MANAGEMENT OF CORN STALK WASTE AS REINFORCEMENT FOR POLYPROPYLENE INJECTION MOULDED COMPOSITES

Jirleska Flandez, Israel González, Jordi Bayer Resplandis, Nour-Eddine El Mansouri,*
Fabiola Vilaseca, and Pere Mutjé

The main objective of this study was the management of corn stalk waste as reinforcement for polypropylene (PP) injection moulded composites as an alternative to wood flour and fibers. In the first step, corn stalk waste was subjected to various treatments, and four different corn stalk derivatives (flour and fibers) able to be used as reinforcement of composite materials were prepared and characterized. These derivatives are corn stalk flour, thermo-mechanical, semi-chemical, and chemical fibers. They were characterized in terms of their yield, lignin content, Kappa number, fiber length/diameter ratio, fines, coarseness, viscosity, and the length at the break of a standard sheet of paper. Results showed that the corn stalk derivatives have different physico-chemical properties. In the second step, the prepared flour and fibers were explored as a reinforcing element for PP composites. Coupled and non-coupled PP composites were prepared and tested for tensile properties. For overall trend, with the addition of a coupling agent, tensile properties of composites significantly improved, as compared with non-coupled samples. In addition, a morphological study revealed the positive effect of the coupling agent on the interfacial bonding. The composites prepared with semichemical fiber gave better results in comparison with the rest of the corn stalk derivatives due to its chemical characteristics.

Keywords: Corn stalks; Agricultural wastes; Biocomposites; Natural fibers; Polypropylene

*Contact information: Group LEPAMAP, Department of Chemical Engineering, University of Girona, c/ M. Aurèlia Capmany, nº 61, Girona 17071, Spain. *Corresponding author:nour_eddine.elmansouri@udg.edu*

INTRODUCTION

During the last few years, biomass from crops has been the main target in the search of new materials applicable in several industrial areas, such as composites, textiles, pulp, and paper manufacture (English et al. 1996; Reddy and Yang 2005). Lignocellulosic wastes from crops are of particular interest since they represent an abundant, cheap, widely available worldwide renewable material. They represent a good option for substituting wood (Hurter 1997). Within the group of agricultural wastes, corn stalk can be considered as one of the most important in terms of production, as can be seen in Table 1. This is due mainly to the dramatic increment of corn crops used as a source for bioethanol production. In addition, in Europe and in U.S.A., most of these wastes are simply burnt or put underground in situ, thus increasing the risk of infestations and fire.

Table 1. Production of Agricultural Wastes (Hurter 1997).

Agricultural Waste	**BDMT/Year**
Cereals straw	1,250,000,000
Corn stalks	750,000,000
Grain and sweet sorghum stalks	252,000,000
Cotton stalks	68,000,000
Grass seed straw	3,000,000
Total	2,323,000,000

The potential uses of lignocellulosic materials from agricultural wastes as an alternative to wood for wood-plastic composites have received considerable attention in the literature. In our research group, several lignocellulosic fibers such as hemp, cannabis sativa, jute, sisal, flax, *alfa*, abaca, and pine fibers have been explored as reinforcement in composite materials (Vallejos et al. 2006; Girones et al. 2007; Méndez et al. 2007; Mutjé et al. 2007; Vilaseca et al. 2007a, 2007b, 2010). The corn stalk has a chemical composition similar to that of hardwood, and its fiber shows good strength properties (Han and Rowel 1997; Rodriguez et al. 2010). Therefore, corn stalk fibers can be considered a potential lignocellulosic agricultural waste product that could be used to replace wood as a fiber source in the production of wood-plastic composites.

Lignocellulosic raw materials can be processed in four different ways: mechanical, thermo-mechanical, semi-chemical, and chemical treatment. The first one comprises merely the mechanical milling of the lignocellulosic materials into flour. The rest of the treatments comprise the use of temperature and chemicals for extracting the fibers (Reddy and Yang 2005). The type and concentration of chemicals as well as time and temperature of treatment regulate the quality and characteristics of the fibers obtained. Thus, thermo-mechanical pulping (TMP) requires steam and a mechanical defibration treatment; the method provides a high yield of fibers, exceeding 90%. Semi-chemical pulping (SCP) requires the use of a NaOH solution and anthraquinone, a temperature of 155 ºC, and a period of 30 minutes; the yield is of about 65%. Chemical pulping (CP) delivers the lowest yield (50%) and requires more severe experimental conditions. The use of chemical and mechanical modified lignocellulosic materials as filler or reinforcement in thermoplastic composites is highly beneficial in terms of its properties, economics, and environmental aspects (Sreekala et al. 1997). Cost effective, easily available, and renewable lignocellulosic materials can be obtained from corn stalk wastes.

Natural fibers can be used as reinforcing materials in different polymeric matrices. One of the most important matrices is the group known as polyolefins. These oil-derived polymers are widely used as commodity plastics in a great variety of fields, ranging from packaging to car accessories (Scott 2000). Among them, polypropylene is a cheap, recyclable polyolefin that offers interesting properties that make it suitable for composite fabrication, such as good chemical resistance, dimensional stability, and processability. Because of that, PP is an interesting matrix for the fabrication of fiber-polymer based composites. On the other hand, natural fibers represent a good alternative as reinforcing materials, although fibreglass is still the most used reinforcement in industry (Vilaseca et al. 2007a). Fibreglass as a filler enhances mechanical properties of the polymeric matrices when it is added. However, the environmental disadvantages (non-biodegradability, difficult recycling, and origin from a non-renewable source), as well as wear in the processing equipment stand as its main disadvantages. Because of that, the main goal of the present study was the management of corn stalk wastes as a fiber source for reinforcement of composite materials. Thus, this paper deals with the preparation and characterization of four corn stalks derivatives (flour and fibers) by means of different treatments, and explores their suitability to be used as reinforcement in PP injection-moulded composites. In addition, the development of an efficient treatment/ modification method for corn stalk wastes to obtain fibers suitable for PP composites application is a target of this paper.

