Preparation and Properties of Biocomposites Based on Jute Fibers and Blend of Plasticized Starch and Poly(β-hydroxybutyrate)

Ramzi Belhassen,[1] José Alberto Méndez,[2] Sami Boufi,[1] Joan Pere López,[2] Josep Puig,[2] Angels Pèlach,[2] Pere Mutjé[2]

[1]*LMSE, Faculte des Sciences de Sfax, University of Sfax, Sfax BP 802-3018, Tunisia*
[2]*LEPAMAP Group, University of Girona, Campus Montilivi, Girona 17071, Spain*

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ABSTRACT: In this work, preparation and properties of biocomposites based on jute fibers and blend of plasticized starch and poly(β-hydroxybutyrate) (PHB) have been investigated. Different amounts of glycerol and aliphatic polyesters (PHB) have been added to native starch to obtain a processable biodegradable matrix. In the same way natural jute fibers up to 30 wt % loading were added to improve the mechanical and thermal stability of the material. Tensile mechanical, thermal, and thermomecahnical analyses have been performed to characterize the ensuing materials. Significant enhancement in the mechanical properties and water sensitivity were noted by the addition of 8 wt % PHB. The fibers incorporation into the biopolymer matrix brings about an increase in both the mechanical strength and modulus as much higher as the fibers loading is important. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 313–321, 2009

Key words: biopolymers; cellulose; composites; mechanical properties

INTRODUCTION

Synthetic polymeric materials have been widely developed for ease processibility, possibility to provide large variety of cost effective items, durability, and high resistance to different degradation forms. However, the above cited features that make the polymer so useful have contributed to generate a negative environmental impact due to their accumulation and difficulty to recycle. The development of commodity plastic material has to take accounts all the constraints and policy regulation dealing with postconsume of plastic waste. In this regard, when a long life span is not required, the recourse to biopolymer constitutes an interesting alternative to petroleum-based polymer. To date, among the different commercially available bio-based material, starch polymers are one of the most important groups and cost effective.[1,2]

Starch is a natural polymer composed by two polymers of D-glucose: amylose and amylopectin. Native starch can be a thermoplastic material by adding different plastisizers such as water, alcohols, oligomers.[3–5] The resulting material is a biodegradable polymer with limited mechanical properties depending on the plastisizer content.[6,7]

The limits in the usefulness of thermoplastic starches are managed by his high-water sensibility leading to a deterioration of the mechanical properties. One of the strategy that is widely adopted to overcome the inherent shortcomings of plasticized starch (PST) consists in the association of PST with other polymer in the form of blend or multilayer product.[8–10] In this regard, polycaprolactone (PCL) is often mixed with starch at a level ranging from 30 up to 60 wt % to produce water-resistant biopolymer easy to process displaying properties comparable with low-density polyethylene.[11–13] Apart from PCL, which is well advanced in terms of reaching large-scale production, a number of other polyesters derived from a bio-based feedstock were mixed with starch. Among them, polyhydroxyalkanoates such as PHB attracted much attention given its qualities for thermoprocessing applications, water insolubility, good resistance to hydrolytic degradation, and high crystallinity (60–70%). However, most of the reported studies were rather concerned with blend of PHB with PST acting as a functional filler at a level of PHB ranging from 90 to 70%. The main objective for the addition of starch is cost reduction without compromising the physical properties[14] and also to control the rate of degradation or disintegration. Lai et al.[15]

Correspondence to: S. Boufi (sami.boufi@fss.rnu.tn).

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prepared a blend of PHB and TPS with a glycerol content ranging from 33 to 39% based on starch and a PHB amount up to 7%. Up to 3% in PHB level, they showed a significant increase in tensile and tear strength with respect to pristine TPS.

To improve the properties of the final material, starch matrix can be strengthened by means of reinforcing agents. In this sense, natural fibers can be used as reinforcing agent of starch biopolymer, without loosing the environmental benefits associated with the biodegradable matrix. Natural fibers, derived from annually renewable resources, provide positive environmental benefits and often bring about an improvement in the mechanical properties of the ensuing material.[16-21]

In the present work, the effect of PHB addition on the properties of PST was studied. Biocomposite based on jute fibers at different fibers loading and blend of PST and PHB were also prepared. Mechanical properties, thermomechanical [dynamic mechanical thermal analyzer (DMTA), differential scanning calorimetry (DSC)], and water uptake were investigated.

MATERIALS AND METHODS

Materials

Both thermoplastic materials and composites prepared in this work were formulated with a polymer matrix based on native starch coming from corn crops, which was provided by Roquette Laisa España, S.A. (Barcelona, Spain). This material is a nonmodified starch used as modifier agent in paper technology. Glycerol (Gly) provided by Quimivita, S.A. (Sant Adrià de Besòs, Spain) was used as plasticizer without any prior purification. 4,4′-Methylene-bis(phenylisocyanate) (MDI) obtained from Aldrich (Madrid, Spain) was used as bifunctionalized agent to induce coupling between the components of the polymer matrix during its processing. Triethylamine supplied by Scharlau, S.L. (La Jota, Spain) was used as catalyst in the modification reaction with MDI. Triethylamine was purified by distillation prior use. Poly(β-hydroxybutyrate) (PHB) was supplied by Biomer™ (Krailling, Germany) and was applied to the formulated thermoplastic starch for improving mechanical properties as well as water absorption resistance. Lignocellulosic fibres derived from jute crops were supplied by Mas Clarà de Domeny (Girona, Spain) to be used as reinforcing component.

