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Effect of raw and chemically treated oil palm mesocarp fibers on thermoplastic cassava starch properties

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ABSTRACT

Composites of thermoplastic cassava starch (TPS) and oil palm mesocarp fibers (OPMF) were prepared using a screw extrusion rheometer. Two types of OPMF were used: raw and alkaline treated oil palm fibers. TPS composites using raw fiber showed an improvement of 193% in the elastic modulus and 153% for maximum stress, while the elongation at break was kept constant when compared to the neat TPS matrix. The high improvement in the mechanical and thermal properties of the TPS matrix by the raw fiber is due to the presence of silica, which influences the interaction of the matrix and OPMF fibers. The present work shows that TPS composites with 10 wt% raw fiber have greater mechanical properties than higher OPMF raw fiber content or alkaline treated fibers and provides the use of OPMF residue to produce an eco-friendly composite for various applications.

1. Introduction

The potentialof biodegradable polymers has long been recognized due to the possibility of replacement of some polymers based on fossil resources. Starch, for example, is an inexpensive, renewable, fully biodegradable and widely available raw material that after processing under some specific conditions of shear, time and temperature, is transformed into the so-called thermoplastic starch (TPS), usually in the presence of a plasticizer (Avérous and Halley, 2009; Rosa et al., 2009; Corradini et al., 2006; Cao et al., 2008). However, TPS shows high water absorption and rather weak mechanical properties when compared to the current synthetic polymers (Wan et al., 2009). To overcome these weaknesses, different strategies have been examined, such as chemical modification of starch, blending TPS with other biodegradable polymers and the addition of reinforcements (Avérous and Boquillon, 2004; Avérous et al., 2000; Dufresne and Vignon, 1998; Curvelo et al., 2001; Duanmu et al., 2007).

The use of natural fibers as reinforcement is a growing trend, due to their remarkable advantages: renewable source, deformability and biodegradability, high specific strength, low density and low cost (Bledzki and Gassan, 1999; Bhardwaj et al., 2006; Paquet et al., 2010).

In recent years, oil palm production has grown at rate of 9% (Souza et al., 2015) and the production of this crop is one of the most increased, worldwide. The oil palm waste generates environmental problems when kept on the soil, where it can attract unexpected animals and diseases (Sreekala et al., 1997). The raw materials obtained from industrial processing can be used as a natural reinforcement for polymers with or without any chemical and physical treatments (Souza et al., 2015; Ferrer et al., 2012), once the fibers obtained have desirable properties.

Oil palm mesocarp fibers (OPMF) is a large source of lignocellusic material that can be obtained from the palm oil industry and it is a low cost and renewable material, turning it into a suitable candidate for various applications such as bioethanol production and as reinforcement in polymer composites (Bahrin et al., 2012; Harmaen et al., 2015). OPMF have numerous silica-bodies attached to craters on their surface that are connected to a network of siliceous pathways within the fibrous matrix (Law et al., 2007) that can benefit its use in composites with TPS (Wang et al., 2011). Law et al. (2007) analyzed the oil palm empty fruit brunch (OPEFB) that quantified 0.9% of silica. OPEFB fibers were studied by Izani et al., as well as other ligno-cellulosic fibers, such as oil palm mesocarp (OPMF) ones, that had superior tensile strength and elongation at break when compared to OPEFB fibers.

Another advantageous use of this cellulose source is the nature of its fibers, which can align and orient along the matrix, improving the mechanical properties. Previous studies have shown an increase of the

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tensile strength when natural fibers were added on a TPS matrix. This fact is due to the great adhesion among the fibers and the matrix caused by their chemical affinity.

Chemical treatments, such as alkali treatment, were employed to enhance fiber-matrix interaction by removing lignin, oils, waxes and silica. These treatment causes, along the removal of hydrophilic components, the fiber fibrils opening, in a process called fibrillation (Campos et al., 2012; Wang et al., 2011; Haafiz et al., 2013; Ma et al., 2005; Lins et al., 2002). However, silica may act as a reinforcement agent when incorporated in polymeric ester or hydroxyl matrices due to the interaction between the silica oxygen and those polar groups.

In order to take advantage of the availability of oil palm mesocarp fibers (OPMF) and the good properties of TPS, two types of OPMF were used in this work to obtain the composites: raw and alkali treated fibers, mixed with thermoplastic cassava starch (TPS). There is a lack of information about the impact of the raw and alkali treated OPMF on the TPS matrix. As such, this work intends to investigate the mechanical, thermal and crystallinity properties when different content (5–20% w/w) of raw and alkali treated OPMF are incorporated in TPS.

2. Experimental

2.1. Materials

Raw oil palm mesocarp fibers (OPMF) were supplied by Embrapa Amazônia Oriental (Belém-PA, Brazil). NaOH (Qhemis) was used for alkali treatment of OPMF. Cassava starch was supplied by Amazon Amidos and glycerol by TecLab – Hexis Cientifica.

