RESEARCH ARTICLE

Use of starch granules melting to control the properties of bio-flour filled polypropylene and poly(butylene succinate) composites: Mechanical properties

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The feasibility and industrial potential of using bio-flours from tropical crop residues, in particular starch containing bio-flours, for the manufacture of bio-composites was investigated. Polypropylene (PP) and poly(butylene succinate) (PBS) were compounded with bio-flours from pineapple skin (P) and from non-destarched (CS) and destarched (C) cassava root by twin-screw extrusion. In CS composites, two levels of starch granules melting were achieved by adjusting the extrusion temperature, enabling control of morphological and mechanical properties. The use of bio-flours reduced tensile strength by 26–48% and impact strength by 14–40% when the proportion of bio-flour was increased to 40% w/w, while flexural strength initially increased upon addition of bio-flours, before decreasing at higher loads. The use of compatibilizers, in particular maleic anhydride-polypropylene (MAPP) in PP composites with 30% bio-flour resulted in tensile strength similar to non-compatibilized composites with 10% bio-flour (34–35 MPa). MAPP also increased flexural strength to higher levels than pure PP, resulting in a stronger, but less flexible material.

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1 Introduction

The sharp rise in the price of oil in recent years and environmental concerns spurred research efforts to develop materials based on renewable and biodegradable resources, in order to reduce the use of conventional polyolefins such as polyethylene (PE) and polypropylene (PP). One approach is to develop composites of polyole-

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Abbreviations: AAPP, acrylic acid-polypropylene; **MAPP,** maleic anhydride-polypropylene; **PBS,** poly(butylene succinate); **PE,** polyethylene; **PP,** polypropylene

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fins and natural bio-flours to reduce the amount of non-renewable polyolefin consumed [1–4]. Furthermore, when possible replacing polyolefins with biodegradable polymers, for instance poly(butylene succinate) (PBS) or polylactic acid (PLA), is desirable to achieve fully renewable materials [5, 6]. The use of PE and PP in bio-flour filled composite materials has been studied extensively [7–10]. Biodegradable polymers (PBS, PLA) are now commercially available, and their use for the production of bio-composites is also under investigation [11, 12].

Wastes from agricultural production are an abundant source of natural bio-flours, which can be used as filler for the production of plastic bio-composites. For instance, wood flour and rice husk flour have been tested in PE and PP matrixes with satisfactory results in terms of dispersion and mechanical properties [13]. Typically the addition of bio-flours decreases the tensile strength of the plastic matrix, but the mechanical properties remain acceptable with up to 40–50% bio-flour w/w for applications with low levels of stress, such as some construction materials (decks, window frames, and panels) and car parts (door panels and dashboards) [14]. With extensive agricultural production, Thailand generates large quantities of natural bio-flours, in particular rice husks (5 million tons/year), rice straw (7 million tons/year), bagasse from sugar cane (16 million tons/year), cassava root flours (1.5 million tons/year), and pineapple leaf fibers and skin flours (1 million tons/year) [5]. These bio-flours are generally cheap ($<$0.3 USD/kg) and are therefore good potential alternative sources of raw materials.

While most bio-flours are composed of lignocellulosic particles, a few also contain starch after processing, for instance cassava root flour which comprises up to 69% starch, dry basis [15]. Native starch is a semi-crystalline polysaccharide in the form of discrete granules [16, 17]. Under heat and pressure, starch forms a continuous, amorphous material made of molten granules, a process known as gelatinization [18]. Depending on the severity of the treatment, different degrees of gelatinization can be obtained, resulting in a continuum of morphological states from discrete to partially melted granules, to fully amorphous material. In pure starch materials and in composites containing starch, the degree of gelatinization contributes to the determination of mechanical properties [19].

Due to the hydrophobic nature of the polymer matrix and the hydrophilic nature of the bio-flours, compatibilizers are useful to reduce interface tension and to improve adhesion between the two phases. The use of compatibilizers typically results in an increase in tensile strength, thus at least partially compensating for the weaker mechanical properties caused by the addition of bio-flours [13]. To be effective, compatibilizers must interact well with both the hydrophilic and the hydrophobic fractions of the material. In the case of PE and PP, a family of compatibilizers based on PE or PP grafted with maleic anhydride has been developed [4] and is commercially available. Maleic anhydride has the ability to interact with the bio-flours either via the formation of covalent bonds with hydroxyl groups carried by the bio-flours (esterification) or via hydrogen bonds [20]. Following the same principle, another type of compatibilizer based on PP grafted with acrylic acid is also commercially available, with the carboxylic acid playing the same role as maleic anhydride in MAPP.

The objective of this work was to test whether the degree of starch granules melting obtained by extrusion under different temperatures can influence the morphological and mechanical properties of PP- and PBS-based bio-composites filled with a starch-containing cassava bio-flour. Bio-flours without starch were used as controls and to further demonstrate the industrial potential of using low-cost bio-flours obtained from tropical crops by-products for the development of bio-composites with satisfactory mechanical properties.

2 Materials and methods

2.1 Materials

Polypropylene (PP) and polybutylene succinate (PBS), used as the matrix polymer, were supplied as homopolymer pellets by LG Chem. Ltd. (Seoul, South Korea) and by IRe Chemical Ltd. (Wonju, South Korea), respectively. Two of the bio-flours used as reinforcing fillers were pineapple skin (P) and non-destarched cassava root bio-flour (CS) obtained from pineapple and cassava starch processing factories in Thailand, and further powdered, washed, and dried at the Cassava and Starch Technology Research Unit (CSTRU, Bangkok) facilities. A third bio-flour was prepared at the CSTRU by treating CS bio-flour with α-amylase (2 h, 100°C) and glucoamylase (overnight, temperature below 60°C) to remove the starch fraction (up to 69% dry weight basis [15]), resulting in destarched cassava root bio-flour (C). The proximate analysis and rough particle size distribution (as determined by sieving), of the bio-flours are summarized in Tables 1 and 2. The maleic anhydride-polypropylene (MAPP) and acrylic acid-polypropylene (AAPP) compatibilizers were obtained from Crompton Corporation (Chemtura Corporation, Middlebury, CT, USA) in the form of Polybond 3200 (1% weight maleic anhydride) and Polybond 1002 (6% weight acrylic acid), respectively. MAPBS was synthesized at Seoul National University by reactive extrusion at 145°C and 200 rpm, using PBS, maleic anhydride (Merck, Whitehouse Station, NJ, USA) and dicumyl peroxide (Aldrich, St. Louis, MO, USA) as a catalyzer in the proportions 100:7:0.7 w/w.