Methods

Fibre conditioning

The length of jute strands was reduced upto 10 mm to facilitate fiber dispersion. Natural strands were cut by means of a manual guillotine (Metrotec™, San Sebastián, Spain) and were submitted to a drying process in an oven at 80 °C for 24 h (Dycometal, Sant Boi de Llobregat, Spain).

Polymer matrix plastification

The preblend made of native starch, water, and glycerol was carried out in a low density polyethylene (LDPE) bag. The components were mixed for 45 min by hand until obtaining a homogeneous mass with a quite high viscosity.

The preblend and the other components of the final thermoplastic matrix or reinforced composites were added in an internal mixer (Brabender Plastograph™, Duisburg, Germany) working at 140° C and 80 ×*g*. The addition process of each component was optimized and is summarized in Table I. After complete water evaporation, MDI (4 wt % regarding starch content) was added followed by PHB. To classify the materials prepared in this work the following nomenclature has been established: $ST_{aa}GLY_{bb}W_{cc}PHB_{dd}$, with ST, GLY, W, and PHB being starch, glycerol, water and PHB, respectively. The subscripted number on the right of each acronym reflects the wt % of each component regarding the final material weight. The absence of one label in the name reflects the absence of this component in the final formulation.

Compression molding processing

Each formulation obtained after mixing in the internal mixer was pelletized to obtain a particle size able to be processed by compression molding. The materials were grinded using a mill (Agrimsa™, Sant Adrià del Besos, Spain) equipped with a set of knifes and sieves. Once the material was milled, it was introduced in a stainless mold for obtaining specimens for mechanical characterisation according to ASTM D638 standard specifications. The mold filled with the material was introduced in a hydraulically operated laboratory press LabEcon300 (Fontijne Grotnes™, Vlaardingen, The Netherlands). The procedure for compressing the material is summarized in Table II. The first stage in the compression molding (first line Table II) was carried out by

TABLE I
Procedure of Addition of Each Component to Obtain the Thermoplastic Starch or the Composites (When Fibres Are Added)

Time (min)	Component
0	Preblend
5	Natural fibres
9	MDI
12	PHB
15	End of processing

TABLE II
Temperature/closing Pressure vs. Time Sequence Applied for Compression Moulding of Thermoplastic Starch and Reinforced Composites

Time (min)	Temperature (°C)	Closing pressure ($kg_f \cdot cm^{-2}$)
0	180°C	0
8	180°C	6
13	180°C	30
21	Cooling until 55°C	30
26	Acquisition of specimens at 55°C	0

approaching the warm plates of the press to force the softening of the material prior compression.

Water uptake

Different fractions of specimens of each material obtained after compression molding were submitted to a controlled environment of 23°C of temperature and 50% of moisture by using a climate chamber Dycometal (Sant Boi de Llobregat, Spain). Each material was studied by triplicate, evaluating the water uptake by weighing the samples after different periods of time. The water uptake was determined by using eq. (1):

$$WU = \frac{(W_2 - W_1)}{(W_1)} \times 100 \tag{1}$$

where W_1 is the weight of the sample before conditioning and W_2 is that obtained after the corresponding period of time. With the values of water uptake, a kinetic study of the water diffusion was carried out applying the Fickian theory [eqs. (2) and (3)]:

$$\left(\frac{M_t}{M_\infty}\right) = k \cdot t^n \tag{2}$$

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

where M_t and M_∞ are the values of water uptake at t time and once the water equilibrium is reached, k and n are constants, L is the thickness of the sample, and D is the diffusion coefficient. Equation (3) can be applied only for materials with Fickian behavior ($n = 0.5$) and for values of $\left(\frac{M_t}{M_\infty}\right) \leq 0.5$.

Mechanical properties

Tensile test was carried out by means of a Universal testing machine (Instron 1122, Zamudio, Spain), equipped with a load of 5 kN, according to ASTM D638 standard specifications. The specimens were assayed after 48 h of conditioning at 23°C and 50 wt % of moisture to determine the properties of the material just after processing. Because of the hydrophilic nature of native starch, another set of specimens was tested after reaching the water content equilibrium (M_∞), after 41 days. A minimum of five specimens were tested for each batch.

Thermal properties

Crystallization behavior and thermal degradation of different samples were evaluated by means of DSC (Mettler Toledo DSC 820) and thermogravimetry analysis (Mettler Toledo TGA/851). The heating rate was 10°C min^{-1} and the range of temperatures was −80–220°C and 50–700°C, respectively. The glass transition temperature was computed as the midpoint of heat capacity increase. The analyses were performed under a nitrogen flow of 40 mL min^{-1}.

SEM observation

The area of fracture of the specimens tested under tensile stress was observed by means of a scanning electron microscope (Zeiss DMS 960, Oberkochen, Germany). The samples were coated with gold prior characterization.

Dynamic mechanical thermoanalysis

Dynamic mechanical analysis was conducted in a tension mode using a Diamond (Perkin-Elmer). Temperature scans were run from −80 to 100°C at a heating rate of 2 °C/min, frequency of 1 Hz, and amplitude deformation of 10 μm. The storage (E') and the loss (E'') modulus of the sample and the loss factor tan δ = (E''/E') were measured as a function of temperature. Sample dimensions were about 20 mm length, 5 mm width, and 2 mm thick. The main relaxation temperature T is defined as the temperature where the maximum of tan δ is reached.

