Carbohydrate Polymers 90 (2012) 1550–1556

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Physical, chemical and mechanical properties of pehuen cellulosic husk and its pehuen-starch based composites

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ARTICLE INFO

Article history:
Received 16 April 2012
Received in revised form 3 July 2012
Accepted 7 July 2012
Available online 16 July 2012

Keywords:
Pehuen starch
Biofiber
Biodegradable
Composite

ABSTRACT

Pehuen cellulosic husk was characterized and employed as reinforcement for composite materials. In this research, thermoplastic pehuen starch (TPS) and TPS/poly(lactic acid) (PLA)/polyvinyl alcohol (PVA) composites, reinforced with 5 and 10% of pehuen husk, were prepared by melt-blending. Comparative samples of pehuen TPS and TPS/PLA/PVA blend were also studied. Physical, thermal, structural and mechanical properties of composites were evaluated.

Pehuen husk mainly consists of cellulose (50 wt%), hemicellulose (30 wt%) and lignin (14 wt%). In respect to lipids, this husk has only a 0.6 wt%. Its surface is smooth and damage-free and it is decomposed above 325 °C.

The incorporation of pehuen husk improved considerably the thermal stability and mechanical properties of the studied composites, mainly in TPS composites. Their thermal stability enhances since biofiber hinders the "out-diffusion" of volatile molecules from the polymer matrix, while mechanical properties could raise due to the natural affinity between husk and starch in the pehuen seed.

1. Introduction

Biocomposite materials produced from non-renewable or renewable polymer matrixes and nonwood biofibers such as kenaf, jute, flax, banana, hemp and husk have potential applications for several sectors, including aircraft parts, sports goods, construction, automotive components and food containers (Ku, Wang, Pattarachaiyakoop, & Trada, 2011). The primary advantages of using biofiber as fillers are their availability, low cost and self-weight; also, biofibers produce an eco-friendly biocomposite. Biocomposite performance is affected by size, orientation and aspect ratio of the fibers, and by the interfacial adhesion between the fiber and the polymer matrix (Abdul, Bhat, & Ireana, 2012; Satyanarayana, Arizaga, & Wypych, 2009). The latter is a major challenge in obtaining biocomposites with superior mechanical properties. In the case of biocomposites with the similar chemical nature of both fiber and polymer matrix, no surface modification of the fibers or addition of coupling agent are necessary for obtaining a good adhesion with the matrix, decreasing the final cost of manufacturing biocomposites (Satyanarayana et al., 2009). The properties of biocomposites are also influenced by fiber content and processing conditions (Sykacek, Hrabalova, Frech, & Mundigler, 2009).

Thermoplastic starch reinforced with lignocellulosic fibers offers a promising alternative to synthetic polymer composites, especially for short-lived applications. Few studies have investigated the preparation of thermoplastic starch biocomposites, most of them oriented to obtain starch-based foam materials. Thus, for example, Reolon and Borges (2010) reported the effect of eucalypt cellulose fiber concentration on mechanical properties of the foam based on cassava starch and dolomitic limestone. The increase of cellulosic fiber content produces a decrease of tensile strength of the foam material; however, the values of tensile strength were higher than those of expanded polystyrene used as food container. Foam materials with 5 wt% of cellulose fibers increased by 51% the tensile strength in respect to the foam of expanded polystyrene. A similar study was performed by Kaisangsri, Kerdchoechuen, and Laohakunjit (2012) with cassava starch-based foam, but using kraft fiber as a filler and chitosan in low proportion (0–6 wt%). Foams with 30 wt% of fiber and 4 wt% of chitosan had a tensile strength, density and elongation at break close to polystyrene foam. On the other hand, Soykeabkaew, Supaphol, and Rujiravanit (2004) concluded that mechanical properties of starch-based composite foams reinforced with jute- and flax-fiber improved considerably when 5–10 wt% of the fibers is added; also, these properties depend

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http://dx.doi.org/10.1016/j.carbpol.2012.07.029

on aspect ratio and orientation of the fiber in the biocomposites. In the case of biofiber/thermoplastic starch composites as bulk material, it is also reported that the use of biofiber as reinforcement improves the thermo-mechanical properties and water resistance of the composite in respect to TPS matrix. Guimarães, Wypych, Saul, Ramos, and Satyanarayana (2010) prepared and characterized corn starch composites reinforced with banana and bagasse fibers; as a result, improvements in tensile modulus and yield strength of these composites were obtained in respect to those of the matrix. Bagasse fiber/starch composite displayed higher mechanical properties, which have been attributed to parallel alignment of the bagasse fibers in the fractured surface observed by SEM (Dufresne & Vignon, 1998).

