Contents lists available at ScienceDirect

Industrial Crops and Products

Composite materials of thermoplastic starch and fibers from the ethanol–water fractionation of bagasse

Maria E. Vallejos [a,b], Aprigio A.S. Curvelo [c], Eliangela M. Teixeira [d], Fernanda M. Mendes [c], Antonio J.F. Carvalho [e], Fernando E. Felissia [a], Maria C. Area [a,b,*]

[a] Programa de Investigación de Celulosa y Papel, Facultad de Ciencias Exactas, Químicas y Naturales, Universidad Nacional de Misiones, Félix de Azara 1552, 3300 Posadas, Misiones, Argentina
[b] Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Argentina
[c] Instituto de Química de São Carlos, Universidade de São Paulo, São Carlos, 13560-970 São Paulo, Brazil
[d] Embrapa, 13560-970, São Carlos, São Paulo, Brazil
[e] Department of Materials Engineering, University of São Paulo, São Carlos, São Paulo, Brazil

ARTICLE INFO

ABSTRACT

The aim of this study was to evaluate the potential of the fibrous material obtained from ethanol–water fractionation of bagasse as reinforcement of thermoplastic starches in order to improve their mechanical properties. The composites were elaborated using matrices of corn and cassava starches plasticized with 30 wt% glycerin. The mixtures (0, 5, 10 and 15 wt% bagasse fiber) were elaborated in a rheometer at 150 °C. The mixtures obtained were pressed on a hot plate press at 155 °C. The test specimens were obtained according to ASTM D638. Tensile tests, moisture absorption tests for 24 days (20–23 °C and 53% RH, ASTM E104), and dynamic-mechanical analyses (DMA) in tensile mode were carried out. Images by scanning electron microscopy (SEM) and X-ray diffraction were obtained. Fibers (10 wt% bagasse fiber) increased tensile strength by 44% and 47% compared to corn and cassava starches, respectively. The reinforcement (15 wt% bagasse fiber) increased more than fourfold the elastic modulus on starch matrices. The storage modulus at 30 °C ($E_{30 °C}'$) increased as the bagasse fiber content increased, following the trend of tensile elastic modulus. The results indicate that these fibers have potential applications in the development of biodegradable composite materials.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

The reinforcement of polymer composites with fibers to obtain materials with improved properties is one of the most important fields in the material science. Within this field, the use of natural cellulosic fibers as reinforcement of polymer matrices is increasing, due to their low cost and easy processability. Fibers have interesting mechanical and physical properties (Bledzki and Gassan, 1999; Eichhorn et al., 2001; Mohanty et al., 2000, 2002). Their renewable nature and their biodegradability are also interesting characteristics of natural fibers, which are an alternative to non-biodegradable inorganic reinforcements/fillers like glass, mica and calcium carbonate.

In recent years, there has been a great interest towards a more efficient use of renewable agro-industrial waste for obtaining value-added bio-products. This represents an increased value for the agro-based components besides that these composites are environment-friendly materials. On the other hand, synthetic and natural biodegradable polymers can also be considered as polymer matrices for preparing composites. Synthetic materials such as poly(L-lactic acid), poly(e-caprolactone), poly(hydroxyl-butyrate), poly(hydroxyl-alkanoate), and others, have been applied mainly in the field of the biomaterials (Averous and Digabel, 2006; John and Thomas, 2008; Bismarck et al., 2005). The use of natural matrices is being increased due to the non-toxicity of their degradation products and their renewable sources. One of the natural polymer most researched is starch (Averous and Digabel, 2006; Avérous and Halley, 2009) and its composites (Avérous et al., 2001; Averous and Boquillon, 2004; Curvelo et al., 2001; Carvalho et al., 2003). The studies showed a good compatibility between the cellulosic fibers and the biodegradable matrices, without compatibilizers or fibers modification. Sugarcane bagasse is a fibrous waste remaining after sugar extraction, which is produced in large quantities by the sugar and alcohol industries in several countries. Sugarcane bagasse is

* Corresponding author at: Programa de Investigación de Celulosa y Papel, Facultad de Ciencias Exactas, Químicas y Naturales, Universidad Nacional de Misiones, Félix de Azara 1552, 3300 Posadas, Misiones, Argentina. Tel.: +54 3752 422198; fax: +54 3752 422198.
E-mail address: m_c_area@fceqyn.unam.edu.ar (M.C. Area).

conventionally used as fuel for energy production or as cellulose fibers in the pulp and paper industry. Sugar mills generate around 0.13–0.15 tons of bagasse (dry weight) per metric ton of sugarcane. About half of this amount is burned as fuel to supply energy to the same industry. Currently, the remaining stored bagasse constitutes an environmental problem due to the risk of combustion.

Sugarcane bagasse is an abundant source of lignocellulose material. It can be used as an alternative low-cost fibrous resource, with suitable properties as reinforcement of composites in biodegradable polymer matrices, increasing the economy of the process. In a previous work, we presented results of ethanol–water fractionations of bagasse (Area et al., 2009). In that work, we separated three of its major components (cellulosic fraction, hemicelluloses and lignin), following the concept of biorefinery, and applying economically competitive and environmentally compatible technologies. In the present work, non-conventional sugar cane derivatives using bagasse as reinforcement of composites were prepared, as an alternative to conventional materials such as non-biodegradable plastics. Bagasse pulp fibers–starch composites can be used in different short-lived applications, such as packaging (Avérous and Halley, 2009). The research on starch polymers has focused on several areas, including the use of commodity starches in composites, building materials and polymer blends. The main drawbacks of thermoplastic starches (TPSs) are their brittleness, moisture absorption and low mechanical properties. The incorporation of natural fibers is an alternative to improve their thermal and mechanical properties and to preserve their biodegradability.

Lignocellulosic fibers can be used for the development of new composites because of their good mechanical and physical properties. Both treated or untreated chopped sugarcane bagasse fibers reinforced with different polymers such as polypropylene (Ramaraj, 2007; Cao et al., 2007; Ashori and Nourbakhsh, 2009; Nourbakhsh and Kouhpayehzadeh, 2009; Zabihzadeh et al., 2010; Zabihzadeh, 2010), epoxy (Vilay et al., 2008; Lee and Mariatti, 2008; Acharya et al., 2008; Saw and Datta, 2009; Acharya et al., 2009; Mishra and Acharya, 2010), polyethylene (Lei et al., 2007; Youssef et al., 2008; Mulinari et al., 2009; Zabihzadeh, 2010), polyvinyl chloride (Zheng et al., 2007; Xu et al., 2010, 2008), biopolyester (Hodzic et al., 2007), ethylene vinyl acetate (Stael et al., 2001), among others, have been studied in recent works. The results of these works suggest that bagasse–polymer composites can be used for commercial applications. However, although there are some reports on the use of cellulosic and lignocellulosic fibers in starch composites, such as *Eucalyptus urograndis* bleached kraft pulp (Curvelo et al., 2001; Carvalho et al., 2003), cassava bagasse (Teixeira et al., 2005), wheat straw (Averous and Digabel, 2006) and bleached fibers (Avérous et al., 2001; Averous and Boquillon, 2004), few reports exist about bagasse fibers or bagasse pulp fibers as reinforcement of starch matrices or biodegradable polymers. The results of the present work can be extended to the use of commercial wood pulp, available in large quantities at relatively low cost, with known and guaranteed properties.

