RESEARCH ARTICLE

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

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Bio-composites made from polypropylene (PP) and poly(butylene succinate) (PBS) compounded with pineapple skin (P) bio-flour, non-destarched (CS), and destarched (C) cassava root bio-flours were prepared by twin-screw extrusion. In CS composites, different degrees of starch granules melting were achieved by adjusting extrusion temperature, thus enabling control of the morphological and mechanical properties. FTIR analysis indicated the formation of ester bonds between bio-flours and compatibilizers during extrusion, which confirmed the effectiveness of these compatibilizers for improving interfacial interactions between PP and bio-flours. Thermogravimetric analysis showed that the composites had reduced thermal stability compared to pure PBS and PP materials, due to the lower degradation temperature of the bio-flours (261–351°C). DSC data indicated that bio-flours improved nucleation and crystallinity, whereas, compatibilizers reduced molecular mobility and hence propagation and crystallinity.

1 Introduction

Composites made of conventional polyolefins such as polypropylene (PP) or biodegradable polymers such as poly(butylene succinate) (PBS) blended with bio-flours typically have weaker mechanical properties than pure polyolefins, with lower tensile strength, and lower flexural strength, but increased stiffness [1, 2]. In addition to mechanical properties, the development of a bio-composite requires the characterization of its physico-chemical properties, in order to check the stability and durability of the material under the conditions of intended use. Relevant properties include thermal stability and crystallinity, and biodegradability as well as properties related to user perception and health, such as color stability, odor release, and release of volatile organic chemicals during the lifetime of

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Abbreviations: AAPP, acrylic acid-polypropylene; **C,** destarched cassava root; **CS,** non-destarched cassava root; **MAPBS,** maleic anhydride poly(butylene succinate); **MAPP,** maleic anhydride polypropylene; **P,** pineapple skin; **PBS,** poly(butylene succinate); **PP,** polypropylene

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the product [3]. The inclusion of bio-flours typically reduces the thermal stability of the material, as bio-flours degrade at lower temperatures than polyolefins [3], and can influence the crystallinity of the plastic matrix due to nucleation.

Compatibilizers grafted onto the hydrophobic polymer and carrying hydrophilic groups intended to improve interface interactions between the hydrophobic phase and the hydrophilic bio-flour phase, such as maleic anhydride polypropylene (MAPP), can have different mechanisms of action that will influence the mechanical properties of the material [4]. The formation of covalent bonds is the strongest mode of compatibilization, typically through esterification of the compatibilizing agent with the hydroxyl groups carried by the lignocellulosic fibers [5]. Alternatively, hydrogen bonds between bio-flour and compatibilizer can also reduce interfacial tensions [5].

The objective of this work was to characterize the physicochemical properties of blends of PP or PBS with pineapple, non-destarched cassava, and destarched cassava bio-flours, previously analyzed for their mechanical properties, so as to demonstrate the influence of different bio-flours on thermal stability and crystallinity. The mechanism of action of compatibilizers used in the same blends was also investigated.

2   Materials and methods

2.1   Materials and sample preparation

PP and PBS were compounded by twin-screw extrusion with pineapple skin (P), non-destarched cassava root (CS), and destarched cassava root (C) bio-flours, as described in Part I of this study.

The 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. Maleic anhydride poly(butylene succinate) (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 at proportions of 100:7:0.7 by weight.

2.2   Thermal properties

2.2.1   Thermogravimetric analysis (TGA)

The thermal degradation of the composites was characterized using a thermogravimetric analyzer TGAQ500 (TA Instruments, New Castle, DE, USA) on 10 mg samples, over a temperature range from 25 to 700°C at a heating rate of 20°C/min. Experiments were conducted in a high quality nitrogen (99.5% nitrogen and 0.5% oxygen content) atmosphere at a flow rate of 20 mL/min in order to avoid unwanted oxidation.