Thermoplastic starch reinforced with residual lignocellulosic fibers, e.g. husk, from the same source where starch is extracted, is a promising composite material due to the natural affinity between the fibers (husk) and the seeds where starch is formed. Recently, our working group published the results of investigations related with the processing and characterization of starch-based materials from pehuen seeds (Castaño, Bouza, Rodríguez-Llamazares, Carrasco, & Vinicius, 2012), showing that pehuen starch is a good precursor for starch-based materials with adequate performance characteristics. As is well known, alternatives to improve the performance of starch-based materials are its reinforcement with biofibers and the blending of starch with other bioplastics, such as poly(lactic acid) PLA and polyvinyl alcohol (PVA). Hence, the aim of this study is to prepare and characterize pehuen cellulosic husk/pehuen starch-based composites. The effect of pehuen husk content on the thermo-mechanical properties of thermoplastic pehuen starch (TPS) and TPS/PLA/PVA composites is investigated. The properties of TPS/PLA/PVA blend are also studied.

2. Experimental

2.1. Materials

Starch isolated from ripe pehuen seeds collected in the Chilean forest was used to prepare starch-based composites. PVA (Mw: 31–50 kg/mol, 98–99% hydrolyzed) and PLA (Mw = 200 kg) were purchased by Aldrich and Nature Works, respectively. The trade name of PLA is PLA 2003D. Pehuen husks with particles sizes less than 1.0 mm and glycerol (99.5%) provided by Winkler (USA) were used as filler and plasticizer, respectively.

2.2. Characterization of pehuen cellulosic husk

Husk appearance and morphology were analyzed by means of scanning electron microscope (SEM) with the conditions subsequently described in Section 2.4.1.

Fiber aspect ratio was evaluated using an L&W Fiber Tester (Kista, Sweden); for this analysis, pehuen husk was previously pretreated as described earlier (Sykacek et al., 2009). Measurements of particle lengths and diameters were performed using 0.1 g of husk suspended in 100–200 mL of water. The content of insoluble acid lignin (Klason) and cellulose of extractive-free husk was analyzed according to TAPPI standard T 280 and Kurschner & Hoffer method, respectively. Ash, lipids, proteins and humidity content were evaluated according to ASTM D1102-84(01), AOC 2003, Kjendhal and Chilean Standard 176/1, respectively.

Thermal stability and particle size-distribution of pehuen husk were assessed by using thermogravimetric analyzer and by sieve analysis, respectively. The measurement conditions of thermogravimetric analysis (TGA) are described in Section 2.4.2.

2.3. Preparation of TPS and TPS/PLA/PVA composites

Before melt-blending, the respective components of the samples were premixed by hand at room temperature. A Haake internal mixer (Polysystem Rheocord, Waltham, USA) was used to prepare the composites. TPS composites were blended at 120 °C with a rotor speed of 60 rpm for 15 min. TPS/PLA/PVA blend and TPS/PLA/PVA composite were mixed at 160 °C and 40 rpm for 15 min. The composition of each sample is shown in Table 1.

The composites were injection-molded by using a Minijet II (Haake Thermo Scientific, Waltham, USA). TPS composites were processed under the following conditions: 170 °C of cylinder temperature, 50 °C of mold temperature, and 300 bar of injection pressure. The processing conditions of TPS/PLA/PVA blend and TPS/PLA/PVA composites were 190 °C of cylinder temperature, 40 °C of mold temperature and 270 bar of injection pressure.

2.4. Characterization of blend and composites

2.4.1. Scanning electron microscopy

The molding specimens were cooled in liquid nitrogen and fractured. Fracture surfaces were observed through a scanning electron microscope (JEOL-JSM 6380 LV, Tokyo, Japan). The fracture surfaces were coated with a gold thin film of ca. 50 nm and the images were taken at an accelerating potential of 20 kV.

