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Recovered and recycled Kraft fibers as reinforcement of PP composites

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Abstract

Recycled Kraft fibers coming from old sacs were used for the preparation of polypropylene (PP) composites. Composites up to 50 wt.% of reinforcement were obtained and maleated polypropylene (MAH-PP) was used as coupling agent for improving the fiber–matrix compatibility and adhesion. In the present work, the mechanical properties of the obtained composites as well as the evaluation of interfacial behavior are studied. The results discussion is based on the analysis of the mechanical properties of composites, measurements of surface polarity, specific surface, fiber dimensions, spectroscopic and microscopic analysis. Different adhesion mechanisms at fiber–matrix interface must be presumed depending on the existence of MAH-PP coupling agent, as revealed the analysis of the modification reaction and the conducted proofs. The results showed that the addition of maleated polypropylene favored the incorporation of the relatively high amounts of this natural reinforcement and promoted the stress transfer inside the composite. Thus, an increase up to 50 wt.% of recycled Kraft fibers increased two times the ultimate tensile strength of the non-reinforced matrix. Additionally, the intrinsic mechanical properties of recycled Kraft fibers are deduced by means of modified rule of mixtures and compared to those available in the literature. Finally, an approach of the industrial competitiveness of these fibers, daily present in the market, with respect to E fiberglass is carried out. For this reason a comparison between the mechanical properties and the final cost of PP composites from recycled Kraft fibers or E fiberglass has been considered.

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1. Introduction

The recovery and recycling of lignocellulosic fibers has experienced an important increase in the last years. In 2004, the apparent consumption of virgin cellulosic fibers for papermaking purposes was around 188 millions tones in all over the world. The apparent consumption of recovered paper in the world during the same year was 177 millions tones. This value was only a 6.2% lower than the apparent consumption of virgin fibers [1]. From these values, it can be observed that the availability of this raw material is really important and their importance will grow when the consumption per capita of paper in developing countries achieves comparable values of developed countries.

For the paper industry, the main attraction of secondary fibers is their low economic cost as well as their assured existence in the market. This raw material is extensively used as fiber provider in papermaking industries but the processes associated to their preparation are relatively complicated. It is necessary to remove ink and contaminants from the fiber source to obtain a good quality of new paper. All depuration processes related with their adaptation decreases the final yield of the process, being in some cases around 75%.

Recovered paper coming from old sacs is mainly composed of unbleached softwood fibers. These fibers might impart high mechanical properties to the paper, once submitted to refining process, because they show better intrinsic mechanical properties compared to hardwood fibers. Additionally, the bibliographic data held that the intrinsic mechanical properties of softwood fibers are higher than those of natural fibers from annual plants [2].

The recovered paper could be totally included as reinforcement in polymeric matrices with a yield around 100%. Moreover, it also has to be considered the market prices of these pulps, because while virgin softwood fibers cost around 0.55 €/kg and hemp fiber (annual plant) around 0.4 €/kg, the cost of recycled softwood fibers from recovered paper is roughly 0.1 €/kg.

In general, cellulosic fillers/fibers can be classified under three categories depending on their performance when

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incorporated in a plastic matrix. Wood flour and other low cost agricultural based flour can be considered as particulate fillers that enhance the tensile and flexural moduli of the composite with little effect on the composite strength. Wood fibers and recycled newspaper fibers have higher aspect ratios and contribute to an increase in the moduli of composite and can slightly improve stress transfer between the matrix and the fibers. The most efficient cellulosic additives are some natural strands such as kenaf, jute, flax [3]. However, this fact is not in accordance with the intrinsic mechanical properties stated by some bibliography for softwood fibers and plant strands [2]. According to this literature, the tensile strength (1000 MPa) and Young's modulus (40 GPa) of softwood fibers would be significantly higher than those of cotton, jute, hemp, flax or sisal [2]. Conversely, looking at the mechanical properties of the composite, the specific Young's modulus and specific flexural modulus of composites with plant strands are significantly higher than those possible with wood fibers. Therefore, the specific modulus of high fiber volume fraction bast strands-PP composites is in the range of glass fibers-PP composites [3].

Among all thermoplastic matrices, polypropylene (PP) is one of the commodity thermoplastics with greater properties because its low density, high vicat softening point, good surface hardness, good flex life, scratch resistance, abrasion resistance and very good electrical properties [4].

In this study, recycled Kraft fibers (recycled softwood fibers) coming from old sacs were used as reinforcement for the preparation of polypropylene composites. Composites comprising 20, 30, 40 and 50 wt.% of reinforcement were obtained and the use of maleated polypropylene as coupling agent was studied. Additionally, the quality of the interface was evaluated in terms of plausible chemical bonding at fiber–matrix interface. Spectroscopic (FTIR), microscopic (SEM) techniques and the polarity of the fiber surface before and after treatment were used to evaluate the fiber–matrix interactions. The mechanical properties of the obtained composites were also analyzed.

2. Experimental methods

2.1. Materials

Recycled packaging sacs were used as cellulosic fiber resource. The packaging sacs were originally composed of cellulose Kraft fibers coming from softwood. The wetness of the recycled softwood fibers was 22–24 °SR measured according to ISO 5267-1. The Kappa number (lignin amount) of the recycled softwood fiber was 27.6, measured according to TAPPI 236 cm-85. Alkyl ketene dimmer (AKD) emulsion from Eka Chemicals Iberica S.A. (Barcelona, Spain) was used for chemical treatment of recycled softwood fibers. E fiberglass from Vetrotex (Chambéry Cedex, France) were supplied by Maben SL (Banyoles, Spain). The average length of glass fibers was around 3.3 mm and contained a sizing agent for compatibilization. PP (Isplen 090 G2M, Repsol-YPF$^{\text{TM}}$) was used as polymer matrix. Poly(propylene)-co-maleic anhydride (MAH-PP) (Epolene G 3015, Eastman [acid number: 15 mg KOH/g, Mn: 24.8×10^3 Da]), was used as coupling agent as received. Commercial toluene supplied by Sigma Aldrich S.A. was used as solvent for the modification reaction. Commercial xylene from Sigma Aldrich S.A. was used to wash the chemically modified Kraft cellulosic fibers.

2.2. Disintegration process

Packaging sacs composed of different paper layers were submitted to disintegration process for cellulose fiber individualization. The disintegration was carried out in alkali medium (1% of NaOH respect to pulp weight) at 50 °C using a helicon rotor. The disintegration was kept for 15 min and the suspension was then neutralized and filtered to obtain the individualized cellulose fibers. Cellulose fibers were dried in stove at 80 °C until the moisture content was 12%.