2.2.2   DSC analysis

DSC analysis was carried out using a TA Instrument DSC Q1000 (TA Instruments) at NICEM-Seoul National University on 8–10 mg of sample. Each sample was scanned from -80 to 200°C at a heating rate of 10°C/min, then cooled, and reheated at the same rate under nitrogen atmosphere. The thermal properties including T_g, melting temperature (T_m), and melting enthalpy (ΔH) were determined during the second heating scan. T_m was defined as the onset of the endothermic melting peak and T_g as the onset of the baseline shift. The relative degree of crystallinity (X_c) of the specimens was calculated according to the following equation [6]:

$$X_c(\%) = \frac{\Delta H_f}{\Delta H_f^0 \times w} \times 100 \tag{1}$$

where ΔH_f is the heat of fusion of the PP, PBS, and composites, ΔH_f^0 the heat of fusion of 100% crystalline PP ($\Delta H_f^0 = 138$ J/g) and PBS ($\Delta H_f^0 = 210$ J/g), and w is the mass fraction for PP and PBS in the composites [6, 7].

2.3   Attenuated total reflectance FTIR measurements (FTIR-ATR)

The FTIR-ATR infrared spectra of MAPP, PBS, compatibilizers, composites, and compatibilizing agent-treated composites were obtained using a Nexus 870 FTIR spectrophotometer (Thermo Nicolet Instrument Corp. Madison, WI, USA). A diamond was used as ATR crystal. The samples were analyzed over the range of 500–4000 cm^{-1} with a spectrum resolution of 4 cm^{-1}. All spectra were averaged over 30 scans. The measurement was performed at point-to-point contact with a pressure device.

2.4   Statistical analyses

Statistically significant differences between sample means were determined using Student's *t*-test at 95% confidence level.

3   Results

3.1   FTIR evidence of ester covalent bond formation between compatibilizer and bio-flours

In relation to SEM evidence of the improvement of adhesion between polymer and bio-flour fractions, Fig. 1 shows the FTIR spectra of PP composites with 0–40% P,
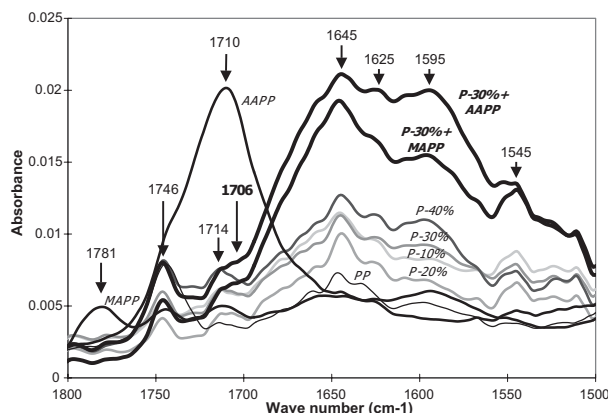
Figure 1. FTIR analysis of PP composites with pineapple bio-flour. PP: Pure PP; P-10%, P-20%, P-30%, and P-40%: Composites of PP with 10–40% pineapple bio-flour, respectively; P-30% + MAPP: Composite of PP with 30% pineapple bio-flour and 3% MAPP; P-30% + AAPP: Composite of PP with 30% pineapple bio-flour and 3% AAPP; MAPP: Pure MAPP; AAPP: Pure AAPP.

Figure 2. FTIR analysis of PBS composites with pineapple bio-flour. PBS: Pure PBS; P-10%, P-20%, P-30%, and P-40%: Composites of PBS with 10–40% pineapple bio-flour, respectively; P-30% + MAPBS: Composite of PBS with 30% pineapple bio-flour and 3% MAPBS; MAPBS: Pure MAPBS. (A) Main FTIR spectrum; and (B) enlargement of the base of the main succinate peak.