RESULTS AND DISCUSSION

Thermoplastic polymer matrix preparation

To obtain homogenous blend both of the polymer matrices as well as composites were mixed in an internal mixer following the sequence time reported in Table I. In the absence of the jute fibers, the typical torque vs. mixing time profile is shown in Figure 1. The torque starts to increase the level off, after 1-2 min, to a plateau ranging from 25 to 8 N m according to the glycerol and PHB content. Thereafter, the torque starts to increase again after the addition of MDI and drop to a lower value at 13 min after the PHB incorporation. The higher the glycerol content with respect to starch, the lower is the torque attained in the first plateau. This effect is expected given the well-known plasticizing action of glycerol for starch that favors proccessibility and enhances flexibility.[22]

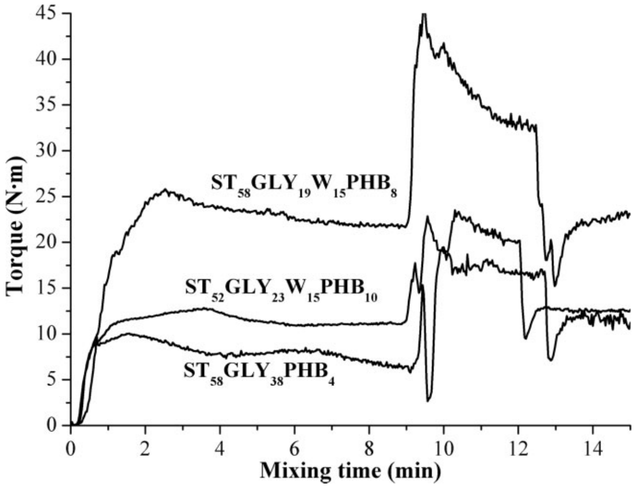

Figure 1 Torque profiles vs time during the mixing process, for the different composition system in the preparation of starch-based thermoplastic matrices.

Once MDI is added after 9 min mixing, an abrupt raise in the torque is noted, attesting an increase in the melt viscosity resulting from the reaction of the terminal isocyanate groups of MDI with the hydroxyl groups of starch and glycerol, thus giving rise to ramification and partial crosslinking among starch macromolecules. Through this effect, we intend improving the mechanical resistance of the ensuing material and reducing the water sensitivity. This coupling agent has been used successfully in the coupling of polymer blends of PLA and starch by urethane bonding between the two phases.[23] The reactivity of MDI additive is attested by comparing the FTIR spectra of the composition $ST_{58}GLY_{19}W_{23}$ with and without incorporation of MDI. Indeed, as shown in Figure 2, the emergence of new bands at 1712 and 1543 cm^{-1} attributed, respectively, to CO and NH stretching vibration of urethane linkage confirmed the occurrence of condensation reaction between the terminal isocyanate function of MDI and the hydroxyl one of starch and glycerol. One can note that other additive such as sodium trimetaphosphate have been reported to impart some crosslinking and hydrophobic effect.[24] The decrease in the torque value after 12 min consecutive to the addition of PHB is indicative of a reduction in the melt viscosity of the PST, probably as consequence of the high fluidity of melted PHB. This hypothesis is corroborated by the high melting flow index of PHB (MFI: 11.99 $g \cdot (10\ min)^{-1}$, $T = 180\ °C$, load: 1.20 kg_f).

The melt flow index evaluation of the thermoplastic starch revealed a material with a very high viscosity. MFI was tried to be measured at 180 °C and 2.16 kg_f of load without any success. Because of this result the material was processed by compression molding where lower flow index is needed compared with that for injection molding.

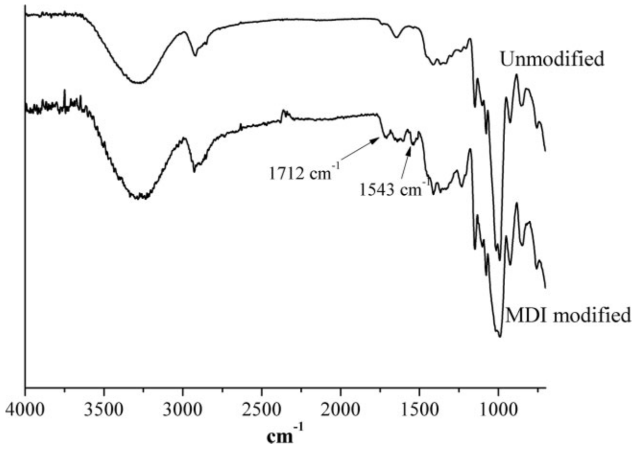

Figure 2 FTIR spectra of $STt_{58}GLY_{19}W_{23}$ modified and nonmodified with MDI.

Water uptake at controlled temperature and moisture

Different formulations were developed to determine the influence of the content of glycerol as well as the presence or absence of PHB. The prepared formulation as well as the maximum water uptake (MWU) and diffusion coefficient (D) are given in Table III. The n coefficient calculated by means of eq. (2) was close to 0.5 what indicates that the materials display a Fickian behavior.[25] The MWU content was reached after more than 1.000 h under controlled conditions. As can be seen, this MWU is dependent on the glycerol content in the samples, being higher with the increase of this component in the formulation. Thus, small implementations in the glycerol content produced growing values of MWU. This effect well known for PST with polyol[26] is attributed to the higher hydrophilic character of glycerol compared to starch, which is associated to the presence of three hydroxyl groups per glycerol molecule imparting higher interaction with water. With this argument a decrease in glycerol content should improve the

TABLE III
Study of the Water Uptake Behaviour of formulations of Thermoplastic Starch plasticized with Glycerol and PHB.

