

Thermoplastic Starch-based Composites Reinforced with Rape Fibers: Water Uptake and Thermomechanical Properties

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Fully biodegradable composite materials were obtained through reinforcement of a commercially available thermoplastic starch (TPS) matrix with rapeseed fibers (RSF). The influence of reinforcement content on the water sorption capacity, as well as thermal and thermomechanical properties of composites were evaluated. Even though the hydrophilic character of natural fibers tends to favor the absorption of water, results demonstrated that the incorporation of RSF did not have a significant effect on the water uptake of the composites. DSC experiments showed that fibers restricted the mobility of the starch macromolecules from the TPS matrix, hence reducing their capacity to crystallize. The viscoelastic behaviour of TPS was also affected, and reinforced materials presented lower viscous deformation and recovery capacity. In addition, the elasticity of materials was considerably diminished when increasing fiber content, as evidenced in the TMA and DMTA measurements.

Keywords: Rape fibers; Thermoplastic starch; Biocomposites; Thermo-mechanical properties

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INTRODUCTION

The design of environmental-friendly polymers has drawn increasing attention due to problems resulting from the current disposal of large volumes of plastics. There are many biodegradable polymers on the market; however, the relatively high cost of most of them has limited their extensive use as substitutes for traditional polymers (Fowler *et al.* 2006; Gandini 2008). By contrast, when converted into a thermoplastic material, starch-based biopolymers are one of the least expensive biodegradable materials that are available in large supply (Averous and Halley 2009; Coombs and Hall 1998). Thermoplastic starches (TPS) are becoming a notable alternative to synthetic polymers, particularly when long-term durability is not needed. In fact, TPS generally present very poor mechanical properties and fast degradation kinetics (Shin *et al.* 2004). As a result, in addition to decreasing their water uptake and degradation kinetics, increases in strength and stiffness are needed in order to enable industrial applications (Gaspar *et al.* 2005). To achieve this goal, one of the most common strategies involves the reinforcement of matrix materials with other polymers and/or fibers (Kaseem *et al.* 2012; Yu *et al.* 2006). In fact, the preparation of fiber-reinforced composite materials is a field under constant development (Faruk *et al.* 2012; Satyanarayana *et al.* 2009). However, the use of non-

biodegradable reinforcing fibers may interfere with the decomposition of the residues at the end of the composites' lifetime. As a consequence, the utilization of biodegradable fibers from renewable sources, and particularly from agricultural residues, as reinforcement is attracting particular attention (Dogossy and Czigany 2011; Ma *et al.* 2005; Teixeira *et al.* 2009).

On the other hand, the increasing usage and depletion of the global supply of fossil fuels is prompting the development of bio-combustibles. In fact, the European Union has approved several directives in an attempt to promote the development and use of fuels derived from biomass conversion (biofuels). In order to meet the target for biofuels set by the EU (10% in 2020), it is assumed that the biodiesel industry would need about 30 million tons of oilseeds, mostly rapeseed, soybean, and sunflower. However, such production of oilseeds will deliver a huge amount of agricultural residues.

In recent years, our research group has focused its investigations on the viability of using these agricultural residues as an abundant, cheap, and renewable source of lignocellulosic fibers. (Peña *et al.* 2012; Vallejos *et al.* 2012) In fact, we have developed thermo-mechanical processes making it possible to obtain cellulosic fibers from rape stalks with over 85% yield. In addition, we have demonstrated that the physical properties of such fibers can be higher than those of thermo-mechanical pulp obtained from wood. As a result, thanks to their high mechanical properties, low density, and eco-friendly character, rape stalk fibers (RSF) can be effectively used as filler/reinforcement for injection-moldable polymers. (Espigule *et al.* 2013a; Espigule *et al.* 2013b)

In this work, a commercially available thermoplastic starch was reinforced with up to 40% wt. rape stalk fibers. The water uptake, thermal, and mechanical properties of the resulting composites materials were evaluated.