2.3. Specific surface measurement

Specific surface area of fibers was determined with a Pulmac instrument [5] based on the Kozeny–Carman equation. Assuming a linear flow of a Newtonian liquid it is possible to obtain a value of the hydrodynamic specific surface by application of the following equation:

$$\left(\frac{C_i}{\mathrm{Rp}_i}\right)^{1/3} = \left(\frac{1}{h_{\mathrm{k}}\sigma^2}\right)^{1/3}(1 - \alpha C_i) \tag{1}$$

where h_{k} is the Kozeny–Carman constant (equal to 5.55), σ the hydrodynamic specific surface ($\mathrm{m^2\,kg^{-1}}$), α the specific volume of particles ($\mathrm{m^3\,kg^{-1}}$), C_i the consistency of suspension ($\mathrm{kg\,m^{-3}}$) and Rp_i is the specific filtration resistance ($\mathrm{m\,kg^{-1}}$).

2.4. Polarity measurement

Polarity of recycled softwood fibers and polypropylene was evaluated through colloidal titration with methyl-glycol chitosan (MGCh). The cationic demand of fiber or polymer suspensions was calculated using the colloidal titration technique developed by Terayama [6] and later applied by different research teams [7,8]. Four milliliters of MGCh from Wako Chemicals GmbH (Neuss, Germany) was added to 25 ml suspension of finely powdered substrates at 1% consistency. After magnetic stirring for 1 min, the suspension was centrifuged for 15 min at 3000 rpm. Afterwards, 10 ml of the above suspension was submitted to titration with the standard potassium polyvinyl sulphate (PVSK) solution (N/400 concentration, fa activity) from Wako Chemicals GmbH (Neuss, Germany) and cationic polymer not fixed on the substrate was measured. *O*-Toluidine blue from Sigma–Aldrich Chemie (Steinheim, Germany) was used as indicator. Polarity results are given in μequiv. of MGCh per gram of substrate, so polar substrates will show higher cationic polymer absorption than non-polar substrates.

2.5. AKD treatment

Recycled softwood fibers were submitted to chemical treatment with AKD. Recycled softwood fibers were soaked for

20 min in a 2.4% AKD emulsion at 60 °C. The consistency in the emulsion was 10 g l^{-1}. The treated recycled softwood fibers were rinsed several times with water and distilled water and let to dry at room temperature before being oven dried at 105 °C until constant weight was achieved. Un-treated recycled softwood fibers were also oven dried.

2.6. Modification reaction

The modification reaction between the cellulose fibers and maleated polypropylene was studied. Recycled cellulose fibers previously dried were placed in a reaction flask equipped with refrigerator and a 3 wt.% of Epolene G-3015 was added. The mixture was kept under refluxing for 20 min and then was filtered and washed with hot toluene. Afterwards, modified cellulose fibers were dried at 80°C for 12 h and washed with xylene in a soxhlet apparatus for 8 h to remove the non-covalent bonded material.

2.7. Floatability test

The hydrophobicity of recycled softwood fibers, before and after modifications, was evaluated by means of a floatability test [9]. The un-treated or modified recycled softwood fibers were introduced in an aqueous/organic mixture of water–hexane 50:50. The relative position of the recycled softwood fibers in the mixture was evaluated.

2.8. Composite preparation

Recycled softwood fibers comprising 12% of moisture content were used as reinforcement of PP composites. Composites at 20, 30, 40 and 50 wt.% of reinforcement were obtained by means of an internal mixer (Brabender plastograph). Maleated polypropylene (MAH-PP) Epolene G-3015 was incorporated as coupling agent to improve the fiber–matrix compatibility. For the composite blend preparation, PP was melted at 190 °C with a mixing rate of 80 rpm and the reinforcement was added directly without pre-drying. Afterwards, blends were obtained working at 80 rpm for recycled softwood fibers composites and 20 rpm for E fiberglass composites. Volatiles were allowed to be removed from the mixture. For those composites containing MAH-PP coupling agent, PP and MAH-PP were mixed before the addition of the reinforcement. Composite blends were granulated in a blade mill (Agrimsa) equipped with a strainer of 10 mm nominal size. The pellets were moulded using an injection-moulding machine (40-Mateu&Soler) to obtain specimens. The steel mould was according to ASTM D3641 standard. The specimens were conditioned according to ASTM D618 standard before testing (23 °C and 50% relative humidity for 3 days).

2.9. Mechanical tests

Tensile properties of polypropylene and composites were determined using an INSTRON testing machine (model 1122). Tensile strength measurements and three-point bending tests were carried out following ASTM D638 and ASTM D790 standard methods. The impact strength was measured according to ASTM D6110 using a Charpy apparatus provided with a hammer of 2.074 kg weight and 382 arm length. All the results were taken as the average of five samples. For each composite blend, five specimens were tested.

2.10. Characterization methods

ATR-FTIR technique was used to validate the modification reaction. FTIR spectra of recycled softwood fibers, AKD treated recycled softwood fibers and recycled softwood fiber

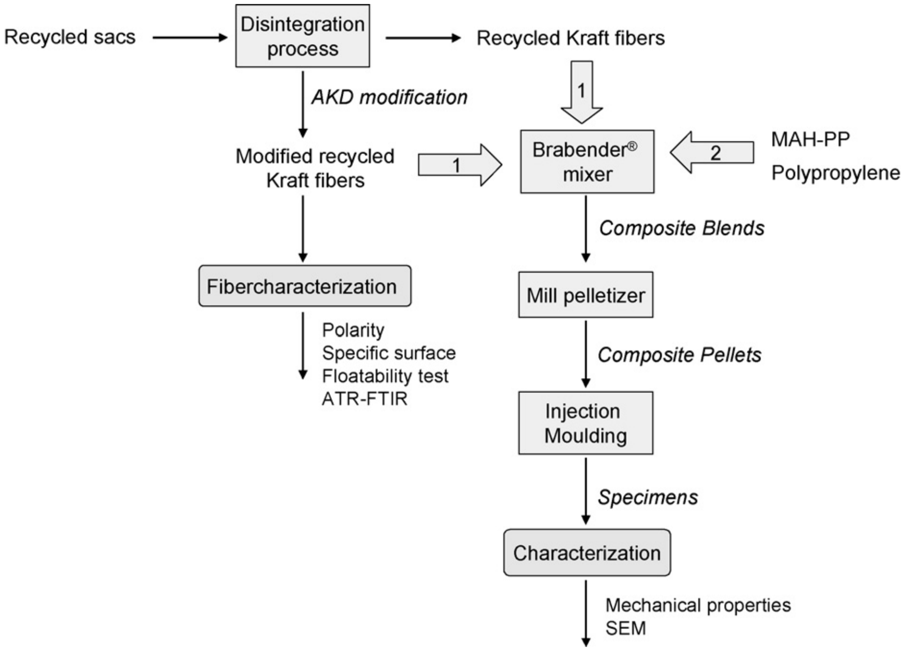

Fig. 1. Flow chart for composite preparation and characterization.

