend of 50:50 BioPBS grape pomace decreased slightly. Other researchers have attributed the decrease in the properties to the high ash content of the grape pomace in comparison to other fruit pomaces. The increased stiffness of the BioPBS matrix after the addition of the GP filler is thought to be the reason for this increase. The flexural strength of the composites improved slightly in samples with 40% filler, but it decreased with a filler content of 50%. The tensile strength and flexural strength insignificantly change because the MA-g-BioPBS acts as a toughening agent, and therefore, increases the strength of the composites but not their ductility. If the reactive sites on the BioPBS are fully consumed, then more amounts of MA-g-BioPBS will not change the strength. The flexural modulus increased with the increasing filler content up to 50% filler. The flexural modulus was further improved with the addition of compatibilizer into the system. The compatibilized samples had an improvement in flexural strength, but the amount of filler did not seem to change the strength at 40 and 50% filler content. The flexural modulus showed very little difference between compatibilized and uncompatibilized samples, which is a contrast to the improvement in flexural strength with compatibilizer. Compared to neat BioPBS, the biggest improvement in flexural modulus was the BioPBS/grape pomace/compatibilizer (55:50:5 wt %) blend, with a flexural strength of 45.6 MPa and a flexural modulus of 2.89 GPa. This results in an increase of 135.5 and 371%, respectively. The improvements can be associated with the reinforcing effect of grape pomace.

The Izod notched impact strength of BioPBS, BioPBS/GP composites, and compatibilized BioPBS/GP composites can be seen in Figure 7b. Neat BioPBS had an impact strength of around 24 J/m. The impact strength of the BioPBS/GP composites improved significantly with the addition of filler at 40% compared to the neat BioPBS, however, at 50% filler the impact strength decreased by a very slight amount. The impact strength was improved with the addition of compatibilizer, but not drastically. The highest improvement was seen in the BioPBS/grape pomace/compatibilizer (57:40:3 wt %) blend. An impact value of 38.8 J/m was obtained, a 159% improvement over neat BioPBS. The improvement can be attributed to enhanced adhesion between components. The impact strength started to decrease with a higher filler content, regardless if the compatibilizer was present. The impact strength increased with the addition of GP because it absorbed the energy transferred during the test. GP reinforces the BioPBS matrix, allowing it to withstand more added energy. With the higher addition of GP the matrix became overloaded, and the GP started to behave as a stress concentration factor, causing the impact strength to decrease.

Surface Morphology. The surface morphology of the grape pomace, neat BioPBS, and composites were all examined to determine the interfacial bonding between the filler and the

---

**Figure 6.** Expected reaction schematics between hydroxyl groups of GP and MA-g-BioPBS as proposed and redrawn in refs 49, 50.

**Figure 7.** (a) Flexural properties of BioPBS and BioPBS/GP composites. (b) Izod notched impact strength of BioPBS and BioPBS/GP composites (A) neat BioPBS, (B) BioPBS/GP (60:40 wt %), (C) BioPBS/GP (50:50 wt %), (D) BioPBS/GP/MA-g-BioPBS (59:40:1 wt %), (E) BioPBS/GP/MA-g-BioPBS (57:40:3 wt %), (F) BioPBS/GP/MA-g-BioPBS (55:40:5 wt %), (G) BioPBS/GP/MA-g-BioPBS (47:50:3 wt %), and (H) BioPBS/GP/MA-g-BioPBS (45:50:5 wt %).
matrix through scanning electron microscopy (SEM). The degree of grape pomace dispersion in the matrix can also be determined. As shown in Figure 8A below, there are many different structures found in the grape pomace. These can be broken down into two separate categories: long, straw like particles, and round particles. The straw like particles can be from the stems found in the pomace. The round particles could be from the seeds of the grapes. The very different morphologies of the pomace suggest that the pomace is not completely uniform in composition.