Table 1. Proximate analysis (% dry weight basis) of non-destarched cassava, destarched cassava, and pineapple bio-flours

Proximate analysis	Non-destarched cassava	Destarched cassava	Pineapple skin
Crude fiber (%)	16.10 ± 0.04	39.40 ± 0.05	23.49 ± 0.04
Starch (%)	55.84 ± 0.01	–	2.65 ± 0.03
Protein (%)	2.27 ± 0.02	4.22 ± 0.00	4.52 ± 0.01
Ash (%)	5.23 ± 0.03	6.52 ± 0.03	2.66 ± 0.00

Table 2. Particle size distribution of non-destarched cassava, destarched cassava, and pineapple bio-flours

Particle size (μm)	Non-destarched cassava (%)	Destarched cassava (%)	Pineapple skin (%)
<100	4.97	7.35	0.02
100–200	19.98	23.74	14.14
200–500	68.19	63.15	84.88
>500	6.86	5.79	0.96

2.2 Compounding and sample preparation

The bio-flours were oven dried at 105°C for 24 h to adjust the moisture content to 1–3% and then stored in sealed PE bags before compounding. The matrix polymers, PP and PBS, were blended with each bio-flour and compatibilizing agents (MAPP, AAPP, and MAPBS) in a laboratory size, co-rotating, twin screw extruder (model BA-19, Bau Technology, Uijungbu, Kyungki, South Korea) using three general processes: melt blending, extrusion, and pelletizing. The extruder barrel had a diameter of 19 mm and was divided into eight zones with the temperature in each zone being individually adjustable. The temperature of the mixing (central) zone in the barrel was maintained at, respectively, 185°C for PP-based samples and 145°C for PBS-based samples, that is 25–30°C above the melting temperatures of the polyolefins in order to reduce melt viscosity to a suitable level for processing [20, 21]. The screw speed was set at 200 rpm. Volatiles were extracted using a venting hole placed near the extruder die and connected to a water-vacuum pump. The extruded strand was cooled in a water bath at room temperature and pelletized using a pelletizer (Bau Technology, Uijungbu, Kyungki, South Korea). Extruded pellets were oven dried at 80°C for 1–2 h and compounded a second time in the extruder to improve blending, before being dried again at 80°C for 6 h, and then stored in sealed PE bags. To investigate the effect of the proportion of bio-flour on mechanical properties, composite samples were prepared at 10, 20, 30, and 40 wt% bio-flour. To investigate the effect of compatibilizing agents on the mechanical and thermal properties, composite samples were prepared with 30 wt% bio-flour loading and incorporating MAPP, AAPP, and MAPBS at 3 wt%, based on the total weight of composite.

Extruded pellets were injection molded into tensile (ASTM D638), Izod impact (ASTM D256), and three-point bend test bars (ASTM D790) using an injection molding machine (Bau Technology, Uijungbu, Kyungki, South Korea) at 185°C (PP composites) and 145°C (PBS composites) with an injection pressure of 1200 psi and a device pressure of 1500 psi. The tensile specimens had the following dimensions: $L = 10.8$ mm, $W = 3.2$ mm, $T = 3.1$ mm, where L, W, and T are the length, width, and thickness of the narrow section, respectively. The specimens for the impact and three-point-bend tests had the following dimensions: $L = 75$ mm, $W = 12.5$ mm, $T = 3.1$ mm, where L, W, and T are the length, width, and thickness of the test bar, respectively.

2.3 Mechanical properties of the composites

The tensile test of the composites was conducted according to ASTM D638-99 (ASTM, 1999) with a Universal Testing Machine (Zwick Co., Ulm, Germany) at a crosshead speed of 100 mm/min and a temperature of 24°C. The notched Izod impact strength was measured on an impact tester (model DYD-103C, DaeYeong Precision Co., Kunpo, Kyungki, South Korea) using the ASTM method D256-97 (ASTM, 1999) at 24°C. The notch depth and the fracture length were 2.5 and 10 mm, respectively. The three-point bend tests of the composites were carried out according to ASTM D790 (ASTM, 1999) with a Universal Testing Machine (Lloyd Instrument LR30, Fareham, Hampshire, UK). The span was set to 49.6 mm, so that the span to depth ratio was 16:1, and the tests were carried out at a crosshead speed of 5 mm/min. All measurements were replicated five times.

2.4 Morphology of the composites

The morphology of the fracture surface of samples after tensile tests was investigated by SEM. The microscope used was a Philips model XL30 with an acceleration of 13 kV. The samples were coated with a layer of gold under vacuum before the experiment.

2.5 Statistical analyses

Statistically significant differences between sample means were determined using Student's *t*-test at 95% confidence level. Multivariate linear discriminant analysis was used to identify differences among the samples based on their mechanical properties. Statistical analyses were performed with JMP IN 5.1.2 software (SAS Institute Inc., SAS Campus Drive, Cary, NC, USA).

3 Results and discussion

3.1 Effect of the proportion of bio-flours on mechanical properties

3.1.1 Tensile and impact tests

The mechanical properties of all samples are summarized in Table 3. For both PP and PBS, the tensile strength, strain at maximum force, and impact strength weakened with increasing proportions of bio-flour. Tensile strength decreased from 39.3 MPa for pure PP to 24.9–29.0 MPa at 40% bio-flour in PP composites, and from 34.8 MPa