Table 1
Mechanical properties of recycled Kraft fiber/PP composites

Reinforcement (%)	σ_t (MPa) [S.D.]	ε_t (%) [S.D.]	E_t (GPa) [S.D.]	σ_f (MPa) [S.D.]	E_f (GPa) [S.D.]	I (kJ m^{-2}) [S.D.]
Recycled Kraft fiber/PP composites without MAH-PP						
0	27.6 [0.5]	9.3 [0.2]	1.1 [0.1]	40.2 [1.0]	1.1 [0.1]	–
20	29.8 [0.3]	3.8 [0.3]	2.0 [0.2]	51.8 [0.8]	1.9 [0.3]	21.1 [1.5]
30	32.4 [0.9]	3.5 [0.3]	2.51 [0.3]	54.2 [1.5]	2.6 [0.3]	17.8 [1.4]
40	34.3 [0.6]	3.3 [0.4]	3.08 [0.2]	55.2 [1.1]	4.0 [0.04]	17.8 [1.4]
50	33.1 [0.8]	3.1 [0.2]	3.68 [0.2]	53.4 [1.4]	4.5 [0.1]	16.1 [1.1]
Recycled Kraft fiber/PP composites with 6% of MAH-PP						
0	27.6 [0.5]	9.3 [0.2]	1.1 [0.1]	40.2 [1.0]	1.1 [0.1]	–
20	36.5 [0.2]	4.9 [0.2]	2.1 [0.03]	55.2 [1.0]	2.2 [0.04]	22.6 [1.9]
30	40.6 [0.8]	4.4 [0.4]	2.54 [0.04]	64.4 [3.2]	2.9 [0.2]	20.0 [1.4]
40	49.0 [0.7]	4.2 [0.2]	3.15 [0.2]	81.9 [1.2]	3.8 [0.07]	21.2 [1.4]
50	55.1 [0.7]	3.7 [0.1]	3.70 [0.09]	88.9 [2.5]	4.4 [0.2]	20.1 [0.2]

S.D., standard deviation.

extracted from the composites were recorded using a Mattson Satellite spectrometer equipped with a MKII Golden Gate Reflection ATR System. Each spectrum was recorded by co-adding 64 scans at 4 cm^{-1} optical resolution within the range 600–4000 cm^{-1}. The ATR-FTIR technique is capable of probing functional groups present both above and just below the top molecular layer of flat surfaces.

The tensile fractured surfaces of the composites were used for morphological study using scanning electron microscopy (SEM). A Zeiss DSM 960 microscope operating at 25 kV was used and the samples were glued onto tube, gold sputtered and dried prior to study (Fig. 1).

3. Results and discussion

3.1. *Effect of recycled Kraft fibers on the mechanical properties of PP composites without coupling agent*

The mechanical properties of recycled Kraft fiber/PP composites without MAPP coupling agent are shown in Table 1. The results point out that recycled Kraft fiber increased both tensile and flexural properties compared to those of non-reinforced matrix for those composites without coupling agent. The increase in tensile and flexural strengths for composites reinforced up to 40 wt.% without coupling agent was by 24% and 37%, respectively. The improvement of the strength was observed in spite of the lack of good compatibility at fiber matrix interface. It is well known that recycled Kraft fibers based on cellulose are hydrophilic while PP matrix is essentially hydrophobic. The different polarity of both constituents produced poor adhesion at fiber–matrix interface. In composite materials the stress transfer efficiency is related with good compatibility and adhesion at interface. Different interaction mechanisms can take place at fiber–matrix interface according to the intrinsic nature of each constituent: London-Van der Walls forces, hydrogen bonds, electrostatic interactions or covalent bonds. Additionally, mechanical anchoring due to the surface roughness of some constituent contributes to the reinforcement effect and stress transfer in the composite. In the case of absence of coupling agent no covalent bonding can take place at fiber–matrix interface. The evaluation of the surface polarity of recycled Kraft fibers and polypropylene matrix was obtained by colloidal titration in terms of cationic polymer adsorbed to the substrate surface. The results of the polarity are given in microequivalents of methyl-glicol-chitosan (MGCh) per gram of material. The results showed that while 10.53 μequiv. of MGCh were absorbed to 1 g of recycled Kraft fibers, only 4.46 μequiv. of MGCh were absorbed to the same amount of polypropylene. This different polarity stated that no strong chemical interactions can be found at fiber–matrix interface for composites without MAH-PP. For this type of composites the mechanical anchoring should be one of the main adhesion mechanisms at interface. This interaction mechanism is established looking at the surface morphology of recycled Kraft fibers showed in Fig. 2. The microphotography corresponds to a fractured tensile specimen, from which the roughness of the fiber surface is illustrated. Additionally, non-effective adhesion at fiber–matrix interface can be established, as shown by the gap between the fiber and the matrix. However, the occurred fiber fracture is

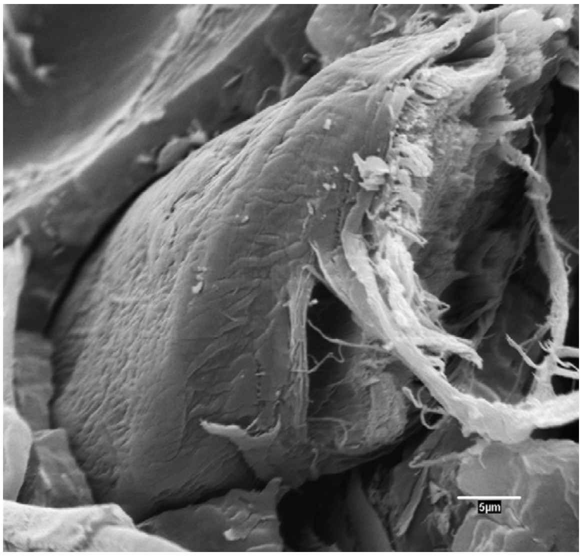

Fig. 2. SEM microphotography of the fractured surface of recycled Kraft fiber/PP composites.