SEM fracture surfaces of uncompatibilized composites as seen in Figures 9A and 10A show interfacial gaps between the matrix and filler and filler pull out from the filler—matrix. With the increasing filler content, an increase in filler bundles/aggregates were seen up to a filler content of 50 wt %. The morphology was more uniform in the blend with lower amounts of GP (Figure 10A). Similar findings have been seen in PBS/miscanthus composites, PLA/kenaf composites, PHBV/kenaf composites, PHBV/PLA/miscanthus composites, PBS/bamboo composites, PBS/kenaf fiber composites, and PP/bioflour composites. Weak interfacial adhesion can cause debonding from the matrix which can be seen in the fracture surface morphology. Figures 9B and 10B show the SEM fracture surface of compatibilized BioPBS composites. The compatibilized composite does not show as much filler pull out and it has good filler dispersion in the matrix due to the improved interfacial adhesion. The compatibilized composite has a more uniform appearance, which can be attributed to the addition of compatibilizer. Each of the compatibilized samples have better performance than the uncompatibilized samples with the same ratios of BioPBS to GP due to the enhanced interfacial adhesion. Similar results have been seen for PBS/miscanthus fiber composites as well.³

■ CONCLUSIONS

Grape pomace (GP), an abundant byproduct of the wine industry was used as a filler in a bio-based PBS matrix to increase its value and to increase the sustainability of the BioPBS blends. GP-reinforced BioPBS composites were prepared with various amounts of fillers, up to 50% GP by weight. MA-g-BioPBS was successfully grafted with a grafting level of 3.88%. TGA results show that the GP was thermally stable at processing conditions. The use of a compatibilizer enhanced both mechanical and thermal properties when compared to uncompatibilized counterparts and neat BioPBS. Flexural and impact properties improved with the addition of GP up to 50% by weight. The improvement in the properties can be attributed to the enhanced interfacial interaction between the GP filler, the BioPBS matrix, and the maleic anhydride-grafted compatibilizer. A balance of both mechanical and thermal properties was found with a blend of (57:40:3) BioPBS/GP/MA-g-BioPBS, indicating that a high level of GP can be successfully incorporated into a polymer matrix. The interfacial interaction improvement was confirmed by SEM analysis. Overall, this study shows that a food by product can be utilized as a low-cost filler to create bio-based composites with improved mechanical and thermo-mechanical properties.

Figure 8. Surface morphology of grape pomace at 2000× magnification.

Figure 9. Fracture surfaces of uncompatibilized and compatibilized 50% BioPBS/GP composites at 500× magnification: (A) BioPBS/GP (50:50 wt %) and (B) BioPBS/GP/MA-g-BioPBS (45:50:5 wt %).
**EXPERIMENTAL SECTION**

**Materials.** Grape pomace was obtained from Andrew Peller Winery, Grimsby ON, Canada. Injection molding bio poly-(butylene succinate) (BioPBS) grade FZ71PM was purchased from PTT MCC Biochem Co., Ltd., Bangkok, Thailand. It has manufacturer specifications for density, melt flow rate (at 190 °C/2.16 kg), melting point, yield stress, strain at break, flexural modulus, flexural stress, and heat deflection temperature (HDT), respectively, of 1.26 g/cm³, 40 MPa, 170%, 630 MPa, 40 MPa, and 95 °C.\(^{58}\) Maleic anhydride purchased from Acros Organics, and the initiator, Luperox 101 (2,5-bis(tert-butylperoxy)-2,5-dimethylhexane) technical grade, purchased from Sigma-Aldrich, were used in compatibilization.

**Composite Fabrication.** Grape Pomace Preparation and Conditioning. Grape pomace was air-dried inside a laboratory fume hood for 6 days until the moisture content of the grape pomace was around 2.5%. The pomace was then milled using a 1 mm sieve on a Retsch ZM 200 grinding machine at 6000 rpm (Retsch GmbH, Germany). The pomace was then dried overnight in an oven at 60 °C before reaching a final moisture content of below 2.5%. It was sealed in zip lock plastic bags and kept below zero for further processing.

