Tailoring the Properties of Thermoplastic Starch with Bamboo Powder and/or Hollow Glass Microspheres

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ABSTRACT: In this study, bamboo powder and/or hollow glass microspheres were added to thermoplastic cassava starch in order to overcome its drawbacks. The composites were characterized by scanning electron microscopy (SEM), tensile testing, water contact angle measurement and X-ray diffractometry (XRD), in addition to their thermal properties. The mechanical strength of the composites showed a general decline with increasing bamboo powder content while the water contact angles increased up to 15% of bamboo powder content (% w/w dry starch). The addition of hollow glass microspheres provides an optimal balance between hydrophobicity and mechanical strength. The results pointed to improved properties that are expected to make thermoplastic starch more attractive and hence more competitive with synthetic polymers.

KEYWORDS: Thermoplastic starch, bamboo powder, hollow glass microspheres, wettability

1 INTRODUCTION

Thermoplastic starch, a renewable, biodegradable biopolymer, is considered one of the most promising candidates to replace synthetic polymers. However, the poor mechanical properties of starch along with its high hydrophilicity limit its wider use [1]. In recent years, the use of biobased fillers as reinforcing agents in polymers has attracted much attention. They offer a number of lucrative advantages, viz., low cost, low density, high specific strength and stiffness, eco-friendliness, and biodegradability [2]. Versino and García [3] have reinforced cassava starch films with the residue derived from starch extraction. This interesting research enables adding value to this industrial waste, with the consequent diminution of waste volumes. The importance of bamboo has been acknowledged for many years by the rural people in many tropical countries as traditional material for houses and bridges, handicraft items, fishing rods, foods, and other traditional uses [4]. Nowadays, the use of bamboo has been expanded to include modern applications. One of these is composites based on urethane diacrylate photopolymer and bamboo fiber for use in digital light rapid prototyping (DLRP) [5]. Another example is the processing of bamboo culm with polyvinyl chloride (PVC) to obtain composites with various loading ratios of bamboo particles [4]. According to the authors, despite the fact that the modulus of rupture was not increased, the inclusion of bamboo particles enhanced the flexural modulus of elasticity. In another study, bamboo particles were thermomechanically processed with low density polyethylene (LDPE) to produce composites [6]. In this case, the results of the oxidation induction time from differential scanning calorimetry (DSC) suggest the existence of some antioxidant activity of bamboo. This could lead to composites with enhanced potential in food packaging applications. On the other hand, inorganic fillers added to the starch matrix generally lead to composites with better overall properties [7]. Hollow glass microsphere (HGM) is an interesting inorganic filler for producing low density TPS composites. HGMs consist of an outer stiff glass and an inner inert gas, which results in some unique properties such as light weight and low thermal conductivity [8]. Composites have been prepared using HGMs; for example, the composites fabricated with poly(butylene succinate) (PBS) with various HGM contents [9]. As reported by the authors, the addition of HGM significantly decreased the density of the composites. The storage modulus and viscosity were enhanced with the increase of HGM content,

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while the crystalline structure was not affected. A combination of nanofillers and biobased fillers could offer additional possibilities for starch modification. Such hybrid composites may fulfill the need for potential lightweight and high-strength materials [10]. The work of Azwar and Hakkarainen [11] has evaluated the possibility of tuning the mechanical properties of cassava starch through utilization of different combinations of plasticizers, inorganic and biobased fillers. They have found that Halloysite, milled wood flour and rice bran improved the strength at break of the starch films, while addition of kaolin in most cases resulted in materials with intermediate strength at break and strain at break. Also, the addition of liquefied rice bran significantly improved the strain at break. In this context, the aim of the present study is to tailor the properties of thermoplastic cassava starch films through the addition of bamboo powder and/or glass hollow microspheres.

2 EXPERIMENTAL

2.1 Materials

Bamboo of *Phyllostachys heterocycla* species, aged approximately three years, was provided and collected by Bambuzeria Southern Cross, located in Ravenna, Sabará City district in Minas Gerais (Brazil). Cassava starch was acquired from Starch Nivaraí (Brazil). Commercially available glass microspheres with sizes ranging from 9 to 13 μm and glycerol were purchased from Sigma-Aldrich (MO, USA) and Synth (Brazil) respectively.

