RESEARCH ON THE SUITABILITY OF ORGANOSOLV SEMI-CHEMICAL TRITICALE FIBERS AS REINFORCEMENT FOR RECYCLED HDPE COMPOSITES

Nour-Eddine El Mansouri,[a] Francesc X. Espinach,[b,*] Fernando Julian,[b]
Narcís Verdaguer,[b] Lluís Torres,[c] Miquel F. Llop,[a] and Pere Mutje [a]

The main objective of this research was to study the feasibility of incorporating organosolv semi-chemical triticale fibers as the reinforcing element in recycled high density polyethylene (HDPE). In the first step, triticale fibers were characterized in terms of chemical composition and compared with other biomass species (wheat, rye, softwood, and hardwood). Then, organosolv semi-chemical triticale fibers were prepared by the ethanolamine process. These fibers were characterized in terms of its yield, kappa number, fiber length/diameter ratio, fines, and viscosity; the obtained results were compared with those of eucalypt kraft pulp. In the second step, the prepared fibers were examined as a reinforcing element for recycled HDPE composites. Coupled and non-coupled HDPE composites were prepared and tested for tensile properties. Results showed that with the addition of the coupling agent maleated polyethylene (MAPE), the tensile properties of composites were significantly improved, as compared to non-coupled samples and the plain matrix. Furthermore, the influence of MAPE on the interfacial shear strength (IFSS) was studied. The contributions of both fibers and matrix to the composite strength were also studied. This was possible by the use of a numerical iterative method based on the Bowyer-Bader and Kelly-Tyson equations.

*Contact information: a: Group LEPAMAP, Department of Chemical Engineering, University of Girona, c/ M. Aurèlia Capmany, nº 61, Girona 17071, Spain; b: Design, Development and Product Innovation, Dept. of Organization, Business, University of Girona, c/ M. Aurèlia Capmany, nº 61, Girona 17071, Spain; c: Analysis and Advanced Materials for Structural Design (AMADE), Polytechnic School, University of Girona c/ M. Aurèlia Capmany, nº 61, Girona 17071, Spain;
Corresponding author: Francisco.espinach@udg.edu

INTRODUCTION

Polymer materials reinforced with natural fiber have received considerable attention in the scientific literature during the past few years due to their cost-effectiveness versus fiber glass composites, and due to their environmental friendly aspects (Vilaseca *et al*. 2010; Ashori and Nourbakhsh 2009). Usually the matrices used for natural fiber-based composites are polyolefinic thermoplastics, mainly polypropylene (PP) and polyethylene (PE). They represent the largest fraction of polymer wastes; therefore, their recycling and use in composite materials is an alternative to landfill disposal (Favaro *et al.* 2010). Generally, lignocellulosic natural fibers can be classified into three groups based on their origin: annual plant strands, wood fibers, and agroforestry waste fibers. On the other hand, depending on the pulping process and the raw material yield, the fibers can also be classified as mechanical pulp (MP),

thermomechanical pulp (TMP), chemi-thermomechanical pulp (CTMP), semi-chemical pulp (SCP), and chemical pulp (CP). The resulting pulps are fibers with different physico-chemical properties that can be used as a reinforcing element for composite materials. Within the group of agroforestry wastes, cereal straws are the most abundant, amounting to 1,250 million tons/year, which represents about 46% of the worldwide production (Hurter 1997). In 2007, the production of wheat straws was estimated to be 540 million tons/year (Reddy and Yang 2009). Therefore, the existence of low-cost wheat straw as raw material for the preparation of composite fibers in the global market is guaranteed. Within the wheat straw group, triticale is a cereal straw resulting from a cross between wheat (*Triticum*) and rye (*Secale*). When compared with other cereals such as wheat, barley, or rye, triticale produces more kilograms of straw with respect to the kilograms of seed. Triticale can be considered a potential lignocellulosic raw material from which to obtain polymer-reinforcing fibers.