Maleic Anhydride Grafting Reaction. The coupling agent was in-lab synthesized by reactive extrusion using BioPBS, maleic anhydride (MA), and Luperox as initiators. The BioPBS was used and dried to 1% or less before processing according to manufacturer recommendations for this process. These components were mixed by hand in a closed container until reaching a homogeneous mixture. This reactive extrusion was performed in a twin-screw extruder, Leistritz Micro-27, having a length to diameter ratio (L/D) 48:1 and 27 mm screw diameter (Leistritz advanced technologies corp.). The ratio of reactants was of 5% of MA and 1% of initiator based on the total weight of the polymer. The temperature profile was 160 °C at a feeding rate of 4 kg/h which was controlled through a balanced-feed mechanism. The screw speed was 60 rpm in a co-rotating configuration. Strands were produced using a die with openings of 3 mm and cooled using a water bath, and pelletized and vacuum dried to remove the free maleic anhydride before composite manufacturing.

**Purification of Maleic Anhydride-Grafted Bio-PBS and Maleic Anhydride Grafting Percentage.** Purification of MA-g-BioPBS was performed following a modified procedure.\(^{59}\) To ensure that unreacted maleic anhydride was removed, it was vacuum dried at 80 °C for 3 days. For the test, the vacuum dried MA-g-BioPBS was then dissolved in 50 mL chloroform. The MA-g-BioPBS was then selectively precipitated in methanol and filtered. The filtered samples were then dried at 80 °C under vacuum for 24 h.

Back-titration was performed to determine the amount of maleic anhydride grafting onto the BioPBS backbone, following a modified method from Nabar et al.\(^{59}\) Approximately 1 g of purified MA-g-BioPBS was dissolved in 50 mL of chloroform at room temperature for 2 h. The free grafted maleic anhydride groups potentially found in the solution were then hydrolyzed with the addition of eight drops (2 μL) of water at room temperature. The solution was then titrated with 0.1 N KOH solution and five drops of phenolphthalein were added as an indicator. The MA-g-PBS is soluble in chloroform and did not precipitate out of the solution during titration with KOH. The grafting percentage was calculated as follows

\[
grafting\;\text{percentage}\; (\%) = \frac{V_{\text{KOH}}N_{\text{KOH}}}{2W} \times 98.06 \times 100 \tag{1}
\]

where \(V_{\text{KOH}}\) is the volume of KOH in liters, \(N_{\text{KOH}}\) is the normality of KOH solution, \(W\) is the weight of MA-g-BioPBS in grams, and 98.06 is the molecular weight of MA in g/mol.

The grafting level of the MA-g-BioPBS was 3.88%. The grafting was higher than that calculated by Muthuraj et al. at 2.56%, which can be due to the different source of PBS.

**Composite Preparation.** Grape pomace was dried overnight at 80 °C prior to processing and the BioPBS according to manufacturer recommendation. The moisture content of the GP was less than 2% after drying. The biocomposites were prepared through an extrusion–injection molding process by using a DSM Xplore 15 cm³ micro compounder and micro 12 cm³ injection molding machine (The Netherlands). The extruder has three independent control heating zones, with twin screws of 150 mm length and an aspect ratio of 18. Compounding was done with the following parameters: a screw speed of 100 rpm, processing temperature of 140 °C in all heating zones, with a residence time of 2 min. All the