Table 3. Mechanical properties of the PP and PBS bio-composites

	Tensile strength (MPa)	Strain at Fmax	Impact strength (kJ/m^{2})	Flexural strength (MPa)	Flexural modulus (MPa)
PP	39.34 (1.19)^{a}	0.402 (0.017)^{bc}	4.68 (0.18)^{efgh}	32.25 (1.99)^{n}	966.7 (23.7)^{o}
PP-C10%	34.19 (1.36)^{de}	0.314 (0.010)^{e}	3.79 (0.60)^{lmno}	37.10 (0.28)^{h}	1512.6 (26.6)^{k}
PP-C20%	33.28 (0.49)^{e}	0.299 (0.012)^{efghi}	4.03 (0.26)^{ijklm}	36.12 (0.57)^{hi}	1783.8 (82.9)^{gh}
PP-C30%	29.71 (1.72)^{gh}	0.267 (0.016)^{jkl}	3.42 (0.26)^{no}	33.51 (0.50)^{l}	1931.7 (85.9)^{f}
PP-C40%	29.02 (0.55)^{hi}	0.248 (0.001)^{lmno}	3.82 (0.31)^{klmno}	29.24 (1.12)^{r}	2198.9 (50.9)^{cd}
PP-C30% + MAPP	36.06 (0.95)^{bc}	0.299 (0.008)^{efgh}	3.79 (0.17)^{lmno}	39.92 (0.99)^{fg}	2148.7 (104.2)^{d}
PP-C30% + AAPP	31.42 (1.45)^{f}	0.277 (0.027)^{ijk}	3.85 (0.46)^{klmno}	35.84 (0.82)^{i}	2021.0 (59.5)^{e}
PP-CS10%	33.97 (1.05)^{de}	0.300 (0.016)^{efgh}	3.85 (0.27)^{klmno}	34.76 (0.49)^{jk}	1337.1 (26.0)^{l}
PP-CS20%	31.49 (0.59)^{f}	0.283 (0.015)^{ghij}	3.72 (0.40)^{mno}	33.90 (0.54)^{kl}	1602.8 (90.0)^{j}
PP-CS30%	28.57 (0.27)^{hij}	0.268 (0.014)^{jkl}	3.79 (0.35)^{lmno}	31.12 (0.28)^{op}	1604.8 (23.1)^{j}
PP-CS40%	24.90 (0.11)^{l}	0.230 (0.010)^{o}	4.03 (0.45)^{ijklm}	27.06 (1.19)^{s}	1788.9 (76.8)^{gh}
PP-CS30% + MAPP	36.60 (1.53)^{b}	0.300 (0.006)^{efgh}	3.66 (0.48)^{mno}	40.17 (0.26)^{f}	1814.8 (59.3)^{g}
PP-CS30% + AAPP	29.75 (2.10)^{gh}	0.261 (0.021)^{klm}	3.36 (0.43)^{o}	33.71 (0.68)^{l}	1742.7 (55.7)^{hi}
PP-P10%	35.01 (0.71)^{cd}	0.304 (0.015)^{efg}	4.35 (0.58)^{ghijk}	48.02 (1.10)^{a}	1895.4 (28.1)^{f}
PP-P20%	31.35 (0.58)^{f}	0.295 (0.012)^{efghi}	3.85 (0.27)^{klmno}	45.26 (0.29)^{c}	2369.9 (50.1)^{b}
PP-P30%	31.43 (0.89)^{f}	0.288 (0.015)^{ghij}	3.74 (0.29)^{lmno}	45.74 (1.07)^{bc}	2224.4 (102.8)^{c}
PP-P40%	27.12 (0.50)^{k}	0.241 (0.014)^{mno}	3.66 (0.22)^{mno}	38.92 (0.65)^{g}	2661.5 (58.5)^{a}
PP-P30% + MAPP	33.84 (1.11)^{de}	0.269 (0.011)^{jkl}	3.66 (0.37)^{mno}	46.60 (0.55)^{b}	2178.9 (72.3)^{cd}
PP-P30% + AAPP	31.86 (1.03)^{f}	0.279 (0.020)^{ijk}	3.60 (0.40)^{mno}	43.34 (0.30)^{d}	2174.3 (91.7)^{cd}
PBS	34.83 (1.07)^{cd}	0.458 (0.038)^{a}	6.56 (1.08)^{a}	29.43 (0.40)^{r}	516.0 (2.5)^{r}
PBS-C10%	30.90 (0.69)^{fg}	0.411 (0.013)^{b}	5.25 (0.66)^{cde}	35.98 (0.49)^{i}	783.4 (26.4)^{p}
PBS-C20%	27.60 (0.66)^{jk}	0.349 (0.010)^{d}	4.52 (0.26)^{ghi}	35.71 (0.88)^{ij}	1007.2 (48.8)^{no}
PBS-C30%	23.25 (0.65)^{m}	0.298 (0.013)^{efghi}	4.58 (0.31)^{fghi}	30.69 (0.55)^{pq}	1297.2 (42.2)^{lm}
PBS-C40%	19.60 (0.43)^{o}	0.251 (0.015)^{lmn}	3.97 (0.31)^{jklm}	23.93 (0.57)^{t}	1565.7 (48.3)^{jk}
PBS-C30% + MAPBS	23.43 (2.56)^{m}	0.312 (0.026)^{ef}	4.50 (0.46)^{ghij}	33.46 (0.08)^{lm}	1357.6 (56.8)^{l}
PBS-CS10%	29.40 (0.20)^{h}	0.400 (0.015)^{bc}	5.56 (0.45)^{bc}	31.83 (0.52)^{no}	644.1 (26.0)^{q}
PBS-CS20%	25.06 (0.35)^{l}	0.343 (0.010)^{d}	5.13 (0.33)^{cdef}	32.42 (0.32)^{mn}	821.4 (5.9)^{p}
PBS-CS30%	20.74 (0.78)^{no}	0.292 (0.008)^{fghi}	4.05 (0.15)^{ijklm}	29.76 (0.42)^{qr}	1053.4 (9.0)^{n}
PBS-CS40%	18.11 (0.37)^{p}	0.235 (0.017)^{no}	3.91 (0.33)^{klmn}	24.93 (0.70)^{t}	1239.0 (30.2)^{m}
PBS-CS30% + MAPBS	21.14 (1.29)^{n}	0.281 (0.014)^{hijk}	4.27 (0.37)^{hijkl}	30.67 (0.50)^{pq}	1061.3 (24.1)^{n}
PBS-P10%	31.26 (0.74)^{f}	0.389 (0.017)^{c}	6.03 (0.88)^{ab}	39.64 (0.39)^{fg}	826.3 (23.3)^{p}
PBS-P20%	27.97 (0.45)^{ijk}	0.342 (0.013)^{d}	5.37 (0.46)^{cd}	41.23 (0.69)^{e}	1060.7 (36.2)^{n}
PBS-P30%	24.44 (1.34)^{lm}	0.302 (0.027)^{efgh}	4.88 (0.22)^{defg}	41.76 (1.78)^{e}	1518.7 (56.2)^{k}
PBS-P40%	20.64 (0.40)^{no}	0.243 (0.005)^{mno}	4.50 (0.15)^{ghij}	35.22 (0.56)^{ij}	1704.4 (25.9)^{i}
PBS-P30% + MAPBS	24.92 (0.19)^{l}	0.290 (0.018)^{ghi}	4.88 (0.25)^{defg}	43.55 (1.76)^{d}	1517.5 (98.9)^{k}

C, CS, and P represent destarched cassava, non-destarched cassava and pineapple bio-flours, respectively. The percentages indicate the proportion of bio-flours in the composites.
SDs are in brackets. Statistically significant differences are indicated with superscript letters.

for pure PBS to 18.1–20.6 MPa at 40% bio-flour in PBS composites. Strain at maximum force decreased from 0.40 for pure PP to 0.23–0.25 at 40% bio-flour in PP composites, and from 0.46 for pure PBS to 0.24–0.25 at 40% bio-flour in PBS composites. Impact strength decreased from 4.68 kJ/m^2 for pure PP to 3.66–4.03 kJ/m^2 at 40% bio-flour, and from 6.56 kJ/m^2 for pure PBS to 3.97–4.50 kJ/m^2 at 40% bio-flour. No statistically significant differences were identified between the three types of bio-flours (pineapple (P), non-destarched cassava (CS), and destarched cassava (C)) in terms of strain at maximum force and impact strength. Comparable results were obtained in other studies using pineapple leaf fibers [22] and rice husk flour and wood flour [20].