The most cited transformation techniques reported are extrusion, thermoforming, and injection molding (Panthapulakkal *et al.* 2006; Panthapulakkal and Sain 2007; Zou *et al.* 2010). The reviewed literature discusses composite materials prepared from fibers from different pulping processes, with an emphasis on their mechanical behavior. Pan *et al.* (2010) studied compression-molded composite materials with wheat straw fibers, produced by MP or TMP, and coupled with PP and maleated polypropylene (MAPP). The tensile strength (σ_t^c) for the 40 wt. % composites was about 42.5 MPa, and the Young's modulus (E_t^C) was about 2.5 GPa. Even if the increase of the σ_t^c is noticeable, the value of the Young's modulus is low, possibly due to its measurement without an extensometer. The same authors have evaluated the influence of several surface treatments on the thermal, mechanical, and rheological properties of the composite materials (Pan *et al.* 2009). In the same way, Panthapulakkal *et al.* (2006) prepared injection-molded composites using wheat straw MP or TMP, and CP fibers as reinforcement, with PP as the matrix and MAPP as the coupling agent. The σ_t^c for MP/TMP 30 wt. % composites was 40.5 MPa, a value similar to that found by Pan *et al.* (2009), though they used a lower substitution percentage. The low values of σ_t^c and E_t^C obtained with CP is rather surprising. This is likely due to the chemical composition of CP fibers, with a low lignin percentage that had a higher ability for the creation of hydrogen bonds that hindered its dispersion within the matrix. The obtained low values for the Young's modulus is likely due to tensile testing without an extensometer. Similarly, Sykacek *et al.* (2011) used a wheat straw kraft pulp that was flash-dried as reinforcement fiber for PP, which was coupled with various agents. The σ_t^c for 30 wt. % composites varied depending on the coupling agent. The Young's modulus was in line with the abovementioned literature reports. To the best of our knowledge, there has not been scientific literature published on the tensile properties of composite materials with semi-chemical fibers (SC) used as reinforcing element for thermoplastic composites.

The increasing concern with the environment and its preservation have exposed the need to replace the classical pulping processes (*e.g.* kraft, sulphite) that use sulphur-containing reagents, the release of which can cause serious pollution problems. Ethanolamine possesses a high-boiling point and can thus be used at pressure levels similar to those of classical processes. Rodriguez *et al.* (2008) discussed the technical, economical, and environmental advantages of organosolv processes.

In this research work, triticale straws were used as reinforcement for recycled high density polyethylene composites. The objective was to obtain semi-chemical pulps

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of triticale straws produced by an organosolv cooking process. Coupled and uncoupled recycled high density polyethylene (HDPE) composites were prepared and tested for their tensile properties and their Young's modulus. Finally the Bowyer-Bader methodology (Bowyer and Bader 1972) and the Kelly-Tyson modified equation (Kelly and Tyson 1965) were used to determine the interfacial shear strength (IFSS), the fiber orientation factor, the coupling factor, and the contribution of the fibers and the matrix to the final properties of the composite.

MATERIALS AND METHODS

Materials

Integral triticale straws were provided by Fundació Mas Badia (la Tallada d'Empordà, Spain). Recycled high density polyethylene HDPE supplied by Mas Clara de Domeny, S.L. (Girona, Spain), was used as the thermoplastic matrix. Polyethylene was grafted with maleic anhydride, MAPE (Fusabond MB100D, 0.9%), in order to enhance the interface between the polymer matrix and the organosolv triticale fibers (OTF). Diglyme was supplied by Clariant as a dispersing agent. Decalin (190 ℃ boiling point; 97% purity) was supplied by Fisher Scientific and used to dissolve recycled HDPE matrix during the fiber extraction from composites. Acetone (reagent grade; 95% purity) from Sigma Aldrich was used as received.

Preparation of Triticale Fibers

Integral triticale straws were chopped using a knives mill from Agrimsa (Torelló, Barcelona, Spain). For the preparation of the OTF, the chopped triticale straws were pulped by an organosolv cooking process using ethanolamine as the solvent in a liquid-to-fiber ratio of 4:1, at 170 ℃ for 90 minutes. Afterward, the pulp was rinsed with excess water, defibrated by a Sprout-Waldrom single-disk refiner, and oven dried.

Triticale fibers were dispersed in water-diethyleneglycol dimethyl ether (diglyme) (1:3) mixture to obtain single fibers and eliminate fiber flocks; the resulting single fibers were filtered and oven dried. The use of diglyme in the previous step limits the formation of hydrogen bonds between the cellulosic fibers resulting in fiber-fiber entanglement (Rodriguez *et al.* 2010).

Characterization of Triticale fibers

The viscosity of the OTF was determined by the capillary viscometer method (TAPPI Standard, T230 om-94), and the OTF kappa number was determined by TAPPI standard T236 cm-85. The OTF length and diameter were determined for the prepared fibers. Both lengths and diameters of the fibers were analyzed using 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.

Composites Fabrication

Recycled HDPE, together with OTF and MAPE coupling agent, were blended at different weight ratios by using an intensive kinetic Gelimat mixer. The mixing process was carried out at 3000 rpm for 2 minutes until the discharged temperature of approximately 210 ℃ was reached. Composite blends comprising 10 to 40 wt. % of OTF without and with 4 wt. % of MAPE (with respect to the fiber content) were produced.