EXPERIMENTAL

Materials

Corn stalks were provided by Fundació Mas Badia (La Tallada d'Empordà, Spain). The polymeric matrix used was polypropylene ISPLEN 090 G2M (Repsol-YPF, Spain). In order to improve the compatibility between the polymer matrix and the reinforcing fiber, a maleic anhydride-grafted polypropylene (MAPP) coupling agent was used: Epolene® G3015 from Eastman (Netherlands). According to manufacturer, this material has an acid number of 17.4 mg KOH/g, and the number average and weight average of its molecular weights are M_n = 24800 g/mol and M_w = 47000 g/mol.

Preparation of Corn Stalks Derivatives

Corn stalks flour (CSf/M)

Integral corn stalks were chopped using a knives mill from Agrimsa (Torelló, Barcelona, Spain) equipped with a set of sieves. The obtained splits were sieved and classified by means of a strainer with a 10 mm pathway.

Corn stalk fibers

Corn stalk thermo-mechanical fibers (CSF/TMP) were prepared by subjecting chopped corn stalks to steam-water treatment, without further classification, maintaining the water-to-fiber ratio at 6:1. The corn stalks were heated at 160 ºC for 15 minutes, and the obtained pulp was rinsed with distilled water and then passed through Sprout-Waldron equipment. With this process, the final fiber increased its reactant surface due to a defibration mechanism. After this, the pulp was subjected to a classification stage using a Somerville screen in order to remove uncooked corn stalk chips.

For corn stalk semi-chemical fibers (CSF/SCP), the corn stalks were submitted to a sodium hydroxide/anthraquinone (AQ) cooking process (12.5% NaOH: 0.1% AQ) in a liquid to fiber ratio of 4:1, working at 160 ºC for 30 minutes. In the case of corn stalk chemical fibers (CSF/CP), corn stalks were submitted to a NaOH/anthraquinone (AQ) cooking process (20% NaOH: 0.1% AQ) in a liquid to fiber ratio of 4:1, working at 160 ºC for 60 minutes. Afterwards, the obtained pulped materials from semi-chemical and chemical treatments were rinsed profusely with water, passed through a Sprout-Waldrom single-disk refiner, and oven dried.

Finally, all the prepared corn stalk fibers were dispersed in a water-diglyme mixture (3:1) in order to facilitate their individualization during composite preparation. After dispersion, the pulp was filtered and dried at room temperature.

Composites Preparation

Polypropylene, corn stalk fibers or flour, and MAPP were dried before use in an oven (80 ºC without vacuum for 48 h). The composites were prepared by the addition of the polymer matrix and the reinforcement inside a Brabender plastograph internal mixer. The mixing procedure was carried out at 180 ºC and 80 rpm for 8 minutes. The obtained composites were pelletized with an Agrimsa Pelletizer. The pellets were then dehumidified with an oven at 80 ºC during 24 h.

Injection Molding

Pellets were injection-moulded into a Meteor-40 injection machine to obtain tensile specimens. The injection molding temperatures were in the range of 175 to 190 ºC. The first and second pressures were 120 and 37.5 kgf/cm^2, respectively.

Mechanical Characterization

Processed materials were placed in a conditioning chamber (Dycometal) at 23 ºC and 50% relative humidity during 48 hours, in accordance with ASTM D618, prior to testing. Afterwards, composites were assayed by using a universal testing machine (Instron^{TM} 1122), fitted with a 5 kN load cell. Tensile properties were analyzed according to ASTM D618. Results were obtained from the average of at least five samples.

Characterization of Corn Stalk Materials

For corn stalk wastes (CSW) and corn stalks derivates, the Klason lignin was determined by the conventional method as the fraction left insoluble after two-step acid hydrolysis (TAPPI standard, T222 om-98). Acid-soluble lignin was determined by applying the spectrophotometric method (TAPPI Standard, UM 250), viscosity by the capillary viscometer method (TAPPI Standard, T230 om-94), kappa number (TAPPI standard, T236 cm-85), coarseness (TAPPI Standard, T234 cm-84), and the length at break of a standard sheet of paper (ISO 1924-2). The standard sheet of paper was prepared according to TAPPI standards (TAPPI T205 sp-95).

The corn stalk fiber length and diameter were determined for the prepared fibers. Both lengths and diameters of the fibers were analyzed with a MORFI analyzer. An aqueous suspension of each fiber was prepared, and the average fiber length and diameter were calculated from the analysis of 30,000 fibers for each analysis.

Thermal Gravimetric Analysis

The thermal stabilities of the flour and fiber samples were measured using a Mettler Toledo instrument operating from 25 ºC to 800 ºC at 10 ºC/min heating rate under a nitrogen atmosphere. TGA analysis measures the weight change of the samples as a function of temperature or time under an inert atmosphere.

Morphological Study

Studies on the morphology of the fractured tensile samples of the composite were carried out by means of scanning electron microscopy (SEM) in order to visualize the fiber-matrix interface. Microphotographs of the samples were taken by means of a Zeiss DMS 960 SEM microscope. The microscope was operating at 25 kV, and the samples were gold sputtered and dried (10 nm layer coating) prior the observation.