MATERIALS AND METHODS

Materials

Rape biomass (*Brassica napus*; whole stalks, leaves and husks) were supplied by Fundació Mas Badia (La Tallada d'Empordà, Spain). Composed of 74% rape stalks and 26% leaves, prior to use, rape biomass was submitted to a steam-water treatment. The water to fiber ratio was kept at 6:1, and the temperature was kept at 180 °C during 15 min. The pulp obtained was rinsed with water and passed through a Sprout-Waldron refiner in order to increase fiber individualization. Finally, the pulp was centrifuged and dried. The main characteristics of the rape seed fibers obtained have been presented elsewhere. (Espigule *et al.* 2013a)

Supplied by Avebe (Holland), the starch-based Biopar® polymer was used as the matrix. Based on potato starch and other biodegradable polymers, Biopar® is a completely biodegradable thermoplastic material used in the preparation of thin water resistant films. This biopolymer has a specific gravity of 1.25 g/cm³ and a melt flow index of 4 to 5 g/10 min (measured at 130 °C and 10 kg load).

Composite Preparation

Composites were prepared with up to 40% wt/wt rapeseed stalk fibers. Dry individualized fibers and the polymer matrix were mixed by means of a Brabender® Plasti-corder PL2x00/Plastograph (Duisburg, Germany) operating at 150±3 °C for 10 min. The composite materials obtained were granulated in a blade mill (Agrimsa, St.

Adrià del Besós, Spain) provided with a 10 mm mesh. In order to prevent/eliminate moisture absorption, composites were kept in an oven at 80 °C until required (at least 24 h). Test specimens were moulded in a Meteor-40 injection-molding machine (Mateu & Soler, Barcelona, Spain) using a steel mould complying with the ASTM D3641 specifications. Prior to testing, processed materials were conditioned in accordance with ASTM D618. The tensile, flexural, and impact characterization of the composites prepared has been reported elsewhere. (Espigule *et al.* 2013b)

Water Absorption

Samples with 2 mm thickness were dried in an air-circulating oven at 105 °C for 24 h. Water uptake was determined gravimetrically as the weight increase of samples immersed in distilled water at different periods of time. Following the Fick theory, the water absorption kinetics was evaluated by adjusting experimental data to the equation,

$$\log \frac{M_t}{M_\infty} = \log(k) + n \cdot \log(t) \quad (1)$$

where M_t is the water uptake at time t , M_∞ is the water uptake at equilibrium, whilst k and n are Fickian constants. Note that for materials showing a Fickian behavior, the value of n should be close to 0.5.

On the other hand, the water diffusion coefficient (D), representing the ability of solvent molecules to penetrate inside the structure of the tested composite material, was determined from the lineal section of the graphical representation of,

$$\left(\frac{M_t}{M_o} \right) = \frac{4}{L} \left(\frac{D}{\pi} \right)^{0.5} \cdot t^{0.5} \quad (2)$$

where L represents the thickness of the sample assayed and t the exposition time.

Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry measurements were conducted in a Mettler - Toledo DSC822 (Greifensee, Switzerland). Placed in unsealed aluminum pans, 10 to 20 mg test samples were heated to 210 °C and kept at this temperature for 5 min in order to eliminate their water content and erase their thermal history. After cooling down to room temperature, DSC measurements were carried out under nitrogen atmosphere from room temperature to 210 °C at a heating rate of 10 °C/min.

Thermomechanical Analysis (TMA)

Compression creep recovery tests were conducted by means of a high-performance modular ThermoMechanical Analyzer SETSYS Evolution (SETARAM Instruments, Caluire, France). Experiments were conducted at 25 °C in samples obtained from injection-molded impact test specimens (approximate sample size: 6 x 6 x 3.2 mm).

Dynamic Mechanical Thermal Analysis (DMTA)

DMTA measurements were performed in a Mettler-Toledo DMA/SDTA 861e operating in dual cantilever mode at 1 Hz with a pre-load of 0.01 N. The temperature was raised from -80 °C to 140 °C at a 3 °C/min heating rate.

RESULTS AND DISCUSSION

The characterization of the rapeseed fibers used as reinforcement, including the determination of their intrinsic mechanical properties has been reported elsewhere. In previous studies, the tensile, flexural, and impact properties of composites based on the commercially available thermoplastic starch Biopar® reinforced with up to 40% weight of rapeseed fibers were discussed (Espigule *et al.* in press). In the present work, the water uptake, and thermal and dynamic-thermomechanical properties of these materials are analyzed.