Afterward, the composite blends were cut down to a particle size in the range of 5 mm by using a hammer mill equipped with a set of knives. The resulting pellets were dried and stored at 80 ºC for 24 h before injection molding. Tensile test specimens were produced by the injection molding machine, Meteo-40 from Mateu & Solé. The injection moulding temperatures were in the range of 168 to 185 ºC. The first and second pressures were 120 and 37.5 kgf/cm^2. A scheme of the experimental procedure is shown in Fig. 1.
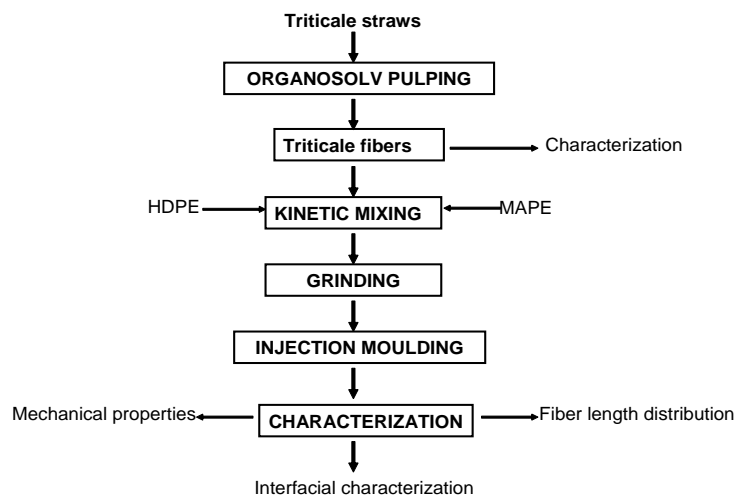

Fig. 1. Flow chart of the experimental procedure

Tensile Properties Determination

After fabrication, all of the specimens were placed in a conditioning chamber (Dycometal) at 23 ºC and 50% relative humidity for 48 h. Mechanical properties under tensile stresses were determined by using an INSTRON universal testing machine fitted with a 5 kN load cell. Tensile properties were analyzed in accordance to the ASTM D790 standard. Reported results were the average of at least 5 sample replicates.

Fiber Extraction from Composites

Reinforcing fibers were extracted from composites by matrix solubilization using a Soxhlet apparatus and decalin as the solvent. Small pieces of composites were cut and placed inside specific cellulose filter and set into the Soxhlet extractor. A small cotton tap was used to prevent the matrix fibers from getting out of the filtering tube. The fiber extraction was completed after 48 h. Once the fibers were extracted, they were rinsed with acetone and then with distilled water in order to remove the residual solvent. Finally, the fibers were dried in an oven at 105 ºC for 24 h.

Micromechanics

Determination of the Young's modulus of the fiber (E_t^F)

The intrinsic tensile modulus of the triticale straws was determined using the Hirsch model (Eq. 1) (Vilaseca *et al.* 2010; Lopez *et al.* 2011; Rodriguez *et al.* 2010; Hirsch 1962),

$$E_t^C = \beta\,(E_t^F V^F + E_t^m (1 + V^F)) + (1 - \beta)\,\frac{E_t^F E_t^m}{E_t^m V^F + E_t^F (1 - V^F)} \tag{1}$$

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where $E_t^{\,C}$, $E_t^{\,F}$, and $E_t^{\,m}$ represent the Young's modulus for the composite, the strands, and the matrix respectively. The factor β determines the transference of the stress between the fiber and the matrix, and usually has a value of 0.4 for this kind of composite (Kalaprasad *et al.* 1997).

Determination of the interfacial shear strength (τ) and the fiber orientation factor (χ₁)

With current standard processing techniques, perfect fiber alignment is almost impossible, and the orientation factor (χ_1) must be taken into account. The calculation of τ can be accomplished through the Kelly-Tyson modified equation (Eq. 2) (Kelly and Tyson 1965; Thomason 2002).

$$\sigma_t^{\,C} = \chi_1 \left(\sum_i \left[\frac{\tau \cdot l_i^{\,F} \cdot V_i^{\,F}}{d^{\,F}} \right] + \sum_j \left[\sigma_t^{\,F} \cdot V_j^{\,F} \left(1 - \frac{\sigma_t^{\,F} \cdot d^{\,F}}{4 \cdot \tau \cdot l_j^{\,F}} \right) \right] \right) + (1 - V^{\,F}) \cdot \sigma_t^{\,m*} \qquad (2)$$

In Equation 2, $\sigma_t^{\,C}$ and $\sigma_t^{\,F}$ represent the ultimate tensile strength of the composite and the reinforcing fibers. The $\sigma_t^{\,m*}$ term is the contribution of the matrix at failure. The $d^{\,F}$ and $l_{i,j}^{\,F}$ terms represent the fiber diameter and the length, respectively. The $V^{\,F}$ term is the volume fraction of reinforcement in the composite. The characteristics of the reinforcing fibers are given by: strength ($\sigma_t^{\,F}$), orientation (χ_1), IFSS (τ), diameter ($d^{\,F}$), and length distribution ($l^{\,F}$). Equation 2 can be simplified to $\sigma_t^{\,C} = \chi_1(X + Y) + Z$, where $\chi_1 \cdot X$, $\chi_1 \cdot Y$, and, Z are the contributions of the subcritical fibers, the fibers, and the matrix to $\sigma_t^{\,C}$, respectively.

