VII Congreso Internacional de MATERIALES del 29 de octubre al 1 de noviembre de 2013 MEDELLÍN • Colombia

Physical, structural, thermal and mechanical properties of starch-based materials from pehuen seeds (Araucaria araucana (Mol) K. Koch)

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ABSTRACT

Starch isolated from pehuen seed (Araucaria araucana (Mol) K. Koch) was employed for producing thermoplastic starch (TPS) and pehuen cellulosic husk was used as reinforcement for starch-based materials composites. Starch, husk, TPS and composites were characterized. Granules pehuen starch are rounded and small (12-21 μm), with an amylose content range 38–40%, a crystalline C-type structure and thermally stable, with decomposition temperature above 300 ◦C. The effect of plasticizer type (glycerol and sorbitol) and starch/plasticizer ratio on TPS properties was also investigated. X-ray diffraction patterns of TPS showed the formation of processing-induced crystallinity, which depended on plasticizer employed. Sorbitol plasticized TPS provided a material with more brittles and less flexibility. In contrast, glycerol plasticized TPS was tough and ductile. The tensile strength of TPS decreased with the increase in plasticizer content. The incorporation 5 y 10 wt.-% of pehuen husk improved considerably the thermal stability and mechanical properties of the studied composites.

Palabras Clave: Pehuen, starch, husk, biocomposite.

1 INTRODUCTION

In the past decade of growing environmental concerns, the use of starch-based resources in non-food applications has been developed, in response to the need for finding substitutes to petroleum-based plastics. In particular, granular starch produced by green plants has attractive characteristics such as natural availability, biodegradability, low cost and easy chemical and physical modifications that permit new applications [1].

2 Experimental

2.1 Materials

Starch was isolated from ripe pehuen seeds collected in the Chilean forest, using the isolation method proposed by Henríquez et al. (2008). Pehuen husks with particles sizes less than 1.0 mm.

The plasticizers used were glycerol with a 99.5% purity (Winkler, USA) and sorbitol with moisture content of 30% (Reutter China).

2.2 **Preparation of thermoplastic starch (TPS) and composites**

Before melt-blending, pehuen starch and liquid plasticizers were premixed by hand at room temperature. A Haake internal mixer (Polysystem Rheocord, Waltham, USA) was used to prepare the TPS and composites. The samples were blended at 120 °C with a rotor speed of 60 rpm for 15 min. The TPS and composites compositions are shown in Table 1. The TPS and composites materials were injection-molded by using a Minijet II (Haake Thermo Scientific, Waltham, USA).

In this work, starch isolated from pehuen seed was employed to prepare pehuen-TPS and pehuen-TPS composites using as filler 5 and 10 wt-% of the pehuen husk. Pehuen starch-based materials were prepared by melt-blending method and characterized physical, thermal, structural and mechanically. Pehuen husk was also characterized.

Table 1. Sample compositions and their codes.

Identification of sample	**Glycerol** (wt-%)	**Sorbitol** (wt-%)	**Pehuén starch** (wt-%)	**Husk** (wt-%)
APG37	30		70	
APG46	40		60	
APS37		30	70	
APS46		40	60	
TPS	40		60	
TPS5H	36		57	5
TPS10H	38		54	10

3 RESULTS AND DISCUSSION

3.1 Results Starch

Starch used as thermoplastic materials is an alternative for biopolymer production. Thermoplastic starch (TPS) properties depend on the physical and chemical characteristics of the starch, such as amylose/amylopectine ratio, granule size distribution and mineral content, among others.

Starch from pehuen seed (Araucaria araucana (Mol) K. Koch) presents physic-chemical properties, such as granule surface is smooth, with no irregularities or erosion; besides, most of them showed a flat surface on one side (see fig.1). The most of the granules of pehuen are small granule size (12–21 µm), 38–40% of amylose content, crystalline C-type structure and decomposition temperature above 300 °C, Castaño et al. [2] that make it a good precursor for starch-based materials with adequate performance characteristics.

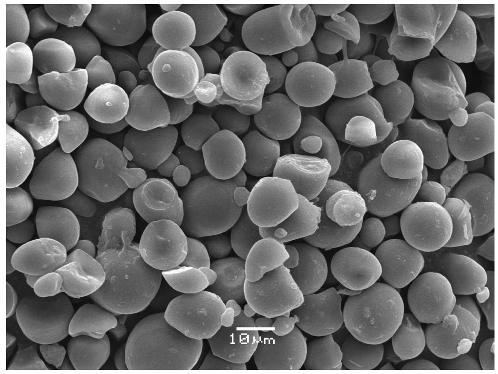

Figure 1. SEM micrograph of pehuen starch

3.2 Results TPS

X-ray diffraction patterns of TPS are presented in Fig. 2. Residual C-type crystallinity is not observed in thermoplastic pehuen starches, since there were not characteristic peaks in X-ray diffraction patterns. This indicates that the energy input in the torque rheometer was sufficient to plasticize the pehuen starch completely. However, the processing-induced crystallinity caused by the recrystallization of amylose complex with plasticizer (complexing agent) into single-helical structures was formed. The diffraction pattern of glycerol plasticized TPS can be assigned to the V_H type structure (peak at around 20°), while sorbitol plasticized TPS, to the E_H type structure (peak at around 17°) Van Soest, et al., 1996 [3].