Water Uptake

For many applications, biodegradation kinetics and dimensional changes caused by water uptake are major concerns when working with thermoplastic starches. Water uptake can be defined as the weight increase of samples after immersion in distilled water. The profiles of water uptake vs. immersion time for the tested materials are shown in Fig. 1.

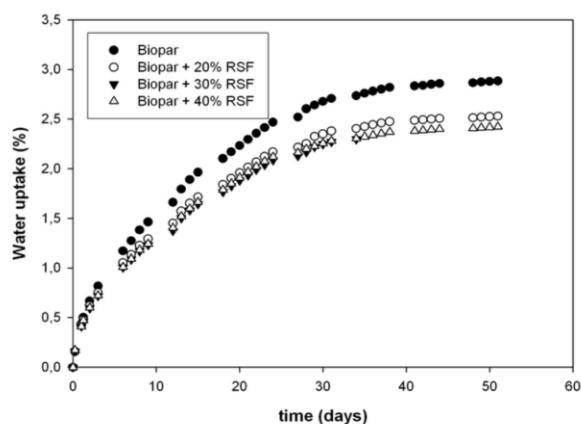


Fig. 1. Effect of fiber content on water uptake of Biopar-based composites

As can be observed, the incorporation of the reinforcing fibers had little effect on the water absorption capacity of the composites. Nevertheless, the general trend suggests that fibers diminish both the kinetics and equilibrium water content of composites.

As can be observed from the experimental values listed in Table 1, all the materials tested showed values of n close to 0.5 (see Eqs. 1 and 2). This result suggests a Fickian behavior in which the diffusion of water is controlled by the concentration gradient between the centre and the outside of the polymer matrix. Whilst non-Fickian processes related to polymer relaxation are common in glassy materials (Davis *et al.* 2011), this is an expected behavior for water sorption in rubbery polymers. With experimental temperature above the glass transition temperature, polymers are able to respond almost instantaneously to the stress caused by water ingress, preventing the

observation of polymer relaxation phenomena within the experimental time scale (Davis *et al.* 2012; Russo *et al.* 2007). No statistically significant differences could be detected between the three composites studied. However, neat Biopar presented a slightly higher n coefficient, which might suggest the presence of some crystalline domains in the polymer matrix.

Table 1. Fick's Law Parameters Representing the Water Uptake Kinetics and the Diffusion Coefficient of Water in Rapeseed Stalk Fiber-reinforced Biopar

Sample	n	K	$M_{\infty(50days)}$	D (m ² /s)
Biopar	0.539	$3.39 \cdot 10^{-4}$	2.8828	$4.7 \cdot 10^{-13}$
Biopar + 20% RSF	0.510	$5.13 \cdot 10^{-4}$	2.5291	$4.7 \cdot 10^{-13}$
Biopar + 30% RSF	0.507	$5.27 \cdot 10^{-4}$	2.5189	$4.7 \cdot 10^{-13}$
Biopar + 40% RSF	0.509	$5.23 \cdot 10^{-4}$	2.4215	$4.7 \cdot 10^{-13}$

In general, the hydrophilic character of natural fibers tends to favor the inclusion of water molecules inside the composite material. By contrast, in the case analyzed here, although minimal, the presence of the rapeseed fibers caused a reduction in the water uptake of composites at equilibrium. This behavior can be explained by the utilization of fibers with high lignin content.

On the other hand, the incorporation of rapeseed fibers had a negligible effect on diffusion coefficient (D) of water in the composite. In fact, there was no statistical difference in the D value for the four materials tested.

Differential Scanning Calorimetry

The DSC thermograms of neat Biopar and Biopar-composites reinforced with 20, 30, and 40% (w/w) of RSF are presented in Figure 2. Due to the hygroscopic character of TPS, data shown correspond to the second scan DSC. By performing this test under these conditions, the true nature of the TPS is changed, since water and other volatile components of the matrix will be lost. However, we judged that this was the best option to analyze and compare the crystalline properties of the composites under the same conditions. The melting temperature, melting enthalpy, and normalized enthalpy of materials tested are also summarized in Table 2.