RESULTS AND DISCUSSION

Characteristics of Corn Stalk Derivatives

Table 2 shows the results of chemical composition of corn stalk wastes (CSW), compared with softwood and hardwood results from literature. A comparison of these results revealed that the lignin content in corn stalk wastes was lower than softwoods and hardwoods investigated by Hurter (1997). The cellulose content in corn stalk wastes was in the ranges of those of softwoods and hardwoods, while the hemicellulose content was higher than those of softwoods and hardwoods.

Table 2: Chemical Composition of Wood and Corn Stalks

Source	Cellulose (%)	Pentosan (%)	Lignin (%)
Softwood[a]	40-50	8-12	26-32
Hardwood[a]	38-50	15-25	18-28
Corn stalks	48	28	16

a:(Hurter 1997)

Afterwards, corn stalk wastes were submitted to different treatments, and different corn stalk derivatives were obtained. The characteristics of these corn stalk materials, all of them suitable to be extruded for the preparation of plastic composites, are shown in Table 3. Milling, the simplest treatment, involves the size reduction of CSW to obtain a flour-like material, named corn stalk flour (CSf). This treatment is almost 100% yield, and the obtained corn stalk flour had the identical chemical composition of the original CSW. Its main characteristics are high content in fines (particles shorter than 200 μm), high coarseness, and short fiber length, compared to the other studied corn stalk products. The aspect ratio of corn stalks flour (CSf) was of 10.45, lower than the those obtained with corn stalk fibers of 30.45, 43.60, and 34.85 for CSF/TMP, CSF/SCP, and CSF/CP, respectively.

Similar to wood, corn stalk wastes were also transformed to thermo-mechanical fibers (CSF/TMP) by means of a process based on fiber steaming and further mechanical defibration. This high yield treatment mainly removes extractives such as fats, waxes, and pectin. Therefore, the thermo-mechanical pulp from corn stalks (CSF/TMP) practically conserves the same chemical composition of corn stalk wastes regarding the holocellulose and lignin. After defibration, the obtained final product is a fibrous material with an aspect ratio similar to thermo-mechanical pulp (TMP) fibers from wood (Mendez et al. 2007).

Table 3. Characteristics of Different Corn Stalk Materials Obtained from Corn Stalk Wastes (CSW)

Materials	CSf/M	CSF/TMP	CSF/SCP	CSF/CP
Treatment	Milling	Steam + defibration	NaOH:AQ + defibration	NaOH:AQ
Yield (%)	99.0	93.0	65.6	51.44
Lignin (%)	17.67	15.45	8.03	0.64
Kappa number	105	92	55	4.29
Fiber length (l^f) (μm)	242.22	676.33	1078.25	748.70
Fiber diameter (d^f) (μm)	23.17	22.28	24.73	21.48
Aspect Ratio (L/D)	10.45	30.35	43.60	34.85
Fines (%)	93.6	82.6	51.3	58.3
Coarseness (mg/100m)	795.4	47.79	16.04	15.07
Viscosity (mPas)	---	---	974.8	762.87
L_R (m)	---	650	2682	1691

AQ: anthraquinone, L_R: length at break of a standard sheet of paper.

Corn stalk wastes were also submitted to a soda-anthraquinone process. This method was chosen because it offers several advantages. In addition to a high yield, no acid residues are produced, and liquors from the process can be reutilized in composite materials. Depending on NaOH concentration and temperature, the process allows the preparation of semi-chemical pulps, whose yield is between 65 and 85%. In the present work, a procedure giving 65% yield was chosen, resulting in semi-chemical fibers with excellent morphological properties and low fines content compared to CSF/TMP. Coarseness also decreased compared to CSF/TMP. Considering the chemical composition indicated in Table 3, it can be seen that during pulping, a high amount of lignin was removed. An indication of the intrinsic strength of CSF/SCP fibers can be found in the length at break of a standard sheet of paper (ISO 1924-2) made from CSF/SCP fibers (TAPPI T205 sp-95). The length at break increased up to 4 times, demonstrating important changes in CSF/SCP compared to CSF/TMP, both chemically and morphologically. In the same way, its behaviour is similar to unbleached kraft fibers from hardwood (Mutjé et al. 2005; Mendez et al. 2007).

Finally, under strong NaOH concentrations, more time, and high temperature, the chemical pulp from corn stalks (CSF/CP) was obtained. For this type of corn stalk pulp, the content of lignin was almost negligible, and low coarseness was obtained, which is typical for chemical pulps. The aspect ratio of the obtained fibers was higher than CSf/M and CSF/TMP and lower than CSF/CP. The length at break of CSF/CP was inferior to CSF/SCP. The behaviour of CSF/CP is similar to that found for bleached and unbleached eucalyptus fibers (Mutjé et al. 2005).

Thermogravimetric Analysis

The changes in the corn stalk composition can be followed by thermogravimetric analysis. The thermogravimetric analysis applied to the four types of obtained corn stalk materials showed the presence of three main products in the corn stalk derivatives, as can be seen in Fig. 1. The first weight-loss temperature starting at 75 ºC corresponds to water and volatile matter, and is related to the extractives present in corn stalk derivatives. Apart from milling, the subsequent treatment applied to corn stalk wastes provided a decrease in the matter in this step, indicative of the extractives removal. Another weight loss is evident at T_{onset} of 250 to 260 ºC. The maximum weight loss at this step is found in corn stalks flour (CSf), and is progressively decreased in CSF/TMP, CSF/SCP, and CSF/CP, respectively. This weight change corresponds to the presence of lignin in the raw material, which is gradually eliminated in the different treatments, and it is almost zero in the chemical pulp of corn stalks fibers (CSF/CP). Finally, a weight loss temperature at 320 to 340 ºC corresponding to the degradation of hemicellulose and cellulose is found. This peak is the main component of every corn stalk material and represents around 50% in CSF/CP.