---

**Figure 10.** Fracture surfaces of uncompatibilized and compatibilized samples at 500× magnification: (A) BioPBS/GP (60:40 wt %) and (B) BioPBS/GP/MA-g-BioPBS (55:40:5).
samples were formed with a mold temperature of 30 °C, with an averaged injection pressure of 10 bar, and injection holding time of 20 s. The PBS/GP composites were made with up to 50% GP filler and 5% MA-g-PBS. Blends of 20, 25, 30, 40, and 50% GP were prepared. Compatibilized samples of 40 and 50% grape pomace were made with 1, 3, and 5% MA-g-BioPBS, only 3 and 5% were made for 50% GP. Fourier Transform Infrared Spectroscopy (FTIR). Fourier transform infrared spectroscopy (Nicolet 6700, Thermo Fisher Scientific) was used on an infrared-attenuated total reflectance mode (FTIR-ATR). The analysis was performed by plotting transmittance versus wavenumber in the range of 4000–400 cm⁻¹ with 128 consecutive scans at a resolution of 2 cm⁻¹ under an air atmosphere. Thermal Analysis. Thermogravimetric analysis (TGA) was performed by using a TA instrument (TGA Q500, TA Instruments) and according to ASTM E1131-08. The grape pomace, BioPBS, and BioPBS/GP composites were placed into a platinum pan and heated to 800 °C at a temperature ramp rate of 10 °C/min under a nitrogen environment. The tests were performed in duplicates. The data was analyzed using a software from TA Instruments, Universal Analysis 2000, version 4.5A. Dynamic mechanical analysis (DMA) (DMA Q800, TA Instruments) was used to determine the heat deflection distortion temperature (HDT) under the three-point bending setting, following the standard ASTM D648. Injection molded samples were tested until they reached a distortion of 250 μm. The results were done in duplicates. DMA was also used to determine the temperature dependent storage modulus (E’), as per ASTM standard D4065. The heating ramp rate for this test was of 3 °C/min. E’ measurements were determined in dual cantilever mode with a strain of 1 Hz and 15 μm oscillating amplitude. All tests were first stabilized at −50 °C for 5 min before being heated in the thermal spectral range of −50–100 °C. These tests were performed in an air atmosphere in duplicates. Differential scanning calorimetry (DSC) was performed using a DSC Q200, TA Instruments. For each sample, between 5 and 10 mg of sample was sealed in an aluminum pan, which was heated from room temperature to 180 °C at a rate of 10 °C/min and held at that temperature for 2 min, then cooled to −60 °C with liquid nitrogen at a rate of 5 °C/min and held for 2 min, before a second heating scan to 180 °C at 10 °C/min. The nitrogen flow was kept at 50 mL/min throughout the test. The samples were dried overnight prior to testing. Two duplicates were prepared for each sample. Three cycles were run to erase the thermal history from the first cycle. The second heating cycle and first cooling cycle were used for analysis and tests were done in duplicates. The percent crystallinity of the neat BioPBS was calculated as follows

\[ X = \frac{\Delta H_c}{\Delta H_m} \times 100\% \]  

(2)

The percentage of crystallinity of the composites were calculated as follows

\[ X = \frac{\Delta H_c}{\Delta H_m(1 - W_f)} \times 100\% \]  

(3)

where \( \Delta H_c \) is the crystallization enthalpy of the composite sample, \( \Delta H_m \) is the theoretical melting enthalpy of 100% crystalline PBS, assumed to be 200 J/g and \( W_f \) is the weight fraction of the grape pomace in the composites. Equation 3 was used to calculate the crystallinity of the composites because the percentage of GP added is taken into consideration. Mechanical Testing. The mechanical properties of the composites were tested using an Instron Universal Testing Machine (Instron-3382, Massachusetts). Type IV specimens were tested according to ASTM D638-14 with a test speed of 5 mm/min for the composites and 50 mm/min for the neat BioPBS at 50% relative humidity. Flexural properties were tested according to ASTM D790-15 procedure B, with a crosshead speed of 14 mm/min and a span length of 52 mm, in the three-point bending mode. Izod Notched impact properties were tested using ASTM D256-10. The impact tester used was a TMI monitor impact tester (Testing machine Inc. DE). The test was performed at room temperature by using a 6.779 J (5 ft.lb) pendulum. Surface Morphology. Scanning electron microscopy was performed with a Phenom ProX (Phenom World BV, Netherlands) on the grape pomace to visualize the shape and structure of the particles. Fracture surface morphology was observed using scanning electron microscopy (SEM) on a Phenom ProX (Phenom World BV, Netherlands) equipped with back scattering electron at 10 kV acceleration voltage. The samples used for the SEM images were fractured with a pendulum hammer to provide a cross section for imaging.