Formulation	n	MWU (wt %)	$D \times 10^{-10}$ (m^2/s)
$ST_{58}GLY_{19}W_{23}$	0.57	7.55	3.71
$ST_{58}GLY_{20}W_{22}$	0.57	7.40	3.74
$ST_{58}GLY_{21}W_{21}$	0.58	7.88	3.59
$ST_{58}GLY_{22}W_{20}$	0.62	8.09	4.08
$ST_{58}GLY_{23}W_{19}$	0.59	8.38	4.63
$ST_{58}GLY_{19}W_{15}PHB_{8}$	0.64	6.10	3.06
$ST_{58}GLY_{27}W_{11}PHB_{4}$	0.56	8.59	9.44

MWU: Maximum Water Uptake in the Equilibrium state; D: Diffusion coefficient; n: Fick coefficient.

TABLE IV
Tensile Mechanical Properties of Formulations of Thermoplastic Starch

Formulation	σ_t (MPa)	E_t (MPa)	ε_t (%)
$ST_{58}GLY_{19}W_{23}$[a]	1.90 [0.2]	133 [40]	22.08 [1.0]
$ST_{58}GLY_{22}W_{20}$[a]	1.67 [0.2]	76 [8]	28.90 [1.5]
$ST_{58}GLY_{27}W_{15}$[a]	0.66 [0.4]	22 [5]	34.88 [2]
$ST_{58}GLY_{27}W_{11}$ PHB_4[a]	4.98 [0.8]	580 [12]	1.04 [0.5]
$ST_{58}GLY_{19}W_{15}$ PHB_8[a]	7.30 [0.5]	1726 [13]	0.65 [0.4]
$ST_{58}GLY_{19}W_{15}$ PHB_8[b]	4.01 [0.4]	201 [28]	17.06 [1.0]
$ST_{58}GLY_{19}W_{23}$[b]	0.60 [0.4]	21 [5]	48 [2.5]

[a] After 48 h at 23°C/50% humidity.

[b] After 1.000 h at 23°C/50% humidity; [SD]: standard deviation.

water uptake resistance of the material, but glycerol is required to bring about plasticizing of starch. In this sense, the addition of a third component less sensitive to water may balance the water sensitivity imparted by the presence of glycerol. With the incorporation of the aliphatic polyester PHB, reduction in the water uptake was noted as shown in Table III. The formulation $ST_{58}GLY_{19}W_{15}PHB_8$ showed an important decrease in MWU with respect to the one without PHB and with comparable content in glycerol. Thus, comparing the composition $ST_{58}GLY_{19}W_{15}PHB_8$ with $ST_{58}GLY_{19}W_{23}$, the value of MWU was decreased by 19%. To confirm which component, glycerol or PHB, imparts a higher influence in water uptake behavior, the formulation $ST_{58}GLY_{27}W_{11}PHB_4$ with a high content in glycerol (27 wt %) and in the presence of low amount of PHB was prepared. As can be seen in Table III, MWU was again increased, pointing out the high dependence of the thermoplastic starch with the content of glycerol.

Static mechanical properties

Tensile test was carried out to evaluate the influence of the different components of the prepared thermoplastic matrices based on native starch. Ultimate tensile strength (σ_t), Young modulus (E_t), and strain at break (ε_t) of different starch-based polymer matrices were obtained after 48 h and after 41 days of conditioning at 23°C and 50% humidity, and the results are listed in Table IV. In the absence of PHB, the level of glycerol significantly affects the mechanical properties. The higher the glycerol content, the lower were the ultimate tensile strength (σ_t) and the Young Modulus (E_t). Thus, increasing glycerol content from 19 to 27 wt % (formulations $ST_{58}GLY_{19}W_{23}$ and $ST_{58}GLY_{27}W_{15}$, respectively) leads to a drop in the tensile strength and modulus by a factor 2.8 and 6, respectively, and bring about an increase in the elongation at break by a ratio of 1.5. This result is in line with the high plasticizing effect of glycerol toward starch[3–5] being able to be inserted among amylopectin chains thus decreasing the intermolecular interaction between them.

The addition of PHB brings about an important increase in σ_t as well as E_t both at high and medium amount of glycerol. Thus, the two compositions $ST_{58}GLY_{27}W_{11}$ PHB_4 and $ST_{58}GLY_{19}W_{15}$ PHB_8 displayed a strength at 4.98 and 7.3 MPa and a modulus at 580 and 1726 MPa, respectively. These value are much higher than their homologous without PHB $ST_{58}GLY_{19}W_{23}$ and $ST_{58}GLY_{27}W_{15}$ with a strength value at 1.9 and 1.67 MPa, and a modulus at 133 and 76 MPa, respectively. The enhancement in the mechanical properties imparted by the addition of PHB could be ascribed to the high strength of PHB and a good compatibility between PST and PHB. This result is in agreement with the work reported by Lai et al.[15] As will be shown later, phase separation and the PHB morphology within the continuous starch phase contributed to this improvement.

One can also note a significant decrease in the mechanical properties of the different composition after being conditioned for 41 j (1.000 h at 23°C and 50% of humidity) (last row, Table IV). This phenomenon is likely due to the water uptake by PST that contributes to enhance the plasticization degree of the material. Indeed, similar to glycerol water molecules are able to share hydrogen bonding with starch contributing to lose the interaction among amylose chains. the time dependence of the mechanical properties evolution is also the consequence of the kinetic aspect of water diffusion inside the material that need more than 30 days to attain the absorption equilibrium, as shown in Figure 3.