Table 2. Melting Temperature, Melting Enthalpy, and Weight Fraction (Φ) Normalized Melting Enthalpy of Rapeseed Fiber-reinforced Biopar

Sample	$T_{m \max}$ °C	ΔH_m (j/g)	ϕ	Normalized ΔH_m (j/g)
Biopar	118.78	8.12	1.0	8.12
Biopar + 20% RSF	127.91	4.03	0.8	5.04
Biopar + 30% RSF	127.69	3.61	0.7	5.15
Biopar + 40% RSF	127.51	3.41	0.6	5.68

The degree of crystallinity (X_c) of a semicrystalline polymer can be determined considering the normalized melting enthalpy ΔH_m of the polymer (calculated from the integral of the endothermal peak in the DSC curve) and the heat of fusion of 100% crystalline polymer ($\Delta H_m^{100\%}$). However, Biopar, as any thermoplastic starch, is not a crystalline polymer, and as such, a value for a 100% crystalline polymer does not exist.

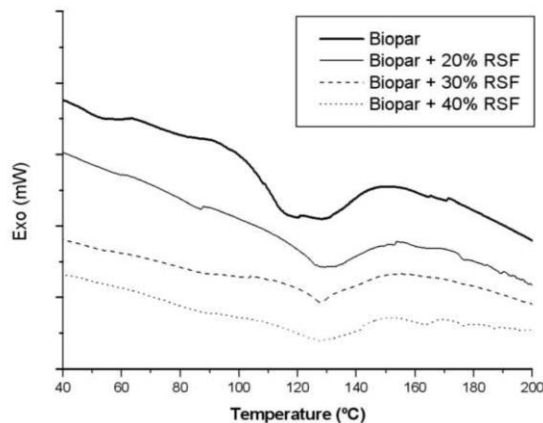


Fig. 2. DSC thermograms of Biopar and rapeseed fiber-reinforced Biopar at different weight percentages

As a consequence, the effect of fiber addition onto the degree of crystallinity cannot be achieved. Nevertheless, since $\Delta H_m^{100\%}$ is a constant, the comparison of the melting enthalpy of composites after correcting the polymer fraction (φ) in the material offers a direct qualitative insight onto the changes in polymer crystallinity.

$$X_c = \frac{\Delta H_m}{\Delta H_m^{100\%}} \cdot \varphi \quad (3)$$

Results of DSC experiments shown in Table 2 provide evidence that the incorporation of RSF caused a slight increase in the melting temperature of the composites. Studies have demonstrated that the influence of the reinforcing fibers on crystallization is not only fiber-specific but also strongly dependent upon surface conditions (Ning *et al.* 2012). Nevertheless, it has been generally accepted that in reinforced thermoplastics, natural fibers can act as heterogenous nucleating agents (Arbelaiz *et al.* 2006; Pengfei *et al.* 2011). The capacity of natural fibers to act as nucleating agents might explain the slight increase in crystallinity detected when comparing composites with increasing fiber content. However, this explanation seems to be in clear disagreement with results obtained for the crystallinity of composites when compared with neat TPS. The collected data suggest that the crystalline degree of the composites was distinctly lower than that of pure TPS (Table 2).

Nevertheless, it must be taken into consideration that the DSC data reported in Table 2 corresponds to second scan experiments. The reason for such experimental conditions was the elimination of the signal caused by the presence of absorbed water from the measurement of TPS melting enthalpy. However, this methodology may result in the loss of some plasticizing agents (water itself being a plasticizer). In turn, by losing these compounds, the properties of the TPS matrix (particularly its elasticity and plasticity) could be severely affected. Thus, under these circumstances, the high fiber content can cause restrictions to the mobility of the polymer matrix, hence reducing its capacity to crystallize, as observed in Table 2 (Li *et al.* 2006).

In order to verify this hypothesis, TGA experiments were conducted on Biopar samples. Figure 3 shows that the degradation of the thermoplastic matrix remained fairly

low at temperatures below 250 °C. Nevertheless, at 210 °C (the temperature used to erase the thermal history of samples in the DSC experiments) the matrix lost about 5% of its original weight, suggesting the loss of plasticizing agents during this preconditioning step.