2.4.2. Thermal analysis

Thermal stability of pehuen husk, blend and composites was evaluated by using a thermogravimetric analyzer NETZSCH 209 F3 TGA (Tarsus, Selb, Germany). TGA curves were recorded at 10 °C/min, in a range between 30 and 900 °C, under nitrogen atmosphere (20 mL/min).

2.4.3. X-ray diffraction (XRD)

The crystalline structure of the blend and composites was analyzed at room temperature by means of a Bruker Endeavor diffractometer (Model D4/MAX-B, Karlsruhe, Germany), operating at 40 kV, 20 mA and Cu Kα radiation (1.541 Å). The scans were obtained in the reflection mode over a 2θ range of 4–40°, in steps of 0.02 at 0.008°/min. Peak fitting analysis was made using a Gaussian distribution function. Degree of crystallinity was calculated using the method reported by Frost, Kaminski, Kirwan, Lascaris, and Shanks (2009).

2.4.4. Tensile properties

Tensile properties were evaluated through a universal testing machine (Emic DL 2000, Parana, Brazil), according to ASTM D-638 standard. Before measurement, specimens were conditioned for 48 h at 23 °C with 50% of relative humidity in agreement with ASTM D618 standard. The crosshead speed was set at 1.0 mm/min. Average value of five specimens is reported.

3. Results and discussion

3.1. Pehuen cellulosic husk

Properties of biofibers depend mainly on the botanic source, growth location, age of the fiber and the extraction method used for obtaining the fiber (Jawaid & Abdul, 2011). A biofiber is a network composed primarily by cellulose, hemicellulose, lignin, and a small amount of protein, lipids, and starch (Bledzki, Mamuna, & Volk, 2010). In pehuen husk, the major component is cellulose, with a content of 50 wt% , hemicellulose of 30 wt% and lignin (total) of 14 wt%; in respect to lipids, this husk has only a 0.6 wt% (see Table 2). Lignocellulosic agricultural residues have a higher