2.2 Methods

Firstly, bamboo culm was ground into a fine powder with the aid of a grinder (IKA A10, IKA Labortechnik, Germany) and passed through a 100-mesh sieve. Starch gelatinization was performed to obtain thermoplastic starch (TPS). For this purpose, 90 wt% of deionized water, 7 wt% of starch and 3 wt% of glycerol were placed in a 500 mL round flask, which was capped with a cork, and mixed under mechanical stirring (Fisatom 713D model). The system was kept under constant stirring (180 rpm) and heated at 80 °C for 20 minutes. Composites from thermoplastic starch (TPS) were prepared by adding the fillers during the gelatinization step. Two different concentrations of BP (5% and 20% w/w) along with 1% (w/w) of hollow glass microspheres, or short glass microspheres (MS) gave rise to composites SBP-5 MS-1 and SBP-20 MS-1, respectively. In addition, a composite prepared with TPS and 10% (w/w) of glass microspheres was prepared and named SMS-10. Films were produced by casting and dried in a vacuum circulating drying oven at 40 °C for 48 h.

2.2 Characterizations

2.2.1 Scanning Electron Microscopy (SEM)

The SEM fracture surface of composites was observed after cryogenic fracture (nitrogen) and coating with gold of samples by using a Shimadzu Superscan SSX-550 model scanning electron microscope.

2.2.2 Contact Angle Measurements

The surface hydrophilicity of the starch film (control) and composites was evaluated by determinig the contact angle through the sessile-drop method. The contact angle measurements were performed using a Krüss DSA100 goniometer. The results represent the average between the right and left angles obtained after droplet deposition with a standardized volume (10 L) on films with dimensions of 2 cm × 2 cm. Three consecutive measurements were made at room temperature by employing Surface Energy mode software that allows the direct measurement of the contact angle (in degrees).

2.2.3 Mechanical Properties

The specimens of pure starch polymer samples (control) and the composites were produced according to the standard ASTM D-638. Mechanical properties were evaluated, such as Young's modulus, stress at break and elongation at break, by tensile test carried out with the help of the Shimadzu Autograph AG-X universal testing machine, with velocity of 50 mm/min and load cell maximum capacity of 10 KN. The spacing between claws was 50 mm.

3 RESULTS AND DISCUSSION

From SEM analyses it was possible to obtain information such as geometry of bamboo powder (BP) and glass microspheres (MS) in addition to the degree of dispersion of the fillers in the starch polymer matrix. The SEM micrographs of BP and MS can be observed in Figure 1. The large and irregular size of BP (Figure 1a) is in agreement with bamboo particles without lignin extraction [12]. The MS morphology presented in Figure 1b suggests a spherical smooth, clean surface, as already shown in the literature [8].

The SEM micrographs of SBP-5 MS-1 and SBP-20 MS-1 composites are shown in Figures 2 and 3 respectively. Regarding the micrographs in Figure 2, no

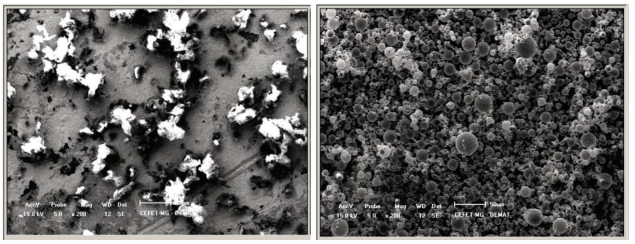

Figure 1 SEM micrographs of (**a**) BP and (**b**) MS.

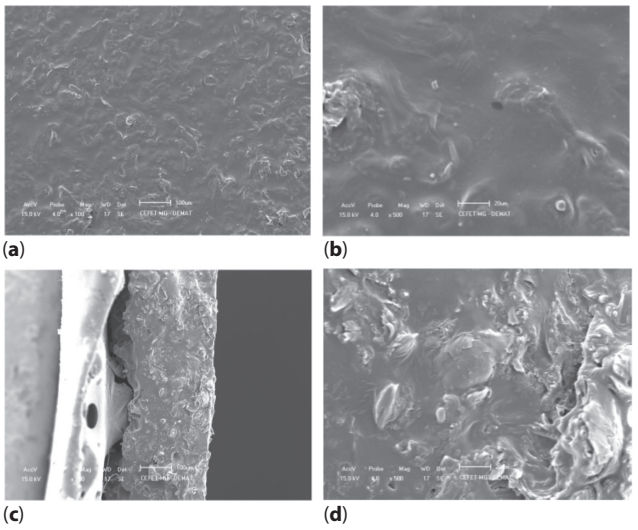

Figure 2 Micrographs (SEM) of the surface of composite SBP-5 MS-1 with magnification of (**a**) 100x and (**b**) 500x; and surface fracture of composite SBP-5 MS-1 with magnification of (**c**) 100x and (**d**) 500x.