The aim of this study was to evaluate the potential of the fibrous material obtained from the ethanol–water fractionation of sugarcane bagasse as reinforcement of thermoplastic starches, and to assess the effect of the type of starch used as a biodegradable polymer matrix.

2. Experimental

2.1. Materials

Corn starch (Amidex 3001) and cassava starch from Corn Products Ltd. (Brazil) were used as biodegradable polymer matrices. Glycerin (30 wt%) and stearic acid (2 wt%) were used as plasticizer

and processing aid, respectively. The fibrous material obtained from ethanol–water fractionation of bagasse was used as reinforcement.

2.2. Fiber preparation

Sugar cane bagasse and ethanol were supplied by a local mill (San Javier Sugar Mill, Misiones, Argentina). Bagasse pith was removed in two stages. In the former, bagasse was wet-depithed to break its structure in a Bauer disc refiner (plate gap of 0.005 in.), after which the bagasse pith was removed by screening, using a plate with 2 mm wide slits (Wenmber). Finally, depithed bagasse was centrifuged. Bagasse was delignified by organosolv ethanol process carried out in a 7 L MK digester (M/K Systems, Inc., MD) with liquor circulation. The ratios of liquor/bagasse and ethanol/water remained constant at 14/1 (v/w) and 50% (v/v), respectively. The time necessary to reach the maximum temperatures was of 30 min.

Fibers (which were agglomerated after drying at room temperature) were separated in a Werk Condux type hammer mill, with a sieve aperture size of 5 mm. The fibrous material processed in the hammer mill was classified in a laboratory-vibrating screen, using standard sieves with opening sizes of 1, 0.42 and 0.25 mm (18, 40 and 60 mesh, respectively). The reinforcement consisted of fibrous material retained on 40 and 60 meshes. The retained material on the 18-mesh sieve was reprocessed in the hammer mill and sieved again. The material that passed the 60-mesh sieve was discarded (about 20 wt% of the starting material). The fiber length distribution was measured in a Zeiss optical microscope with a Leica image analyzer (number of measurements: 130).

2.3. Sample preparation

Starch, glycerol, water, stearic acid and bagasse fibers (0, 5, 10 and 15 wt%) were blended and processed in a HAAKE torque rheometer – Rheomix 600 at 150 °C and 60 rpm for 6 min. The mixtures obtained were pressed in a hot plate press at 155 °C with a force of 10 tons. Test specimens were prepared for tensile tests and dynamic-mechanical analyses (DMA).

2.4. Characterization

The tensile tests were performed according to ASTM D638 M-96 in an EMIC DL3000 universal testing machine, using a load cell of 2 kN and 50 mm min^{-1} speed. These specimens were preconditioned for 30 days at 20–23 °C and 53% RH.

The DMA, in tensile mode, were performed in a Netzsch DMTA 242C equipment equipped with a TASC 414/3A controller and a liquid nitrogen cooling system. The materials were analyzed in the region of linear viscoelastic behavior, with a frequency of 1 Hz and at room atmosphere. The heating rate used was 2 °C min^{-1} and the temperature range −130 to 150 °C. The dimensions of the test specimens were 10 mm × 20 mm × 1 mm.

The morphological structures of the reinforcement materials and the cross section of the specimens for the tensile test of the starch matrices and its composites were studied by scanning electron microscopy (SEM). The photomicrographs were obtained in a Leica-Zeiss LEO 440 SEM-EDX scanning electron microscope equipped with an Oxford solid-state X-ray detector, operated at 20 kV.

The crystal structure of the materials and their proportion were analyzed using small-angle X-ray scattering (SAXS) in a Rigaku X-ray Universal diffractometer at room temperature and an angular range 2θ from 5° to 40°, with a copper electrode operating at 50 kV/100 mA and a rate of 2° min^{-1}.

The thermal analyses of differential scanning calorimetry (DSC) were performed on a Shimadzu TA-50WSI Thermal Analyzer equipped with DSC-50 modules. The scans were carried out from
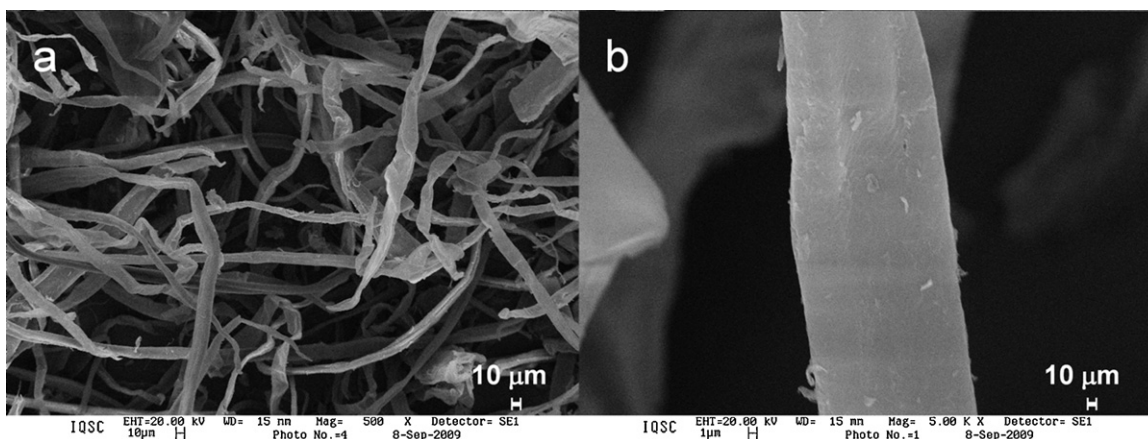
Fig. 1. SEM photomicrographs: (a) fibers individualized by the hammer mill, (b) morphological structure of a fiber.

room temperature to 500 °C at a heating rate of 10 °C min^{-1}, using a nitrogen atmosphere with a flow of 20 mL min^{-1}. Thermogravimetric analysis (TGA) conditions were: a nitrogen atmosphere, a flow rate of 20 mL min^{-1}, a heating rate of 10 °C min^{-1} and a temperature range from ambient to 800 °C.