with and without compatibilizer (MAPP and AAPP), in the 1800–1500 cm^{-1} range. The FTIR spectra of pure MAPP and AAPP are also shown in Fig. 1. In all samples, peaks were detected at 1746, 1714, 1645, 1625, 1595, and 1545 cm^{-1}. These peaks were attributed to carbonyl groups resulting from PP oxidation caused by heat during extrusion or injection-molding, based on observations by other authors of similar peaks related to oxidation after exposure of PP to heat or to visible and UV light [8]. In the pure MAPP and AAPP samples, additional peaks at 1781 and 1710 cm^{-1} were attributed to maleic anhydride and acrylic acid, respectively. The composites samples including the compatibilizers presented an additional shoulder at 1706 cm^{-1}, which was interpreted as evidence of the formation of some ester covalent bonds between the compatibilizer and the bio-flours. Similarly Fig. 2 shows the FTIR spectra of PBS composites with 0–40% P bio-flour, with and without MAPBS compatibilizer, in the 1800–1600 cm^{-1} range. The FTIR spectra of pure MAPBS are also shown in Fig. 2. A large peak corresponding to the carbonyl group of the PBS succinate function was clearly identifiable at 1714 cm^{-1}, with a decrease in the peak intensity with an increase in the proportion of bio-flour. A shoulder at 1685 cm^{-1} was also attributed to the succinate function for the same reason. The pure MAPBS sample showed an additional shoulder at 1778 cm^{-1}, which was attributed to the carbonyl group of the maleic anhydride (Fig. 2B). However, no signal corresponding to ester bonds between MAPBS and bio-flour was identified in PBS composites with MAPBS, either because the signal was masked by the large size of the succinate peak, or because esterification between MAPBS and the bio-flour
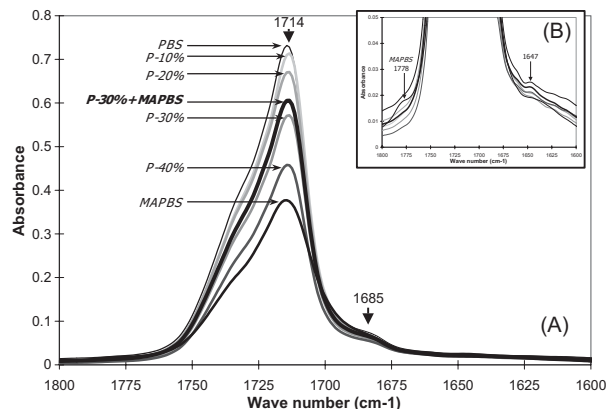
did not occur in significant amounts. Since the MAPBS was an experimental sample, it is possible that the amount of maleic anhydride grafted on the PBS backbone in the first place was too low to allow significant esterification.

The compatibilizers, particularly MAPP, had a clear effect on the morphology and mechanical properties of the composites. The mode of action of the compatibilizers was expected to be ester bond formation, polar interactions with the bio-flours, or a combination of the two. The FTIR data provided limited evidence of the formation of covalent ester bonds in MAPP compatibilized materials, so that polar interactions are likely to be the main factor involved in compatibilization.

3.2 Thermal properties

3.2.1 Thermal gravimetric analysis (TGA)

Figures 3 and 4 shows the dynamic TGA curves of some PP and PBS composites with 30% bio-flours (C, CS, and P), with and without a compatibilizer. The derivatives of the thermogravimetric curves are also shown in the Figs. 3 and 4. The peaks on the derivative curves, corresponding to the highest weight loss rates, were used to determine the degradation temperatures of the bio-flour and polymer fractions. The degradation temperatures are summarized in Table 1. The main weight loss corresponding to the degradation of the polymer matrix occurred in the 391–393°C range for PBS and in the 400–453°C range for PP composites. Hence the bio-flours did not affect the degradation temperature of PBS (393°C for pure PBS; [9]), but reduced the degradation temperature of PP by 30–80°C
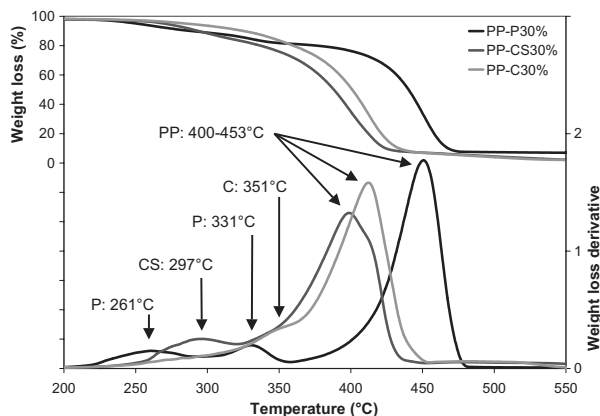
Figure 3. TGA of PP composites with 30% destarched cassava (PP-C30%), non-destarched cassava (PP-CS30%), and pineapple (PP-P30%) bio-flours. Peaks labeled PP, C, CS, and P correspond to the degradation temperatures of the PP, destarched cassava, non-destarched cassava, and pineapple fractions, respectively.