unplasticized starch granules can be observed on the composite surface. Such a finding might indicate that the glass microspheres, through friction, have assisted the blending process during the preparation of the composite, thus contributing to the system homogenization. In addition, despite showing a rough interface, the fracture surface micrographs did not evidence the presence of sharp cracks, which may be indicative that the combination of fillers worked well in respect to matrix adhesion.

On the other hand, in the SBP-20 MS-1 fracture surface micrographs (Figure 3b,d) the presence of cracks can be seen. This fact pointed out the bad adhesion between phases. Probably with the increase of BP content, the amount of microspheres was not enough to aid the system homogenization.

The bad adhesion found in SBP-20 MS-1 could also be explained by the possible occurrence of intramolecular hydrogen bonds between the hydroxyl groups of BP rather than hydroxyl groups BP on one side and those of the starch [13]. In addition, with higher content of BP the irregular fiber morphology (Figure 1a) has more of a negative influence on the system homogenization.

The micrographs corresponding to composite SMS-10 (Figure 4) presented a predominantly homogeneous surface with no unplasticized starch granules. This observation supports the hypothesis that the microspheres have assisted in the mixing process. In the fracture surface micrographs (4c,d), it was noticed that the microspheres did not detach from the matrix during fracture. Such behavior can be attributed to the

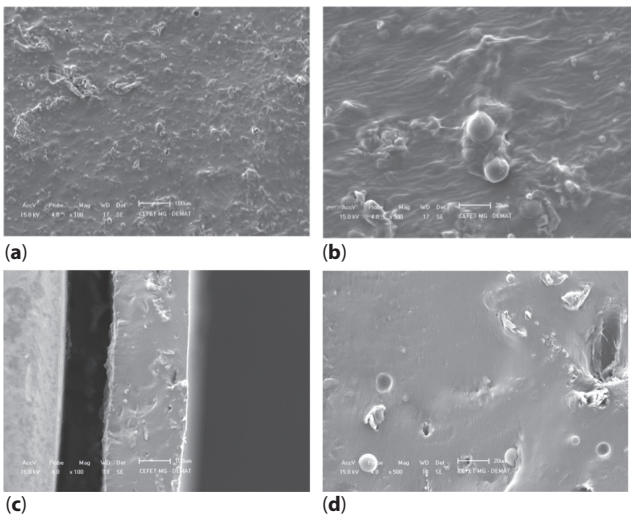

Figure 3 Micrographs (SEM) of the surface of composite SBP-20 MS-1 with magnification of (**a**) 100x and (**b**) 500x; and fracture of composite SBP-20 MS-1 with magnification of (**c**) 100x and (**d**) 500x.

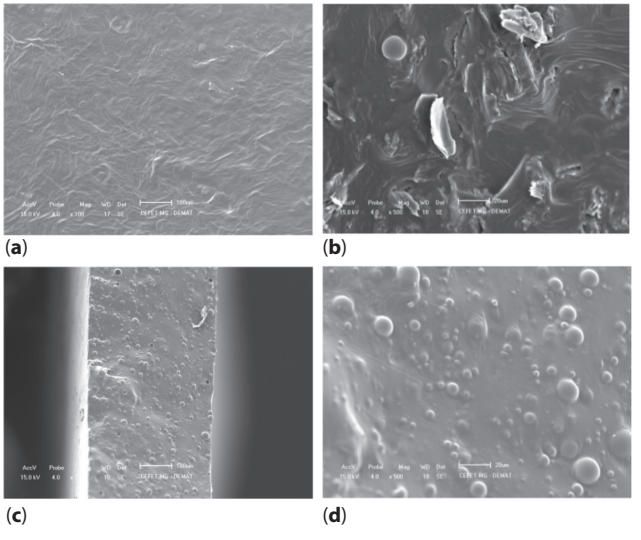

Figure 4 Micrographs (SEM) of the surface of composite SMS-10 with magnification of (**a**) 100x and (**b**) 500x; and fracture of composite SMS-10 with magnification of (**c**) 100x and (**d**) 500x.

hydrophilicity of the glass microspheres, which promotes a good adhesion with the hydrophilic starch matrix.

