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Flexural properties of fully biodegradable alpha-grass fibers reinforced starch-based thermoplastics

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ABSTRACT

This work has the aim of study the flexural properties of alpha-grass reinforced starch-based composites. The composite materials contain alpha-fibers in the range from 5 to 35 wt%. The reinforcing fibers were submitted to an alkali treatment to create a good interphase between the fibers and the matrix. It was observed that a mild 2.5 h cooking process was enough to create a good interphase, while longer periods rendered lesser improvements. The surface charges of the fibers and the matrix were determined by polyelectrolyte titration, and it was found that after the alkaline treatment both were similar. The composite materials were injection molded and tested under flexural conditions. All the flexural properties of the studies composites increased linearly with the reinforcement contents. The micromechanics of the flexural modulus and strength were studied and compared with that of tensile modulus and strength. It was established that the efficiency factors for the tensile and flexural properties were statistically similar. Three different methods were used to compute the intrinsic flexural strength from the available data. Finally the Weibull theory was used to study the best prediction of the standard deviation of the intrinsic flexural modulus.

1. Introduction

In the last two decades there has been a growing interest for the ecofriendly composites, based on natural fiber reinforcements (flax, hemp…) [1–3]. The first steps towards eco-efficiency focused on replacing conventional fibers, like glass fiber (GF), by natural fibers, while maintaining the polyolefin matrix. In that sense polypropylene (PP), high density polyethylene (HDPE) and polyvinylchloride (PVC) have been one of the most used matrices. The high mechanical properties showed by these materials allowed its consideration as an alternative to GF reinforced composites for semi structural engineering applications [4–6]. The main advantages of the natural fibers in front of glass fiber are; its lower density that allows high specific mechanical properties, its comparatively low price and high availability, and its lower equipment abrasion during preparation and manufacturing. On the other hand, from the mechanical properties point of view, their main disadvantage comes from its highly hydrophilic character, in front of the hydrophobicity of the polyolefin matrices, leading to feeble fiber matrix interphases. That aspect has been widely researched, and as a result, a number of fiber treatments have been proposed to obtain better interphases, being the addition of maleated coupling agents one of the most effectively used [7]. As a result, that kind of composite materials are currently used for technical applications, as in the automotive, product design and building [6,8,9].

However, polyolefin matrices do not degrade under normal biodegradation processes, and therefore, at the end of use, the materials have to be incinerated, recycled or dumped [10]. In that sense, the use of thermoplastic biopolymers as matrices for natural fiber reinforced composites seems to be the next logical step. That kind of composite materials retain the advantages of natural fiber reinforcements while adding the biodegradability of the matrix, obtaining fully biodegradable materials, commonly addressed as “green composites” [11–13]. Moreover, some thermoplastic biopolymers, as the starch-based one's, have a chemical affinity with natural fibers, being not necessary the addition of

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coupling agents, while the chemical treatment of the surfaces of the fibers gains importance [14–16]. The thermoplastic biopolymer used in this work, Mater-bi®, is a commercial, fully biodegradable, starch-based biopolymer, made of thermoplastic starch and cellulose derivative, that shows comparatively high mechanical properties and a good affinity with natural fiber reinforcements [17].

Alpha-grass or esparto-grass (Stipa tenacissima), is a plant that belongs to the Graminae family, native to Spain and North Africa. In these regions, alpha-fibers have been used since ancient times to prepare ropes, basketry, and espadrilles due to their toughness and resistance. Nevertheless, at present, the most common utilization of esparto-grass comes from the production of fibers for high-quality lightweight paper [18,19]. The Alpha fibers have proved to be very efficient reinforcements, showing high tensile strengths and high stiffness as PP or Mater-bi® reinforcement. However, semi-aligned natural fiber reinforced composites show significant mechanical anisotropy, being necessary the research on the flexural properties, to properly characterize such materials [20,21]. There are works that showed lesser values, but mainly due to the lack of coupling agents [22]. Presently, and to the best knowledge of the authors, the intrinsic flexural resistance and modulus of alpha-fibers has not been clearly established. Accordingly, the present work will focus on the flexural properties of 5–35% alpha-fibers reinforced Mater-bi®, using three point flexural tests, and comparing the results with conventional GF reinforced PP composites and recyclable stone groundwood (SGW) reinforced PP composites. A second objective of the present study is the effect of a fibers mild chemical treatment and the treatment time on the flexural properties of the composite. Additionally, the micromechanics of the flexural properties of the composites and the intrinsic flexural properties of the alpha fibers are computed, from the experimental data, using some micromechanical models. The study review some relations between the flexural and the tensile strengths present in the literature to predict the flexural properties from the tensile one's [21,23,24]. Finally, the equivalence between the tensile and flexural efficiency fibers factors, used to correct the contribution of semi aligned fibers in the modified rule of mixtures, both in the case of the modulus and the strength, is investigated.