The evolution of water uptake behavior at different fiber content is shown in Figure 3 and the results regarding the Fickian analysis are reported in Table VI. The data showed a decrease in the MWU with the

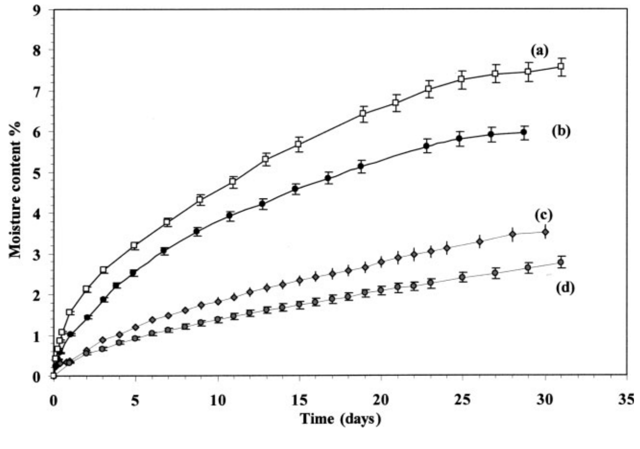

Figure 3 Evolution of the moisture uptake with time of the different composite at 23°C and 50% relative humidity (a) $ST_{58}GLY_{19}W_{23}$, (b) $ST_{58}GLY_{19}W_{15}PHB_8$, (c) $ST_{58}GLY_{19}W_{15}$ PHB_8+20 wt% fibers, and (d) $ST_{58}GLY_{19}W_{15}PHB_8$+30 wt % fibers.

TABLE V
Water Uptake Behaviour of Composite with Different Fibers Content

Composition	[a]V_f (vol%)	σ_t (MPa)	E_t (MPa)	ε_t (%)
ST$_{58}$GLY$_{19}$W$_{15}$ PHB$_8$[b]		7.30 [0.57]	1725 [13]	0.65 [0.04]
ST$_{58}$GLY$_{19}$W$_{15}$ PHB$_8$[c]		4.01 [0.50]	201 [28]	17.06 [7.14]
ST$_{58}$GLY$_{19}$W$_{15}$ PHB$_8$[b] + 10 wt % fibers	0.07	9.24 [0.87]	2148 [142]	0.45 [0.06]
ST$_{58}$GLY$_{19}$W$_{15}$ PHB$_8$[c] + 10 wt % fibers	0.07	7.43 [0.5]	1049 [40]	1.04 [0.2]
ST$_{58}$GLY$_{19}$W$_{15}$ PHB$_8$[c] + 20 wt % fibers	0.11	9.92 [0.6]	1119 [45]	0.75 [0.18]
ST$_{58}$GLY$_{19}$W$_{15}$ PHB$_8$[c] + 30 wt % fibers	0.14	7.42 [0.8]	1861 [65]	0.35 [0.15]

[a] Volume fraction.
[b] Determined after 48 h at 23°C/50% humidity.
[c] Determined after 1.000 h at 23°C/50% humidity.
[SD]: standard deviation.

incorporation of fibers in the matrix. Thus a drop by 21% in the MWU, with respect to unfilled matrix, is noted at 20 wt % fibers content, and if we take into account also the PHB contribution, then the moisture content is decreased by 36% with respect to the matrix based on starch and glycerol at the same composition. This trend is in agreement with other reported studies[27] which commonly associated this result with the lower hydrophilic character of the fiber in comparison with the matrix. Further, Table V revealed an increase in the water diffusion coefficient of the composite compared with the matrix indicating that the fibers favors the water diffusion inside the material probably through the fiber–matrix interface.

Composites reinforced with jute fibers

With all of the characterization procedures showed until now the formulation that displayed the best characteristics was ST$_{58}$GLY$_{19}$W$_{15}$PHB$_8$. This later was used as matrix to prepare biocomposite based on jute fibers. The tensile strength (σ_T), Young's Modulus (E_T), and the elongation at break (ε_{Max}) of the composite at different fibers content ranging from 10 to 30 wt % are listed in Table VI.

The evolution of the Young's modulus (tensile modulus) depicted in Figure 4 showed almost a linear trend with the fiber loading up to 30 wt % (22 vol %) filler content which is in agreement with the general rule of mixtures.[28] Such a linear trend is indicative of thorough fibers dispersion within the matrix and good fibers–matrix adhesion.

TABLE VI
Tensile Mechanical Properties of the Pristine PS Matrix and of the Biocomposite at Different Fibers Content

Composition	n	MWU (wt %)	$D \times 10^{-10}$ (m^2/s)
ST$_{58}$GLY$_{19}$W$_{23}$	0.57	7.5	3.74
ST$_{58}$GLY$_{19}$W$_{15}$PHB$_8$	0.64	6.1	3.06
ST$_{58}$GLY$_{19}$W$_{15}$PHB$_8$ + 10 wt % fibers	0.61	5.7	4.82
ST$_{58}$GLY$_{19}$W$_{15}$PHB$_8$ + 20 wt % fibers	0.60	4.8	4.85
ST$_{58}$GLY$_{19}$W$_{15}$PHB$_8$ + 30 wt % fibers	0.60	4.1	4.76