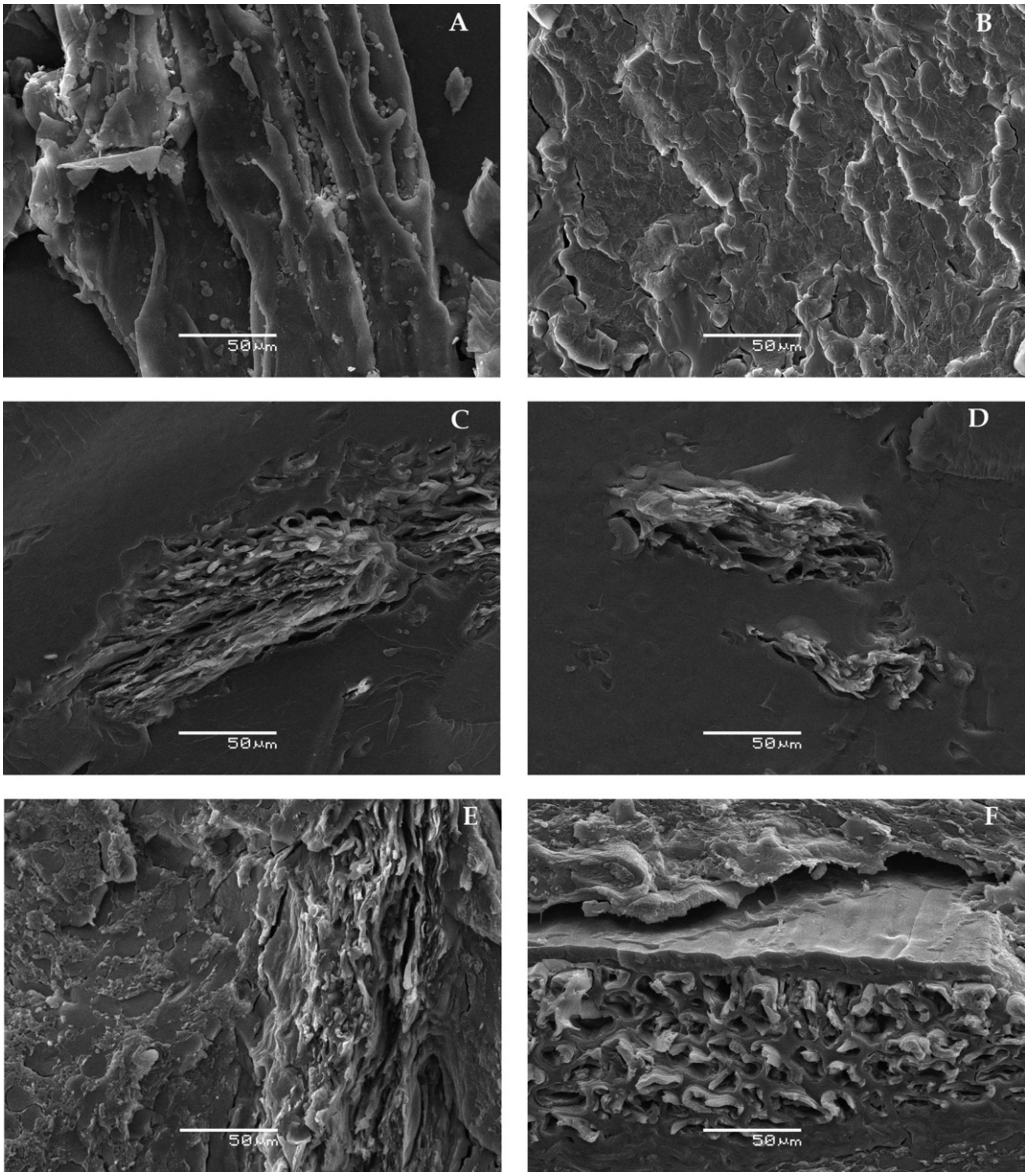

Fig. 1. SEM micrographs of pehuen husk (A) and fracture surfaces of molded specimens: TPS/3P (B), TPS5H (C), TPS10H (D), TPS/3P5H (E) and TPS/3P10H (F).

hydrophilic nature than wood plants, which is related to lower amount of lignin and higher hemicellulose content. On the other hand, as has been reported by Bledzki et al. (2010), lipid content is directly proportional to hydrophobic behavior and higher surface tension of fibers. In this way, it is expected that pehuen husk is hydrophilic and with low surface tension, which are characteristics that favor a good interaction with a hydrophilic polymer matrix.

The aspect ratio of pehuen husk, determined by using fiber tester, was 39. The size distribution of pehuen husk was 22.1, 40.3, 21.4, 6.3, 8.0 and 1.9 on the ranges of +1.0, 0.6–1.0, 0.3–0.6, 0.15–0.3, 0.04–0.3 and less than 0.04 mm, respectively.

External surface features of pehuen husk were observed through SEM (Fig. 1A). It was identified that pehuen husk has smooth and homogeneous surface without defects and damages. Small granules of starch adhered to husk surface were also observed. The fibers surface morphology has influence on the properties of composite materials; microvoids and microcracks can avoid the contact of the matrix with the total surface of the fibers since capillarity effects become more difficult.

Table 1
Sample compositions and their codes.

Sample	Pehuen starch (wt%)	Glycerol (wt%)	PLA (wt%)	Husk (wt%)	PVA (wt%)
TPS	60	40			
TPS/3P	36	24	30		10
TPS5H	57	38	0	5	0
TPS10H	54	36	0	10	0
TPS/3P5H	33	22	30	5	10
TPS/3P10H	30	20	30	10	10

Table 2
Chemical composition (wt%) and physical properties of pehuen husk.