(480°C for pure PP; [5]). In the case of PP, the nature of the bio-flour appeared to influence thermal stability, with P composites degrading at a higher temperature than the C and CS ones (453–455 and 400–433°C, respectively). Secondary weight losses corresponding to the degradation of the bio-flour fraction were observed at different temperatures, depending on the type of bio-flour: P bio-flour presented two peaks at 261–268 and 331–339°C, indicating the presence of two components in the pineapple fraction, while CS bio-flour degraded at 297–298°C. The C bio-flour degraded at 350–351°C and was partially hidden by the degradation peak of the polymer matrix,
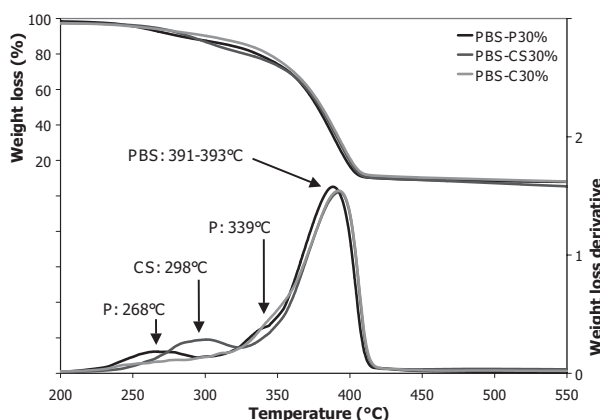
Table 1. Degradation temperatures of the polymer and bio-flour fractions of the bio-composites determined by TGA.

	Degradation temperature (°C)		
	Flour 1st peak	Flour 2nd peak	Polymer
PP [3]	–	–	480
PP-P30%	261	331	453
PP-P30% + AAPP	261	331	455
PP-CS30%	297	–	400
PP-C30%	351	–	414
PP-C30% + MAPP	351	–	428
PP-C30% + AAPP	351	–	433
PBS [9]	–	–	393
PBS-P30%	268	339	391
PBS-P30% + MAPBS	268	339	393
PBS-CS30%	298	–	393
PBS-CS30% + MAPBS	298	–	393
PBS-C30%	(350)	–	393
PBS-C30% + MAPBS	(350)	–	393

particularly in the case of PBS. In the case of C bio-flour, the compatibilizers MAPP and AAPP increased the degradation temperature of PP from 414 to 428–433°C, while no effect of the compatibilizers was observed in the case of other bio-flours. This observation may be related to destarching of the cassava bio-flour, which could have acted as a conditioning treatment of the bio-flour surface and enhanced the interactions between the bio-flour and the compatibilizers.

3.2.2 DSC

The glass transition and melting characteristics of PP and PBS composites are summarized in Table 2. Measurements on the series of composites with CS indicated that the proportion of bio-flour did not influence the glass transition, and reduced the onset melting temperature by 1–2°C for both PP and PBS. The degree of crystallinity of PP in non-compatibilized PP composites ranged from 58.9 to 67.6%. The presence of bio-flours in the PP matrix increased the degree of crystallinity, as the crystallinity of pure PP was measured at 48.1%, which is in agreement with values reported in the literature (49.3%; [10]). However, a direct linear correlation could not be identified between the degree of crystallinity and the proportion of bio-flours. In non-compatibilized PBS composites, bio-flours also increased the degree of crystallinity of PBS from 38.4% in pure PBS to 48.6% in the sample with 40% CS bio-flour. One hypothesis to explain the increase in crystallinity in presence of bio-flours would be enhanced nucleation caused either by the bio-flours directly, or by

Figure 4. TGA of PBS composites with 30% destarched cassava (PP-C30%), non-destarched cassava (PP-CS30%), and pineapple (PP-P30%) bio-flours. Peaks labeled PBS, CS, and P correspond to the degradation temperatures of the PBS, non-destarched cassava, and pineapple fractions, respectively.

Table 2. Glass transition, melting characteristics, and crystallinity of PP and PBS bio-composites determined by DSC.

