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Natural fiber-reinforced thermoplastic starch composites obtained by melt processing

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ABSTRACT

Thermoplastic starch (TPS) from industrial non-modified corn starch was obtained and reinforced with natural strands. The influence of the reinforcement on physical–chemical properties of the composites obtained by melt processing has been analyzed. For this purpose, composites reinforced with different amounts of either sisal or hemp strands have been prepared and evaluated in terms of crystallinity, water sorption, thermal and mechanical properties. The results showed that the incorporation of sisal or hemp strands caused an increase in the glass transition temperature (T_g) of the TPS as determined by DMTA. The reinforcement also increased the stiffness of the material, as reflected in both the storage modulus and the Young's modulus. Intrinsic mechanical properties of the reinforcing fibers showed a lower effect on the final mechanical properties of the materials than their homogeneity and distribution within the matrix. Additionally, the addition of a natural latex plasticizer to the composite decreased the water absorption kinetics without affecting significantly the thermal and mechanical properties of the material.

1. Introduction

The environmental problems originated by the disposal of large volume of plastics, together with the depletion of petroleum stocks, have prompted to an increasing interest on the design of new environmental-friendly polymers [1,2]. In the market many biodegradable polymers, like polycaprolactone (PCL) and polylactic acid (PLA), are already available. However, their massive use as substitutes of traditional polymers like polypropylene (PP) is restricted by their comparatively high cost [3]. In the search of economically attractive alternatives materials, research groups have been dealing with the preparation of biodegradable materials from natural, low cost raw materials [4]. In this sense, due to its wide availability and renewable character, thermoplastic materials obtained by the plasticization of starch (TPS) are among the most promising [5,6]. The understanding of the different processes involved on the transformation of starch into TPS has been greatly increased due to the work of several research groups [7–9]. In recent years, the development of new compositions, plasticizers and processing techniques is continuous [10,11]. Nowadays, converted into a thermoplastic material, starch is already and interesting alternative for synthetic polymers in applications that do not require long-term durability nor elevated mechanical performance. In order to fulfill their potential utilization as synthetic thermoplastic alternative, the mechanical properties of TPS must be enhanced [12,13]. The reinforcement of the thermoplastic matrix with natural lignocellulosic fibers seems to be the logical alternative in order to increase their mechanical performance and to preserve the environmental-friendly character of the final material.

Our research groups have centered their attention to the preparation and characterization of new TPS formulations [14,15], the utilization of natural fibers as reinforcement of thermoplastic matrices [16,17] and the search of new applications for starch-based polymers and composites [18–20]. In the present investigation, our experience in developing TPS and natural fiber composites is applied to the preparation of new fiber-reinforced thermoplastic starch formulations. Mechanical and physicochemical properties of these new materials are analyzed and evaluated.

2. Materials and methods

2.1. Materials

Thermoplastic starch (TPS) was prepared from industrial non-modified starch obtained from corn, with a 28% content of amylose and 72% amylopectin, (Corn products, Brazil). Supplied with 10% humidity, it was used as polymeric matrix mixed with 30% w/w of glycerol (Synth). Fiber strands from sisal and hemp were supplied by CELESA (Spain) and used as reinforcement at various proportions

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ranging from 5% to 20% w/w referred to the glycerol/starch matrix. The long fibers supplied were cut to 10–15 mm prior to their use. Determined by SEM, the average diameter of single strands was 31.5 μm for hemp and 31.8 μm for sisal. Determined by the Klason method (TAPPI T222 om-98), sisal strands contained 12.6 wt.% of lignin. Prior to compounding, fibers were submitted to a reflux in a cyclohexane/ethanol mixture for 24 h. This light treatment allowed the removing of pectin, waxes and other minor components present on the surface of the fibers without affecting the main morphological characteristics of the fibers (i.e. diameter). Yield was 90–95%. The latex used was directly extracted from Hevea Brasilensis and was stabilized with 2.5% of concentrated ammonia aqueous solution. The suspension presented a 35% of solids.

2.2. Composites preparation

Fig. 1 describes the experimental procedure used for the preparation of TPS and TPS-based composites. In brief, the main components of the matrix (corn starch and glycerol) were manually premixed in polyethylene bags. After this preliminary step, the resulting blend was further processed, together with the corresponding amount of fiber-reinforcement, for 6 min in a rheometer (Haake Rheomix 600) at 120 °C and 60 rpm. In those formulations containing latex, this was added in a proportion of 2.5% w/w during this processing stage [21]. After processing the composites, these were granulated (by means of a blade mill equipped with a nominal 10 mm mesh) and thermo-pressed in order to obtain either 210 × 160 × 2 mm film plates or mechanical assay specimens according to ASTM D638. For this purpose a Carver thermo-press was operated for 10 min at 150 °C with a controlled pressure increase from 5 up to 10 Tm. Samples were kept in the press for another 40 min in order to cool down to 50 °C.