Properties of pehuen husk	
Extractive-free (wt%)	8.6 ± 0.7
Cellulose (wt%)	50 ± 6
Hemicellulose (wt%)	31 ± 3
Lignin insoluble (wt%)	11.7 ± 0.3
Protein (wt%)	2.1 ± 0.1
Lipids (wt%)	0.60 ± 0.02
Ash (wt%)	1.4 ± 0.3
Humidity (wt%)	6 ± 1
Length (mm)	0.89 ± 0.02
Aspect ratio	39
Density (g/cm^3)	0.305 ± 0.001

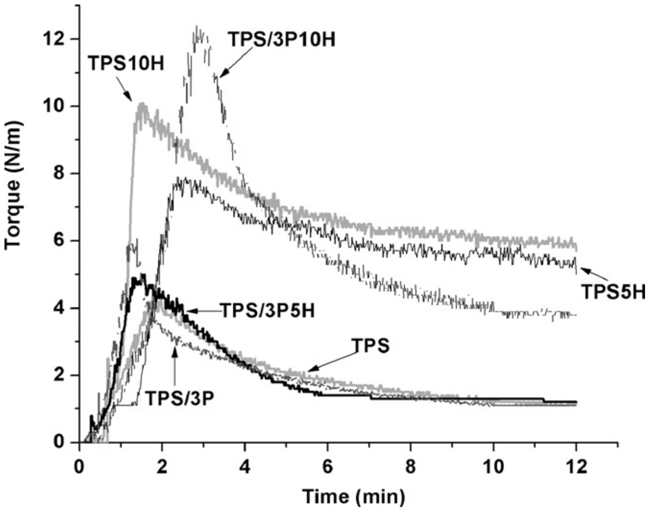

Fig. 2. Torque variation as a function of time for samples.

3.2. Processing properties

Processing properties of the blend and composites were evaluated by monitoring the evolution of torque over time during mixing in a Haake rheometer (see Fig. 2). All tested samples, i.e., blend and composites, showed a similar tendency in the change of torque with time during processing, increasing rapidly to maximum and then decreased gradually up to steady state. Steady state torque is related to the viscosity of the polymer matrix during melt-blending. As was expected, the data from Haake torque rheometer indicates that the viscosity (steady torque) of the composites increases as biofiber content increases in the formulation. Solid biofibers offer certain resistance to the free rotation of the blades and, therefore, the torque increases. Thus, for example, steady state torque of TPS sample was 1.1 Nm while the value increased to 5.9 Nm for TPS10H sample (see Table 3). It is important to note that the torque values corresponding to steady state conditions were kept almost constant after 8 min, which indicates that there was neither chain degradation, or cross-linking or loss of glycerol during the samples processing. Similar results have been reported by Corradini, Felix de Carvalho, Curvelo, Marcondes, and Capparelli (2007).

Table 3
Processing properties and degree of crystallinity.

Sample	Plasticization energy (Nm/min)	Steady torque (Nm)	Crystallinity (%)
TPS	3.93	1.10	9.85
TPS/3P	8.01	1.11	6.75
TPS5H	10.88	5.21	7.89
TPS10H	18.03	5.90	8.07
TPS/3P5H	10.61	1.12	5.19
TPS/3P10H	15.09	3.79	5.35

The plasticization energy was also calculated from the torque rheometry data; these values are summarized in Table 3. The integral of torque curve, from initial time (when all the components were in the mixing chamber) until the time where the maximum torque is reached, is reported as the plasticization energy (Córdoba, Cuéllar, González, & Medina, 2008). In this region, mainly, the diffusion of glycerol inside the starch occurs, and the melting of PLA in those formulations with PLA. The plasticization energy showed similar tendency to viscosity when biofiber content increases.

3.3. Characterization of blend and composites

3.3.1. Scanning electron microscopy

The fractured surface of pehuen TPS sample was previously described by Castaño et al. (2012) observing a continuous, 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 (Fig. 1B–F). SEM images of samples TPS5H and TPS10H showed no specific pehuen husk orientation; the fibers were randomly distributed in starch matrix (see Fig. I). There were also no obvious gaps at husk/matrix interface, indicating a good adhesion between hydrophilic TPS phase and hydrophilic fibers (Fig. 1C and D). When fiber content increased from 5 to 10 wt%, TPS composite had no fiber agglomeration.