2.2. Preparation of OPMF alkali treated

The OPMF were milled in a Wiley (sieve with diameter of 3 mm) and dried in oven with air circulating during 24 h, 50 °C. The alkali treatment of OPMF was carried out with a solution of NaOH 2% (w/v) at 70 °C, under constant stirring for 60 min. The solution was brought to room temperature (25 °C), filtered and neutralized with milli-q water. After neutralization, the fibers were dried in an oven with air circulation (50 °C) until constant weight.

2.3. Preparation of composites

The composites were processed, as the formulations presented in the Table 1, in a HAAKE Rheomix 600 internal mixer connected to a torque rheometer (50 rpm, 120 °C, 6 min). The materials were thermally pressed (150 °C, 5 ton and 10 min) and cooled at 25 °C to obtain ribbons for tensile analyses. Stearic and citric acids were used to prevent early degradation and stabilize the composite.

2.4. Scanning Electron Microscopy (SEM)

The morphology of raw and alkali treated fibers and its composites with TPS were analyzed by scanning electron microscopy (JEOL microscope, model JSM 6510) at 2 kV. Fractured surfaces of polymers were obtained by submerging samples in liquid nitrogen, fracturing with tweezers and placing them in a desiccator. Samples were mounted with the fractured surfaces facing up onto aluminum specimen stubs using double-sided adhesive carbon tape. Specimens were sputter-coated with a thin layer of gold and photographed.

An energy dispersive spectroscopy (EDS) system (model JEOL 6742A–Ultradry Silicon Drift) with an active area of 10 mm^2 and 132 eV resolution was used to detect SiO_2 particles at the fiber surface.

Table 1
Samples designated and its constituent's content.

Samples	Starch (g)	OPMF (g)	Glycerol (g)	Milli-q water (g)	Stearic acid (g)	Citric acid (g)
TPS	60	0	26	14	1	1
TPS5RF	42	2.1	18	10	0.7	0.7
TPS10RF	42	4.2	18	10	0.7	0.7
TPS20RF	42	8.4	18	10	0.7	0.7
TPS5AT	42	2.1	18	10	0.7	0.7
TPS10AT	42	4.2	18	10	0.7	0.7
TPS20AT	42	8.4	18	10	0.7	0.7

2.5. Mechanical tests

From the pressed plates obtained from the formulations, samples 6 mm in width, 78 mm in length and thickness varying between 2 and 2.7 mm were cut. These samples were submitted to tensile tests using an EMIC universal testing machine, model DL 3000, rate of 5 $mm.mm^{-1}$, cell load of 50 kgf, 50 mm of claw distance and 50% relative humidity at 25 °C.

2.6. Thermogravimetric analysis (TGA)

Thermal degradation was evaluated using TA Q500 equipment (TA Instruments, New Castle, DE, USA) under the following conditions, foreseeing the ones used on extrusion processes: atmosphere of synthetic air flowing at 60 $mL.min^{-1}$; heating rate of 10 °C min^{-1} and temperature range from 25 °C to 600 °C.

2.7. X-Ray diffraction measurements (XRD)

The samples were analyzed by XRD in a Shimadzu LABX-XRD 6000 diffractometer, operating at 30 kV, 30 mA and CuKα (λ 1.5406 Å). The assays were performed at 25 °C, with 2Θ angles at 15° and 30° (2°/min).

The crystallinity degrees (Xc) were calculated by the ratio of the crystalline peak and the total area (crystalline + amorphous peaks), using deconvolution of the peaks, employing the Origin 7.5 software, using Gaussian function, after baseline correction.

3. Results and discussion

Fig. 1 shows the micrography of OPMF raw (Fig. 1a) and alkali treated fibers (Fig. 1b). The raw fibers presented average length of 440–1000 μm and diameter of 100 μm. There was observed some structures adhered to the surface, indicating the presence of amorphous substances such as lignin, polysaccharides and waxes. After the alkali treatment, a large part of these substances was removed, but part of the silica remained adhered on the fiber surface (Fig. 1a and b), what is confirmed by SEM-EDS as shown in Fig. 2. Silica removal is observed by craters in the surface (Fig. 1b).

Izani et al. (2013) and Then et al. (2015) studied the influence of alkali treatment on OPMF and stated that treated fibers presented the craters already mentioned on this work, which means that part of the silica was withdrawn by the alkali treatment. Those craters, along with the fibrillation, increase the interaction between the OPMF and the matrix by increasing their interlocking phenomena.

A cross-section of TPS composites with raw and alkali tread fibers (Fig. 1c–h) shows that the polymer matrix covered the fibers and promoted a strong adhesion among them. The fiber-polymer interaction was favored by residual silica presence, whose oxygen atoms interact very strongly with the TPS hydroxyl groups, which contradicts Izani et al. (2013) and corroborates Friedlander (1999). Silica can approach unsaturated bonds of polymer macromolecules and interact with the electrons of the unsaturated bonds of fiber (Wang et al., 2011; Lins et al., 2002). The silica in the fibers interacts with the hydroxyl groups of TPS resulting in strengthened molecular interaction in the adhesive system (Wang et al., 2011).

Composites with high fibers content (20% w/w) showed pull-out of