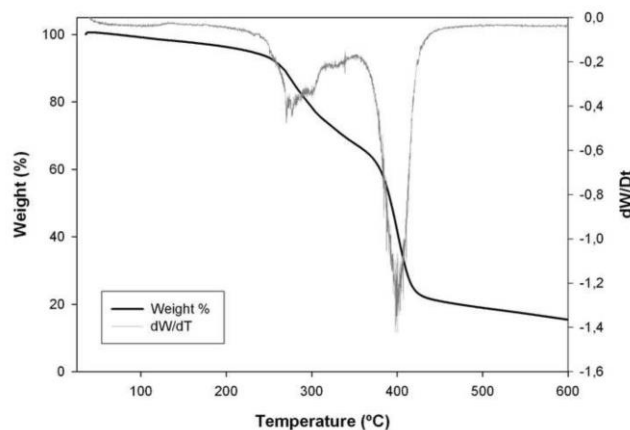


Fig. 3. TGA thermogram of Biopar

Creep Recovery Tests (thermo-mechanical analysis)

Creep recovery testing is one of the most direct methods for evaluating the elasticity of materials. In a compression creep recovery test, a constant weight is applied to the sample and the resultant deformation is measured as a function of time. At a certain time, the weight is removed and the sample is allowed to recover. The recovered deformation is a direct measure of the materials' elasticity. Results of creep recovery tests of the TPS matrix Biopar with and without reinforcing fibers are represented in Fig. 4 and summarized in Table 3.

Table 3. Summary Data of Time-Dependent Compressive Creep-Recovery Curves for Biopar-based Composites Reinforced with Rapeseed Fibers

Sample	Elastic deformation (%)	Viscous deformation (%)	Elastic recovery (%)	Viscous recovery (%)	Permanent set (%)
-	0.73	0.69	0.57	0.54	0.31
20% RSF	0.73	0.60	0.34	0.35	0.63
40% RSF	0.76	0.36	0.22	0.14	0.77

At the start of the creep recovery test, immediately after applying weight onto the sample, the material suffered an elastic deformation that was mostly independent of reinforcement content and accounted for 23 to 24 μm . Considering that samples had a thickness of 3.2 mm, this represents a deformation of about 0.75%. In contrast, the time-dependent viscous deformation that followed was clearly dependent on reinforcement, with the capacity of materials to deform diminishing with increasing fiber content. This behavior can be explained by the higher rigidity introduced by the reinforcing fibers and the limitation caused to the reorientation of the macromolecules comprising the TPS matrix.

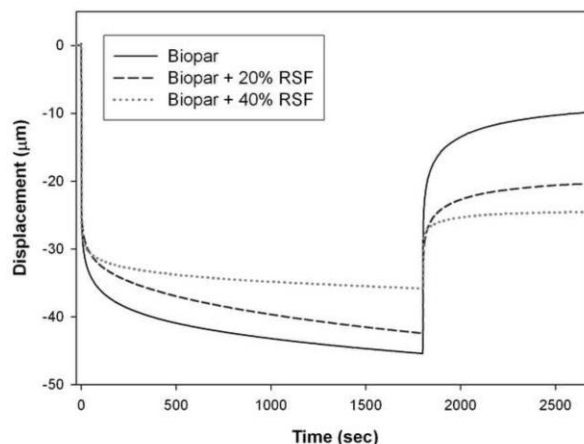


Fig. 4. Compressive creep - recovery curves for Biopar - based composites reinforced with rapeseed fibers

After relieving the weight applied (15 min), the recovery phase of the test started. Creep recovery curves suggest that the duration of the test was large enough to cause an irreversible disentanglement of the macromolecules. As a result, the viscoelastic recovery of test samples was affected and both the immediate (elastic) and the delayed (viscoelastic) recoveries presented values below their respective deformation counterparts. In addition, recovery clearly decreased with increasing RSF content.

The evaluation of the irreversible deformation (permanent set) is evidencing that, even at moderate fiber content (20%), the incorporation of the reinforcing fibers significantly reduced the elasticity of the materials.