Moisture absorption tests in samples conditioned at 20–23 °C and 53% RH were performed according to ASTM E104. The diffusion coefficients (D) of the materials were determined from the curves of water absorption. In general, the diffusion behavior in crystalline polymers is given by the relative mobility between the fluid and the polymer segments. This behavior can be established theoretically by the shape of the absorption curve. The absorption curve can be represented by the following equation:

$$\frac{M_t}{M_e} = kt^n \tag{1}$$

The constant k is related to the characteristics of the macro-molecular network system and penetration. The dimensionless diffusional exponent n can be used as an indicator of the diffusion mechanism for a particular system (a value of n of about 0.5 is indicative of diffusion according to Fick's law). In the case of diffusion according to Fick's law, the diffusion rate is much smaller than
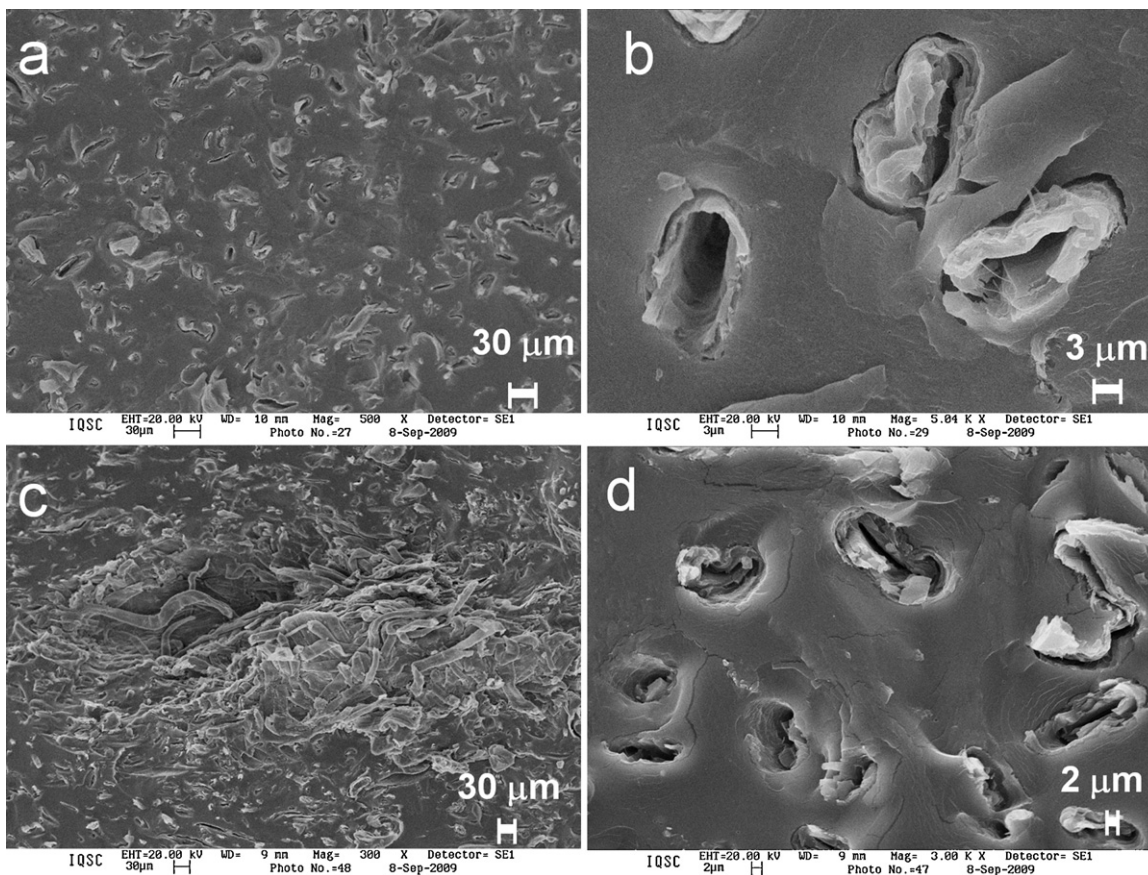

Fig. 2. SEM photomicrographs of the corn TPS composite (a and b) and cassava TPS composite (c and d) with 15% (w/w) bagasse fibers.

the mobility of polymer segments. The equilibrium within the polymer is reached quickly and is maintained independently of time. M_t and M_e are the percentages of moisture absorption at time t to reach the equilibrium.

The analysis of the diffusion mechanism was based on Fick's law, fitting the experimental values to Eq. (2), derived from Eq. (1):

$$\log \left(\frac{M_t}{M_e} \right) = \log k + n \log t \tag{2}$$

The coefficient is a parameter that shows the ability of the fluid molecules to penetrate inside the composite structure. For short times ($M_t/M_\infty \leq 0.5$), Eq. (3) was used, where L is the thickness of the sample:

$$\frac{M_t}{M_e} = \frac{4}{L} \left(\frac{D}{\pi} \right)^{0.5} t^{0.5} \tag{3}$$

Eq. (3) was used to determine the diffusion coefficient D from the linear portion of the slope of the curve of M_t/M_∞ as a function of $(t)^{0.5}L^{-1}$.

3. Results and discussion

3.1. Microscopy

The average fiber length was 667.3 μm (number of measurements: 585), the average fiber width 17.5 μm, and the length/width ratio 38. The fibers presented a wide range of fiber length distribution, between 351 and 1541 μm (50% of fibers between 590 and 1541 μm). The use of fibers as reinforcement to obtain a homogeneous material capable of being uniformly distributed in the matrix requires a good separation of the fibers. The processing of fibrous material in the hammer mill consisted in the application of mechanical impact energy to separate the fibrous agglomerates into fibers, without losing their length and morphological structure. The morphology of the bagasse fibers after the processing in the hammer mill is shown in Fig. 1.

The structure of the composites was characterized by SEM. Samples were fractured by immersion in nitrogen. The fractured surface of corn TPS with 15 wt% fibers is shown in SEM photomicrographs (Fig. 2), which revealed the dispersion of bagasse fiber in corn TPS. The bagasse fibers appeared well dispersed and coated by corn TPS, which was attributed to the fiber–matrix affinity. However, cassava TPS composites (15 wt%) presented agglomerated fibers, which indicate lower dispersion efficiency, when the fiber contents exceeded 10 wt% (Fig. 2c). Starch granules were not observed, which show that the disruption of the structure of starch granules was not affected by the bagasse fiber during the thermoplastic processing of TPS.