**AUTHOR INFORMATION**

**Corresponding Authors**

*E-mail: mohanty@uoguelph.ca (A.K.M.).

*E-mail: mmisra@uoguelph.ca (M.M.).

**ORCID**

Amar K. Mohanty: 0000-0002-1079-2481

Manjusri Misra: 0000-0003-2179-7699

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

The authors are thankful to the Ontario Ministry of Agricultural, Food and Rural Affairs (OMAFRA), Canada/University of Guelph-Bioeconomy for Industrial Uses Research Theme Project #030177, and the Natural Sciences and Engineering Research Council (NSERC) Canada Discovery Grants Project #400320 for their financial support to carry out this research. A special thanks to Dr. Mahendra Thimmanagari, Ontario Ministry of Agriculture, Food and Rural Affairs (OMAFRA), Canada, for collaborating on this project and to Andrew Peller Winery, 697 South Service Road, Grimsby, Ontario L3M 4E8, Canada, for the donation of the grape pomace samples.

**REFERENCES**

(1) Raynaud, J. Valuing Plastics: The Business Case for Measuring, Managing and Disclosing Plastic Use in the Consumer Goods Industry; UNEP, 2014.

(2) Zhang, K.; Mohanty, A. K.; Misra, M. Fully biodegradable and biorenewable ternary blends from polylactide, poly(3-hydroxybutyrate-co-hydroxyvalerate) and poly(butylene succinate) with balanced properties. ACS Appl. Mater. Interfaces 2012, 4, 3091–3101.