Dynamic Mechanical Thermal Analysis (DMTA)

Similar to most thermoplastic starches, Biopar showed a biphasic behavior, presenting two different transitions in the $\tan \delta$ curves (Fig. 5a). The first transition, from minus 20 to minus 30 °C, corresponds to a plasticizer-rich phase. This relaxation peak appears slightly more intense in composite blends presenting high fiber content. Such a shift can be assigned to restrictions to the cooperative motion of the segmental chains of TPS matrix in the vicinity of the reinforcement. The second transition observed in $\tan \delta$ curves, occurring at 30/50 °C, is commonly assigned to the glass transition of TPS (Averous and Boquillon 2004; Averous and Halley 2009). In contrast to previous results for other fiber-reinforced TPS matrices, a shift towards higher temperatures could not be observed in the $\tan \delta$ curves of composites with high fiber content (Girones *et al.* 2012). Nevertheless, the decrease observed in the relative intensity of the $\tan \delta$ signal with increasing fiber content, suggest that the presence of the reinforcing fibers leads to stiffer systems.

This result is corroborated by the storage modulus curves of RSF-reinforced Biopar (Fig. 5b). Curves followed the typical pattern of semi-crystalline polymers, and displayed a plateau below the glass transition temperature. The stiffening effect of the reinforcing fibers is evidenced in the E' modulus curves, where an increase in E' proportional to the amount of fibers added to the TPS matrix can be observed throughout the range of temperatures analyzed. These results are in agreement with the tensile tests

data, (Espigule *et al.* 2013a) when increases in tensile strength of up to 95% were observed after the addition of RSF to the polymeric matrix.

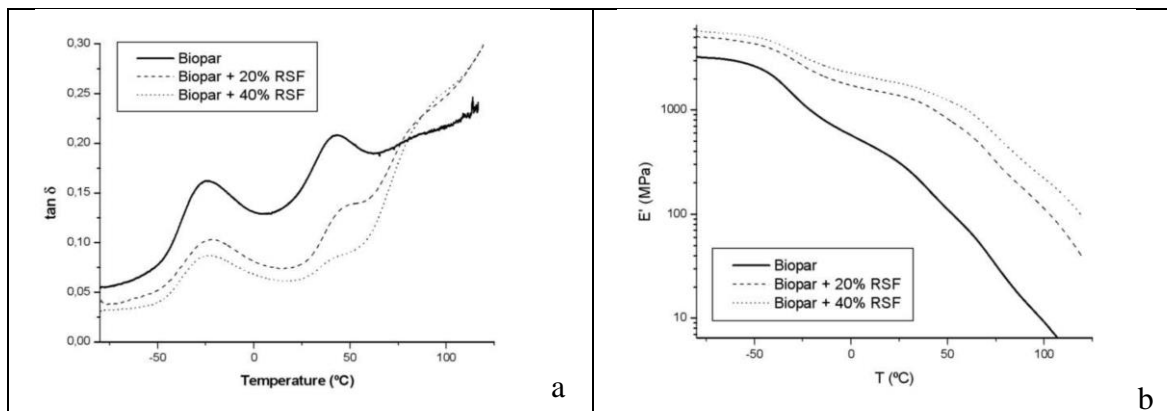


Fig. 5. Effect of rapeseed fibers on the $\tan \delta$ (a) and the storage modulus (b) of Biopar -based composites

CONCLUSIONS

Composite materials were obtained through reinforcement of a commercially available thermoplastic starch (TPS) matrix with rapeseed fibers. The water sorption, and mechanical and thermal properties of the resulting composites were analyzed and evaluated. Even though the hydrophilic character of natural fibers tends to favor the inclusion of water molecules inside the composite material, the results obtained demonstrate that the incorporation of RSF to formulations did not significantly affect the water uptake of composites.

The capacity of the TPS matrix to crystallize was reduced when high reinforcement content was used. This behavior was related to the restrictions on mobility of starch macromolecules caused by the reinforcement. In addition, the viscoelastic behaviour of TPS was also affected by fiber content. Thus, reinforced materials presented lower viscous deformation and recovery capacity than the matrix. The elasticity of materials was also considerably diminished when the amount of reinforcing fibers was increased from 20 to 40%. The higher stiffness of materials was further evidenced in the DMTA measurements, with storage modulus increasing with fiber content, although no significant effects were detected on the damping coefficient ($\tan \delta$).

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