indicating that some mechanical linkage was possible between the composite constituents. This irregular topography of recycled Kraft fibers can help the inter-diffusion of the polymer on the surface of the reinforcement [10]. Additionally, it has to be considered that these recycled Kraft fibers (from recycled sacs) were submitted to a refining process during their manufacturing. The effect of refined lignocellulosic fibers to the mechanical properties of their composites was previously studied in our group [11]. In general terms, the refining process produce an increase in the specific surface of the cellulose fibers by increasing its surface fibrillation, although the fiber length is slightly decreased [7]. The increase in the fibrillation involves an increase of the flexibility and the specific surface of the fibers. Thus, higher specific surface leads to higher anchoring capacity of the reinforcement resulting in an increase of the mechanical properties of the composite. The mechanical anchoring is facilitated by the surface roughness of the fibers and the inter-diffusion phenomenon of the polymer. For this specific case, the specific surface of recycled Kraft fibers was measured. After disintegration process, recycled Kraft fibers exhibited a specific surface of 2.97 $m^2 g^{-1}$ while virgin cellulose fibers showed 1 $m^2 g^{-1}$ specific surface. Higher specific area improved the fiber impregnation and mechanical adhesion at interface. Additionally, the fiber impregnation was facilitated because of the low viscosity of the used polypropylene (MFI = 30 g/10 min). Besides this, the porosity of cellulose fibers assists the inter-diffusion of the matrix throughout the fiber. All these factors explain the strengthening of polypropylene using recycled Kraft fibers as reinforcement without the addition of maleated coupling agent when the fiber percentage increased up to 40 wt.%. In the absence of MAH-PP, higher fiber percentage did not give an increase of the tensile or bending stresses. This phenomenon could be explained because of a saturation of the mechanical anchoring mechanism and an inefficient incorporation of the reinforcement into the matrix, as evidenced the similar or lower tensile or bending strengths of the composite comprising 50 wt.% of reinforcement compared to that at 40 wt.%.

Respect to the tensile and bending modulus, they increased proportionally with the fiber percentage. The Young's modulus of composites reinforced at 20, 30, 40 and 50 wt.% of recycled Kraft fiber increased by 80, 125, 180 and 235%, respectively, compared to that of non-reinforced PP. The increase was more noticeable for the bending modulus. Thus, the flexural modulus of composites including 40 wt.% of recycled Kraft fibers increased up to 260% with respect to that of the PP matrix. It is accepted that the modulus increases with the percentage of reinforcement, and this depends on the degree of dispersion of the reinforcement in the matrix [12,13]. As expected, the reinforcement produced a decrease in the breaking strain of the matrix. Thus, the formulation comprising 20 wt.% of reinforcement decreased by 60% the breaking strain of the non-reinforced matrix.

The impact strength behaved accordingly to the stiffening of the composites. The incorporation of fibers into the matrix decreased the absorbed energy under impact conditions. This behavior can be explained due to a change from ductile to brittle fracture with the presence of rigid elements. The addition of short-fiber reinforcement assisted the fracture initiation and propagation inside the composite.

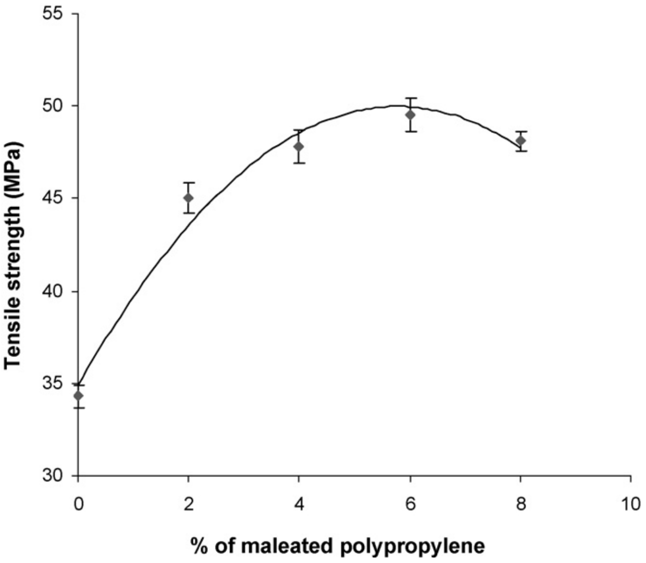

Fig. 3. Tensile strength of PP composites comprising 40% by weight of recycled Kraft fiber at different percentages of MAPP coupling agent.

3.2. *Effect of maleated polypropylene (MAH-PP) coupling agent on the mechanical properties of composites*

In order to improve the wettability, chemical adhesion and compatibility at fiber–matrix interface maleated polypropylene (MAH-PP) was incorporated as coupling agent during the preparation of recycled Kraft fiber/PP composites. The quality of the stress transfer at fiber–matrix interface affects essentially the final tensile stress of the composite materials. According to this, the measurement of the tensile stress of composites is related to the fiber–matrix compatibility and their efficient stress transmission. The values of the tensile strength for composites comprising 40 wt.% of recycled Kraft fibers at different MAH-PP percentages are presented in Fig. 3. Remarkably increments on the tensile strength of composites were obtained by the addition of small quantities of maleated polypropylene coupling agent. Thus, the addition of 2–8 wt.% MAH-PP with respect to the fiber content produced increments from 32 to 45% on the tensile strength of the composites with regarding the same formulation without MAH-PP. Concretely, the formulation at 6 wt.% of coupling agent gave rise to the highest increase in the tensile stress of the composites.