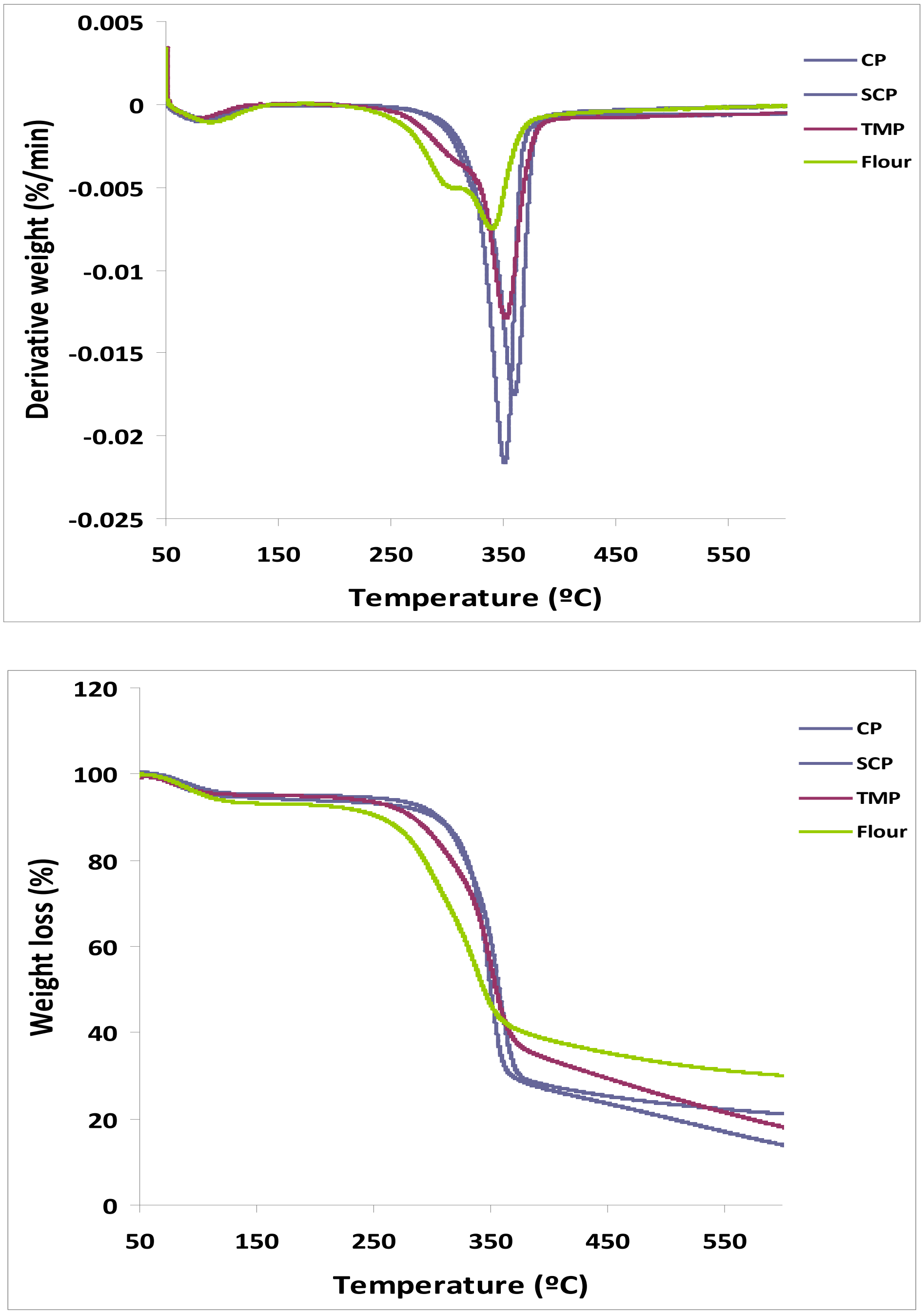

Fig. 1. (a) DTG and (b) TG curves of CSF/M, CSF/TMP, CSF/SCP, and CSF/CP

Tensile Properties of Corn Stalks Composites

Tensile properties of different corn stalk derivatives in PP matrix with and without coupling agent are shown in Table 4. It is clear that filler/fiber is of polar nature, and in order to achieve good tensile properties of the composites, it is necessary to use an interfacial coupling agent such as maleated polypropylene MAPP (Sanadi and Caulfield 2000; Sain et al. 2005). The amount of coupling agent was optimized for PP composites of CSF/SCP and was found to be 6% (wt/wt) with respect to the fiber content (Rodriguez et al. 2010). Afterwards, the same amount of coupling agent was applied to the rest of the composites in view to a comparative study.