When we analyzed the reinforcing effect of the jute fibers, one can note that the Young's modulus (E_T) of the composite (after 41 days aging at 23 °C and 50% humidity) with 10, 20 and 30 wt % fibers content reached a value about 5, 6 and 9 times, respectively, that of the unfilled matrix. An enhancement in the

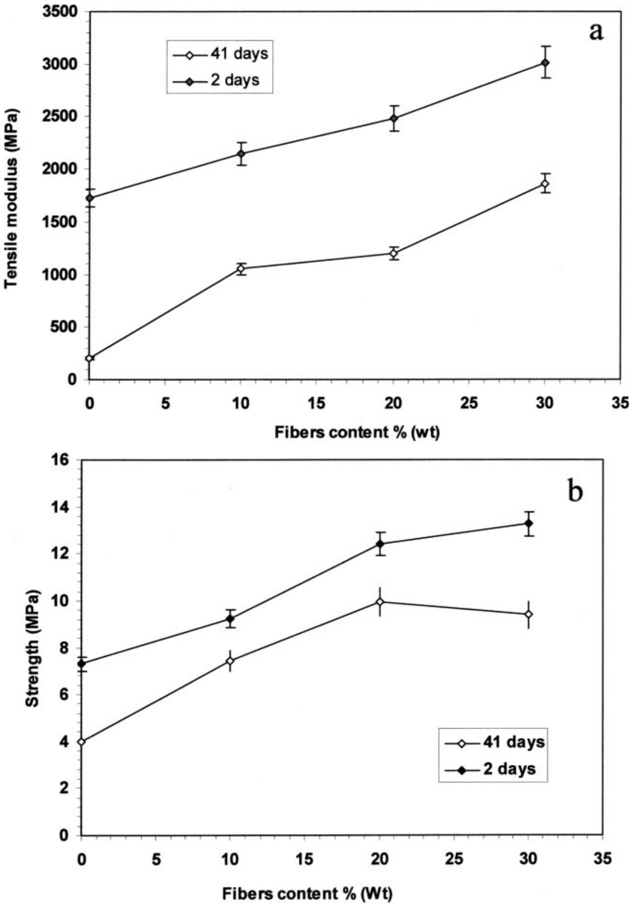

Figure 4 Evolution of (a) the tensile modulus and (b) the tensile strength versus fibers loading for the composite based on ST$_{58}$GLY$_{19}$W$_{15}$PHB$_8$ matrix and jute fibers measured after 2 and 41 days aging at 23 °C and 50% humidity.

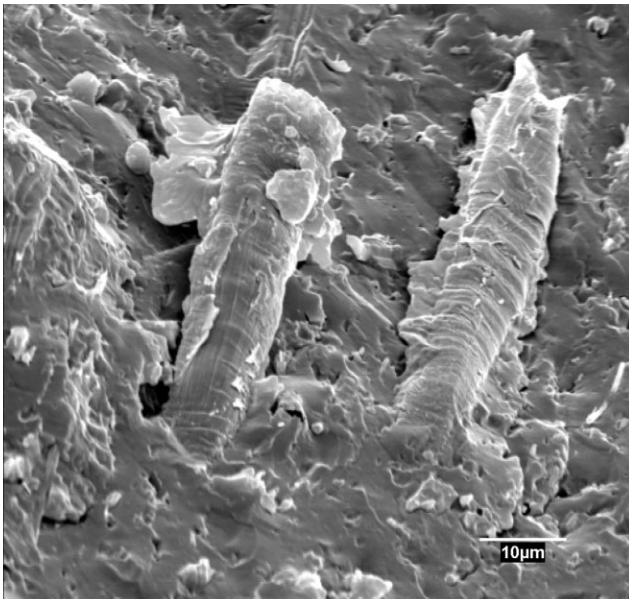

Figure 5 SEM micrographs of the breaking area of tensile specimens of $ST_{58}GLY_{19}W_{15}PHB_8$ with 10 wt % fibers.

mechanical strength is also noted with an increment in the tensile strength being 1.8, 2.5, and 2.3 times that of the nonreinforced matrix at the same fibers content, respectively. This result is in agreement with other reported studies which pointed out a similar trend regarding the enhancement effect brought by fiber addition to biopolymer based on starch.[17,29] However, contrary to the modulus, the strength attained the highest value at 20 wt% fibers content, above which it started to decrease.

The addition of fibers to starch matrix brings about a significant drop in the elongation at break, which evolved from 17% for native matrix to about 1, 0.75, and 0.4% after incorporation of 10, 20, and 30 wt % of jute fibers. This effect is expected if we consider that the fibers incorporation impart rigidity and restrain the deformation on the matrix leading inevitably to a drop in the ductility degree of the material.

In the same way as the pure matrix, the mechanical properties of the composite undergo significant evolution after being conditioned for a long period enough to attain the water adsorption equilibrium. This effect is likely related to the plasticizing action of water.

The enhancement in mechanical strength is indicative of a good degree of adhesion between the fibers and the matrix but also to a relatively high aspect ratio exceeding the critical level. The good fiber–matrix adhesion is quite expected in composites based on starch matrix and cellulose fibers, thanks to the chemical similarity between the two phases. This property ensures an efficient wetting of the fibers by the matrix under melt state favorable to the establishment of a good interfacial adhesion through hydrogen bonding between the two phases. Evidence to this property is corroborated by SEM observation (Fig. 5) of fractured surface, which clearly shows thorough adhesion and wetting of cellulose fibers by the matrix face.