Therefore, composites comprising 20, 30, 40 and 50 wt.% of reinforcement and 6 wt.% of MAH-PP with respect to the fiber content were prepared. The values of the mechanical properties of such composites are also summarized in Table 1. It can be observed that the addition of maleated polypropylene to the composites at 20, 30, 40 and 50% of recycled Kraft fibers increased the tensile stress of the non-reinforced matrix respectively by 32, 47, 77 and 100%. However, the enhancement with the addition of MAH-PP was different at every fiber percentage, compared to the same formulation without MAH-PP. Thus, while the tensile strength of the composite comprising 20 wt.%

of reinforcement increased by 20% with respect to the same formulation without coupling agent, the increment was by 25, 43 and 66% for the formulations at 30, 40, and 50 wt.%, respectively. This can be explained because the amount of MAH-PP was incorporated with respect to the amount of reinforcement. The formulation at 6 wt.% of MAH-PP with respect to the fiber percentage corresponded to the addition of 1.5, 2.5, 4 and 6 wt.% of MAH-PP with respect to the matrix content. According to this, higher amounts of maleated polypropylene were added with respect to PP as much reinforcement was incorporated. The effect of the amount of MAH-PP with respect to the PP matrix was already studied in our laboratory [14]. Thus, the amount of MAH-PP should not increase too much to avoid a diminishing of the mechanical properties due to the effect of the low molecular weight of the PP chains of MAH-PP. The addition of 8 wt.% of MAH-PP would produce a decrease on the mechanical properties of the final composite [14].

Nevertheless, better mechanical performance of composites comprising coupling agent was observed even at high fiber content (50 wt.%). The reason presumes a mechanism of covalent interaction between the anhydride groups of MAH-PP and the hydroxyl groups of cellulose-based fibers [9,15] as well as the establishment of hydrogen bonds between the hydroxyl groups of the fibers and the remaining carboxyl groups of MAH-PP. The reaction between the MAH-PP coupling agent and the reinforcement leaves an aliphatic PP chain on the fiber surface that will enhance the wettability and compatibility at fiber–matrix interface. According to this, a significant improving of the transfer stress inside the composite is expected. The microphotography from Fig. 4 shows the tensile fractured surface of PP composites reinforced with 40 wt.% of recycled Kraft fibers with and without coupling agent. The figure illustrates that the use of MAH-PP coupling agent is preventing the pull out of the reinforcement from the polymer. The addition of MAH-PP also improved the flexural strength, which was 37, 60, 104 and 122% higher than that of non-reinforced matrix for composites comprising 20, 30, 40 and 50 wt.% of reinforcement, respectively. The increment on the flexural strength between composites with and without MAH-PP was also depending on the quantity of MAH-PP respect to the matrix. Thus, the formulations gave increments of 6.5, 19, 48 and 66%, respectively with respect to the same formulation without coupling agent.

In relation to the Young's modulus, the use of coupling agent gave a slight stiffening of the composites. It is well known that the rigidity of composites should not be significantly affected by the interface but for the dispersion and the amount of reinforcement [16]. Generally, Young's modulus reflects the capability of both fiber and matrix material to transfer the elastic deformation in the case of small strains without interface fracture. According to this, the tensile modulus is less sensitive to the variation of interfacial adhesion than the tensile strength, which is strongly associated with interfacial failure behavior. In this case the Young's modulus variation was between 7.5 and 10%. The effect of the coupling agent to the bending modulus followed similar trend. Moreover, the addition of MAH-PP coupling agent improved strain at break by 26–29% over the uncoupled ones. This behavior can be explained for the better wettability and stress transfer between both phases of the composite. These results were in agreement with the small enlargement of the average impact strength obtained for composites including MAH-PP coupling agent. However, considering the standard deviation, the improvement was not significant.

Some bibliographic data [2] support the superior intrinsic mechanical properties of softwood fibers compared to those of annual plant fibers. Opposite to this, other authors [3] hold that cellulose fibers from annual plants are expected to impart higher mechanical strength to the final composites. Experimental results from our laboratory [14], obtained following analogous procedures, demonstrated that values of elastic and bending modulus from PP composites reinforced with softwood fibers are lower to those of PP reinforced with annual fibers such as hemp [14] or kenaf [17]. These results are in concordance to some literature [3], but in conflict to the others [2]. It is well known that the intrinsic mechanical properties of the reinforcement are the key point for obtaining composites with improved mechanical performance. The measurement of the

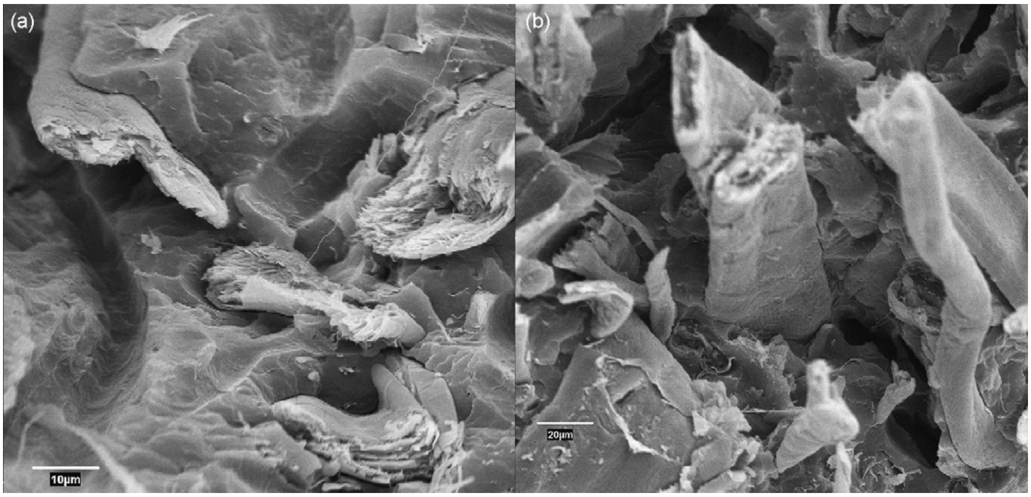

Fig. 4. Tensile fractured surface of recycled Kraft fiber/PP composites with (a) and without (b) coupling agent.

intrinsic mechanical properties of single cellulose-base fibers is possible for annual plant fibers but cannot be performed for Kraft fibers, which are actually too short. In this case a modeling of the elastic modulus can be done according to Hirsch model [18,19], a combination of parallel and series rule of mixture models, which predict quite accurately the elastic modulus of the composite materials from Eq. (2):

$$E_c = \beta(E_f \cdot V_f + E_m \cdot (1 - V_f)) + (1 - \beta)\frac{E_f E_m}{E_m V_f + E_f(1 - V_f)} \quad (2)$$

where β is the factor of efficient stress transfer between fiber and matrix, E the Young's modulus and V the volume fraction, and c, m and f refers to the composite, matrix and fiber, respectively. The factor of efficient stress transfer β was according to that of randomly oriented fibers of 3/8 [20]. The Hirsch model was applied to experimental data from other fibers (feasible to be measured) and it reproduced accurately the elastic modulus of the measured fibers. For this reason, the Hirsch model was used to deduce the intrinsic Young's modulus of recycled Kraft fibers. As a result, the calculated Young's modulus of recycled Kraft fibers into PP composites at 20, 30 and 40 wt.% of reinforcement was between 17.4 and 19.5 GPa. This value is considerable lower than the one stated in literature of 40 GPa [2]. However, Neagu et al. [21] found effective values of the Young's modulus between 17.4 and 19.0 GPa, which are comparable to these obtained by the application of the Hirsch model to our experimental results.