3.2. Rheological behavior

Native starches present hydrogen bonds between the hydroxyl groups in starch molecules, associated to their semi-crystalline structure. The thermal processing of starch-based polymers consists in the disruption of the structure of starch granules using plasticizers to form an amorphous material called thermoplastic starch (TPS). The rheological behavior of starches (plasticized with 30 wt% glycerol) and that of the blends with the bagasse fiber in the Haake rheometer are shown in Fig. 3. The Haake rheometer measures torque variation with time and temperature. The torque peaks are attributed to the phase transition of starch granules under shear stress. The measured torque was dependent on bagasse fiber content. The fiber–matrix interactions reduced the mobility of the polymer chains and increased the viscosity of the fiber–starch TPS blends. The bagasse fiber content increased the viscosity of the corn TPS more than the cassava TPS composites, which evidenced an
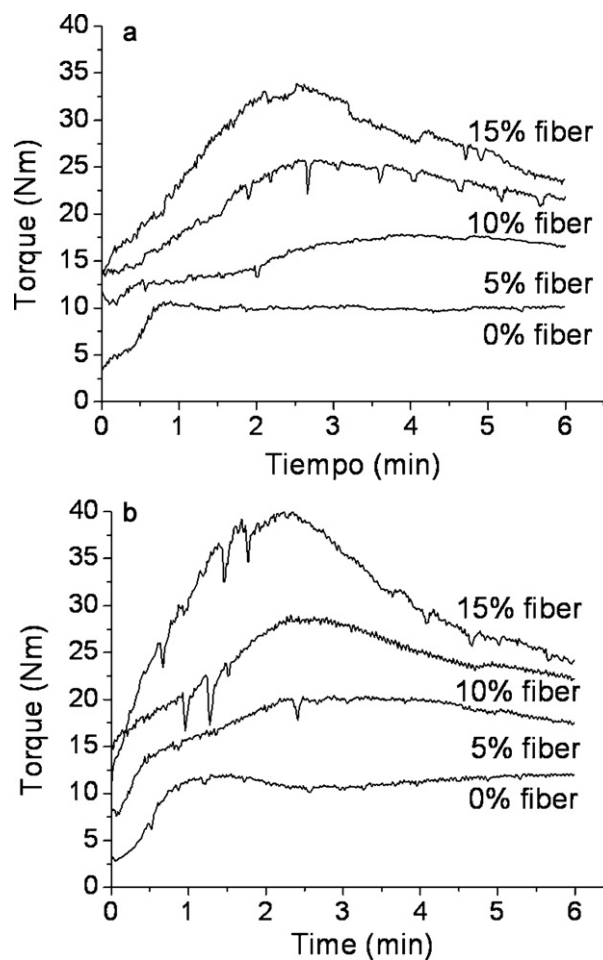

Fig. 3. Rheological behavior of cassava TPS composites (a) and corn TPS composites (b) with bagasse fibers.

insufficient dispersion of fibers during the processing of cassava TPS composites.

3.3. Mechanical properties

The results of the tensile mechanical tests (tensile strength (σ), modulus of elasticity (E) and tensile strain (ε)) of corn and cassava TPSs and their composites are presented in Table 1. The statistical analysis of the results of the tensile mechanical tests was performed by two-way ANOVA. The addition of bagasse fibers significantly improved the tensile strength and stiffness of the materials, respect to cassava and corn TPSs ($p < 0.05$). In the case of tensile strength, the tensile strength means of the materials with fibers differ significantly than those without fibers.

Table 1
Tensile properties of cassava and corn TPSs and their composites.

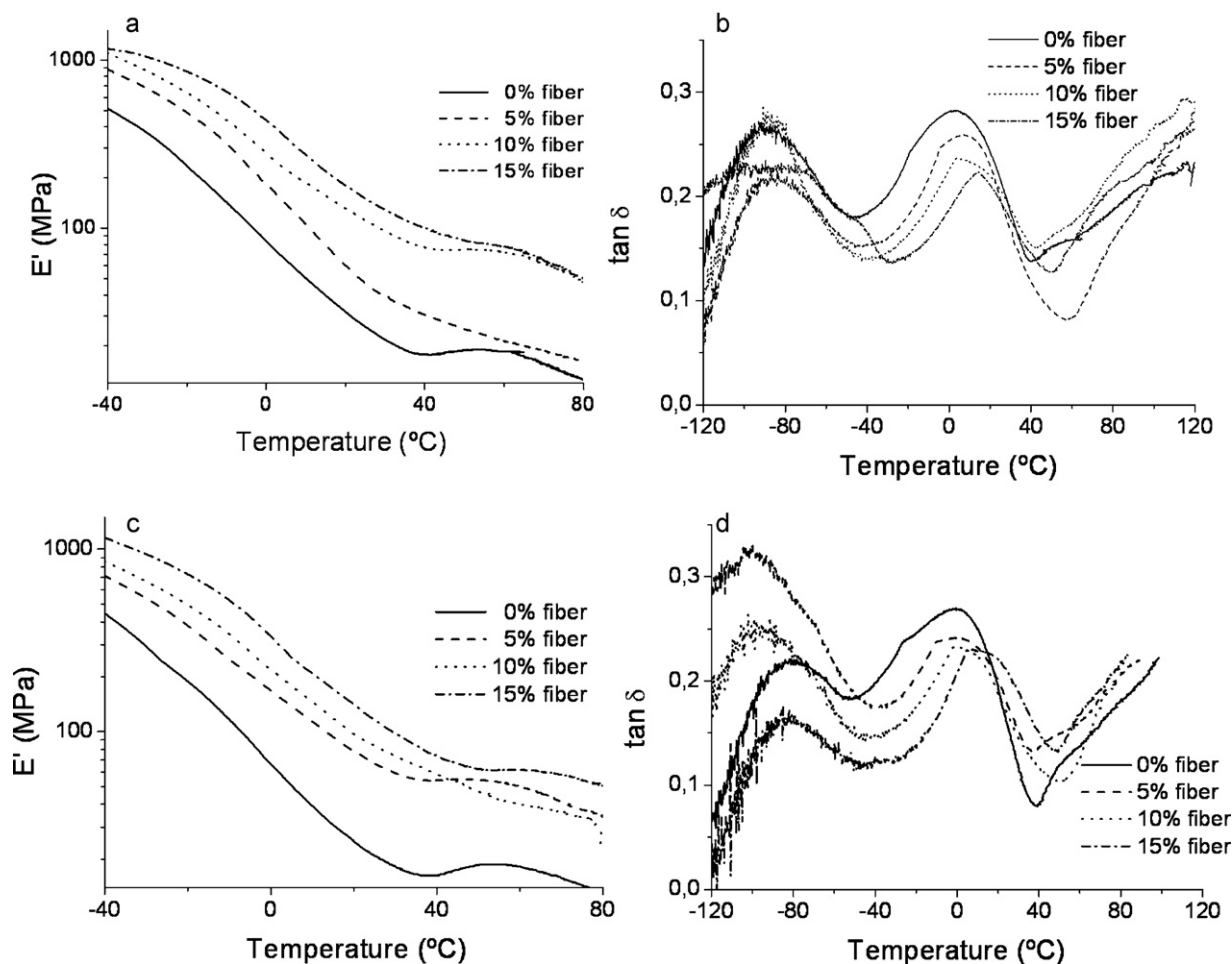| TPS	Bagasse fiber (wt%)	σ (MPa)	E (MPa)	ε (%)
Cassava	0	2.2 ± 0.3	13.3 ± 1.5	57.2 ± 15
Cassava	5	2.7 ± 0.3	23.6 ± 3.6	30.8 ± 7.6
Cassava	10	3.2 ± 0.5	38.0 ± 5.6	22.5 ± 2.8
Cassava	15	3.2 ± 0.7	56.4 ± 9.3	21.0 ± 2.5
Corn	0	2.6 ± 0.3	28.5 ± 3.1	33.4 ± 8.6
Corn	5	3.4 ± 0.5	58.5 ± 4.2	20.7 ± 5.4
Corn	10	3.8 ± 0.3	97.1 ± 4.1	13.7 ± 2.2
Corn	15	3.7 ± 0.7	131 ± 10	10.4 ± 3.5