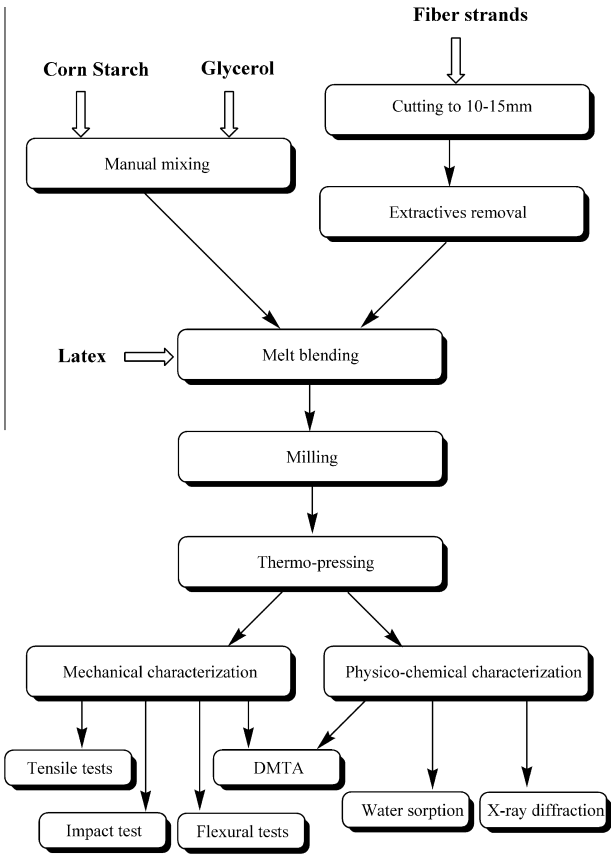

Fig. 1. Flow chart for the preparation of composites based on TPS.

2.3. Mechanical tests

Stress–strain tests were performed according to ASTM D638M-90 in an Emic DL 3000 testing machine. Tensile tests were performed to determine the ultimate tensile strength (UTS), the secant modulus at 1% strain ($E_{1\%}$) and strain at break (ε_r). All specimens were initially dried at 70 °C for 120 h and subsequently conditioned for 20 days in a 53% relative humidity atmosphere before testing. 5–10 specimens were tested for each material and mechanical test.

2.4. Water sorption

Samples with 2 mm thickness were dried in an air circulating oven at 70 °C for 120 h. Water uptake was measured regularly from samples conditioned at 53% relative humidity by adjusting a saturated solution of $Mg(NO_3) \cdot 6H_3O$ (according to ASTM E 104-85).

2.5. Dynamic mechanical thermal analysis (DMTA)

DMTA measurements were performed in a DMA 2980 TA Instrument, working in tension mode at 1 Hz with a pre-load of 0.01 N (maximum deformation of 0.025, corresponding to amplitudes in the range of 16 μm). The temperature was raised from −110 °C to 200 °C, and measurements were carried out in steps of 5 °C. The samples (35 × 5 × 1 mm) were cut from 1 mm thick hot-pressed molded plates. Analyses were performed after equilibrating the samples in the conditions described above.

2.6. Scanning electron microscopy (SEM)

The fragile fracture surfaces of the composites were studied in a scanning electron microscope LEO 440. The tungsten filament was operated at 20 KV. The fractures were produced from samples frozen in liquid nitrogen.

2.7. X-ray analysis

The crystallinity of the composites were determined by diffractometry using a Carl–Zeiss–Jena, URD6 X-ray analyzer. Assays were conducted at room temperature. The angle (2θ) interval 5–40° was analyzed at a speed of 1.2°/min. Crystallinity was calculated according to the peak at 19.6°.

3. Results and discussion

3.1. Characterization of TPS matrix

The physicochemical properties of the natural corn starch used in this work centered the first studies, paying special attention to the changes occurring during its processing. Fig. 2 shows the diffractogram corresponding to the corn starch before and after processing with glycerol.

The results displayed in Fig. 2 demonstrated important changes in the structure of the starch after processing. The analysis of the native starch showed a predominance of *type A* crystallinity, characteristic for cereals, with peaks of higher intensity at Bragg angles of 17.9°, 18.2° and 23.3°. Calculated according to the method proposed by Hulleman [22] the crystalline fraction in this starch sample was found to be about 32%, in agreement with literature values [23,24].

The change in the crystalline structure of starch after processing with glycerol is clearly visible in the X-ray diffractograms, where predominance of crystallinities *type B*, with a characteristic signal $2\theta = 16.8°$, and specially *type Vh* ($2\theta = 12.9°$, 19.7° and 22.4°) are