TPS/3P sample showed a rough surface and some partial miscibility or co-continuous phase with some small holes. This phase morphology is an evidence of poor compatibility of starch and PLA by the use of PVA compatibilizer. SEM images of fractured surfaces of TPS/3P5H and TPS/3P10H composites showed microcracks and discontinuities in the interface between husk and polymeric matrix (Fig. 1E and F). The random dispersion of the husk and their pullout from TPS/3P matrix was also observed. The poor adhesion could be attributed to hydrophobic nature of PLA (Satyanarayana et al., 2009).

3.3.2. Thermal analysis

Thermal stability of pehuen husk, polymer matrixes and composites were analyzed by TGA. The weight loss during heating of the pehuen husk, thermoplastic pehuen starch, TPS/PLA/PVA blend and their composites occurred in two steps, as shown in Fig. 3. In the case of pehuen husk, the first step corresponded to water evaporation, which began immediately after the temperature increased and finished at around 110 °C (Fig. 3A). Similar results have been reported by Rosa et al. (2009) for coir fiber. The percentage of weight loss in this step was 4% and the maximum rate of water evaporation occurred at 73 °C. The second mass-loss step of the pehuen husk is attributed to the thermal decomposition process that started around 170 °C. The decomposition peak at about 340 °C is due to the thermal decomposition of cellulose, the principal component of pehuen husk. There are two large shoulders before the degradation of cellulose, due to of the degradation of lignin and hemicellulose. The first shoulder is related to degradation of lignin, which firstly degrades at a slower rate than the other constituents of biofiber. As reported previously, the degradation peak of lignin overlapped with the hemicellulose and cellulose peaks, finishing at 500 °C (Bledzki et al., 2010). The remaining mass obtained at 900 °C is around 24%, associated to silicate compounds (Ludueña, Fasce, Álvarez, & Stefani, 2011).

The first mass-loss step of pehuen TPS occurred between room temperature and 200 °C and it is attributed to the loss of molecules of low molecular weight, mainly glycerol and water. The second step corresponds to degradation of starch components; the