(3) Muthuraj, R.; Misra, M.; Mohanty, A. K. Injection Molder Sustainable Biocomposites from Poly(butylene succinate) Bioplastic
and Perennial Grass. ACS Sustainable Chem. Eng. 2015, 3, 2767–2776.
(4) Nagarajan, V.; Mohanty, A. K.; Misra, M. Sustainable green composites: Value addition to agricultural residues and perennial grasses. ACS Sustainable Chem. Eng. 2013, 1, 325–333.
(5) García-Lomillo, J.; Gona, L. Applications of Wine Pomace in the Food Industry: Approaches and Functions. Compr. Rev. Food Sci. Food Saf. 2017, 16, 3–22.
(6) Dwyer, K.; Hosseini, F.; Rod, M. The Market Potential of Grape Waste Alternatives. J. Food Res. 2014, 3, 91.
(7) Jiang, Y.; Simonsen, J.; Zhao, Y. Compression-molded biocomposite boards from red and white wine grape pomaces. J. Appl. Polym. Sci. 2011, 119, 2834–2846.
(8) Toscano, G.; Riva, G.; Duca, D.; Pedretti, E. F.; Corinaldesi, F.; Rossini, G. Analysis of the characteristics of the residues of the wine production chain finalized to its industrial and energy recovery. Biomass Bioenergy 2013, 55, 260–267.
(9) Cáceres, C. X.; Cáceres, R. E.; Hein, D.; Molina, M. G.; Pia, J. M. Biogas production from grape pomace: Thermodynamic model of the process and dynamic model of the power generation system. Int. J. Hydrogen Energy 2012, 37, 10111–10117.
(10) Kim, H. S.; Yang, H. S.; Kim, H. J. Biodegradability and mechanical properties of agro-flour-filled polybutylene succinate biocomposites. J. Appl. Polym. Sci. 2005, 97, 1513–1521.
(11) Fujimaki, T. Processability and properties of aliphatic polyesters. ‘BIONOLLE’, synthesized by polycondensation reaction. Polym. Degrad. Stab. 1998, 59, 209–214.
(12) Moussa, H. Life Cycle Assessment of a Hybrid Poly Butylene Succinate Composite. M.Sc. Thesis, University of Waterloo: Canada, 2014.
(13) Zini, E.; Scandola, M. Green Composites: An Overview. Polym. Compos. 2011, 32, 1905–1915.
(14) Hamma, A.; Kaci, M.; Mohd Ishak, Z. A.; Pegoretti, A. Starch-grafted-polypolyethylene/kenaf fibres composites. Part 1: Mechanical performances and viscoelastic behaviour. Composites, Part A 2014, 56, 328–335.
(15) Nanda, M. R.; Misra, M.; Mohanty, A. K. Performance Evaluation of Biofibers and Their Hybrids as Reinforcements in Biocomposites. Macromol. Mater. Eng. 2013, 298, 779–788.
(16) Saheb, N.; Jo, J. Natural Fiber Polymer Composites: A Review. Adv. Polym. Technol. 1999, 2329, 351–363.
(17) Fuqua, M. A.; Huo, S.; Ulven, C. A. Natural fiber reinforced composites. Polym. Rev. 2012, 52, 259–320.
(18) Yu, T.; Jiang, N.; Li, Y. Study on short ramie fiber/poly(lactic acid) composites compatibilized by maleic anhydride. Composites, Part A 2014, 64, 139–146.
(19) Liu, N. C.; Baker, W. E. Reactive polymers for blend compatibilization. Adv. Polym. Technol. 1992, 11, 249–262.
(20) Yang, H. S.; Kim, H. J.; Park, H. J.; Lee, B. J.; Hwang, T. S. Water absorption behavior and mechanical properties of lignoncellulosic filler-polylefin biocomposites. Compos. Struct. 2006, 72, 429–437.
(21) Spiridon, I.; Nicoleta, R.; Nita, D.; Kozlowski, M.; Netchia, A.; Ursu, R. G. Influence of Accelerated Weathering on the Performance of Polylyactic Acid based Materials. Cellul. Chem. Technol. 2016, 50, 5–6.
(22) Spiridon, I.; Darie-Nita, R. N.; Hitric, G. E.; Ludwiczak, J.; Cianga Spiridon, I. A.; Niculaia, M. New opportunities to valorize biomass wastes into green materials. J. Cleaner Prod. 2016, 133, 235–242.
(23) Park, Su-II; Jiang, Y.; Simonsen, J.; Zhao, Y. Feasibility of creating compression-molded biocomposite boards from berry fruit pomaces. J. Appl. Polym. Sci. 2010, 115, 127–136.
(24) Kim, H.-S.; Kim, H.-J. Enhanced hydrolysis resistance of biodegradable polymers and bio-composites. Polym. Degrad. Stab. 2008, 93, 1544–1553.