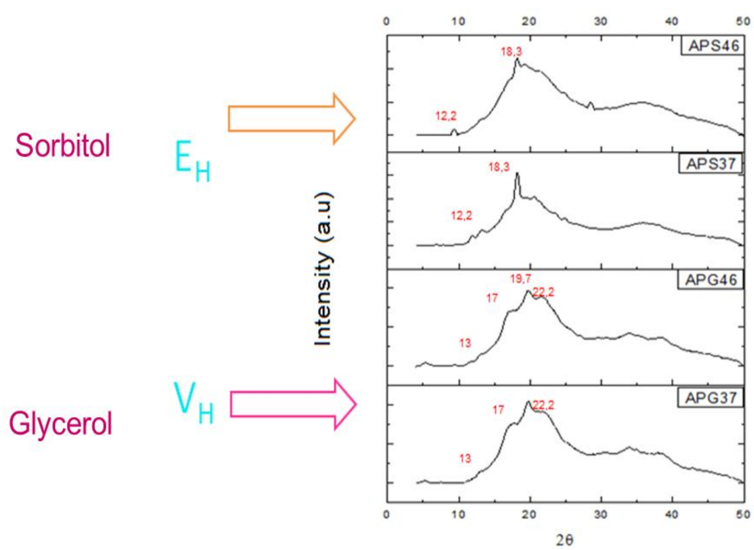

Figure 2. X-ray diffraction pattern of studied TPS.

Mechanical and thermal properties of pehuen-TPS depended on glycerol content; thus, tensile strength decreased with the increase of plasticizer content, while the elongation at break also increased, and pehuen-TPS with 30 wt-% of glycerol had highest thermal stability.

3.3 Results composites

Pehuen husk mainly consists of cellulose (50 wt-%), hemicellulose (30wt-%) and lignin (14wt-%). Its surface is smooth and damage-free and it is decomposed above 325°C. Thermal stability of polymer matrix and composites were analyzed by TGA. In the first step, the maximum rate of weight-loss of TPS occurred at 143°C, while the composites with 5wt-% (TPS5H) and 10wt-% (TPS10H) of biofiber were 179°C and 192°C, respectively. The presence of husk in TPS composites increases considerably the traction resistance of the samples; hence, TPS5H and TPS10H increase this resistance in 305% and 330%, respectively. The incorporation of pehuen husk improved the thermal stability and mechanical properties of pehuen-TPS [4].

The thermal stability enhances since biofiber hinders the "out-diffusion" of volatile molecules from the polymer matrix. Mechanical properties could raise due to the natural affinity between husk and starch in the pehuen seed.

The fractured surface of pehuen TPS sample was homogeneous and little rough surface. Similar aspects show the fracture surfaces of pehuen starch/husk composites. In all cases, the absence of starch granules is an evidence of plasticization of pehuen starch under the used processing conditions. SEM images of samples TPS5H and TPS10H showed no specific pehuen husk orientation; the fibers were randomly distributed in starch matrix. There were also no obvious gaps at husk/matrix interface, indicating a good adhesion between hydrophilic TPS phase and hydrophilic fibers (Fig. 3). When fiber content increased from 5 to 10 wt%, TPS composite had no fiber agglomeration

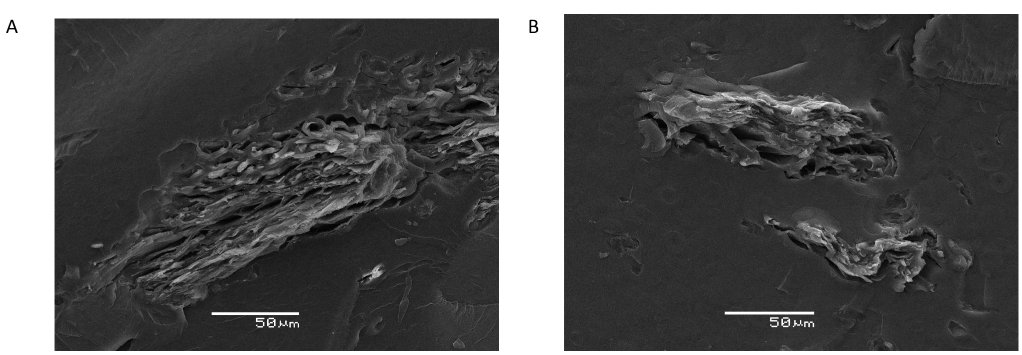

Figure 3 SEM micrographs of fracture surfaces: TPS5H (A), TPS10H (B)

4 CONCLUSIONS

Starch isolated from pehuen seeds of A. araucana (Mol) K. Koch was characterized physicochemical, morphological, structural and thermally. The main characteristics observed were: (a) amylose content ranging between 38 and 40%, (b) small rounded starch granules (12–21µm), (c) crystalline structure of a typical C-type pattern and (d) thermally stable, with decomposition temperature above 300 ◦C.

The effect of type and content of plasticizer on thermoplastic pehuen starch properties was also studied showing the potential of this starch as an excellent precursor for starchbased materials. No retained crystallinity was observed in studied TPS, while processing-induced crystallinity depends on plasticizer employed: glycerol plasticized TPS presented V_H-type structure, while sorbitol plasticized TPS presented the E_H-type structure.

Thermal analysis studies showed that the type and concentration of plasticizer had influence on the thermal stability of TPS. Sorbitol plasticized TPS was more stable, since sorbitol has a higher thermal stability than glycerol. According to tensile properties, sorbitol plasticized pehuen starch provided a material with more brittleness and less flexibility. In contrast, glycerol plasticized pehuen starch made it more resistant and ductile.

Thermo-mechanical properties of thermoplastic pehuen starch composites reinforced with pehuen husk showed the potential of this biofiber as an excellent reinforcement for composite materials. The thermal stability enhances because biofiber hinders the “out-diffusion” of volatile molecules from the polymer matrix. Mechanical properties could raise due to the natural affinity between husk and starch in the pehuen seeds. The adequate thermal and mechanical properties of pehuen TPS composites allow industrial processing and use in applications such as agricultural and packaging industries.

5 REFERENCES

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