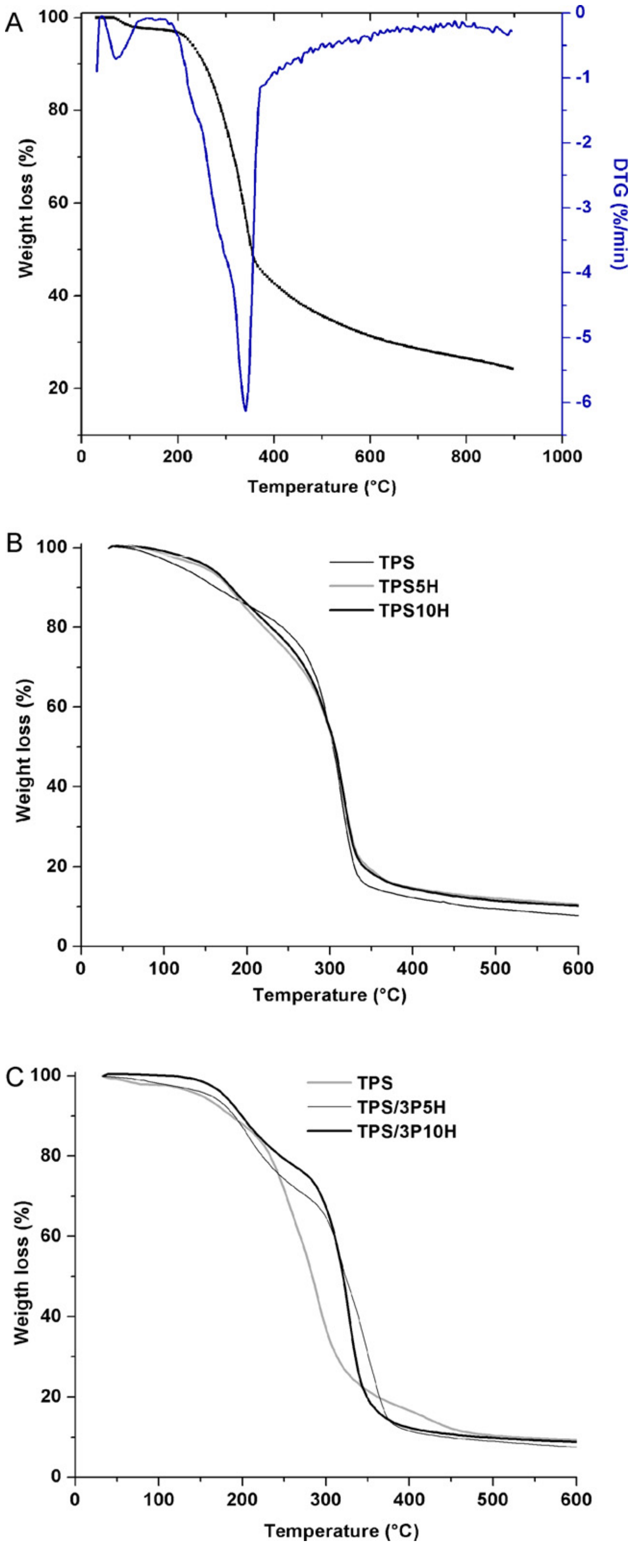

Fig. 3. TGA and DTG curves of pehuen husk (A); TGA curves of TPS composites (B) and TPS/PLA/PVA composites (C).

maximum rate of the starch degradation takes place at 310 °C. TGA curves of TPS composites showed that the temperature ranges of the two mass-loss steps aforementioned are similar to TPS; however, the initial rate of weight-loss was slower in the composites (Fig. 3B). In the first step, the maximum rate of weight-loss of TPS occurred at 143 °C, while the composites with 5 wt% and 10 wt% of biofiber were 179 °C and 192 °C, respectively. The incorporation of biofiber improved the thermal stability of TPS since biofiber hinders the “out-diffusion” of the volatile molecules (e.g. glycerol) as well as the diffusion of oxygen into the polymer matrix. Both factors retard the decomposition process of TPS composites.

Regarding to thermal stability, TGA curves of TPS/PLA/PVA blend and its composites showed a similar tendency than TPS composites. Increasing biofiber content decreased the initial decomposition rate of these composites (see Fig. 3C). As expected, TPS/PLA/PVA blend (TPS/3H) had higher initial thermal stability than TPS. The decomposition temperature at which the 5% of weight loss occurs ($T_{5\%}$) on TPS was 27 °C lower than that on TPS/3H.

The apparent activation energy at temperature of maximum decomposition rate of the samples was calculated from TGA curves by integral method reported by Wang, Yu, Chang, and Ma (2008). The values of activation energy, summarized in Table 4, are in a range of 70–75 kJ mol^{-1} K^{-1}. This narrow range of variation on the activation energy suggests that fiber incorporation does not change the decomposition mechanism for TPS and TPS/PLA/PVA composites (Satyanarayana et al., 2009).

3.3.3. *X-ray diffraction (XRD)*

It has been reported that the processing-induced crystalline structure of starch-based material is assigned to interactions established between starch and plasticizer, for example, plasticizer-amylose complex form a single-helical structure with V-type crystallinity (Girones et al., 2012; Van Soest, Hulleman, De Wit, & Vliegenthart, 1996). As pointed out in a previous report by Castaño et al. (2012), the pehuen TPS presents V_H type structure with characteristic peak at 19.7°. The TPS composites showed a similar X-ray diffraction pattern when compared with the polymer matrix, although a slight reduction of degrees of crystallinity was obtained (see Table 3).

The TPS/PLA/PVA blend showed XRD pattern typical of amorphous materials with a broad peak around 20 (see Fig. II). As was expected, the samples containing PLA/PVA had a lower degree of crystallinity, because a lower amount of amylose was available to form a single helical structure of amylose-glycerol complex (Table 3).

Similar to TPS composites, TPS/PLA/PVA composites exhibited an XRD pattern close to that of TPS/PLA/PVA blend, indicating that biofibers have a little influence on the degree of crystallinity of polymer matrix (see Fig. II) (Zhou, Cui, Jia, & Xie, 2009).

The reduction on the crystallinity of the composites, both with matrixes of TPS and TPS/PLA/PVA, can be related to a decrease in the mobility of starch molecules caused by the presence of the stiffer reinforcing fibers. In Fig. II it is observed that the full width at half maximum of the diffraction peaks of the composites increases when husk content increases too, indicating that the crystallite size diminishes and, in this way, the total crystallinity of the samples diminishes too.