Considering the low plastic deformations of cellulosic fibers, the tensile strength of the fibers can be represented as a function of its elongation ($\varepsilon_t^{\,F}$) and its modulus ($E_t^{\,F}$) according to: $\sigma_t^{\,F} = E_t^{\,F} \cdot \varepsilon_t^{\,F}$. Moreover, within the first part of the stress-strain curve of the composite, one can assume low fiber slippage from the polymeric matrix and consider the elongation of the composite to be equal to that of the fiber. Thus the Kelly-Tyson expression can be expressed as:

$$\sigma_t^{\,C} = \chi_1 \left(\sum_i \left[\frac{\tau \cdot l_i^{\,F} \cdot V_i^{\,F}}{d^{\,F}} \right] + \sum_j \left[E_t^{\,F} \cdot \varepsilon_t^{\,C} \cdot V_j^{\,F} \left(1 - \frac{E_t^{\,F} \cdot \varepsilon_t^{\,C} d^{\,F}}{4 \cdot \tau \cdot l_j^{\,F}} \right) \right] \right) + (1 - V^{\,F}) \cdot \sigma_t^{\,m*} \qquad (3)$$

In order to solve the equation, a Bowyer–Bader methodology was used (Bowyer and Bader 1972; Rodriguez *et al*. 2010; Lopez *et al*. 2011; Thomason, 2002) to evaluate χ_1 and τ.

Determination of the intrinsic tensile strength ($\sigma_t^{\,F}$)

In order to solve the modified equation of Kelly–Tyson, it is necessary to know or estimate the values of $E_t^{\,F}$, $E_t^{\,m}$, and the characteristics of the reinforcing fibers: strength ($\sigma_t^{\,F}$), orientation (χ_1), IFSS (τ), diameter ($d^{\,F}$), and length ($l^{\,F}$). By previous extrac-

tion from the polymeric matrix, the fiber distribution can be empirically obtained. However, usually σ_t^F, χ_1 and τ are unknown.

The Bowyer-Bader model suggests that these parameters can be calculated following Eq. 4.

$$R = \frac{\sigma_t^{c1} - Z_1}{\sigma_t^{c2} - Z_2}; R^* = \frac{\chi_1(X_1 + Y_1)}{\chi_1(X_2 + Y_2)} = \frac{X_1 + Y_1}{X_2 + Y_2} \qquad (4)$$

From the equations above, the strength of the composite at two different deformations ($\sigma_t^{c1}; \sigma_t^{c2}$) can be calculated from the experimental stress-strain curve of the composite. Similarly, Z_1 and Z_2 refer to the polymeric matrix at the same deformations and are also quantifiable from the stress-strain curve of the neat matrix. The values of τ and χ_1 can be determined by iteration until $R = R^*$ (Li *et al.* 2009).

RESULTS AND DISCUSSION

Characterization of Triticale Fibers

Table 1 shows the results of chemical composition of triticale raw material as compared to the composition of non-woods (wheat and rye), and of softwood and hardwood literature reports. The comparison reveals that the lignin content in triticale was lower than that of the softwood and hardwood investigated by Hurter (1997), and was in the range of the values reported for wheat and rye. The cellulose content was in the range of those of non-wood and wood materials, while the hemicellulose content was somewhat higher than those of softwood and hardwood, but within the range of those of wheat and rye.

Table 1. Chemical Composition of Triticale Compared to Wood and Non-Wood Raw Materials

Source	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Triticale	49.1	26.05	16.2
Wheat[a]	49-54	26-32	16-21
Rye[a]	50-54	27-30	16-19
Softwood[a]	53-62	7-14	26-34
Hardwood[a]	54-61	19-26	23-30

a: (Hurter 1997).

Afterward, the triticale straw was pulped by an organosolv process using ethanolamine as the solvent. Organosolv pulping has been studied as an alternative to the standard alkaline process, and it has some advantages over kraft pulping (Barbera *et al.* 2011, Gonzalez *et al.* 2008, Rodriguez *et al.* 2008, Jimenez *et al.* 2004). The physical properties of the OTF as compared to industrial eucalypt kraft pulp fibers are listed in Table 2. Depending on the ethanolamine solvent to fiber ratio, reaction temperature, and reaction time, the organosolv pulping process allows the preparation of different semi-chemical pulp qualities with yields between 65% and 85%. In the present work, organosolv pulping was terminated to afford a 77.5% yield, which resulted in semi-chemical pulp with morphological fiber properties comparable to those of unbleached

eucalypt kraft pulp. This is reflected in the aspect ratio of OTF comparable to that of industrial eucalypt kraft pulp. These fibers also show relatively comparable fines content (particles shorter than 200 μm) compared to those of the industrial eucalypt kraft pulp. Considering the result of kappa number indicated in Table 2 (25.3) equivalent to 5.8 % (w/w), it can be seen that during pulping, an important amount of lignin was removed. On the other hand, the cellulose in the OTF fibers had a low viscosity when compared to the industrial eucalypt fibers. The low viscosity is an indication of the depolymerization of cellulose chains, which can affect the final mechanical properties of the prepared composites.