2. Materials and methods

2.1. Materials

Esparto or alpha-grass (Stipa tenacissima), with initial strand lengths of about 30 cm, was kindly provided by Mas Clarà de Domeny, S.L. (Catalonia, Spain). The starch-based polymer (Mater-bi® YI014U/C, TPS from here-on), with a density of 1.3 g/cm^3, was supplied by Novamont (Novara, Italy), and was used as biodegradable thermoplastic matrix. TPS is biodegradable and compostable for rigid and dimensionally stable injection molded items with a biodegradation time of about four months in composting conditions and 30 days in anaerobic conditions (1 mm in thickness). This material is made of thermoplastic starch and cellulose derivative [17].

For comparison, PP based composites, reinforced with glass fiber (GF) and stone groundwood (SGW), were also prepared. The materials used were as follows: polypropylene (PP) Isplen PP099 K2M (Repsol-YPF, Tarragona, Spain). The principal physical properties of the PP are as follows: density 0.905 g/cm^3, tensile strength 28–30 MPa, elongation at break 9.1%, and tensile modulus 1500–1800 MPa. A modified maleic anhydride-grafted polypropylene (MAPP) coupling agent was used: Epolene® G3015 from Eastman (Netherlands). Stone groundwood (SGW) derived from softwood (*Pinus radiata*) was supplied by Zubialde, S.A. (Aizarnabal, Spain) and used as lignocellulosic reinforcement. E glass fiber (GF) was produced by Vetrotex (Chamberly Cedex, France) and provided by Maben, S.L. (Banyoles, Spain).

Sodium hydroxide (Merck KGaA, Darmstadt, Germany) and anthraquinone (BASF AG, Ludwigshafen, Germany) were used for the treatment ("cooking") of the esparto fibers. Chloroform, acetone, and decalin, supplied by Fisher Scientific, were used to dissolve the TPS matrix.

2.2. Methods

2.2.1. Defibration of alpha-fibers

Alpha-grass was cut in a blade mill and classified with a 5-mm grid. The obtained raw material was homogenous and suitable for chemical treatment. Esparto-grasses were submitted to chemical treatments to remove the extractives and a small portion of lignin. Plants were soaked in a thermostatic bath set at 98 ± 1 °C. Then, 5% (w/w) sodium hydroxide and 0.1% (w/w) anthraquinone (based on dry fiber content) were added to the reactor and the mixture was stirred for 150, 210 and 270 min. The cooking process was carried out with 1:6 hydro-module. Although the elimination of extractives is quickly accomplished, due to the relatively mild reactive conditions applied, the elimination of soluble lignin and hemicellulose is expected to be time-dependent.

Complete individualization was achieved with a "Sprout-Waldron" defibrator. The alpha fibers (AF) were then washed and dried.

2.2.2. Characterization of esparto-grass

The determination of the basic chemical composition of esparto-grass was conducted following TAPPI standard protocols. The amounts of extractives, ash, lignin, hemicellulose, and alpha-cellulose were measured according to TAPPI methods T204, T211, T222, and T203, respectively.

2.2.3. Evaluation of polarity

The surface charge of the fibers was determined by polyelectrolyte titration following the adsorption of a polyelectrolyte, p-DADMAC, onto the surface of the cellulose fibers. Due to its high molecular weight, p-DADMAC does not penetrate into fiber pores and the adsorption can be directly linked to the fiber surface charge. The time of adsorption for this cationic polymer was 30 min, after which the fibers were filtered and it was performed a back titration of the filtrate with potassium polyvinyl sulfate (KPVS) [25–27]. A Mütek PCD-04, Particle Charger Detector, by BTG Instruments (UK), was used to measure the colloidally dissolved substances.

2.2.4. Composite preparation

A 20% (w/w) TPS/AF composite was produced using a Brabender internal mixing machine. The working parameters were 80 rpm and 180 °C during 10 min. To avoid the high attrition phenomena common with Brabender internal mixing machine, composite materials comprising 5–35 wt% TPS/AF, PP/SGW and PP/FG were prepared in a Gelimat intensive kinetic mixer at a temperature of 180 °C for 2 min at 2500 rpm, until a discharge temperature of 175 °C was reached. The MAPP was added to the mixer with the PP pellets in the case of the PP-SGW and PP-FG composites.

Composites were granulated in a blade mill provided with a 10-mm mesh. Then, to prevent moisture absorption, they were kept in an oven at 80 °C until required. Test specimens were injection-molded in a Meteor-40 injection-molding machine (Mateu & Soler, Barcelona, Spain) using a steel mold complying with ASTM D3641 specifications.