3.3.4. *Mechanical properties*

The mechanical properties were determined by means of traction test; the corresponding values for analyzed samples are informed in Table 4. As has been previously reported by Castaño et al. (2012), pehuen TPS with 40% of glycerol has a tensile strength of 2.9 MPa and 60% elongation at break. 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. Undoubtedly, this improvement is a consequence of pehuen fiber reinforcement and of an adequate compatibility among the components. Huneault and Li (2007) reported that tensile strength and elongation at break of composites are directly linked to interfacial adhesion between the reinforcing particles and the polymer matrix. On the other hand,

Table 4
Thermal and mechanical properties.

Sample	$T_{5\%}$ (°C)	T decomp. (°C)	Apparent energy activation (kJ M^{-1} K^{-1})	Tensile strength (MPa)	Elongation at break (%)
TPS	117	312	74.7	2.9 ± 0.3	60 ± 2
TPS/3P	144	316	78.6	10.0 ± 0.6	10 ± 1
TPS5H	150	312	74.7	9 ± 2	40 ± 2
TPS10H	160	317	76.2	9.6 ± 0.3	33.0 ± 0.8
TPS/3P5H	162	328	78.5	12.0 ± 0.3	12.0 ± 0.4
TPS/3P10H	178	347	79.1	13.0 ± 0.2	10.0 ± 0.3
Pehuen husk	223	354		17 ± 2	128 ± 10

the elongation at break diminished from 60% to 40% for TPS5H and up to 34% for TPS10H.

When the TPS is blended with PLA/PVA (TPS/3H), the tensile strength of the TPS increases in approximately 350% but the elongation at break decreases in more than 500%, i.e., this is a rigid material. When pehuen husk was added to the TPS/PLA/PVA blend, the tensile strength increased only 20% in respect to the matrix (TPS/PLA/PVA blend); however, the elongation at break also increased 20% in both composites, even when TPS/PLA/PVA composites showed microcracks in the husk–matrix interface. From elongation at break values, it is possible to infer that the husk is a ductile material by itself, which confer a certain degree of plasticity to the composites.

It is noteworthy that the TPS-pehuen husk composites achieved better properties if a compromise between tensile strength and elongation at break is considered. This is related to a strong fiber–matrix-interface interaction, which enables stress transfer from the matrix to the fiber as well as a uniform distribution of the fiber into the polymeric matrix (Sykacek et al., 2009).

4. Conclusions

Pehuen husk biofiber was physicochemical, morphological and thermally characterized. The main characteristics were a cellulose content of 50 wt%, a 30 wt% of hemicellulose, a 14 wt% of lignin, a small percentage of lipids (0.6 wt%), a smooth and damage-free surface and a decomposition temperature above 325 °C.

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. TPS composites showed a good interaction between the fibers and the plasticized starch matrix due to the natural affinity between husk and starch in the pehuen seed. TPS/PLA/PVA blend showed partial miscibility or co-continuous phase and TPS/PLA/PVA composites presented also discontinuities at the biofiber–polymeric matrix interface.

The incorporation of biofiber improved the thermal stability of the composites, increasing the initial decomposition temperature. The biofiber hinders the “out-diffusion” of the volatile molecules (e.g. glycerol), retarding the decomposition process of starch composites. On the other hand, the degree of crystallinity of composites decreases when pehuen husk content increases.

Tensile strength of pehuen TPS increased when it was blended with PLA/PVA as well as when it was reinforced with pehuen husk; however, the elongation at break diminished. Reinforcing TPS/PLA/PVA blend with pehuen biofiber had not a considerable effect on the mechanical properties.

In this study, it was demonstrated that for improving thermal and tensile properties of pehuen TPS, the best way is to reinforce it; pehuen husk is a convenient, economical, biodegradable and abundant material to achieve this purpose.

Acknowledgements

This work has been partially financed by Projects Fondef D08I1191 and D09I1195, Conicyt-Regional R08C1002. Ms. Susana Castillo Miss Creusa Ferreira and Ms. Evelise Fonseca dos Santos for helping in sample preparation and testing.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2012.07.029.

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