Table 2. Properties of Triticale Organosolv Pulp Fibers Compared to Eucalypt Kraft Pulp Fibers

Fibers	Triticale Fibers	Eucalypt Fibers
Yield (%)	77.5	57.1
Fines (%)[*]	30.7	27.8
Kappa number	25.3	14.1
Length (μm)[**]	800.4	750.4
Fiber diameter (μm)	21.3	17.9
Aspect Ratio (L/D)	37.6	41.9
Viscosity (mPa•s)	542	927

[*] Fines in length <200 μm
[**] Weighted in length

Tensile Properties of Triticale Composites

Tensile strength, Young's modulus, and elongation at break of the recycled HDPE composites reinforced by OTF with MAPE coupling agent are summarized in Table 3.

Table 3. Tensile Properties of OTF/HDPE with 6 wt. % MAPE Composites (the standard deviations are inside the parenthesis)

Fiber %	V^F	MAPE wt. %	σ_t^c (MPa)	σ_t^{m*} (MPa)	Elongation Break (%)	E_t^c (GPa)
10	0.066		18.4 (0.09)	14.37	10.70 (0.15)	1.1 (0.11)
20	0.138	6	22.70 (0.26)	14.14	9.30 (0.19)	1.55 (0.14)
30	0.215		26.5 (1.12)	12.90	6.10 (0.25)	1.95 (0.21)
40	0.299		32.90 (0.39)	12.22	5.15 (0.24)	2.55 (0.07)

It is well known that the properties of natural fiber composites are determined by the nature of the fiber, the fiber volume fraction, the fiber orientation factor, the aspect ratio of the reinforcement, and the quality of the fiber/matrix interface. The tensile strength of the 40 wt. % OTF composites without MAPE was evaluated to be 20.1 MPa with a standard deviation of 0.26. It was noticed that the tensile strength increased by 63.6% when compared to the plain matrix. It is remarkable that the tensile strength increased in spite of the lack of good adhesion between the recycled HDPE matrix and the OTF. In general, the addition of lignocellulosic fibers in a non-polar matrix is limited because of the different surface nature of both constituents. Consequently, the tensile strength is expected to decrease with increasing reinforcement content. The increase in the tensile strength can be attributed to the mechanical anchoring between the fiber and matrix, to the diffusion phenomenon of the polymer onto the fiber, and to the aspect ratio

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of the OTF inside the composite material, as will be discussed later. In addition, the phenomenon of transcrystallization, characteristic of semicrystaline thermoplastic matrix composites, must be taken in account because it could be the cause of a part of the enhancement of the tensile strength of the studied materials (Nielsen and Pyrz 2003; Sanadi and Caulfield 2000). Transcrystallization occurs when spherulites are heterogen-eously nucleated on the fiber's surface. The factors that may affect the heterogeneous nucleation are the surface energy of the substrate, the adsorption of molecular entities, and other processing conditions such as melt time, temperature, and cooling rate. This phenomenon will contribute to an increase in the mechanical properties of the final composite, and it may help transfer the stress at the fiber–matrix interface.

Nevertheless, in order to have more competitive materials, and from an engineering point of view, higher tensile properties of composites are required for many applications. For this reason, a high quality fiber–matrix interface must be achieved. Some researchers have demonstrated that chemical modification of the fiber surface is one potential method to improve the wettability and compatibility between the composite constituents. In general, chemical modifications are used to decrease the polarity of the fiber surface in order to make it more compatible to that of the polymer surface. The treatments of the fiber surface with short chain hydrophobic agents such as acetyls, isocyanates, or silanes are not enough to optimize the mechanical properties of the composite materials (Li *et al.* 2007). Actually, coupling agents, which react with the fiber's hydroxyl groups, but additionally are able to interlock with matrix chains are the best treatment to increase the mechanical properties of the composite. In this respect, the use of an interfacial coupling agent, such as maleated polyethylene (MAPE), has yielded good tensile properties of the composites (Sanadi and Caulfield 2000; Sain *et al.* 2005). For this research work, the amount of coupling agent was optimized for the recycled HDPE composites in previous studies and was found to be 6 wt. % with respect to the fiber content (Rodriguez *et al.* 2010). This amount of coupling agent was then applied to the rest of the composites to make a comparative study.