Fig. 4. Module E' and $\tan \delta$ of the cassava composites (a and b) and corn composites (c and d) with bagasse fibers.

In general, the tensile properties of composites differed significantly according to the bagasse fiber content ($p < 0.05$). The bagasse fibers increased the tensile strength of starches from 2.61 to 3.75 MPa (47%) respect to corn TPS, and from 2.21 to 3.24 MPa (44%) respect to cassava TPS. The addition of 15 wt% bagasse fibers did not contribute to the increase in the strength of the composites.

The modulus of elasticity of the composites with 15 wt% bagasse fibers was four times greater than the modulus of elasticity of TPS alone (423% and 458% in cassava and corn TPSs, respectively). This property increased linearly with the bagasse fiber content (cassava TPS and their composites, $R^2 = 0.99$; corn TPS and their composites $R^2 = 0.98$).

In TPS, the tensile strain decreased significantly ($p < 0.05$) as the bagasse fiber content increased. The presence of fiber agglomerates demonstrates that the dispersion of fibers in the matrix was not efficient (Fig. 2c). This is one of the principal drawbacks to exploit the potential of this resource as reinforcement. Smaller contents of bagasse fibers would be
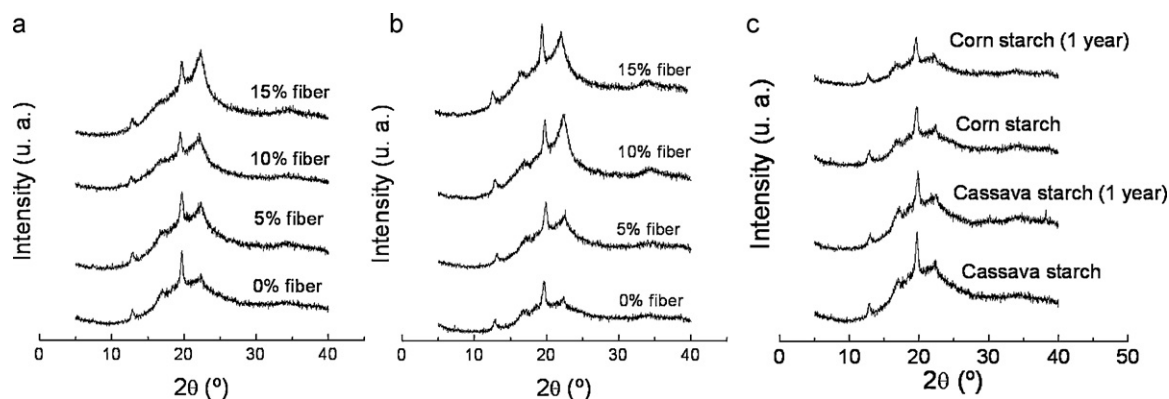

Fig. 5. X-ray diffractogram of the cassava TPS composites (a) and corn TPS composites (b) with bagasse fibers, and cassava TPS and corn TPS after one year (c).

Table 2
Dynamic-mechanical properties of cassava and corn TPSs and their composites.

TPS	Bagasse fiber (wt%)	$E_{30\,°C}'$ (MPa)	T_g (°C)
Cassava	0	21.5	3.7
Cassava	5	39.6	6.8
Cassava	10	95.9	8.2
Cassava	15	128.5	14
Corn	0	18.2	−0.5
Corn	5	59.1	−0.4
Corn	10	73.0	3.1
Corn	15	97.4	13

Table 3
Values of n, k, D and M_e of the composites, depending on the type and content of reinforcement.

| TPS	Bagasse fiber (wt%)	n	k	D (cm² s⁻¹)	M_e (%)
Corn	0	0.60	0.05	3.68×10^{-8}	7.9 ± 0.1
Corn	5	0.61	0.05	4.07×10^{-8}	7.9 ± 0.0
Corn	10	0.63	0.04	3.20×10^{-8}	7.5 ± 0.2
Corn	15	0.63	0.04	3.04×10^{-8}	7.5 ± 0.3
Cassava	0	0.66	0.04	4.03×10^{-8}	8.0 ± 0.2
Cassava	5	0.67	0.04	3.85×10^{-8}	7.8 ± 0.3
Cassava	10	0.64	0.04	3.07×10^{-8}	7.8 ± 0.2
Cassava	15	0.61	0.04	2.88×10^{-8}	7.5 ± 0.1

more appropriate, as their dispersion in the matrix could be facilitated.

3.4. Dynamic-mechanical properties

The dynamic-mechanical test showed the viscoelastic behavior of the corn and cassava TPSs and their composites in a wide range of temperatures. The variation of the storage modulus at 30 °C ($E_{30\,°C}'$) at different bagasse fiber contents is given in Table 2. The storage modulus decreased as temperature increased, and this decrease was more pronounced in cassava and corn TPSs (Fig. 4).