	Onset T_g (°C)	Onset T_m (°C)	Melting enthalpy (J/g sample)	Crystallinity (%)
PP	–	154.6	66.4	48.1
PP-CS10%	−10.3	152.4	82.3	66.3
PP-CS20%	−9.3	152.3	74.6	67.6
PP-CS30%	−6.6	153.0	58.2	60.2
PP-CS40%	−9.4	152.9	55.4	66.9
PP-CS30% + MAPP	−2.3	152.8	64.1	66.4
PP-CS30% + AAPP	−3.4	155.4	65.5	67.8
PP-C30%	−6.0	153.4	56.9	58.9
PP-C30% + MAPP	−5.8	153.9	53.5	55.4
PP-C30% + AAPP	−5.8	153.6	65.1	67.4
PP-P30%	−2.4	152.2	65.3	67.6
PP-P30% + MAPP	−2.5	153.2	48.1	49.8
PP-P30% + AAPP	−2.1	153.1	73.4	76.0
PBS	−33.4	108.7	80.7	38.4
PBS-CS10%	−34.8	104.5	71.1	37.6
PBS-CS20%	−35.1	105.7	66.4	39.5
PBS-CS30%	−34.2	107.0	60.6	41.2
PBS-CS40%	−34.3	107.1	61.2	48.6
PBS-CS30% + MAPBS	−35.6	106.7	55.9	38.0
PBS-C30%	−34.8	107.0	37.2	25.3
PBS-C30% + MAPBS	−34.8	106.2	51.3	34.9
PBS-P30%	−36.4	104.7	86.8	59.0
PBS-P30% + MAPBS	−34.5	107.0	44.1	30.0

impurities introduced in the blends at the same time as the bio-flours.

Measurements on composites with 30% C, CS, and P bio-flours evidenced some effects of the type of bio-flour, in particular a higher T_g for PP-P composites (−2.4°C), compared to PP-CS and PP-C composites (respectively, −6.6 and −6.0°C), and different levels of PP and PBS crystallinity. The T_g increased after compatibilization in most cases, either markedly as in the case of MAPP and AAPP in blends with CS bio-flour with an increase from −6.6°C to, respectively, −2.3 and −3.4°C, or more moderately with increases of between 0.2 and 2°C. This observation indicated that the compatibilizers tended to reduce molecular mobility in the composites. Furthermore, MAPP and MAPBS appeared to reduce the level of PP and PBS crystallinity in composites with pineapple and cassava bio-flours. This reduced crystallinity could be related to the lower molecular mobility in compatibilized composites, as indicated by the T_gs, which could in turn reduce the propagation of the crystallites (lower rate of growth of crystals) during cooling of the composites.

4   Discussion

In addition to altering mechanical properties, the blending of pineapple, destarched cassava, and non-destarched cassava bio-flours with PP and PBS modified the physico-chemical characteristics of the bio-composites. Resistance to thermal degradation was reduced due to the lower degradation temperature of the bio-flours. The crystallinity of PP and PBS in the bio-composites increased, possibly because of a nucleation effect by the bio-flours or by microimpurities in the flours. FTIR provided evidence of the formation of ester covalent bonds between MAPP and AAPP compatibilizers and the bio-flours; however, it is likely that non-covalent polar interactions also play a significant role in improving interfacial interactions between the bio-flour and the matrix. Of the two compatibilizers, MAPP was more effective than AAPP, possibly because the higher reactivity of the maleic anhydride resulted in a higher density of compatibilizer–bio-flour ester bonds. Although MAPBS prepared by reactive extrusion at SNU altered the morphological properties of PBS composites, it was not effective in improving the mechanical properties, and no evidence of esterification between MAPBS and bio-flours was found. We, therefore, hypothesize that the degree of maleic anhydride grafting on PBS was too low to create a significant amount of covalent bonds.

The results of both mechanical and physico-chemical characterization of pineapple/cassava and PP/PBS bio-composites are in accordance with similar studies using rice husk flour and wood flour [11], and confirm the possib-

ility of using bio-flours made from tropical crops for the manufacture of bio-composites.

The authors have declared no conflict of interest.

5   References

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