Differential scanning calorimetry

The DSC and DMTA curves of different samples are presented in Figure 6 (DSC) and 8 (DMTA). The temperatures associated with the different thermal transition are reported in Table VII. The DSC thermograms in the temperatures range from −80 to 200°C for the different samples displayed two glass transition characterized by change in the heat capacity, one at low temperature around −60°C and the second at higher temperature close to 48°C. These two transition well reported for starch plasticized with glycerol are associated with glycerol-rich phase and starch-rich phase, respectively.[30] It is worth noting that the detection of these two transitions was not evident for all the sample, even after a second scan, which is likely due to the moderate change in the heat capacity accompanying the relaxation. A weak endothermic peak at 165°C with a low-melting enthalpy (not exceeding 1 J g^{-1}) was noted for $ST_{58}GLY_{21}W_{19}$ probably linked with the crystalline phase melting of the PST.

For both $ST_{58}GLY_{19}W_{15}PHB_8$ matrix and the composite, the DSC thermogram showed in addition to the above cited glass transition an endothermic peak around 175°C associated with the melting of PHB crystalline phase. This hypothesis is supported by the close position of the endothermic peak with the one arising for pure PHB (Fig. 6). The presence of such a peak suggests that phase separation occurred between the PST and PHB in a similar way as for PCL starch blend.[13]

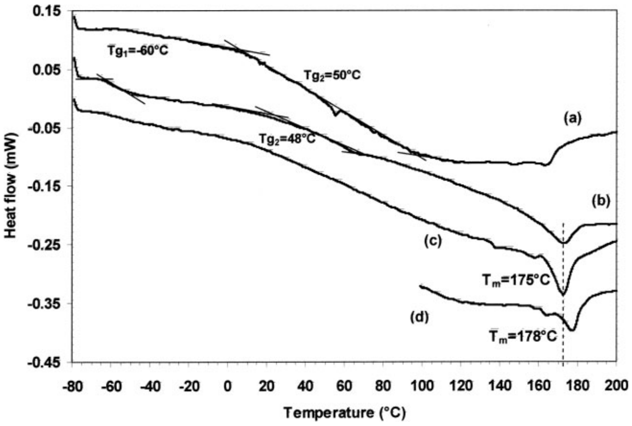

Figure 6 DSC thermogram of (a) $ST_{58}GLY_{21}W_{21}$, (b) $ST_{58}GLY_{19}W_{15}PHB_8$ +10% fibers, (c) $ST_{58}GLY_{19}W_{15}PHB_8$, and (d) pure PHB.

TABLE VII
Thermal Transition Determined by DSC and DMTA and the Crystallinity Degree of PHB Phase in the Different Composition

	First transition		Second transition		Melting		
Composition	T_β[a](DMTA)	T[b](DSC)	T_α[a](DMTA)	T_g[b](DSC)	T_m[c](DSC)	ΔH_{melt} (J/g)	X_c[d](%)
Pure PHB	–	–			178	61.8	42.4
$ST_{58}GLY_{21}W_{21}$	−57	–	52	50	–	–	–
$ST_{58}GLY_{19}W_{15}PHB_8$	−57	−60		48	175	5.53	42
$ST_{58}GLY_{19}W_{15}PHB_8$/10 wt % fibers	−57	−60	55	48	175	6.5	56
$ST_{58}GLY_{19}W_{15}PHB_8$/20 wt % fibers	−57	–	62		175	5.7	51
$ST_{58}GLY_{19}W_{15}PHB_8$/30 wt % fibers	−57				175	5.1	52

[a] Determined at the maximum of the tan δ.
[b] Determined at the midpoint of heat capacity change.
[c] Determined as the maximum of the melting point.
[d] Crystallinity degree of the PHB phase.

The crystallinity degree of the PHB phase can be determined from the ratio of the melting enthalpy ΔH_0 for 100% crystalline PHBV, estimated at 146 $\mathrm{J \cdot g^{-1}}$ according to Barham and Keller,[31] to the melting enthalpy ΔH_s of the sample. The absolute crystallinity can be calculated from these values and weight fraction w of PHB in the blend by using the following equation:

$$Xc = \frac{\Delta H_s}{w.\Delta H_0}\ 0.100 \qquad (4)$$

It can be noted that the melting temperature decreased to a small extent with the addition of PST, from 178°C for pure PHB to 175°C for the blend containing 10 wt % PHB. The small shift of the melting temperature could indicate that some interactions between the two components of the blend exist. Further, one can note an increase in the crystalline degree in the composite, likely to be associated with the nucleating effect of the fibers.

The phase separation between PHB and PST matrix can be confirmed by high magnification SEM observation performed on a fractured surface under cryogenic condition to avoid plastic matrix deformation. As shown in Figure 7, it can be observed that fine spherical particles with average diameters being

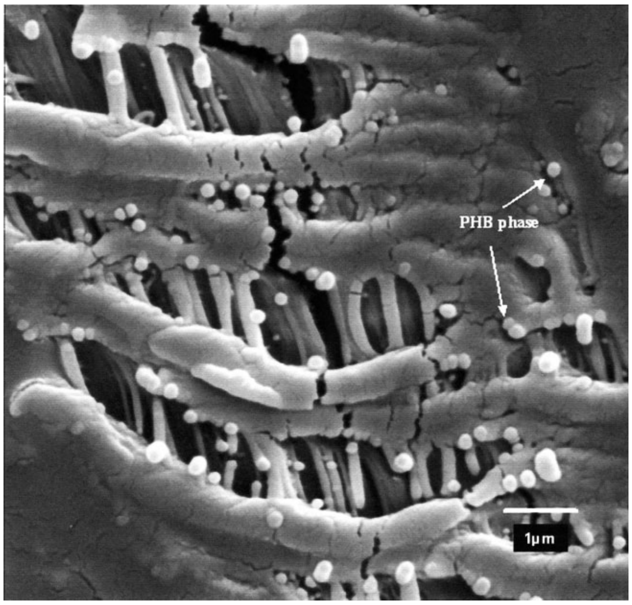

Figure 7 SEM micrographs of the breaking area of tensile specimens of $ST_{58}GLY_{19}W_{15}PHB_8$- 10 wt % of jute fibers cryogenically fractured.