The storage modulus correlated well with the values of elastic modulus obtained in the tensile tests ($R^2 = 0.97$ and $R^2 = 0.94$ for cassava and corn TPSs and composites, respectively). The modulus E' improved as the content of bagasse fibers increased, when comparing with the modulus E' of cassava and corn TPSs. The modulus E' of the composites containing 15 wt% bagasse fiber at 30 °C were about five and six times higher than the corn and cassava TPSs alone, respectively.

The glass transition temperatures (T_g) were determined from the peaks of the curve tan δ–temperature (Table 2, Fig. 4b and d). The first peak observed corresponds to the relaxation of the glycerol-rich phase (the T_g of pure glycerol is in the range of −75 to −80 °C). The second peak is related to the glass transition of thermoplastic starch. The T_g of the thermoplastic starch depends on the content of plasticizer, the moisture conditions and the composition of the starch.

Some studies on the physical properties of TPS (glycerol as plasticizers) have shown discrepancies in the T_g values, even for the same glycerol content, possibly due to differences in the conditions of TPS preparation (Avérous and Halley, 2009). The T_g values for the corn and cassava TPSs (30 wt% glycerol) were −0.5 and 3.7 °C, respectively, at 23 °C and 53% RH. Other authors, who studied the physical properties of the plasticized starches with glycerol, reported higher T_g values (Avérous and Halley, 2009). García et al. (2009) reported a T_g value of approximately −10 °C for cassava TPS.

3.5. X-ray diffractometry

The X-ray diffractograms of the cassava and corn TPSs and their composites are shown in Fig. 5. Both TPSs show the corresponding peak at $2\theta = 12.7°$ (V_a), $2\theta = 16.8–17°$ (B), $2\theta = 19.7°$ (V_h) and $2\theta = 22.4°$ (V_h). The peak $2\theta = 16.8–17°$ is attributed to the recrystallization of amylopectin (B-type crystallization), while the peaks at $2\theta = 19.7°$ and $2\theta = 22.4°$ are characteristic of the induced crystallization process (V_h) produced by the recrystallization of amylose during the cooling of the processed material (Teixeira et al., 2005). The peak at $2\theta = 22.4°$, attributed to the cellulose crystallinity, overlaps with the peak at $2\theta = 22.4°$ (V_h), and becomes progressively greater as the bagasse fiber content increases.

The X-ray diffractograms of cassava and corn TPS composites showed that as bagasse fiber content increased, the peak at 22.4°, which was attributed to cellulose crystallinity, became gradually

stronger. In the X-ray diffractograms of cassava and corn TPS composites stored for twelve months (Fig. 5c), we did not observe the tendency to re-crystallization.

In this work, the peak $2\theta = 19.7°$ (V_h) decreased gradually as the bagasse fiber increased, independently of the type of starch, which was attributed to a decrease in crystallinity.

3.6. Water absorption

The water absorption is a critical criterion for several applications of TPS products. The starches absorb moisture due to their hygroscopic nature. The results of the moisture absorption test (20–23 °C and 53% RH) are presented in Table 3 and Fig. 6 for cassava and corn TPSs and their composites. The absorption equilibrium was reached after twelve days.
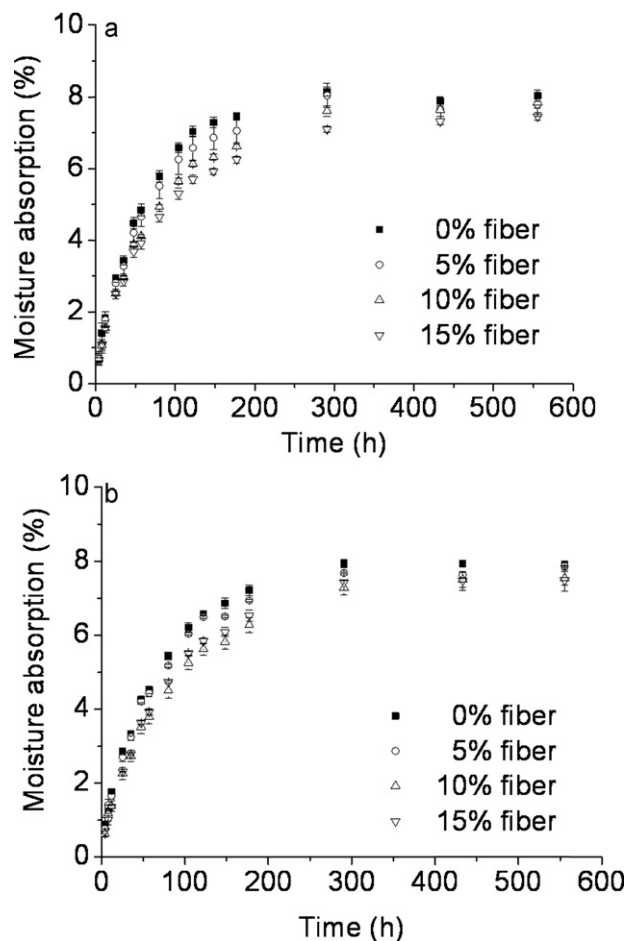
Fig. 6. Moisture absorption of cassava (a) and cassava (b) TPS and their composites with bagasse fibers (53% RH).
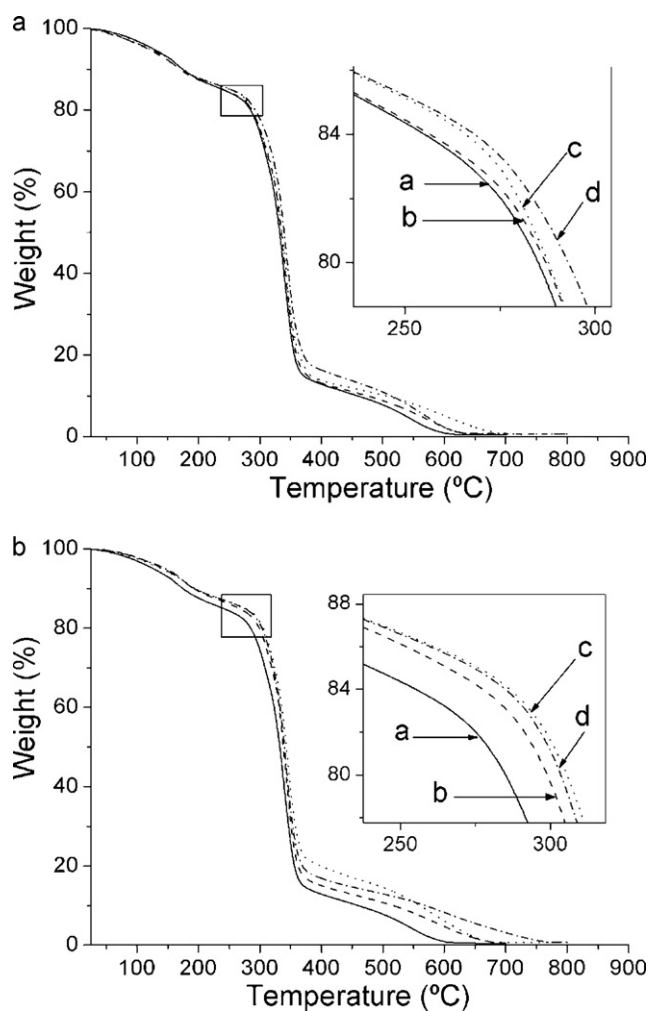
Fig. 7. TGA thermograms of cassava TPS (a) and corn TPS (b) and composites with (a) 0%, (b) 5%, (c) 10% and (d) 15% (w/w) bagasse fibers.