(25) Phua, Y. J.; Chow, W. S.; Mohd Ishak, Z. A. The hydrolytic effect of moisture and hygrothermal aging on poly(butylene succinate)/organo-montmorillonite nanocomposites. Polym. Degrad. Stab. 2011, 96, 1194–1203.
(26) Phua, Y. J.; Chow, W. S.; Mohd Ishak, Z. A. Reactive processing of maleic anhydride-grafted poly(butylene succinate) and the compatibilizing effect on poly(butylene succinate) nanocomposites. eXPRESS Polym. Lett. 2013, 7, 340–354.
(27) Cai, Y.; Lv, J.; Feng, J. Spectral Characterization of Four Kinds of Biodegradable Plastics: Poly (Lactic Acid), Poly (Butylenes Adipate-Co-Terephthalate), Poly (Hydroxybutyrate-Co-Hydroxyvalerate) and Poly (Butylenes Succinate) with FTIR and Raman Spectroscopy. J. Polym. Environ. 2013, 21, 108–114.
(28) Deytothen, S.; Selke, S. E. M.; Narayan, R.; Rubino, M.; Auras, R. Reactive functionalization of poly(lactic acid), PLA: Effects of the reactive modifier, initiator and processing conditions on the final grafted maleic anhydride content and molecular weight of PLA. Polym. Degrad. Stab. 2013, 98, 2697–2708.
(29) Gu, X.; Yang, C. Q. FTIR Spectroscopy Study of the Formation of Cyclic Anhydride Intermediates of Polycarboxylic Acids Catalyzed by Sodium Hypophosphite. Text. Res. J. 2000, 70, 64–70.
(30) Widmann, G. Interpreting TGA curves UserCom 2001, 1 20.
(31) Kim, H.-S.; Yang, H.; Kim, H.; Lee, B.; Hwang, T. Thermal Properties of Agro-Flour-Filled Biodegradable Polymer Bio-Composites. J. Therm. Anal. Calorim. 2005, 81, 299–306.
(32) Khiani, B.; Jeguirim, M. Pyrolysis of Grape Marc from Tunisian Wine Industry: Feedstock Characterization, Thermal Degradation and Kinetic Analysis. Energies 2018, 11, 730.
(33) Yang, H.; Yan, R.; Chen, H.; Lee, D. H.; Zheng, C. Characteristics of hemicellulose, cellulose and lignin pyrolysis. Fuel 2007, 86, 1781–1788.
(34) Sahoo, S.; Misra, M.; Mohanty, A. K. Effect of compatibilizer and fillers on the properties of injection molded lignin-based hybrid green composites. J. Appl. Polym. Sci. 2013, 127, 4110–4121.
(35) Nielsen, L. E. Mechanical Properties of Polymers and Composites. In Mechanical Properties of Polymers and Composites, 2nd ed.; Taylor & Francis Group, CRC Press: New York, 1974; pp 1–880.
(36) Lee, M. W.; Han, S. O.; Seo, Y. B. Red algae fibre/poly(butylene succinate) biocomposites: The effect of fibre content on their mechanical and thermal properties. Compos. Sci. Technol. 2008, 68, 1266–1272.
(37) Lee, S. M.; Cho, D.; Park, W. H.; Lee, S. G.; Han, S. O.; Drzal, L. T. Novel silk/poly(butylene succinate) biocomposites: The effect of short fibre content on their mechanical and thermal properties. Compos. Sci. Technol. 2005, 65, 647–657.
(38) Pothan, L. A.; Oommen, Z.; Thomas, S. Dynamic mechanical analysis of banana fiber reinforced polyester composites. Compos. Sci. Technol. 2003, 63, 283–293.
(39) George, J.; Bhagawan, S. S.; Thomas, S. Thermogravimetric and dynamic mechanical thermal analysis of pineapple fibre reinforced polyethylene composites. J. Therm. Anal. Calorim. 1996, 47, 1121–1140.
(40) Nyambo, C.; Mohanty, A. K.; Misra, M. Polyacryl-Id Based Renewable Green Composites from Agricultural Residues and Their Hybrids. Biomacromolecules 2010, 11, 1654–1660.
(41) Ahankari, S. S.; Mohanty, A. K.; Misra, M. Mechanical behaviour of agro-residue reinforced poly(3-hydroxybutyrate-co-3-hydroxyvalerate), (PHBV) green composites: A comparison with traditional polylactline composites. Compos. Sci. Technol. 2011, 71, 653–657.
(42) Zhang, Y.; Yu, C.; Chu, P. K.; Lv, F.; Zhang, C.; Ji, J.; Zhang, R.; Wang, H. Mechanical and thermal properties of basalt fiber reinforced poly(butylene succinate) composites. Mater. Chem. Phys. 2012, 133, 845–849.