Similarly, the intrinsic tensile strength of Kraft fibers (σ_t^F) cannot be easily determined because of their short-fiber length. The modified rule of mixtures is often used to predict the tensile strength of short-fiber composites assuming a perfect interfacial bond between fibers and matrix [22]. The formula of the modified rule of mixtures is given by

$$\sigma_t^C = \chi_1 \cdot \chi_2 \cdot \sigma_t^F \cdot V_F + \sigma_t^m \cdot (1 - V_F) \quad (3)$$

where σ_t^C and σ_t^F are the ultimate tensile strength of composite and fiber respectively, and σ_t^m the matrix stress at the failure of the composite, V_F the volume fraction of the reinforcement, and χ_1 and χ_2 are, respectively, the fiber orientation and fiber length factors and the product $\chi_1 \cdot \chi_2$ is the fiber efficiency factor for the strength of the composite. Shao-Yun and Lauke [22] found the $\chi_1 \cdot \chi_2$ product for different short-fiber composites. In that case, the mean value of the $\chi_1 \cdot \chi_2$ product was 0.2089 ± 0.0624. According to this, the modified rule of mixtures was used to predict the intrinsic tensile strength of the recycled Kraft fibers for PP composites comprising MAH-PP coupling agent. Again, the obtained tensile strength of the recycled Kraft fibers, shown in Table 2, were lower than 1000 MPa [2], although were close to those reported by Van den Akker et al. [24] and Michel and Wilis [23].

Table 2
Fiber tensile strength for composites at 20, 30, 40 and 50 wt.% predicted from the modified rule of mixtures

Reinforcement (%)	σ_t^C (MPa)	V_F (t/1)	σ_t^F (MPa)
20	36.5	0.13	534.5
30	40.6	0.20	500.7
40	49.0	0.286	529.7
50	55.1	0.375	516.3

3.3. *Recycled Kraft fibers–PP interface study*

In order to study the modification reaction between the coupling agent MAH-PP and the hydroxyl groups of the softwood fiber surface, several samples from dry recycled softwood fibers were submitted to a controlled modification reaction with MAH-PP under refluxing of toluene. After reaction, the materials were totally dried and subsequently washed in a soxlhet apparatus with xylene, to remove any un-covalently linked reagent on the fibers surface. The ATR-FTIR of the treated and un-treated fibers is shown in Fig. 5(a). According to the chemical structure of MAH-PP, the main difference between both spectra was found at the characteristic absorption bands assigned to the polyolefin fraction of MAH-PP. Thus, characteristic absorption peaks between 2900 and 2950 cm^{-1} corresponding to the tensile vibration of the C–H aliphatic bonds and the presence of a new absorption band at 1460 cm^{-1} corresponding to the associated bending vibration of the same aliphatic bonds were found in the treated fiber spectrum. However, the confirmation of the chemical bonding between the MAH-PP coupling agent and softwood fibers was evidenced in the region from 1700 to 1800 cm^{-1}. In Fig. 5(b) the following spectra amplification are shown (by descendant order): MAH-PP spectrum, un-treated recycled softwood fiber, MAH-PP treated softwood fiber and the digital subtraction of un-treated fiber from the treated one. In the MAH-PP spectrum, the absorption band at 1775 cm^{-1} corresponded to the vibration of the carbonyl group of the anhydride function and the absorption band at 1713 cm^{-1} was associated to the tensile vibration of the carboxylic groups in the MAH-PP structure, due to the hydrolysis of some anhydride group. Subsequently, the subtraction of the spectrum of un-treated fiber from the treated one gave three new absorption bands drawn at 1776, 1752 and 1717 cm^{-1}. Thus, while the absorption bands at 1776 and 1717 cm^{-1} were assigned to the presence of unreacted MAH-PP in the treated fiber, the absorption peak at 1752 cm^{-1} was assigned to the ester group consequence of the chemical reaction of the anhydrides of MAH-PP and the hydroxyl groups of the softwood fiber. Actually, Felix and Gatenholm [25] published the esterification reaction of some cellulosic fibers with waxes like MAH-PP with the emergency of absorption bands at these frequencies. The chemical reaction between the MAH-PP coupling agent and the hydroxyl groups of recycled softwood fibers is supporting the high increments of the tensile strengths found in softwood fiber/PP composites comprising 6% of MAH-PP coupling agent.

In order to confirm the chemical reaction between MAH-PP coupling agent and Kraft fibers and its influence on the mechanical properties of the final composite, a negative proof was conducted. For this reason, recycled Kraft fibers were treated with alkyl ketene dimmer (AKD) before being used as reinforcement of PP composites. Then, PP composites reinforced at 40 wt.% of AKD modified Kraft fibers comprising 6 wt.% of

MAH-PP with respect to the fiber content were prepared. The tensile strength and the Young's modulus of the obtained composites were respectively 33.9 ± 0.3 MPa and 3.10 ± 0.1 GPa, indicating that no-interfacial bond did take place. Additionally, the AKD modified Kraft fibers were submitted to floatability test. A blend of AKD-modified and non-modified Kraft fibers was introduced in a 50:50 hexane–water mixture. The non-modified Kraft fibers sunk to the bottom of the flask within few minutes while the AKD modified Kraft fibers remained floating at the interface of the organic/aqueous phase. The AKD modification applied to the Kraft fibers increased their hydrophobic character and decreased the number of the surface –OH hydroxyl groups available for reacting with MAH-PP. This phenomenon supported the idea that non-effective strengthening is accomplished if the chemical reaction at fiber–matrix interface is banned. The reinforcement effect of composites from AKD-modified Kraft fibers containing MAH-PP was similar to that of non-modified Kraft fibers without MAH-PP.