From the results presented in Table 3, the effectiveness of MAPE as a coupling agent is clearly seen. The addition of MAPE coupling agent improved the tensile strength in all cases. Concretely, the addition of 6 wt. % of MAPE provided increments of about 25.1, 54.4, 80.1, and 123.8% in tensile strength of the 10 to 40% reinforced composites, respectively, when compared to the recycled HDPE plain matrix. When compared with the 0 wt. % MAPE composites, the resulting tensile increase was 63.7% for the 40% OTF composites. The tensile strength of the composite increased linearly with the percentage of fibers.

The Young's modulus showed a clear linear and fast evolution (Table 3). Taking in account that the Young's modulus value of the recycled HDPE was 0.75 GPa and of the 40% OTF composite was 2.55 GPa, the modulus increased by a factor of 3.4.

Flandez *et al.* (2012) stated that the proportion of lignin, hemicelluloses, and cellulose varies from the middle lamella to the primary or secondary walls. Therefore, the surface composition of the semi-chemical pulp of triticale fibers will be higher in lignin if the defibering takes place between the middle lamella and the primary wall, or higher in holocellulose if the separation occurs between or within the S1 and S2 layers (Garcia 2007). For the present case, where the defibering was carried out under more severe conditions, the surface composition of the semi-chemical fibers will be rich in cellulose and contain a depolymerised lignin in moderate quantities (Flandez *et al.* 2012).

The improvement in tensile strength observed for this type of composite can be accounted for by two different hypothesized mechanisms. The first one refers to the higher amount of hydroxyl groups at the fiber surface due to the S1/S2 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 polymer caused by ethanolamine organosolv pulping. Therefore, the modified lignin becomes more reactive toward the esterification reaction or hydrogen bonding at the interface. The appearance of new hydroxyl groups after organosolv pulping of lignocellulosic materials with the lignin polymer is due to the cleavage of ether bonds, such as *α*- and *β*-O-4, which are the major linkages in the native lignin polymer (Gilarranz *et al.* 2000). The second hypothesis is related to substantial modification of the chemical composition of the fiber, thus affecting the intrinsic mechanical properties of the reinforcing fibers. Possibly, both mechanisms can occur simultaneously. According to Bledzki and Gassan (1999), alkaline pulping 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 inter-fibrillar 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 the lignin is gradually removed, the middle lamella joining the ultimate cell wall 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 pulping of lignocellulosic fibers (Sharma *et al.* 1995; Sreenivasan *et al.* 1996, Varma *et al.* 1984). The increase in the crystallinity index of alkal-treated fibers occurs because of the removal of the cementing materials, which leads to better packing of cellulose chains (Varma *et al.* 1984).

Micromechanical Analysis

The modified rule of mixtures (Eq. 5) could predict, with enough precision, the behavior of composite materials with natural fibers or natural strands as reinforcements:

$$\sigma_t^C = f_c \cdot \sigma_t^F \cdot V^F + (1 - V^F) \cdot \sigma_t^{m*} \tag{5}$$

In the above equation, σ_t^C and σ_t^F are the ultimate tensile strengths of the composite and the strand, respectively. The σ_t^{m*} term is the matrix tensile stress at the failure point of the composite. The V^F term is the volume fraction of the reinforcement and the f_c term is the compatibility factor. The main problem involves the estimation of the value of the intrinsic tensile strength of the fiber (σ_t^F) needed to predict σ_t^C. The objective is to determine a value of a mean σ_t^F for OTF inside the composite using Bowyer-Bader methodology and the Kelly-Tyson equation. Table 3 shows the evolution of σ_t^C for a 6 wt. % of MAPE. The optimum percentage of MAPE was around 6 wt. % for composites with a 40% of reinforcement (Table 3) (Rodriguez *et al.* 2010). Figure 2 shows the distribution of the lengths of the fibers in the composite after its extraction.
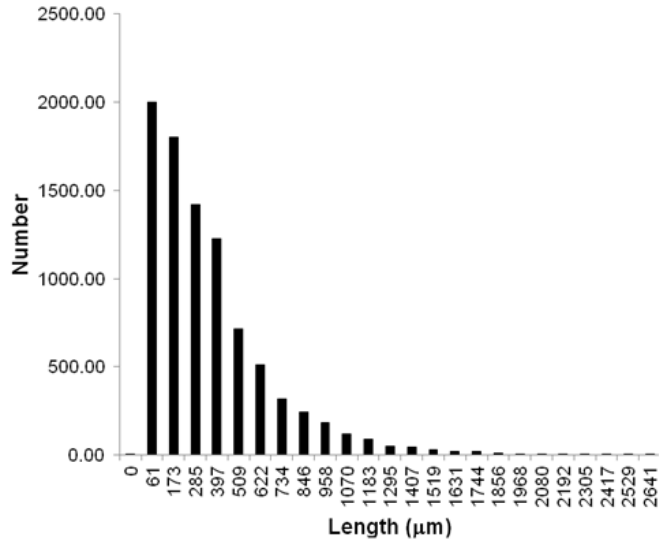
Fig. 2. Length vs. number of fibers