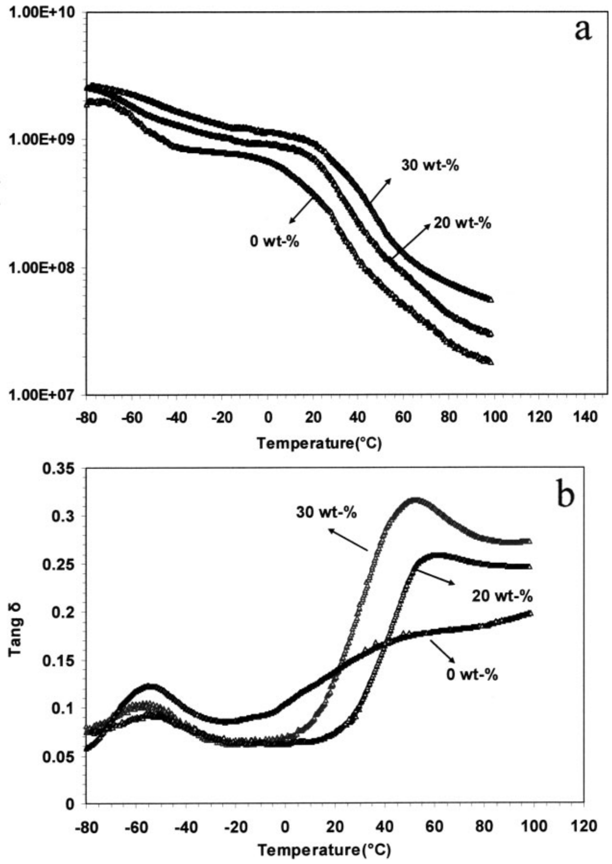

Figure 8 Evolution of the (a) the storage tensile modulus E′, and (b) loss angle tan δ vs. temperature at 1 Hz for $ST_{58}GLY_{19}W_{15}PHB_8$ matrix and composite $ST_{58}GLY_{19}W_{15}PHB_8$- of jute fibers at different loading.

in the range 150 to 250 nm are dispersed throughout the polymeric matrix. The low average particle size of the PHB phase, its high crystalline level, and the good interfacial bonding through hydrogen bonding between the hydroxyls of starch and carbonyl of PHB may account for the enhancement in the strength and modulus of $ST_{58}GLY_{19}W_{15}PHB_8$ compared with $ST_{58}GLY_{21}W_{21}$.

DMTA results are presented in Figure 8(a,b), where the storage modulus (E′) and loss factor (tan δ) of the $ST_{58}GLY_{19}W_{15}PHB_8$ matrix and composites with different filler content were plotted versus temperature. For the unfilled matrix tan δ exhibits two relaxations located around -60°C (labeled β) and around 50°C (labeled α) which are accompanied by a significant drop in E′. The position of these two transitions is in agreement with the DSC results. The difference between the temperature corresponding to the transitions observed by DMTA and DSC is attributed to the frequency of the analysis method.

The addition of fibers brings about an enhancement in the storage modulus E′ before and after T_α, which is consistent with the reinforcing effect of fibers. At 25 °C, the increase in the storage modulus is about 1.9 and 2.6 times with respect to the unfilled matrix at a fiber loadings of 20 and 30 wt %, respectively. Further, it can be seen from tan δ [Fig. 8(B)] plot a shift to higher temperature in the α relaxation from 50 °C for the pristine matrix to about 55 and 62 °C for the biocomposite containing 20 and 30 wt % fibers content. This result is in agreement with those reported by Dufresne et al.[32] and Averous et al.[17] It ascribed to the segmental mobility restriction of polymer molecules in the vicinity of the fiber as a consequence of various molecular interactions, which increased the T_g of the immobilised polymer molecules. Moreover, the fact that only the α relaxation undergoes a shift while the β one maintained its position could be indicative of the preferable contact of the fibers with the starch-rich phase.

CONCLUSIONS

The presence of glycerol in the fabrication of starch-based polymer matrices is indispensable for obtaining a material ready to be processed. But the content of this plastisizer involves a control of important parameters of the material such as water-uptake sensibility and mechanical properties. Higher amounts of glycerol yield better processability by using lower amounts of energy for mixing although the hydrophilicity of the final system is increased and the mechanical resistance is reduced. The addition of aliphatic polyesters PHB controls such water sensibility as well as improves the strength of the material, maintained during a long time under humid conditions. The addition of jute strands to the starch-based polymer matrix leaded to a material with higher capacities to support stresses keeping them even after 1.000 h of exposition under humid environment. The addition of the fibers up to 30 wt % content brings about an enhancement in the strength and modulus of the material as much higher as the fibers loading is important. This decrease in water sensibility and improvement in mechanical resistance leads to a useful material in the field of packaging with the capacity of biodegradation after working life.

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