For this kind of short-fiber composites, the interfacial shear strength can be calculated from the fiber length factor χ_2 according to the equations [22]:

$$\chi_2 = \frac{L_\mathrm{F}}{2 \cdot L_\mathrm{F}^\mathrm{C}} \quad \text{for} \quad L_\mathrm{F} < L_\mathrm{F}^\mathrm{C} \tag{4}$$

$$\chi_2 = 1 - \frac{L_\mathrm{F}^\mathrm{C}}{2 \cdot L_\mathrm{F}^\mathrm{C}} \quad \text{for} \quad L_\mathrm{F} \geq L_\mathrm{F}^\mathrm{C} \tag{5}$$

where L_F is the fiber length and L_F^C is the critical fiber length. The critical fiber length is given by [26]:

$$L_\mathrm{F}^\mathrm{C} = \frac{d_\mathrm{F} \cdot \sigma_\mathrm{t}^\mathrm{F}}{\tau} \tag{6}$$

being d_F the fiber diameter, $\sigma_\mathrm{t}^\mathrm{F}$ the intrinsic fiber tensile strength and τ the interfacial shear strength of the composite. The substitution of L_F^C in Eqs. (3) and (4) gives respectively the Eqs. (7) and (8):

$$\tau = \chi_2 \cdot \frac{d_\mathrm{F} \cdot \sigma_\mathrm{t}^\mathrm{F}}{L_\mathrm{F}} \tag{7}$$

$$\tau = \frac{d_\mathrm{F} \cdot \sigma_\mathrm{t}^\mathrm{F}}{4 \cdot L_\mathrm{F} \cdot (1 - \chi_2)} \tag{8}$$

To apply the Eqs. (7) and (8), the diameter and fiber length of the reinforcement were measured and χ_2 was taken from the bibliography ($\chi_2 = 0.6204 \pm 0.068$) [22]. According to this, the interfacial shear strength of the obtained composites is shown in Table 3. It can be observed that the interfacial shear strengths deduced for the given composites are similar to those obtained by Doan et al. [18] for PP composites reinforced with jute fibers comprising MAH-PP coupling agent.

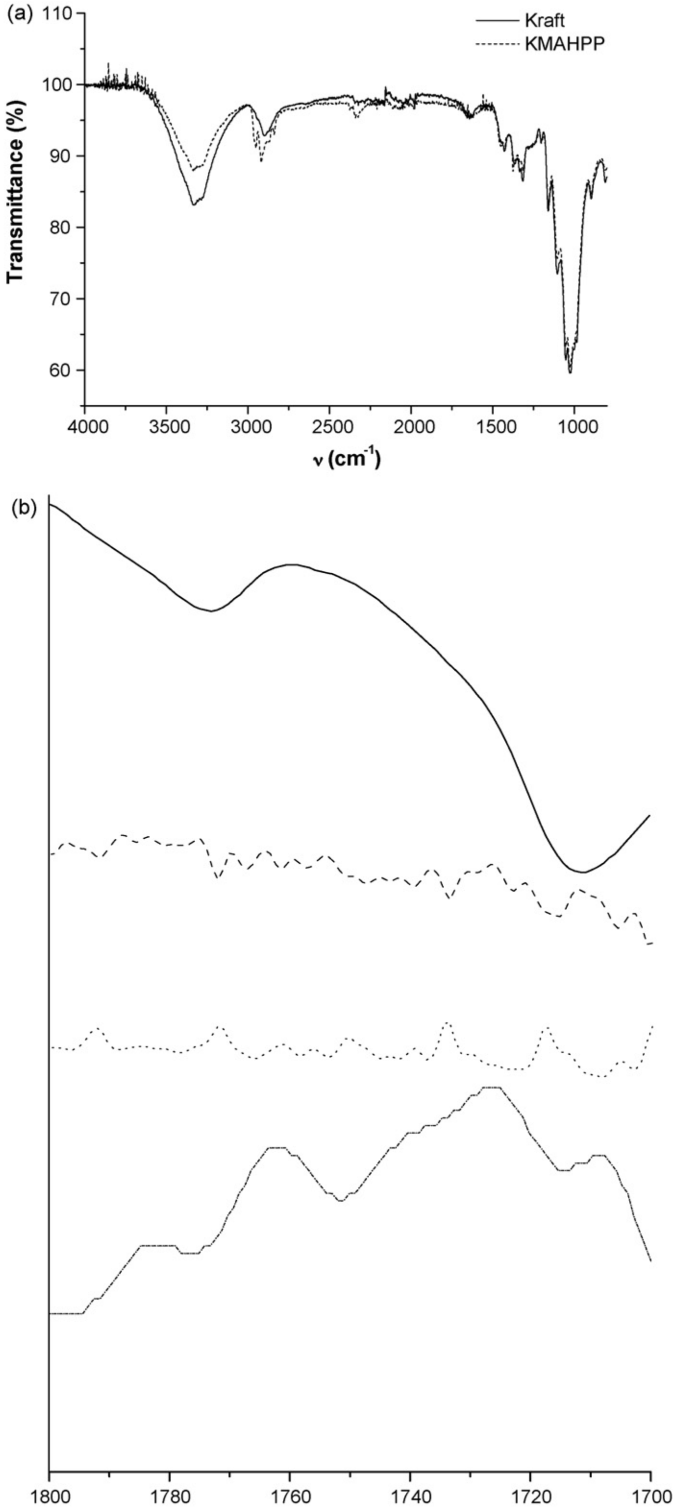

Fig. 5. ATR-FTIR spectra of recycled softwood fibers and MAH-PP treated softwood fibers (a) and the amplification spectra of MAH-PP, un-treated recycled softwood fiber, MAH-PP treated softwood fiber and the digital subtraction of un-treated fiber from the treated one (descendant order) (b).

3.4. Industrial competitiveness

At this point, it is worth noting to look at the real competitiveness of composites with recycled Kraft fiber as reinforcement. At industrial scale, the most widely used reinforcement is fiberglass, E fiberglass for this rank of properties. E fiberglass shows

Table 3
Predicted interfacial shear strength for recycle Kraft fiber/PP composites

Reinforcement (%)	L_F (μm)	d_F (μm)	L_F/d_F aspect ratio	σ_t^F (MPa)	$\tau\ (L_F < L_F^C)$ (MPa)	$\tau\ (L_F \geq L_F^C)$ (MPa)
20	413	24	17.2	534.5	19.26	20.45
30	394	23	17.1	500.7	18.13	19.24
40	370	23	16.1	529.7	20.42	21.68
50	360	24	15	516.3	21.35	22.66

very good mechanical performance, although there are several negative aspects associated to the use of this mineral reinforcement. Thus, many environmental disadvantages can be found because of its non-biodegradability, it cannot be easily recycled and come from a non-renewable resource. Moreover, fiberglass is detrimental for the operational machines and harmful for the human health. Opposite to this, recycled Kraft fibers group all the advantages known for cellulose-based fibers and additionally they come from a recovery process.