The distribution of fibers, with a major presence of relatively short ones, indicates the effects of the shear efforts experienced by the composites. Karmaker and Youngquist (1996) studied the effects of the attrition during the composite fabrication. Figure 3 shows the experimental stress-strain curve for the composite and the plain matrix. The matrix tensile strength function at any strain is obtained by fitting the equation to the experimental stress strain result. The mean result is reflected by a 4th order polynomial found from regression, which in this case is:

$$\sigma_t^m = -0.0041 \, \varepsilon^4 + 0.1062 \, \varepsilon^3 - 1.0825 \, \varepsilon^2 + 5.6284 \, \varepsilon + 0.5213 \tag{6}$$
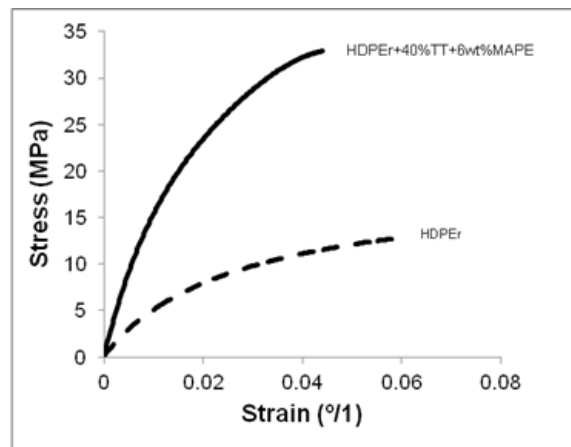

Fig. 3. Stress-strain curve for the recycled HDPE matrix and the
40% triticale + 6 wt. % MAPE composite

We computed the intrinsic Young's modulus for the composites with 10 to 40 wt. % OTF using the Hirsch model (Hirsch 1962). The theoretical mean intrinsic Young's modulus for the triticale fibers was found to be 13 GPa.

The experimental data values required to apply Bowyer-Bader methodology are summarized in Table 4. The strain levels 1 and 2 correspond to 1/3 and 2/3 of the

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composite strength. The recycled HDPE stress was computed by Equation 6. All the data were obtained in accordance with the described methods.

Table 4. Composite Properties, Stress-Strain Input Data, and Parameters

Reinforcement Volume fraction	0.3
Average weighted length (μm)[*]	629
Average diameter (μm)	21.25
Composite strength (MPa)	32.9
Composite modulus (GPa)	2.52
Fiber modulus (GPa)	13
Elongation at break (%)	5.06
Strain level 1 analyzed (%)	1.69
Composite stress at strain level 1 (MPa)	19.75
Strain level 2 analyzed (%)	3.37
Composite stress at strain level 2 (MPa)	29.8
Matrix stress at strain level 1 (MPa)	7.21
Matrix stress at strain level 2 (MPa)	10.68
Matrix stress at break (MPa)	12.15

* Weighted-weighted in length

Figure 3 shows a typical tensile stress-strain curve. In this case, it corresponds to the 40% OTF, 6 wt. % MAPE composite. The Bowyer-Bader model, as an approximation, assumes that: (1) the stress transfer at the interface increases linearly from zero at the fiber end to a maximum value; (2) fiber-matrix debonding does not happen; (3) χ_1 is independent of strain and constant for all fiber lengths; (4) interfacial shear stress is independent of loading angle; (5) porosity in the composite is negligible; and (6) fiber and matrix stress *vs.* strain curves is linear (Li *et al.* 2009). After the application of the Bowyer-Bader methodology, the obtained results are shown in Table 5.

Table 5. Output Data Obtained from the Bowyer-Bader and the Kelly-Tyson Methodologies to Input Data

Reinforcement Volume Fraction	0.3
Orientation factor - χ_1	0.304
Interface shear strength (MPa) - τ	7.63
Fiber's tensile strength at maximum stress (MPa) - σ_t^F	430
Critical length (μm) - l_c^F	598.8

The mean value of the orientation factor (χ_1) was 0.304. This value is very similar to the one obtained for a composite of PP and stone groundwood fibers (Lopez *et al.* 2011). The obtained orientation factor implies a mean orientation angle of 42.05°, taking into account that $\chi_1 = \cos^4 \theta$ (Mittal *et al.* 1987).

The critical fiber length (l_c^F) was calculated from: $l_c^F = (d^F \sigma_t^F)/2\tau$ (Li *et al.* 2009). All the calculations were made according to the described methodology.

