FAST AND SIMPLE METHOD FOR PREDICTION OF THE MICROMECHANICAL PARAMETERS AND MACROMECHANICAL PROPERTIES OF COMPOSITE MATERIALS

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The method described in the present work was assessed through the production of composite materials made of polypropylene reinforced with chemical thermomechanical pulp of hemp core fibers. Composite materials were obtained by extrusion and injection molding, and by the addition of a coupling agent to ensure a good interphase between fiber and matrix. In all cases, the composite materials were considered as semi-aligned reinforced. Tensile strength was selected as a representative parameter and was studied by the Kelly-Tyson model.[1] Since the original Kelly-Tyson equation was formulated for fully aligned reinforced composite materials, the present work uses a modified one, where the orientation factor is included. The fiber length and diameter distribution were determined by the extraction of the fibers from the composite materials and analyzed in a MorFi equipment. The orientation factor was calculated taking into account the predicted tensile strength for fully aligned composites and the experimental value from the semi-aligned ones. The interfacial shear strength was estimated through Tresca and Von Mises criteria. The values obtained through the simulation were compared to the experimental ones, showing a good correlation between the mathematical model and the experimental part.

Keywords: composite, MorFi, Kelly-Tyson model

INTRODUCTION

The statement of the twelve principles of green chemistry[2] is a clear consequence of the growing environmental awareness, which has been a popular topic during recent years. Regarding composite materials, the main concerns are related to the low degradability of plastics, the growing legal aspects that limit the use of landfill space and increase the cost of its use, the CO_2 emissions due to incinerations, and the cost and availability of fossil sources. These considerations have augmented the interest in the use of natural and renewable fibers as reinforcement for composite materials.[3,4] Although there are a lot of potential advantages in favor of this initiative,[4] there are also some inefficiencies in the interface between natural fibers and polymers to deal with, since the polyolefin matrices, such as polypropylene, are hydrophobic, while natural fibers are hydrophilic.[5-9] While there are some studies on the replacement of glass fiber-based composites by natural fiber reinforced composites,[5,10-12] their application in the industry is nowadays scarce. One of the first concerns of an industrialist is knowing all the technical information related to the material. Usually, the total characterization of a series of composite materials implies a lot of expensive and time consuming methods and techniques. While macroproperties, such as tensile strength, Young's modulus or impact strength, are easy to determine with limited equipment, to find out the micromechanical properties of the composites special equipment is needed, the time and the costs also increase geometrically.[13] Nonetheless, the micromechanical properties inform on the degree of optimization of the composite materials.[14] As mentioned above, natural fiber reinforced composites usually show bad interfaces due to the hydrophobic nature of the matrices and the hydrophilic nature of the fibers.[15] This made it necessary to use coupling agents and fiber surface treatments. In this regard, the scientific literature agrees on the use of maleic acid as coupling agent as one of the best alternatives to increase the quality of the interphase.[8,16-19] The coupling agent used in the present work was maleic anhydride-grafted polypropylene.

There are some definite bounds that could inform the researcher on the suitability of the interphase between the reinforcement and matrix. These bounds are determined with different equations or models. In the present research, the coupling factor from a modified rule of mixtures and the interfacial shear tensile strength predicted by Tresca or Von Mises criteria were used.[15,20]

This work proposes a method to evaluate the intrinsic tensile strength of the fibers, and their orientation factor inside the matrix. The method is aimed at characterizing a composite material, reinforced with a percentage of fibers. Then, based on the scientific literature, we propose an estimation of the tensile shear strength and the compatibility factor. These values could be used then to predict the values of the tensile strength of composite materials with different reinforcement percentages. The methodology could determine or narrow the number of composites to fully characterize, thus saving time, costs, materials and expensive or pollutant reagents. To do so, composites with 30 to 50% hemp core fiber reinforced polypropylene were prepared and mechanically tested. The experimental information was used to validate the proposed technique.

EXPERIMENTAL

Materials

The untreated hemp core of *Cannabis sativa* was provided by Agrofibra S.L. (Puigreig, Spain). The polymeric matrix used was polypropylene (PP) ISPLEN® 090 G2M (Repsol-YPF, Spain). Epolene® G3015 from Eastman (Netherlands), a modified maleic anhydride-grafted polypropylene (MAPP) coupling agent, was used as received.

Obtaining hemp core straws

Hemp straws can be separated into two main components, fibers and core. Hemp fibers or strands are long, proceeding from the outer rings of the hemp straw. Core straws are the inner material of the straw. Figure 1[21] shows the straw processing.