The evaluation of the technical industrial competitiveness has been made by comparing the tensile properties of composites reinforced with E fiberglass or recycled Kraft fibers. Fig. 6 shows the evolution of tensile strength of composites with the volume fraction of both types of reinforcement. The tendency followed the equation $\sigma_t^C = 202.57 \cdot V_F^{GF} + 28.695$ for E fiberglass composites and $\sigma_t^C = 74.202 \cdot V_F^{KF} + 26.98$ for recycled Kraft fiber composites. Analogous equations were found for the Young's modulus, $E_t^{GF} = 15.903 \cdot V_F^{GF} + 1.2$ for fiberglass composites and $E_t^{KF} = 9.442 \cdot V_F^{KF} + 1.665$ for recycled Kraft fiber composites. According to these equations, superior ultimate tensile strength and Young's modulus belong to fiberglass composites for identical volume percentage of reinforcement. In fact, the intrinsic mechanical properties of fiberglass are at least four times higher ($\sigma_t^{GF} = 20003500$ MPa and $E_t^{GF} = 7072$ GPa) than those of recycled Kraft fibers ($\sigma_t^{KF} \approx 520$ MPa and $E_t^{KF} \approx 18$ GPa). Moreover, the differences on the effectiveness increase proportionally with the volume fraction of the reinforcement. Thus, while at 5% volume fraction the different effectiveness between both reinforcements is around 30%, the increment grows up to 70% when the volume fraction is around 20%. That is why both reinforcements can only be compared for a rank of properties, since high mechanical performance cannot be achieved using recycled Kraft fibers as reinforcement. According to this, the industrial competitiveness of these reinforcements has been considered for three ultimate tensile strengths, 40, 52 and 62.4 MPa. This last value corresponds to the maximum percentage of Kraft fiber reinforcement allowable (60 wt.%). From the linear equations written above, the volume fraction of the corresponding reinforcement at every tensile strength is calculated. Additionally, by means of the specific gravity the proportion by weight of every composite component is isolated. Finally, the costs per kilo of the obtained composite materials are calculated from the individual cost of the raw materials: 0.9 €/kg for PP, 1.25 €/kg for E fiberglass, 0.09 €/kg for the recycled Kraft fiber and 4 €/kg for the MAH-PP coupling agent. Table 4 shows the costs per kilo for PP composites reinforced with either E fiberglass or recycled Kraft fibers. The values illustrate that for an equal final tensile strength the volume fraction by weight needed is almost three times higher for recycled Kraft fiber than for E fiberglass. It is also worth noticing that, for these formulations, the Young's modulus of composites reinforced with recycled Kraft fiber is 10–13% higher for the recycled Kraft fiber composites. In relation with the cost of materials, the subsequent addition of fiberglass into the polymer increases gradually the final cost of the composite; however, the increase of recycled Kraft fiber into the polymer decreases remarkably the final cost of the composite.

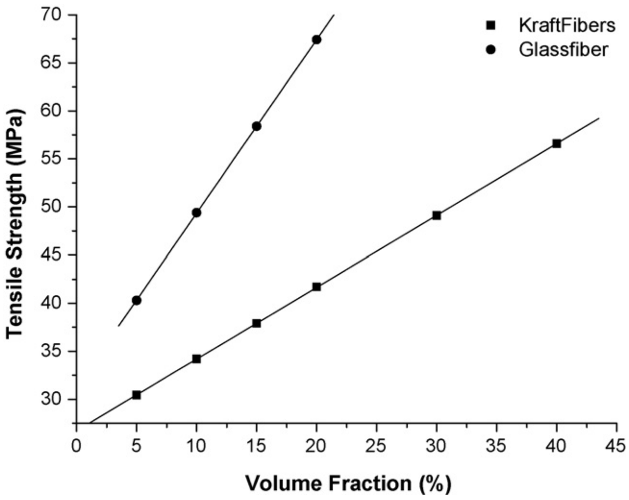

Fig. 6. Evolution of the tensile strength of PP composites reinforced with either glass fiber or Kraft fibers.

Table 4
Cost per kilo of PP composites reinforced with E glass fiber or recycled Kraft fiber

σ_t^C (MPa)	Volume fraction (wt.%)		E_t (GPa)		€/kg	
	KF	GF	KF	GF	KF	GF
40	17.5	5.6	2.3	2.1	0.74	0.95
52	33.7	11.5	3.4	3.0	0.62	0.99
62.4	47.7	16.6	4.3	3.8	0.54	1.02

KF, recycled Kraft fiber, GF, E glass fiber.

4. Conclusions

Recovered paper coming from old sacs has been used as source of cellulose-based reinforcement (Kraft fibers) for the preparation of PP composites. Composites up to 50% of recycled Kraft fibers were prepared and increments of two times the ultimate tensile strength of non-reinforced matrix were achieved for those formulations comprising MAH-PP coupling agent. Regarding the adhesion mechanism at fiber–matrix interface, mechanical anchoring and Van der Waals interaction are the main ways to explain the strengthening of the composite formulations without coupling agent. With the addition of MAH-PP coupling agent, hydrogen bonds as well as covalent linkages were revealed. Measurements of surface polarity, specific surface area, floatability tests and spectroscopic and microscopic analysis were used to demonstrate the interfacial union between the composite components. A negative proof, which banned the existence of hydrogen and covalent bonds at interface, was conducted. It was observed that the inhibition of these chemical interactions gave composites with the same ultimate tensile strength than those without MAH-PP coupling agent.

In the paper, a deduction of the intrinsic mechanical properties of the recycled Kraft fibers is developed by means of modified rule of mixtures. The obtained intrinsic strength and tensile modulus (Young's modulus between 17.4 and 19.5 MPa and tensile strength about 500–534 GPa) were in agreement with some bibliographic data but in discordance with others. Additionally, the calculated interfacial shear strength was also comparable to those obtained by other authors in composites from PP and jute fibers.

The study demonstrates the viability of this type of recovered fibers as reinforcement of polyolefins. The competitiveness of recycled Kraft fibers allows the substitution of E fiberglass for a rank of properties, which involve a maximum tensile strength about 62 MPa and stiffening only 10% lower than that provided with E fiberglass. Likewise, the substitution of E fiberglass for recycled Kraft fibers can halve the saving costs of the final composite materials.

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