The surface wettability was assessed by the contact angle measurements, as presented in Figure 5. The values of contact angle are depicted in Table 1. As can be seen in this table, the composite SBP-5 MS-1 presented a marked increase in the hydrophobicity related to TPS. Whereas in the composite SBP-10 MS-1, the contact angle diminishes again, and the composite SMS-10 presented the highest contact angle.

The behavior is typical of events in which there is more than one factor acting. In this case, two opposing factors are suggested; that is, increased hydrophilicity due to the presence of hydrophilic cellulosic filler and increased hydrophobicity due to surface roughness.

The surface roughness (r) has a considerable influence on the mean contact angle. An important aspect is the length scale involved. For not too rough surfaces (roughness significantly below the wavelength of light) we can describe the effect of surface roughness by the so-called Wenzel regime, in which the liquid penetrates into the grooves. In this case, the contact angle θ_w, which a liquid drop makes with the rough surface, is given by Equation 1.

$$\cos \theta_w = r \cos \theta \quad (1)$$

where θ is the contact angle for a smooth surface, and r is the factor related to the roughness.

This equation states that, for a hydrophobic surface, as roughness increases the surface becomes even more hydrophobic. Likewise, if a hydrophilic surface is roughened it becomes more hydrophilic [14]. On the other hand, Berim and Ruckenstein [14] have shown that, in contrast to the commonly used Wenzel formula, even an extremely small roughness can considerably increase the contact angle. According to them, large contact angles are obtained when the distance between pillars acquires a size at which the liquid can no longer penetrate between them. In such a case, the space between pillars remains empty. In the nomenclature of the macroscopic treatment of wetting, this corresponds to a transition from the Wenzel to the Cassie-Baxter regime [14]. Other authors have reported that the deposition of polystyrene microspheres with aminoethyl groups resulted in a hierarchical topographic pattern suitable for obtaining the superhydrophobic characteristics for starch and its blends [15]. Such authors also related this result to a topography obeying the Cassie-Baxter regime. The improvement in the TPS superficial hydrophobicity was also observed with the addition of 1 and 5% of clay [16].

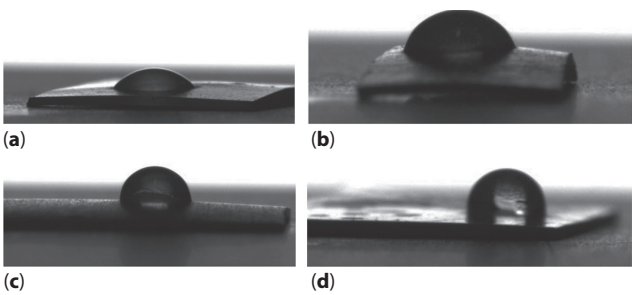

Figure 5 Water drop shape on the surface of the films: (**a**) TPS, (**b**) SBP-5 MS-1, (**c**) SBP-20 MS-1 and (**d**) SMS-10.

The values found in the tensile tests (Table 1) have pointed to a reduction in the tensile strength of the composites when compared with TPS. The composite SBP-20MS-1 presented the lowest tensile strength value, indicating poor adhesion between filler and matrix, as has already been observed by SEM. Figure 6 presents the FTIR spectra of BP (Figure 6a), TPS (Figure 6b), and TPS/BP composite (upper corner) without MS (SBP-20), in an attempt to identify the possible interactions between TPS and BP.

The FTIR spectrum of BP (Figure 6a) shows a broad absorption at 3330 cm^{-1} typical of -OH cellulose hydrogen bonding and absorption at 2876 cm^{-1} (-CH_2-) [17]. Among the bands found by Afrin *etal*. [12] for untreated bamboo, we detected the following bands in BP spectrum: 1740 cm^{-1} attributed to nonconjugated carbonyl stretching; 1596 and 1509 cm^{-1} associated with vibrations of aromatic skeletal vibration; 1240 cm^{-1} identified as belonging to guaiacyl, one of the major components of lignin, and 1037 cm^{-1} assigned to complex vibrations associated with the C–O, C–C stretching and C–OH bending in polysaccharides.

Table 1 Mechanical properties and contact angles of composites.