The value of the mean interface shear strength (IFSS) obtained was 7.63 MPa. This value is in the interval of 8.5 MPa and 7.35 MPa derived from the application of the Von Misses and Tresca criteria, respectively (Pegoretti *et al.* 1996; Vilaseca *et al.* 2010),

considering the σ_t^m of the recycled HDPE. Those values of the IFSS could be denoted as near to the optimum given that the value of σ_t^c is meaningful when compared with other strands or fibers (Lopez *et al.* 2011; Vilaseca *et al.* 2010; Beckermann and Pickering 2009; Sanadi *et al.* 1994).

Once values for χ_1 and τ were obtained, we used the Kelly-Tyson modified equation (Eq. 3) to obtain a value for σ_t^F (Table 5). The mean obtained value of σ_t^F was 430 MPa, and it is comparable with other publications (Bledzki *et al.* 2004; Pickering *et al.* 2007; Niu *et al.* 2011). Once σ_t^F was known, and by means of the modified rule of mixtures (Eq. 5), it was possible the evaluation of the coupling factor f_c (Table 6). Then knowing that $f_c = \chi_1 \chi_2$, we were able to compute $\chi_2 = 0.625$.

Table 6. Coupling Factor Computed by Means of the Modified Rule of Mixtures

% fiber	V^F	MAPE wt. %	f_c
10	0.066		0.175
20	0.138	6	0.180
30	0.215		0.176
40	0.299		0.188

As it could be observed from Table 6, a composite with 6 wt. % MAPE exhibited a mean coupling factor of 0.18. This value is slightly inferior to 0.2 predicted by Sanadi as the optimum (Sanadi *et al.* 1994).

Values for *X*, *Y*, and *Z* were derived from Equation 2, which can be simplified as $\sigma_t^C = \chi_1 (X + Y) + Z$. To estimate the final contribution to the composite, *X* and *Y* must be multiplied by χ_1. Figure 4 shows the contribution of *X* (subcritical fibers), *Y* (super-critical fibers), and *Z* (matrix) to σ_t^c. The contribution of the subcritical fibers remains minimum, but not negligible for the composites with larger amount of reinforcement.
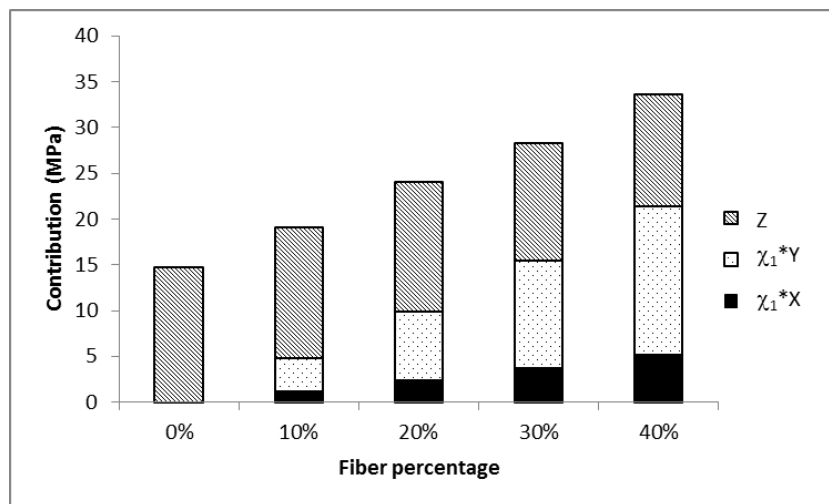

Fig. 4. Contributions of subcritical fibers, supercritical fibers, and matrix to the final composite strength

In all the cases it is clear that there was substantial contribution of supercritical fibers, representing respectively 19%, 31%, 41%, and 48% of the total tensile strength. Taking into account the cumulative contribution of the supercritical and the subcritical fibers ($X+Y$), the contribution increases respectively to 24.8%, 41.2%, 54.4%, and 63.6%. The contribution percentages of the subcritical and supercritical fibers to the tensile strength of the composite material was in line with that shown by hemp strand composites (Vallejos *et al.* 2012).

CONCLUSIONS

1. The organosolv triticale fibers showed its effectiveness as reinforcement for composite materials.

2. The tensile strength of the 40 wt. % OTF composite with 6 wt. % of MAPE increased by more than 120% when compared to that of the high density recycled polyethylene. The increase was higher than that shown by similar composite materials using polypropylene and hemp strands as reinforcement (Vallejos *et al.* 2012).

3. The Young's modulus of the same composite material increased by a factor of 3.4 when compared to that of the recycled HDPE

4. The intrinsic tensile strength of the OTF was not as high when compared to another fiber, but the efficiency shown was very high.

5. The contribution of the supercritical fibers increased quickly with the OTF %, while the contribution of the matrix decreased slightly. The contribution of the subcritical fibers also increased but in a lower percentage. Consequently the real increase of the properties of the composite material was due to the contribution of the supercritical fibers.

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