3.1.2 Flexural test

For both PP and PBS, the addition of a low proportion of bio-flour (10–20%) increased flexural strength, from 32.3 MPa for pure PP to 34.8–48.0 and 33.9–45.3 MPa with 10 and 20% bio-flour in PP composites, respectively, and from 29.4 MPa for pure PBS to 31.8–39.6 and 32.4–41.2 MPa with 10 and 20% bio-flour in PBS composites, respectively. With higher proportions of bio-flour (30–40%), a decrease in flexural strength was observed, which varied with the type of bio-flour: The flexural strength of P bio-flour composites remained higher than that of the pure polymer materials (respectively, 38.9 and 35.2 MPa for PP and PBS composites at 40% bio-flour), whereas the flexural strength of CS and C bio-flours composites became lower than that of pure polymer materials (respectively, 27.1–29.2 and 23.9–24.9 MPa for PP and PBS composites at 40% bio-flour). The increase in flexural strength at 10–20% bio-flour was less marked in composites with CS bio-flour than in composites with C and P bio-flours, which may be interpreted as the ability of starch to mitigate the effect of cellulosic bio-flours, resulting in a composite whose flexural strength is closer to that of the pure polymer. For both PP and PBS, the flexural modulus increased with increasing proportions of bio-flour, from 966.7 MPa for pure PP to 1788.9–2661.5 MPa with 40% bio-flour in PP composites, and from 516.0 MPa for pure PBS to 1239.0–1704.4 MPa with 40% bio-flour in PBS composites. The type of bio-flour had a significant effect on the flexural modulus, with P bio-flour causing a large increase, up to, respectively, 2661.5 and 1704.4 MPa in PP and PBS composites with 40% bio-flour, whereas CS bio-flour caused the smallest increase, up to, respectively, 1788.9 and 1239.0 MPa in PP and PBS composites with 40% bio-flour. These observations may reflect the ability of the starch present in CS bio-flour to create a more ductile, but less strong material.

3.2 Effect of the degree of starch granules melting on the morphology and mechanical properties of the composites

3.2.1 Evidence of starch granules melting during processing

Starch in its native state comes in the form of round granules that are readily observable by SEM [16], and in which the polysaccharide chains are packed in semi-crystalline order [17]. In the case of cassava, granule size distribution is in the range 10–30 μm [23]. When heated to 60–70°C in excess water (>66% water w/w [18]), the granules melt and release starch molecules, thus forming a homogeneous solution or gel depending on the concentration. When water is limited or absent, the starch granules melt at higher temperatures, up to 200°C, depending on the water available, shear rate, and pressure applied during the process. Hence the extrusion conditions used during this study correspond to the possibility that starch granules melting occurred in the blends containing non-destarched cassava bio-flour. SEM observations (Fig. 1) of non-destarched cassava (CS) bio-flour blends confirmed that granules melting occurred at a temperature between 145 and 185°C, as intact starch granules were clearly visible in PBS blends extruded at a lower temperature (145°C), whereas only a few intact granules remained in PP blends extruded at a higher temperature (185°C). To illustrate the difference between blends containing destarched (C) and non-destarched (CS) cassava bio-flours, SEM micrographs of blends of C bio-flour with PBS and PP are also provided in Fig. 2, showing the presence of only cellulosic particles with sizes typically above 50 μm

SEM observations indicated that the extrusion conditions markedly influenced starch granules melting, resulting in two morphologically different categories of materials: At 145°C (PBS composites) the extent of granules melting was limited so that starch remained in discrete granules, whereas at 185°C (PP composites) granules melting was more extensive. Regarding the morphology of the molten starch fraction, SEM observations of molten granules merging into a larger continuous starch phase (Fig. 3) suggest the formation of either pockets or strings of molten starch enclosed in the PP phase, particularly at higher proportions of CS bio-flour (30% and above), as observed by other authors [8, 24].

3.2.2 Effect of starch granules melting on mechanical properties

In PBS composites extruded at 145°C, the non-destarched cassava bio-flour (CS) resulted in significantly lower tensile strengths than the other bio-flours (destarched

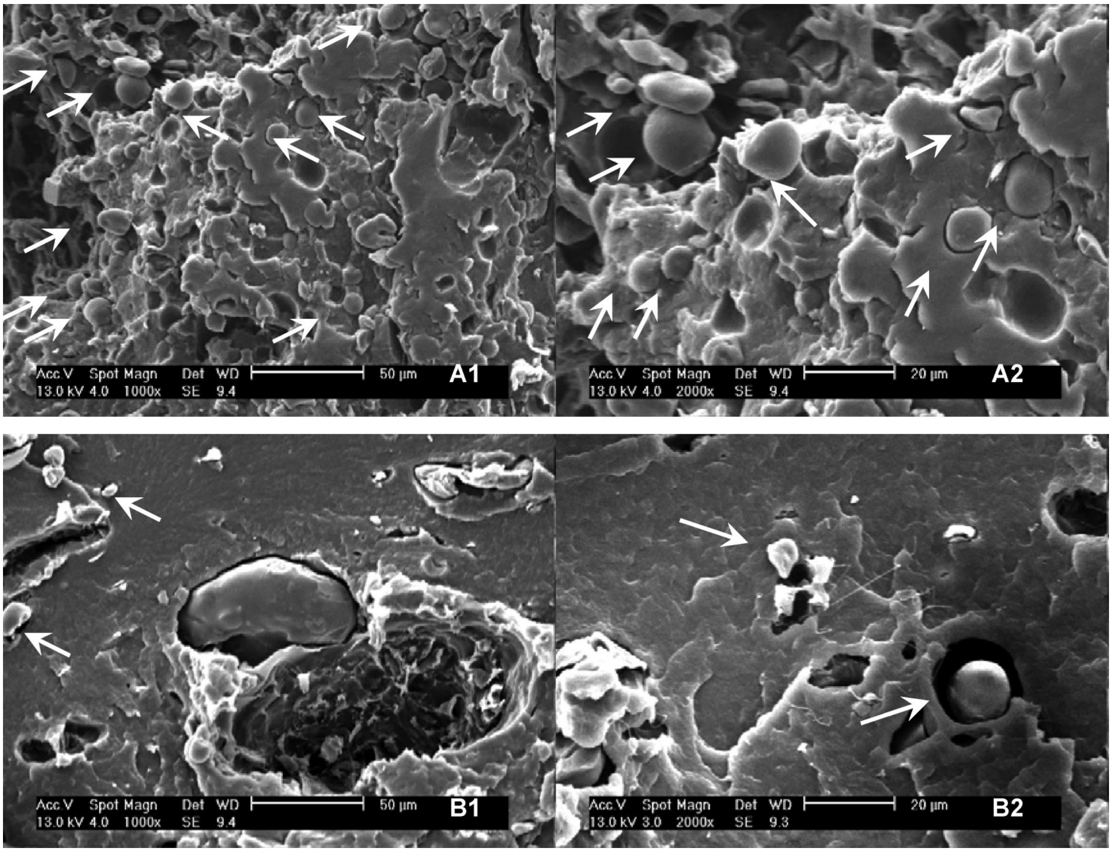

Figure 1. SEM micrographs showing the presence of non-melted starch granules in 70:30 blends of PBS/non-destarched cassava bio-flour extruded at 145°C (A1, A2) and of the few intact starch granules in 70:30 PP/non-destarched cassava bio-flour extruded at 185°C (B1, B2). Starch granules are indicated with arrows. The large particle visible in the center of (B1) is a cellulosic particle.