(43) Chen, R. Y.; Zou, W.; Zhang, H. C.; Zhang, G. Z.; Yang, Z. T.; Jin, G.; Qu, J. P. Thermal behavior, dynamic mechanical properties and rheological properties of poly(butylene succinate) composites filled with nanometer calcium carbonate. Polym. Test. 2015, 42, 160–167.
(44) Yasuniwa, M.; Satou, T. Multiple melting behavior of poly(butylene succinate). I. Thermal analysis of melt-crystallized samples. J. Polym. Sci., Part B: Polym. Phys. 2002, 40, 2411−2420.
(45) Ma, P. M.; Wang, R. Y.; Wang, S. F.; Zhang, Y.; Zhang, Y. X.; Hristova, D. Effects of fumed silica on the crystallization behavior and thermal properties of poly(hydroxybutyrate-co-hydroxyvalerate). J. Appl. Polym. Sci. 2008, 108, 1770−1777.
(46) Song, B.; Wang, Y.; Bai, H.; Liu, L.; Li, Y.; Zhang, J.; Zhou, Z. Crystallization and melting behaviors of maleic anhydride grafted poly(propylene) nucleated by an aryl amide derivative. J. Therm. Anal. Calorim. 2010, 99, 563−570.
(47) Du, Y.; Wu, T.; Yan, N.; Kortschot, M. T.; Farnood, R. Fabrication and characterization of fully biodegradable natural fiber-reinforced poly(lactic acid) composites. Composites, Part B 2014, 56, 717−723.
(48) Igarza, E.; Pardo, S. G.; Abad, M. J.; Cano, J.; Galante, M. J.; Prettarin, V.; Bernal, C. Structure-fracture properties relationship for Polypropylene reinforced with fly ash with and without maleic anhydride functionalized isotactic Polypropylene as coupling agent. Mater. Des. 2014, 55, 85−92.
(49) Mani, R.; Bhattacharya, M.; Tang, J. Functionalization of polyesters with maleic anhydride by reactive extrusion. J. Polym. Sci., Part A: Polym. Chem. 1999, 37, 1693−1702.
(50) Carlson, D.; Nie, L.; Narayan, R.; Dubois, P. Maleation of Polyactide (PLA) by Reactive Extrusion. J. Appl. Polym. Sci. 1999, 72, 477−485.
(51) Csikos, A.; Faludi, G.; Domján, A.; Renner, K.; Móczó, J.; Pukanszky, B. Modification of interfacial adhesion with a functionalized polymer in PLA/wood composites. Eur. Polym. J. 2015, 68, 592−600.
(52) Gao, H.; Xie, Y.; Ou, R.; Wang, Q. Grafting effects of polypropylene/polyethylene blends with maleic anhydride on the properties of the resulting wood-plastic composites. Composites, Part A 2012, 43, 150−157.
(53) Avella, M.; Bogoeva-Gaceva, G.; Bužaroska, A.; Errico, M. E.; Gentile, G.; Grozdanov, A. Poly(lactic acid)-based biocomposites reinforced with kenaf fibers. J. Appl. Polym. Sci. 2008, 108, 3542−3551.
(54) Avella, M.; Bogoeva-Gaceva, G.; Bužaroska, A.; Errico, M. E.; Gentile, G.; Grozdanov, A. Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)-Based Biocomposites Reinforced with Kenaf Fibers. J. Appl. Polym. Sci. 2007, 104, 3192−3200.
(55) Lee, S. H.; Wang, S. Biodegradable polymers/bamboo fiber biocomposite with bio-based coupling agent. Composites, Part A 2006, 37, 80−91.
(56) Thirmizir, M. Z. A.; Ishak, Z. A. M.; Taib, R. M.; Rahim, S.; Jani, S. M. Kenaf-bast-fiber-filled biodegradable poly(butylene succinate) composites: Effects of fiber loading, fiber length, and maleated poly(butylene succinate) on the flexural and impact properties. J. Appl. Polym. Sci. 2011, 122, 3055−3063.
(57) Kim, H. S.; Lee, B. H.; Choi, S. W.; Kim, S.; Kim, H. I. The effect of types of maleic anhydride-grafted polypropylene (MAPP) on the interfacial adhesion properties of bio-flour-filled polypropylene composites. Composites, Part A 2007, 38, 1473−1482.
(58) Ptt MCC Biochem. BioPBS FZ71PM Technical Data Sheet Extrusion Coating Product Description; Technical Report, 2017.
(59) Nabar, Y.; Raquez, J. M.; Dubois, P.; Narayan, R. Production of starch foams by twin-screw extrusion: Effect of maleated poly(butylene adipate-co-terephthalate) as a compatibilizer. Biomacromolecules 2005, 6, 807−817.
(60) Miyata, T.; Masuko, T. Crystallization behaviour of poly(tetramethylene succinate). Polymer 1998, 39, 1399−1404.