Table 4: Tensile Properties of Different Corn Stalks / PP Composites

Materials	MAPP (%)	%, filler/fiber content (w/w)	σ_t (MPa)	E_t (GPa)	ε_t (%)
PP	-	-	27.60 (0.50)	1.10 (0.10)	9.30 (0.20)
PP+CSf/M	0	40	21.05 (0.79)	3.36 (0.10)	2.07 (0.20)
	6	40	32.15 (0.95)	3.38 (0.15)	2.71 (0.10)
PP+CSF/TMP	0	40	26.10 (0.30)	3.75 (0.10)	2.60 (0.10)
	6	40	38.48 (0.60)	3.80 (0.05)	3.35 (0.40)
PP+CSF/SCP	0	40	34.10 (0.70)	4.30 (0.20)	2.10 (0.20)
	6	40	49.50 (0.90)	4.30 (0.10)	4.30 (0.40)
PP+CSF/CP	0	40	25.80 (0.30)	3.70 (0.10)	2.00 (0.20)
	6	40	41.58 (0.83)	3.65 (0.09)	3.97 (0.18)

Composites from corn stalks flour

The tensile strength (σ_t) of coupled composites dramatically improved when compared to the PP matrix and those composites without coupling agent. Thus, the increment was about 16% with respect the plain matrix, and about 52% with the same composite without the coupling agent. It is worth noting that the addition of corn stalk flour drastically decreased the tensile strength of the matrix, as it behaved as a foreign material and resulted in matrix discontinuity. The tensile strength of its composite was really low for both composites, without or with coupling agent. This behaviour indicates that corn stalk flour can be used only as filler in wood-like plastic composites due to the low mechanical properties, compared to the other corn stalk composites, especially to CSF/SCP composites.

In the literature, one can find only one reference concerning corn stalks flour/PP composites (Sain et al. 2005). In that case, corn stalk flour was obtained by means of a Wiley Mill, and they found very good results (tensile strength of about 45MPa for composites comprising 40wt %). These results are also similar to those found with wood flour (Yeh and Gupta 2008; Lee and Kim 2009). Another similarity to wood flour was given by Sain et al. (2005) using HDPE matrix. With respect to Young’s modulus, the obtained results are in the ranges of those found by Sain et al. (2005) and Kim et al. (2009). These results were somehow superior to those given by Lee and Kim (2009), but inferior to the ones provided by Yeh and Gupta (2008). The increase in the rigidity produced a huge diminishing of the plastic deformation, which increased with the addition of coupling agent.

Composites from corn stalks fibers

The corn stalk fibers also resulted in a decrease in the tensile strength of the matrix, with an exception given to semichemical corn stalk fibers (CSF/SCP), which increased the matrix strength by 24%. Therefore, only the addition of MAPP coupling agent showed a positive effect on tensile strength of corn stalk composites. The results from Table 4 show that those coupled composites comprising 40% (wt/wt) of CSF/TMP, CSF/SCP, or CSF/CP had respectively a tensile strength of 38.48, 49.5, and 41.58 MPa. Therefore, the tensile strength of the plain matrix increased by 40% for composites of CSF/TMP, by 80% for composites of CSF/SCP, and by 50.5% for composites of CSF/CP.

After treatment, CSF/TMP fibers are constituted by the same holocellulose and lignin content as corn stalk flour (CSf), with exception of the extractives fraction, soluble in water at 160 ºC. The surface composition of CSF/TMP is determined by the layer from which the defibering has taken place. As shown in Fig. 2, the proportion of lignin, hemicelluloses, and cellulose varies from the middle lamella to the primary or secondary walls. Therefore, the surface composition of the thermomechanical pulp of corn stalk fibers will be higher in lignin if the defibering takes place between the middle lamella and the primary wall, or higher in holocellulose if separation occurs between or within the S_1 and S_2 layers (Garcia 2007). For the present case, where the defibering was carried out under steam conditions at a temperature of 160 ºC, the surface composition should be close to 65% holocellulose and 35% lignin, corresponding to a defibration event within the S_1/S_2 layers (Garcia 2007). This hypothesis justifies the increase in the tensile strength of CSF/TMP composite by the addition of a coupling agent. The hydroxyl groups present at corn stalks thermomechanical pulp surface, mainly due to the amount of holocellulose exhibiting after defibering, will be able to interact with MAPP coupling agent resulting in improved tensile strength of its composite. The OH-groups mainly present in the lignin molecule from thermomechanical fiber at surface fiber are in their condensed state, which renders these groups from lignin polymer less reactive toward esterification reaction or hydrogen bonding with carboxyl groups of the MAPP polymer.

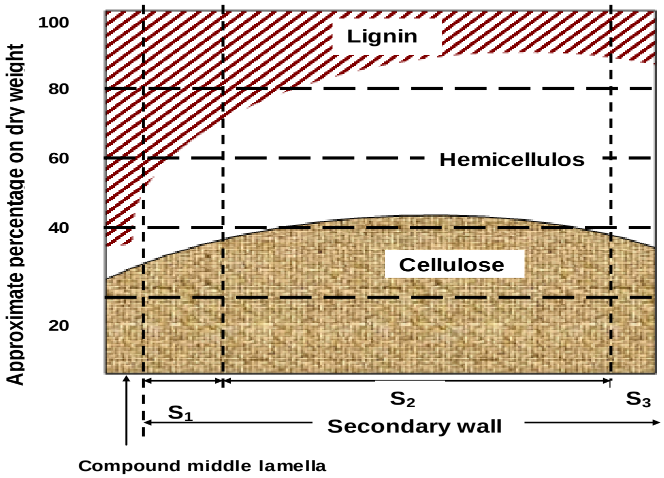

Fig. 2. Chemical composition of wood fiber along the fibril structure

Corn stalk wastes submitted to an alkaline process produced semichemical pulp (CSF/SCP), used as reinforcement of PP composite with elevated tensile strength. The tensile strength of CSF/SCP was about 49.5 MPa, 28.6% over that found for CSF/TMP. Therefore, semichemical pulp of corn stalk wastes can be considered as a reinforcing substitute of composites comprising up to 20% (wt/wt) of sized-glass fiber (Lopez et al. 2011). Considering the treatment itself, the yield to produce semichemical pulp of corn stalks is smaller (65%) than that found for thermomechanical pulp (93%). However, the intrinsic quality of semichemical corn stalks fibers is superior to thermomechanical corn stalks fibers. The theory of the complex lignin-hemicelluloses states that this complex is easily removed as a whole when the chemical treatment is applied to lignocellulosic material (Garcia 2007). This complex represents 44% by weight of corn stalk wastes. After chemical characterization, CSF/SCP showed 8.25% of lignin. According to this, the lignin content was halved during the process, and a higher amount of hemicelluloses must be removed. In this case the defibering was also carried out under conditions that favour the delamination between S_1 and S_2 layers (Garcia 2007). Therefore, the surface composition of the semichemical fibers will be rich in cellulose and contain a depolymerised lignin in moderate quantities.