cassava (C) and pineapple (P)) for the whole range of proportions tested (Table 3): 29.4, 25.1, 20.7, and 18.1 MPa for CS versus 30.9, 27.6, 23.3, and 19.6 MPa for C and 31.3, 28.0, 24.4, and 20.6 MPa for P with, respectively, 10, 20, 30, and 40% bio-flour. In contrast, in PP composites extruded at 185 °C, the CS bio-flour led to significantly lower tensile strength only at the highest proportion of bio-flour, 40% (24.9 MPa for CS versus 29.0 MPa for C and 27.1 MPa for P). Hence, the presence of numerous intact starch granules in PBS/CS composites may weaken the tensile strength of this type of material, whereas the molten starch present in PP/CS composites did affect tensile strength at high proportions of bio-flour, i.e., when molten starch was abundant enough to form a semi-continuous phase enclosed in the PP matrix. The flexural modulus of PP/CS composites increased with the proportion of bio-flour (Table 3), however the increase became slower with more than 30% bio-flour, with a change of 19.9, 0.1, and 11.5% between 10 and 20%, 20 and 30%, and 30 and 40% bio-flour, respectively. Hence the use of CS bio-flour in large enough proportions to form a semi-continuous phase of molten starch (30% and above) appeared to enhance the flexibility of the material, thereby attenuating the stiffening effect of the lignocellulosic particles.

3.3 Effect of the compatibilizer on the morphology and mechanical properties of the composites

3.3.1 Improvement in adhesion between polymer matrix and bio-flours

The morphologies of blends of destarched cassava bio-flour (C) and PP and PBS, with and without compatibilizer were compared by SEM (Figs. 4 and 5). Non-compatibilized composites showed large gaps between bio-flour particles and the continuous polymer phase (5–10 μm, Figs. 4-A and 5-A). This gap was reduced to < 5 μm in PP composites compatibilized with MAPP (Fig. 4-B), as well as in PBS composites compatibilized with MAPBS (Fig. 5-B), thus demonstrating the positive effect of maleic-

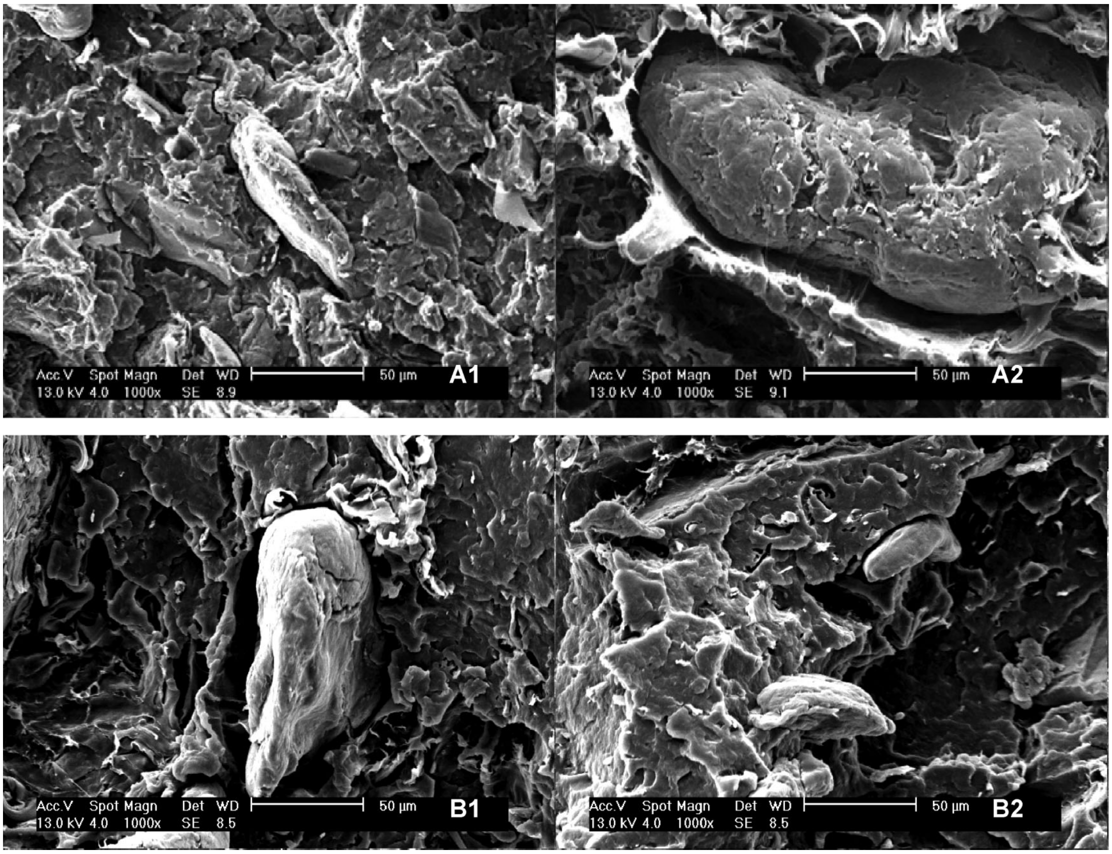

Figure 2. SEM micrographs showing the presence of only cellulosic particles in 70:30 blends of PBS/destarched cassava bio-flour (A1, A2) and PP/destarched cassava bio-flour (B1, B2).

anhydride based compatibilizers. These observations also confirmed that the extrusion conditions used for the "in-house" preparation of MAPBS at SNU were effective. The gap between polymer and bio-flour particles was not reduced in the case of AAPP-compatibilized composites (Fig. 4C), which may be due to the lower reactivity of acrylic acid than of maleic anhydride. Similar observations were obtained with composites containing non-destarched cassava bio-flour (CS).

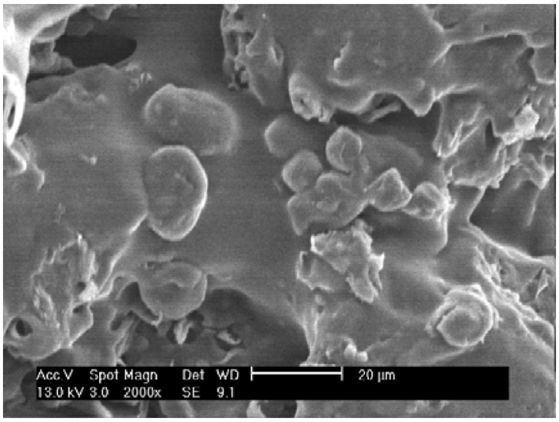

Figure 3. SEM micrographs showing partially molten starch granules merging into a continuous starch phase (white arrows), in a 60:40 blend of PP/non-destarched cassava bio-flour.