The addition of bagasse fibers decreased the moisture absorption rate, excluding the moisture content at equilibrium, except for corn TPS composites. At seven days, the composites with 15 wt% bagasse fibers had a moisture content lower than that of corn and cassava TPSs (9 and 16% lower, respectively). This behavior was related to the differences in the hydrophilic character of the fibers in comparison to starch. The effect of bagasse fibers on the equilibrium moisture content was not evident. The equilibrium moisture for cassava and corn TPSs and their composites was 7.5–8.0%.

The values of D in corn TPS and cassava TPS were 3.68×10^{-8} and 4.03×10^{-8} cm^2 s^{-1}, respectively. The values of D decrease when the amount of fiber increases (10 and 15 wt%). The decrease was of 8 and 28% in corn and cassava composites (15 wt%) respect to TPSs. The lower values of D of the composites are attributed to the lower crystallinity of starch in comparison to cellulose. Therefore, the fibers absorb less moisture and the composites contain less starch when compared to pure starch. In addition, the presence of hydrogen bonding interactions between starch and cellulose crystallites formed at the fiber–TPS interfaces stabilizes the starch matrix when it is in a moist atmosphere (Lu et al., 2005).

3.7. Thermal analysis

The thermal behavior of cassava and corn TPSs and their composites was studied by the TGA. The thermal behavior of the composites is shown in Fig. 7. TGA experimental results (peak maxi-

Table 4
Thermal analysis results, TGA and DTGA.

TPS	Bagasse fiber (wt%)	T_m (°C)	Weight loss at T_m (%)	$T_{onset\,1}$ (°C)	Weight loss at $T_{onset\,1}$ (%)	$T_{onset\,2}$ (°C)
Cassava	0	342	63	313	33	358
Cassava	5	344	59	314	32	366
Cassava	10	340	56	315	32	367
Cassava	15	339	52	317	29	367
Corn	0	340	61	316	30	354
Corn	5	341	58	318	29	360
Corn	10	345	53	319	27	364
Corn	15	344	56	319	28	360

mum temperature, T_m; weight loss at T_m; onset temperature of first thermal event, $T_{onset\,1}$; onset temperature of second thermal event, $T_{onset\,2}$) are presented in Table 4. The thermal stability is limited to temperatures below 200 °C. The weight loss at temperatures below 150 °C was not considered in this analysis because it is related to moisture loss and to the beginning of the degradation of glycerol.

The thermal behavior of the weight loss curve was similar in the thermoplastic starch and their composites. The degradation started at 313–317 °C in cassava TPS and their composites and at 316–319 °C in corn TPS and their composites (loss at the $T_{onset\,1}$ between 29–33% and 27–30%, respectively). The peak of maximum temperature and the weight loss at T_m were obtained from the DTGA curves. The peak of maximum temperature was at 339–344 °C in cassava TPS and their composites and at 340–345 °C in corn TPS and their composites (weight loss at T_m between 52–63% and 53–61%, respectively). The addition of bagasse fiber has decreased the weight loss of the composite respect to pure TPS at T_m. It indicates an improvement in the thermal resistance of the starches.

4. Conclusions

Tensile tests showed that the reinforcement of thermoplastic starches improved their strength and increased their stiffness significantly. The addition of more than 10% of reinforcement did not contribute to strength increase. Bagasse fibers (10%) increased the strength about 44% and 47%, compared to corn and cassava starches, respectively. The reinforcement with 15 wt% bagasse fiber resulted in a more than fourfold increase in the elastic modulus on starch matrices. The tensile strain decreased significantly as bagasse fiber content increased. The presence of fiber agglomerates indicates that the dispersion in the matrix was not efficient in composites reinforced with more than 10 wt% bagasse fiber. This is one of the principal drawbacks that prevents taking advantage of their potential as reinforcement material. Smaller contents of bagasse fibers would be more appropriate, since the dispersion of fibers in the matrix could be facilitated. The storage modulus at 30 °C ($E_{30°C}'$) and glass transition temperature (T_g) determined by DMA increased proportionally with the content of bagasse fibers. The content of bagasse fibers affected the rate of moisture absorption, but not the moisture content at equilibrium, except in the case of corn starch composites. The composites have enhanced performance properties compared to TPS. The results indicate that the fibers obtained by the ethanol–water fractionation of bagasse have potential applications as reinforcement in the development of starch based biodegradable composites (Carvalho, 2008).

Acknowledgements

References

Acharya, S.K., Mishra, P., Mehar, S.K., 2008. Weathering behavior of bagasse fiber reinforced polymer composite. J. Reinf. Plast. Comp. 27, 1839–1846.

Acharya, S.K., Mishra, P.P., Mehar, S.K., 2009. The influence of fiber treatment on the performance of bagasse fiber-reinforced polymer composite. J. Reinf. Plast. Comp. 28, 3027–3036.

Area, M.C., Felissia, F.E., Vallejos, M.E., 2009. Ethanol–water fractionation of sugar cane bagasse catalyzed with acids. Cell. Chem. Technol. 43, 269–277.

Ashori, A., Nourbakhsh, A., 2009. Polypropylene cellulose-based composites: the effect of bagasse reinforcement and polybutadiene isocyanate treatment on the mechanical properties. J. Appl. Polym. Sci. 111, 1684–1689.

Avérous, L., Fringant, C., Moro, L., 2001. Plasticized starch–cellulose interactions in polysaccharide composites. Polymer 42, 6565–6572.

Averous, L., Boquillon, N., 2004. Biocomposites based on plasticized starch: thermal and mechanical behaviours. Carbohydr. Polym. 56, 111–122.

Averous, L., Digabel, F., 2006. Properties of biocomposites based on lignocellulosic fillers. Carbohydr. Polym. 66, 480–493.