The large improvement of the tensile strength observed for this type of composites can be accounted for by two different theories. The first one refers to the higher amount of hydroxyl groups at the fiber surface due to the S_1/S_2 delamination that extends the chemical reaction with the coupling agent. The higher amount of hydroxyl groups is mainly due to the increase of cellulose fraction at the fiber surface, and also the increase of hydroxyl groups present in lignin molecules caused by the alkaline treatment. Therefore, lignin becomes more reactive toward the esterification reaction or hydrogen bonding at the interface. The appearance of new hydroxyl groups after alkaline treatment of lignocellulosic materials in lignin molecules is due to the cleavage of ether bonds, such as α and β-O-4, which are the major linkages in a lignin molecule (El Mansouri et al. 2006). The second theory is related to substantial modification of the chemical composition of the fiber, thus affecting the intrinsic mechanical properties of the reinforcing fibers. Possibly, both theories can occur simultaneously. According to Bledzki and Gassan, alkali treatment tends to remove the lignin and hemicellulose, thus affecting the tensile characteristics of the fibers (Bledzki and Gassan 1999; Gassan and Bledzki 1999). When the hemicellulose is removed, the interfibrillar region is likely to be less dense and less rigid, making the fibrils more capable of rearranging themselves along the direction of tensile deformation. Subsequently, when natural fibers are stretched, the fibril rearrangement would result in better load sharing and, therefore, higher stress development of the fiber. On the other hand, as lignin is removed gradually, the middle lamella joining the ultimate cells is expected to be more plastic and homogeneous due to the gradual elimination of microvoids. Other authors have reported changes in the crystallinity through alkaline treatment of natural fibers (Varma et al. 1984; Sharma et al. 1995; Sreenivasan et al. 1996). The increase in the crystallinity index of alkali treated fibers occurs because of the removal of the cementing materials, which leads to better packing of cellulose chains (Varma et al. 1984).

For CSF/CP composites, the tensile strength drops down until the stress values correspond to those of bleached or unbleached kraft pulp composites. These kraft fibers are provided from low yield processes and generally exhibit very low Kappa numbers (Beg and Pickering 2008; Gironès et al. 2008). According to Neagu et al., when the kappa number is changed (see Table 2), both the carbohydrate chemical composition and cellulose molecular weight of the fibers will simultaneously change (Neagu et al. 2006). A yield pulp process of 50% is equivalent to almost complete removal of lignin and hemicelluloses. In our case, the obtained Kappa number (4.92) was indicative that the percentage of lignin had been significantly reduced. Therefore, the drop on the tensile strength of severe alkaline treated fibers was not only due to the complete removal of lignin and hemicelluloses, but also to a depolymerisation of cellulose chains, which is corroborated by the decrease of viscosity of CSF/SCP and CSF/CP fibers, from 974.8 to 762.87 mPas, respectively. Therefore, the CSF/CP fibers are chemically damaged, and their composites must present poor tensile strength.

The results from Table 4 show that those non-coupled composites comprising 40% (wt/wt) of CSF/TMP, SCF/SCP, and CSF/CP had respectively a Young's modulus of 3.75, 4.30, and 3.70 GPa. Therefore, the young's modulus was 3.41 higher for the composites of CSF/TMP, 3.90 higher for the composites of CSF/SCP, and 3.36 higher for the composites of CSF/CP, than that of plain matrix. Consequently to the stiffness of the composites, the elongation at break (ε_t^c) decreased significantly with the addition of corn stalk fibers. The results are in agreement with the expected increase of the materials' stiffness and the reduction of the capacity to sustain plastic deformation (Vilaseca et al. 2010). For the coupled composites, it can be observed that Young's modulus did not improve the stiffness.

Morphology Characteristics

Scanning electron microscopy (SEM) is an effective characterization method for morphological investigations of composites. The tensile fracture surface for composites of 40% (wt/wt) CSF/SCP (a) without, and (b) with 6% (wt/wt) MAPP coupling agent, are shown in Fig. 3.