3.3.2 Improvement of mechanical properties

3.3.2.1 Tensile and impact tests

The MAPP compatibilizer significantly increased the tensile strength of PP composites with 30% bio-flour, particularly in the case of destarched cassava bio-flour (C) and non-destarched cassava bio-flour (CS), for which the tensile strength increased from 29.7 and 28.6 MPa to 36.1 and 36.6 MPa, respectively (Table 3). Thus the use of MAPP compensated for the decrease in tensile strength caused by the bio-flours, resulting in compatibilized 30% bio-flour composites with similar tensile strength to that of 10% bio-flour composites without MAPP (34.0–35.0 MPa). The AAPP compatibilizer was much less effective than MAPP in improving the tensile strength of PP-based materials.

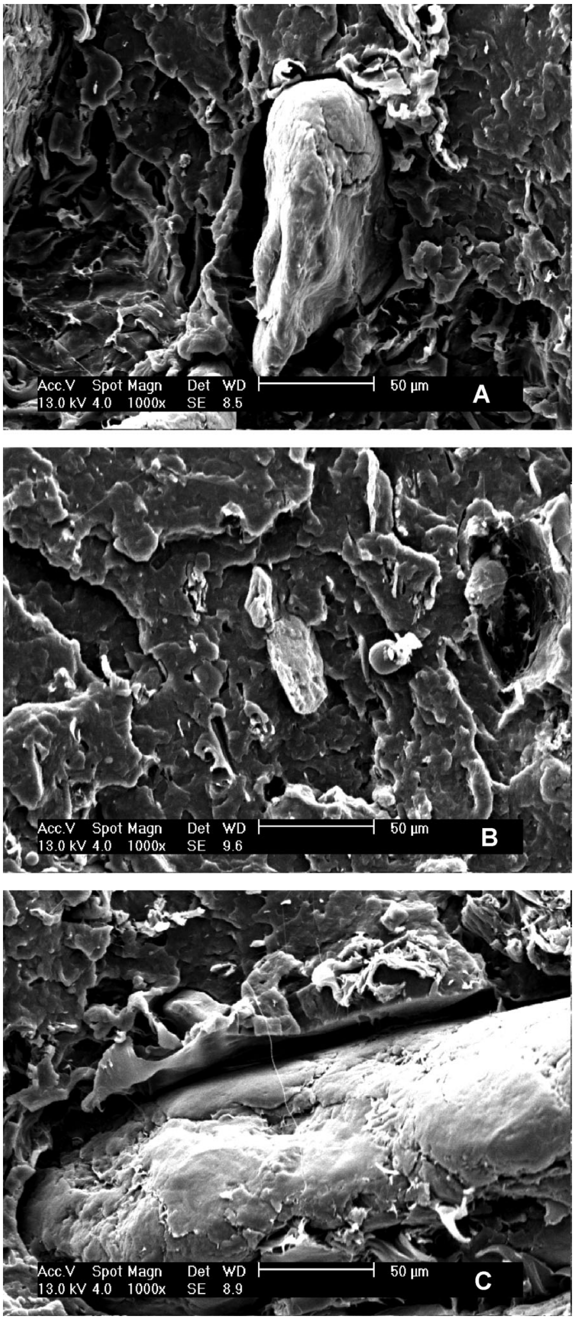

Figure 4. SEM micrographs of PP/destarched cassava bio-flour composites (70:30), (A) without compatibilizer, (B) with MAPP compatibilizer, (C) with AAPP compatibilizer.

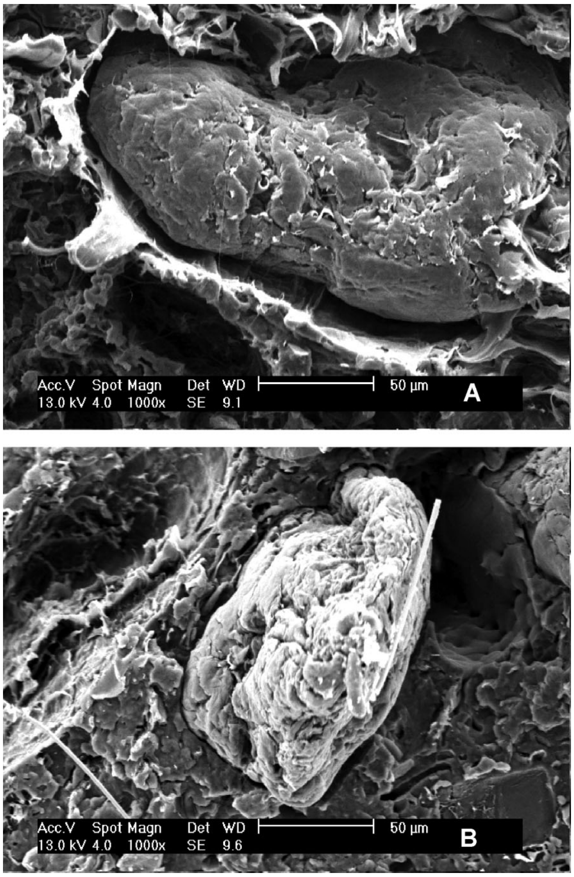

Figure 5. SEM micrographs of PBS/destarched cassava bio-flour composites (70:30), (A) without compatibilizer, (B) with MAPBS compatibilizer.

MAPP significantly increased the strain at maximum force in the case of PP composites with 30% C and CS bio-flours, from 0.27 in the non-compatibilized samples up to 0.30 in the compatibilized ones (Table 3), while no statistically significant effect was evidenced with 30% pineapple bio-flour (P). The AAPP compatibilizer did not have a significant effect on the strain at maximum force in PP and PBS composites with 30% bio-flour.

The MAPBS compatibilizer had no statistically significant effect on the tensile properties of PBS-based materials, possibly because the expected esterification between the maleic anhydride functions and the bio-flours did not take place due to the lower extrusion temperature (145°C for PBS, versus 185°C for PP), resulting in hydrogen bond interactions instead of covalent bonding between the two phases.

The impact resistance of the composites was not significantly improved by the compatibilizers.