Avérous, L., Halley, P.J., 2009. Review: biocomposites based on plasticized starch. Biofuel Bioprod. Bior. 3, 329–343.

Bismarck, A., Mishra, S., Lampke, T., 2005. In: Mohanty, A.K., Misra, M., Drzal, L.T. (Eds.), Natural Fibres, Biopolymers and Biocomposites. CRC Press, p. 37.

Bledzki, A.K., Gassan, J., 1999. Composites reinforced with cellulose based fibres. Prog. Polym. Sci. 24, 221–274.

Cao, Y., Goda, K., Shibata, S., 2007. Development and mechanical properties of bagasse fiber reinforced composites. Adv. Compos. Mater. 16, 283–298.

Carvalho, A.J.F., Zambom, M.D., Curvelo, A.A.S., Gandini, A., 2003. Size exclusion chromatography characterization of thermoplastic starch composites. 1. Influence of plasticiser and fibre content. Polym. Degrad. Stab. 79, 133–138.

Carvalho, A.J.F., 2008. Starch: major sources, properties and applications thermoplastic materials. In: Belgacem, M., Gandini, A. (Eds.), Monomers, Polymers and Composites from Renewable Resources. Elsevier, Oxford, UK, pp. 321–342.

Curvelo, A.A.S., Carvalho, A.J.F., Agnelli, J.A.M., 2001. Thermoplastic starch–cellulosic fibers composites: preliminary results. Carbohydr. Polym. 45, 183–188.

Eichhorn, S.J., Baillie, C.A., Zafeiropoulos, N., Mwaikambo, L.Y., Ansell, M.P., Dufresne, A., Entwistle, K.M., Herrera-Franco, P.J., Escamilla, G.C., Groom, L., Hughes, M., Hill, C., Rials, T.G., Wild, P.M., 2001. Review: current international research into cellulosic fibres and composites. J. Mater. Sci. 36, 2107–2131.

García, N.L., Famá, L., Dufresne, A., Aranguren, M., Goyanes, S., 2009. A comparison between the physico-chemical properties of tuber and cereal starches. Food Res. Int. 42, 976–982.

Hodzic, A., Coakley, R., Curro, R., Berndt, C.C., Shanks, R.A., 2007. Design and optimization of biopolyester bagasse fiber composites. J. Biobased Mater. Bioenergy 1, 46–55.

Lee, S.C., Mariatti, M., 2008. The effect of bagasse fibers obtained (from rind and pith component) on the properties of unsaturated polyester composites. Mater. Lett. 62, 2253–2256.

Lei, Y., Wu, Q.L., Yao, F., Xu, Y.J., 2007. Preparation and properties of recycled HDPE/natural fiber composites. Compos. Part A: Appl. Sci. 38, 1664–1674.

Lu, Y.S., Weng, L.H., Cao, X.D., 2005. Biocomposites of plasticized starch reinforced with cellulose crystallites from cottonseed linter. Macromol. Biosci. 5, 1101–1107.

Mishra, P., Acharya, S.K., 2010. Solid particle erosion of bagasse fiber reinforced epoxy composite. Int. J. Phys. Sci. 5, 109–115.

Mohanty, A.K., Misra, M., Drzal, L.T., 2002. Sustainable bio-composites from renewable resources: opportunities and challenges in the green materials world. J. Polym. Environ. 10, 19–26.

Mohanty, A.K., Misra, M., Hinrichsen, G., 2000. Biofibres biodegradable polymers and biocomposites: an overview. Macromol. Mater. Eng. 276-277, 1–24.

Mulinari, D.R., Voorwald, H.J.C., Cioffi, M.O.H., da Silva, M.L.C.P., Luz, S.M., 2009. Preparation and properties of HDPE/sugarcane bagasse cellulose composites obtained for thermokinetic mixer. Carbohydr. Polym. 75, 317–321.

Nourbakhsh, A., Kouhpayehzadeh, M., 2009. Mechanical properties and water absorption of fiber-reinforced polypropylene composites prepared by bagasse and beech fiber. J. Appl. Polym. Sci. 114, 653–657.

Ramaraj, B., 2007. Mechanical and thermal properties of polypropylene/sugarcane bagasse composites. J. Appl. Polym. Sci. 103, 3827–3832.

John, M.J., Thomas, S., 2008. Biofibres and biocomposites. Carbohydr. Polym. 71, 343–364.

Saw, S.K., Datta, C., 2009. Thermomechanical properties of jute/bagasse hybrid fibre reinforced epoxy thermoset composites. Bioresources 4, 1455–1476.

Stael, G.C., Tavares, M.I.B., d'Almeida, J.R.M., 2001. Evaluation of sugar cane bagasse waste as reinforcement in EVA matrix composite materials. Polym.–Plast. Technol. 40, 217–223.

Teixeira, E.M., Da Róz, A.L., Carvalho, A.J.F., Curvelo, A.A.S., 2005. Preparation and characterisation of thermoplastic starches from cassava starch, cassava root and cassava bagasse. Macromol. Symp. 229, 266–275.

Vilay, V., Mariatti, M., Taib, R.M., Todo, M., 2008. Effect of fiber surface treatment and fiber loading on the properties of bagasse fiber-reinforced unsaturated polyester composites. Compos. Sci. Technol. 68, 631–638.

Xu, Y., Wu, Q., Lei, Y., Yao, F., Zhang, Q., 2008. Natural fiber reinforced poly(vinyl chloride) composites: effect of fiber type and impact modifier. J. Polym. Environ. 16, 250–257.

Xu, Y.J., Wu, Q.L., Lei, Y., Yao, F., 2010. Creep behavior of bagasse fiber reinforced polymer composites. Bioresour. Technol. 101, 3280–3286.

Youssef, H.A., Ismail, M.R., Ali, M.A.M., Zahran, A.H., 2008. Effect of the various coupling agents on the mechanical and physical properties of thermoplastic–bagasse fiber composites. Polym. Compos. 29, 1057–1065.

Zabihzadeh, S.M., Hashemi, S.K.H., Nikoo, H.M., Sepidehdam, S.M.J., 2010. Influence of fungal decay on physico-mechanical properties of a commercial extruded bagasse/PP composite. J. Reinf. Plast. Comp. 29, 1750–1756.

Zabihzadeh, S.M., 2010. Flexural properties and orthotropic swelling behavior of bagasse/thermoplastic composites. Bioresources 5, 650–660.

Zheng, Y.T., Cao, D.R., Wang, D.S., Chen, J.J., 2007. Study on the interface modification of bagasse fibre and the mechanical properties of its composite with PVC. Compos. Part A: Appl. Sci. 38, 20–25.