Composite	Tensile strength (MPa)	Elastic modulus (MPa)	Elongation (%)	Contact angle
TPS	4.78 ± 0.20	17 ± 0.3	120 ± 0.8	43° ± 0.5
SBP-5MS-1	3.78 ± 0,16	51 ± 0,5	63 ± 0,31	95° ± 0,6
SBP-20MS-1	2.49 ± 0,23	15 ± 0,96	103 ± 0,9	79° ± 1,0
SMS-10				111° ± 1,0

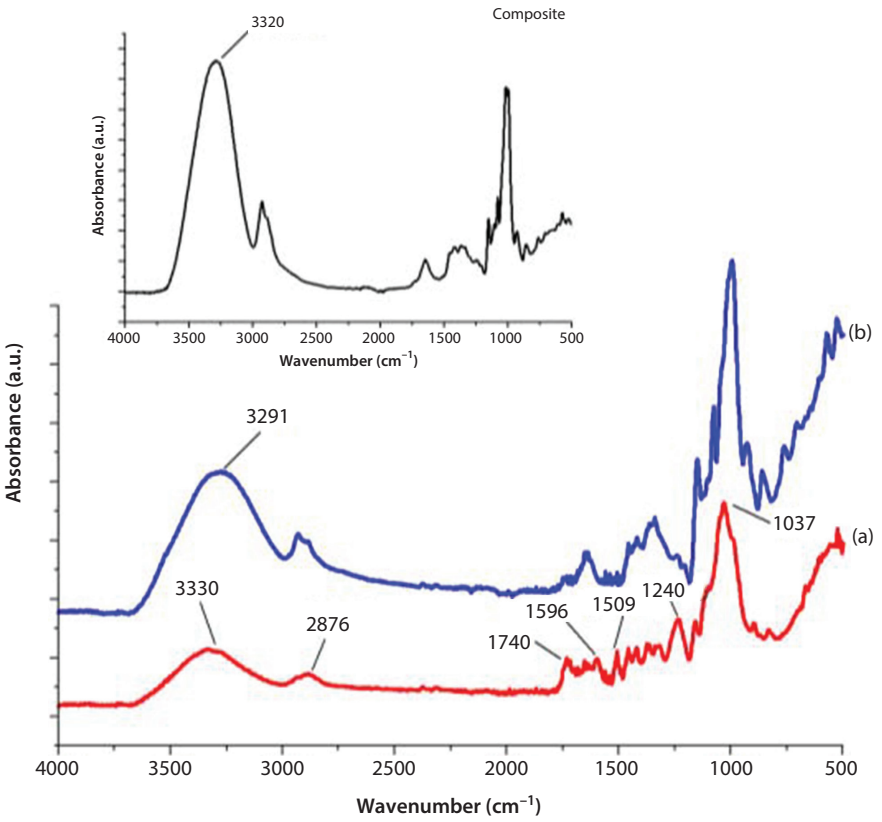

Figure 6 FTIR spectra of BP, TPS, and SBP-20.

Based on the statement of Prachayawarakorn *et al.* [18], the FTIR spectra of TPS (Figure 6b) and TPS/BP composite (upper corner) were similar because the main composition of the starch and BP is based on cellulose structure. These authors, unlike in the spectra of Figure 6, observed a slight shift of the band associated with TPS hydroxyl groups (3300–3500 cm^{-1}) to lower wavenumber for the composites of TPS/jute fiber. According to them, such a result is good evidence for the formation of new hydrogen bonds between the TPS and the cellulosic fibers. This disagreement with our results can be attributed to the difference in processing method. In the case of the authors, an internal mixer was used to blend the components.

The SMS-10 composite was not evaluated in the tensile test. As shown by SEM (Figure 3d), this composite presented a morphology in which the hollow particles were embedded in TPS matrix, and has been classified as syntactic foam [19].

4 CONCLUSIONS

The obtained results provide evidence that the addition of bamboo powder and hollow glass microspheres can modulate the properties of thermoplastic starch.

It can be concluded that there was a poor interaction between the matrix and the bamboo powder. Such failure was supposedly attributed to poor dispersion of the bamboo powder. It was noticed, however, that the glass microspheres, through friction, assisted the blending process during the preparation of the composites, thus contributing to the system homogenization. The surface wettability of the thermoplastic starch varied with the filler contents. The contact angle values were related to the surface roughness and suggested a transition from the Wenzel to the Cassie-Baxter regime. Due to their green character, TPS composites have potential to be used in the packaging industry, provided that very high mechanical properties are not demanded. Further studies should be done in order to achieve TPS composites with better properties.

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