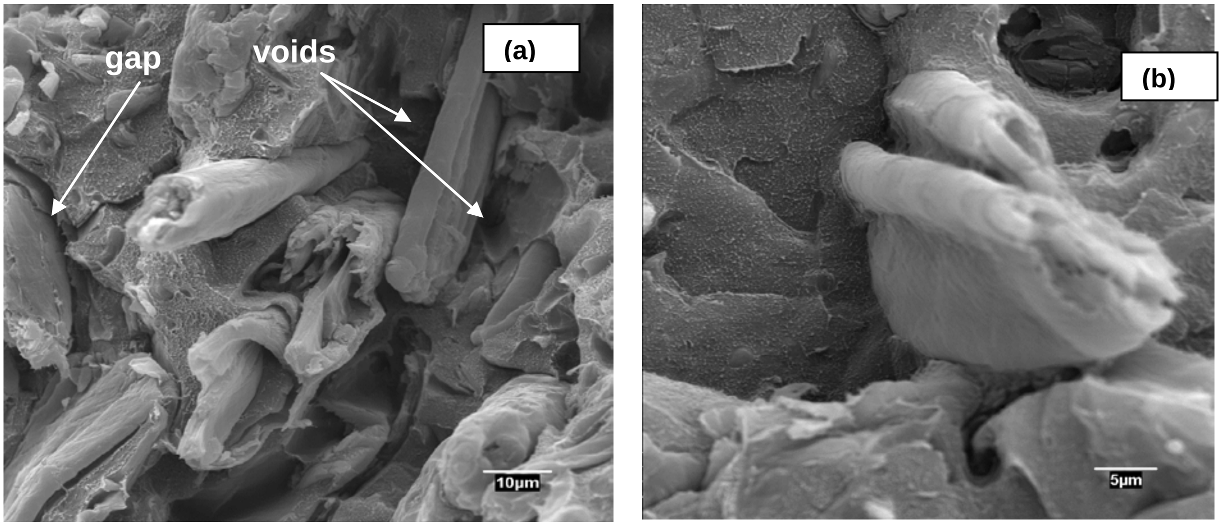

Fig. 3. SEM microphotographs of the tensile fracture surface for composites of 40% (wt/wt) CSF/SCP (a) without, and (b) with 6% (wt/wt) MAPP coupling agent

This formulation was chosen for SEM analysis because of its excellent tensile strength results. In Fig. 3(a), examination of the cryo-facture surface of the composite without coupling agent showed the presence of voids, indicating fiber pull-out and large gaps between the CSF/SCP fibers and PP matrix, which corroborates the weak interfacial adhesion at the interface (Ashori and Nourbakhsh 2010; Poletto et al. 2011). The SEM microphotograph of the coupled composite in Fig. 3(b) shows strong bonding and reduced evidence of fiber pull-out. This result demonstrates that MAPP addition to the composites provides strong interfacial adhesion, as evidenced by the almost complete absence of voids in the polymer matrix and gaps between fiber and the matrix (Ashori and Nourbakhsh 2010; Poletto et al. 2011)

CONCLUSIONS

1. The corn stalk derivatives (flour and fibers) able to be used as reinforcement in composite materials from corn stalk wastes showed different physico-chemical properties.
2. Corn stalk flour (CSF) used as filler and coupled with the matrix can be valuable for the preparation of composites with similar properties to wood-plastic composites because of its lower mechanical properties.
3. Corn stalk fibers from semichemical pulp (SCF/SCP) coupled with the matrix gave PP composites superior mechanical properties and similar technical requirements to fibreglass/PP composites, due to its excellent chemical properties.
4. Corn stalk fibers from thermomechanical (SCF/TMP) and chemical pulp (CSF/CP) do not show interesting properties when used as reinforcing material, and their characteristics seem to be more suitable for the fabrication of paper and boards.
5. The tensile strength and modulus of the composites could be improved by using coupling agent due to the improvement of the interfacial bonding between the fiber and matrix. SEM study also shows that interfacial adhesion between the fiber and the matrix is improved with the addition of MAPP coupling agent.
6. Finally, the present work reveals that corn stalk wastes can be highly beneficial as raw materials for the preparation of plastic composites.

ACKNOWLEDGMENTS

The authors are thankful to the Catalan Government and the University of Girona for funding the research by the specific Research Program.

REFERENCES CITED

Ashori, A., and Nourbakhsh, A. (2010). "Bio-based composites from waste agricultural residues," *Waste Management* 30(4), 680-684.

Beg, M. D. H., and Pickering, K. L. (2008). "Accelerated weathering of unbleached and bleached Kraft wood fibre reinforced polypropylene composites," *Polymer*

Degradation and Stability 93(10), 1939-1946.

Bledzki, A. K., and Gassan, J. (1999). "Composites reinforced with cellulose based fibres," *Progress in Polymer Science* 24(2), 221-274.

El Mansouri, N. E., Farriol, X., and Salvado, J. (2006). "Structural modification and characterization of lignosulfonate by a reaction in an alkaline medium for its incorporation into phenolic resins," *Journal of Applied Polymer Science* 102(4), 3286-3292.

English, B., Chow, P., and Bajwa, D. S. (1996). "Processing into composites," in: Rowell, R. M., Young, R. A., and Rowell, J. K. (eds.), *Paper and Composites from Agro-Based Resources*, CRC Press, Boca Raton.

Gassan, J., and Bledzki, A. K. (1999). "Alkali treatment of jute fibers: Relationship between structure and mechanical properties," *Journal of Applied Polymer Science* 71(4), 623-629.

Garcia, H. J. A. (2007). *Fibras Papeleras*, Edicions UPC, Barcelona.

Girones, J., Mendez, J. A., Boufi, S., Vilaseca, F., and Mutje, P. (2007). "Effect of silane coupling agents on the properties of pine fibers/polypropylene composites," *Journal of Applied Polymer Science* 103(6), 3706-3717.

Girones, J., Pimenta, M. T. B., Vilaseca, F., Carvalho, A. J. F., Mutje, P., and Curvelo, A. A. S. (2008). "Blocked diisocyanates as reactive coupling agents: Application to pine fiber-polypropylene composites," *Carbohydrate Polymers* 74(1), 106-113.

Han, J. S., and Rowell, J. S. (1997). "Chemical composition of fibers," in: Rowell, R. M., Young, R. A., and Rowell, J. K. (eds.), *Paper and Composites from Agro-Based Resources*, CRC Press, Boca Raton.