3.3.2.2 Flexural test

In the case of C and CS bio-flours, the MAPP compatibilizer significantly increased the flexural strength of PP composites with 30% bio-flour by 19.1–29.1% (Table 3), from 31.1–33.5 MPa to 39.9–40.2 MPa, a value higher than pure PP (32.3 MPa). This result reflected the better transmission of the load to the bio-flours due to improved interactions between the bio-flours and the PP matrix [7]. To a lesser extent, both the AAPP and MAPBS compatibilizers also increased the flexural strength of PP and PBS composites with 30% bio-flour, from 31.1–33.5 MPa to 33.7–35.8 MPa and from 29.8–30.7 MPa to 30.7–33.5 MPa, respectively. Results were less clear-cut in the case of P bio-flour, for which MAPP and MAPBS increased flexural strength slightly from 45.7 to 46.6 MPa (1.9%) and from 41.8 to 43.6 MPa (4.3%), respectively, whereas AAPP decreased flexural strength from 45.7 to 43.3 MPa. Hujuri et al. [22] reported a 9.3–38.9% increase in flexural strength for PP composites with 5–20% pineapple leaf fibers compatibilized with MAPP.

MAPP and AAPP significantly increased the flexural modulus in the case of PP composites with 30% C bio-flour, from 1931.7 MPa in the non-compatibilized sample up to 2021.0 MPa (AAPP) and 2148.6 MPa (MAPP) in the compatibilized ones (Table 3). The same trend was observed in PP composites with 30% CS bio-flour, from 1604.8 MPa in the non-compatibilized sample up to 1742.7 MPa (AAPP) and 1814.8 MPa (MAPP) in the compatibilized ones. However, MAPP and AAPP did not have a statistically significant effect on the flexural strength of composites with P bio-flour. In the case of PBS composites, the MAPBS compatibilizer caused a statistically significant increase in flexural modulus only with 30% C bio-flour, from 1297.2 MPa in the non-compatibilized sample up to 1357.6 MPa in the compatibilized one.

3.4 Multivariate discriminant analysis of the composites' mechanical properties

Linear discriminant analysis of pooled data on the mechanical properties (i.e., tests of tensile strength, impact strength, and flexural strength) identified tensile strength, flexural strength, and flexural modulus as the three main discriminating variables. Using this set of three variables to complete the analysis, canonical plots mapping the differences between samples were drawn for the PP- and the PBS-based composites samples, and are shown in Fig. 6. Both pure PP and PBS materials were included in the analyses. The canonical spaces for PP and PBS composites had a similar structure, but were rotated 90°, with samples located in similar positions relative to each other in both spaces. This was interpreted as an indication that the bio-flours behaved in a similar way in both PP and PBS composites. Overall, the composites had lower tensile strength and higher flexural strength and flexural modulus than the pure polymer materials. The proportion and type of bio-flours were the two main factors affecting the mechanical properties of the composites. In particular, samples with a high proportion (40%) of pineapple bio-flour (P) were the furthest from the pure polymer material, while samples with a low proportion (10–20%) of non-destarched cassava bio-flour (CS) were the closest. This confirmed the role of starch in developing mechanical properties different from pure cellulosic bio-flours. One hypothesis is that melted starch granules during extrusion formed a semi-continuous network of merged starch granules, which resulted in more ductile behavior than discrete bio-flour particles dispersed in the PP or PBS matrix. Discriminant analysis also enabled assessment of the effectiveness of the compatibilizers. MAPBS-compatibilized samples appeared close to their non-compatibilized equivalents (Fig. 6-B), while the MAPP-compatibilized samples appeared farthest (Fig. 6-A), illustrating the limited effect of the MAPBS and the major effect of MAPP on mechanical properties, respectively. The AAPP-compatibilized samples (Fig. 6-A) were located between the MAPP-compatibilized samples and the non-compatibilized equivalents, indicating more limited effectiveness of AAPP than of MAPP.

4 Discussion

The use of pineapple (P), destarched cassava (C), and non-destarched cassava (CS) bio-flours in PP- and PBS-based bio-composites reduced tensile strength and impact strength, while the effect on flexural strength depended on the proportion of bio-flours. Elongation, characterized as the strain at maximum force during the tensile test, decreased, and stiffness, characterized as the flexural modulus, increased with increasing proportions of bio-flours. These results are in accordance with similar studies using rice husk flour and wood flour [20], and confirm the possibility of using bio-flours from tropical crops for the manufacture of bio-composites.

The use of compatibilizers reduced the gap between the two fractions, as confirmed by SEM observations. This partially compensated for the loss of tensile strength caused by the bio-flours and increased flexural strength. Of the two compatibilizers, MAPP was more effective than AAPP, possibly because the higher reactivity of maleic anhydride created a higher density of ester bonds in MAPP compatibilized samples. MAPBS prepared by reactive extrusion was not effective in improving the mechanical properties of PBS composites.

Different bio-flours conferred different mechanical properties to the composites, notably pineapple bio-flour led to higher flexural strength, while the non-destarched cassava bio-flour led to lower tensile and flexural strengths, particularly in samples with 30–40% bio-flour. Several factors may explain these differences, including the size and shape of the particles [7], the state of the surface of the particles [22], and the degree of starch granules melting.

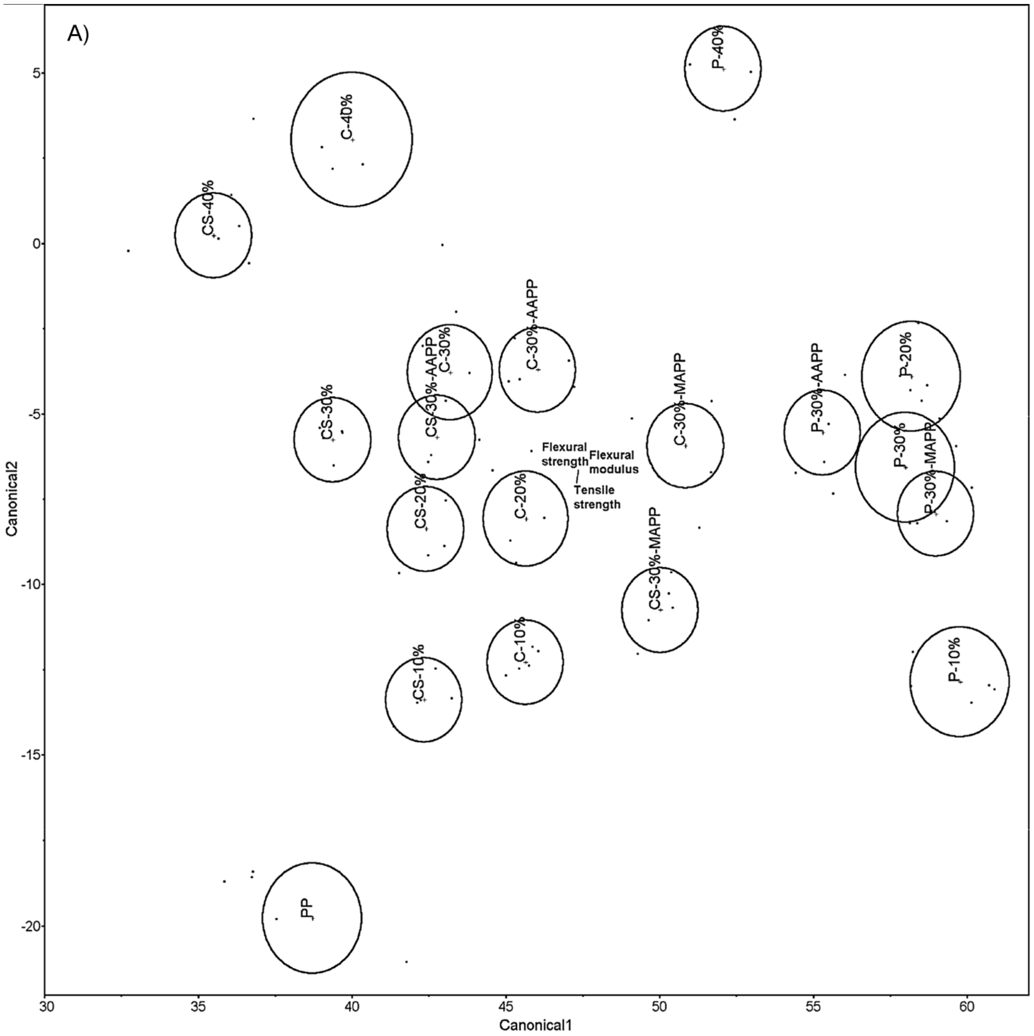

Figure 6. Discriminant analysis canonical plot of mechanical properties of (A) PP and (B) PBS composites. The black dots represent individual samples. The size of the ellipses corresponds to the 95% confidence limit for the multivariate mean of the five replications for each sample. The biplot rays are shown emanating from the grand mean of all samples and indicate the directions of the variables in the canonical space. C, CS, and P represent destarched cassava, non-destarched cassava and pineapple bio-flours, respectively. The percentages indicate the proportion of bio-flours in the composites.

Evidence of starch granules melting in the non-destarched cassava bio-flour confirmed the hypothesis that starch can play a key role in determining the morphology and mechanical properties of composites prepared with this type of bio-flour. SEM observations pointed to a higher degree of starch granules melting in PP-non-destarched cassava bio-flour composites than in PBS-non-destarched cassava bio-flour composites, due to the higher temperature used for the extrusion of PP. As a result, in PBS composites, starch still had a discrete granular structure, whereas in PP composites, granules melted and formed a semi-continuous matrix interlaced with the PP matrix. The consequences for mechanical properties were low tensile and flexural strengths, but also a low flexural modulus indicating greater flexibility of the material. These observations of the role of starch in bio-composites suggest the possibility of fine-tuning mechanical properties by adjusting the proportion of starch added to the material and degree of granules melting. The degree of granules melting can be controlled through extrusion conditions, including temperature, moisture content, shear, and pressure. By increasing both the proportion of starch and degree of granules melting, it may be possible to create a fully continuous starch matrix similar to that obtained in LDPE-starch composites by Rodriguez-Gonzalez et al. [8]. Such a matrix intertwined with the polymer (PP or PBS) matrix may improve the low tensile and flexural strengths observed in our work, while

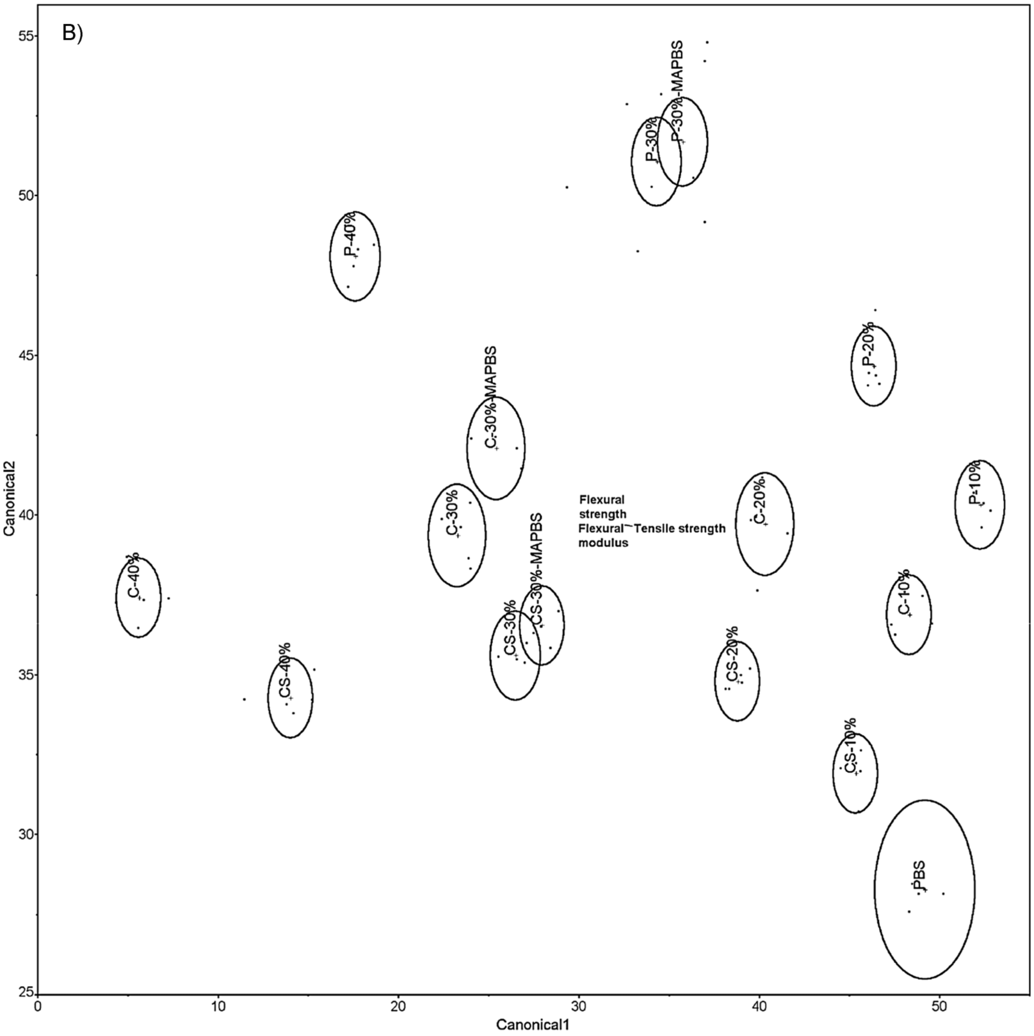

Figure 6. Continued

maintaining a low flexural modulus. Furthermore, additional ingredients may also enhance the ability to control mechanical properties, for instance glycerol and water to improve starch plasticization [25, 26], and higher amounts of compatibilizer to stabilize a large interfacial area between the polymer matrix and the starch matrix. The proportion of cellulosic particles may also be adjusted for their usual role as reinforcing filler. In this respect, non-destarched cassava bio-flour represents a unique, low cost raw material for the bio-composites industry, in that it already contains cellulosic particles and starch with no need for additional preparation.

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