Hurter, R. W. (1997). "Nonwood plant fiber characteristics," *In*: *Agricultural Residues*. TAPPI Nonwood Fibers Short Course Notes.

Kim, J. W., Harper, D. P., and Taylor, A. M. (2009). "Effect of wood species on the mechanical and thermal properties of wood-plastic composites," *Journal of Applied Polymer Science* 112(3), 1378-1385.

Lee, H., and Kim, D. S. (2009). "Preparation and physical properties of wood/ polypropylene/clay nanocomposites," *Journal of Applied Polymer Science* 111(6), 2769-2776.

López, J. P., Méndez, J. A., El Mansouri, N.-E., Mutjé, P., and Vilaseca, F. (2011). "Mean intrinsic tensile properties of stone ground wood fibers from softwood," *BioResources* 6(4), 5037-5049.

Mendez, J. A., Vilaseca, F., Pelach, M. A., Lopez, J. P., Barbera, L., Turon, X., Girones, J., and Mutje, P. (2007). "Evaluation of the reinforcing effect of ground wood pulp in the preparation of polypropylene-based composites coupled with maleic anhydride grafted polypropylene," *Journal of Applied Polymer Science* 105(6), 3588-3596.

Mutje, P., Lopez, A., Vallejos, M. E., Lopez, J. P., and Vilaseca, F. (2007). "Full exploitation of *Cannabis sativa* as reinforcement/filler of thermoplastic composite materials," *Composites Part a-Applied Science and Manufacturing* 38(2), 369-377.

Mutje, P., Pelach, M. A., Garcia, J. C., Presta, S., Vilaseca, F., and Jimenez, L. (2006). "Comparison of cationic demand between olive wood organosolv pulp and eucalyptus kraft pulp," *Process Biochemistry* 41(7), 1602-1607.

Neagu, R. C., Gamstedt, E. K., and Berthold, F. (2006). "Stiffness contribution of various

wood fibers to composite materials," *Journal of Composite Materials* 40(8), 663-699.
Poletto, M., Dettenborn, J., Zeni, M., and Zattera, A. J. (2011). "Characterization of composites based on expanded polystyrene wastes and wood flour," *Waste Management* 31(4), 779-784.
Reddy, N., and Yang, Y. Q. (2005). "Structure and properties of high quality natural cellulose fibers from cornstalks," *Polymer* 46(15), 5494-5500.
Rodriguez, M., Rodriguez, A., Bayer, J., Vilaseca, F., Girones, J., and Mutje, P. (2010). "Determination of corn stalk fibers' strength through modeling of the mechanical properties of its composites," *BioResources* 5(4), 2535-2546.
Sain, M., Suhara, P., Law, S., and Bouilloux, A. (2005). "Interface modification and mechanical properties of natural fiber-polyolefin composite products," *Journal of Reinforced Plastics and Composites* 24(2), 121-130.
Sanadi, A. R., and Caulfield, D. F. (2000). "Transcrystalline interphases in natural fiber-PP composites: Effect of coupling agent," *Composite Interfaces* 7(1), 31-43.
Scott, G. (2000). "'Green' polymers," *Polymer Degradation and Stability* 68(1), 1-7.
Sharma, H. S. S., Fraser, T. W., McCall, D., Shields, N., and Lyons, G. (1995). "Fine structure of chemically modified flax fibre," *Journal of the Textile Institute* 86(4), 539-548.
Sreekala, M. S., Kumaran, M. G., and Thomas, S. (1997). "Oil palm fibers: Morphology, chemical composition, surface modification, and mechanical properties," *Journal of Applied Polymer Science* 66(5), 821-835.
Sreenivasan, S., Iyer, P. B., and Iyer, K. R. K. (1996). "Influence of delignification and alkali treatment on the fine structure of coir fibres (*Cocos nucifera*)," *Journal of Materials Science* 31(3), 721-726.
Vallejos, M. E., Canigueral, N., Mendez, J. A., Vilaseca, F., Corrales, F., Lopez, A., and Mutje, P. (2006). "Benefit from hemp straw as filler/reinforcement for composite materials," *Afinidad* 63(525), 354-361.
Varma, D. S., Varma, M., and Varma, I. K. (1984). "Coir fibers.1. Effect of physical and chemical treatments on properties," *Textile Research Journal* 54(12), 827-832.
Vilaseca, F., Mendez, J. A., Canigueral, N., Turon, X., Barbera, L., Gironses, J., Pimenta, M. T. B., Pelach, M. A., and Mutje, P. (2007a). "Biodegradable composite materials from starch-based biopolymer and hemp strands," *Afinidad* 64(527), 22-24.
Vilaseca, F., Mendez, J. A., Pelach, A., Llop, M., Canigueral, N., Girones, J., Turon, X., and Mutje, P. (2007b). "Composite materials derived from biodegradable starch polymer and jute strands," *Process Biochemistry* 42(3), 329-334.
Vilaseca, F., Valadez-Gonzalez, A., Herrera-Franco, P. J., Pelach, M. A., Lopez, J. P., and Mutje, P. (2010). "Biocomposites from abaca strands and polypropylene. Part I: Evaluation of the tensile properties," *Bioresource Technology* 101(1), 387-395.
Yeh, S. K., and Gupta, R. K. (2008). "Improved wood-plastic composites through better processing," *Composites Part A-Applied Science and Manufacturing* 39(11), 1694-1699.

Article submitted: January 22, 2012; Peer review completed: February 26, 2012; Revised version received and accepted: February 27, 2012; Published: March 1, 2012.