Core straws are a byproduct of the hemp strand obtaining process. The fibers are constituted of holocellulose (70.6%), lignin (24.8%) and ashes (3.3%). Hemp straws were chopped using a knife mill. Then, the straws were separated and classified.

Treatment of hemp core straws

Hemp core straws were pulped in a 15 L batch reactor at 98±2 ºC for 90 minutes. The reactor contained a 7.5% NaOH and 0.1% anthraquinone in a 1:10 solid/liquid ratio. After pulping, the cooked straws were washed and dispersed in a pulp disintegrator. The pulp was then passed through a Sprout-Waldron single-disk defibrator, and oven dried in a Dycometal oven at 80 ºC for 24 h before its use as reinforcement. The process yield was around 70% hemp core fibers (HCF).

Composite preparation and characterization

Composite materials comprising 30, 40 and 50 wt% HCF/PP with 6% of MAPP were prepared in a Brabender® internal mixing machine. The working parameters were 80 rpm during 10 min at a temperature of 180 ºC. The MAPP was added to the mixer with the PP pellets. Thereafter, the blends were cut down to pellets in a blade mill and stored in a climatic chamber for 48 h. The samples for the tensile test were produced with a steel mold in accordance with ASTM D3641 standards in an injection-molding machine. For each composite blend, 10 test specimens were obtained. Tensile tests were carried out with an Instron 1122 universal testing machine following ASTM D638 regulations.

Fiber extraction from composites and morphological analysis

Injection-molded composites were successively refluxed in chloroform, acetone, and decahydronaphthalene (decalin) to eliminate all the components of the polymeric matrix. Fiber aliquots were collected and analyzed using an automatic fiber morphology analyzer.

Micromechanics

A modified rule of mixtures[22] was used to compute the intrinsic strength of the fibers (σ_t^f):

$$\sigma_t^C = f_c \cdot \sigma_t^f \cdot V^f + (1 - V^f) \cdot \sigma_t^{m*} \quad (1)$$

where σ_t^C and σ_t^f are the ultimate tensile strengths of the composite and the strand, respectively; σ_t^{m*} is the matrix tensile stress at the failure point of the composite; V^f is the volume fraction of the reinforcement and f_c is the compatibility factor. The compatibility factor f_c is supposed to be 0.2 in the case of very good interphases, and 0.18 for good ones.[15]

Using the data obtained from the stress-strain tests of the matrix, it was possible to approximate the curve to a 4th degree polynomial, which was used to compute the contribution of the matrix to the final strength of the composite. In the case of the PP matrix used, the polynomial was:[6]

$$\sigma_t^{m*} = -0.0159 \cdot (\varepsilon_t^C)^4 + 0.3712 \cdot (\varepsilon_t^C)^3 - 3.3674 \cdot (\varepsilon_t^C)^2 + 14.8953\varepsilon_t^C + 0.0493$$

The theoretical strength of an aligned fiber composite was calculated using the Kelly and Tyson equation [1] (K&T):

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

where d^f and l^f_j represent, respectively, the fiber diameter and the length, while the intrinsic strength (σ_t^f), orientation (χ_1) and interfacial shear strength (τ) are characteristics of the reinforcing fibers. The equation presents two factors that are unknown and difficult to measure experimentally: τ, and χ_1. The value of the orientation factor χ_1 could be assumed to be 1 if the fibers are aligned with the load direction, and it decreases when the reinforcing fibers mean alignment deviates. On the other hand, Tresca (TrC)($\tau=\sigma_t^m/2$) and Von Mises criteria (VMC)($\tau=\sigma_t^m/3^{1/2}$) have been proven useful to approximate the value of the interfacial shear strength of similar composites.[6,23,24] Usually, the value is enclosed in the interval defined by both criteria, but is closer to the Von Mises one. Accordingly, it seems appropriate to define its theoretical value as:

$$\tau = \frac{VMC+0.5\cdot(VMC+TrC)}{2} \quad (3)$$

With all the assumptions made, it is possible to use equation $K\&T$ to compute the theoretical value of the tensile strength of an aligned composite $\sigma_t^{Cal,al}$.

Attending to the $K\&T$ equation, the only difference between an aligned and a semi-aligned composite is the orientation factor value. Then, the division of the experimental by the theoretical value will tend to χ_1. Thus, it will be possible to use the computed values to predict the theoretical values of the aligned tensile strengths for different percentages of reinforcement ($\sigma_t^{Cal,al}$), recalculate the orientation factors and compare them with the one initially obtained. Figure 2 shows the flowchart of the methodology. All the micromechanical parameters were calculated for the case of the 40% composite and used to compute the theoretical values for the 30 and 50% composites. The values were compared to assess the goodness of the proposed methodology.

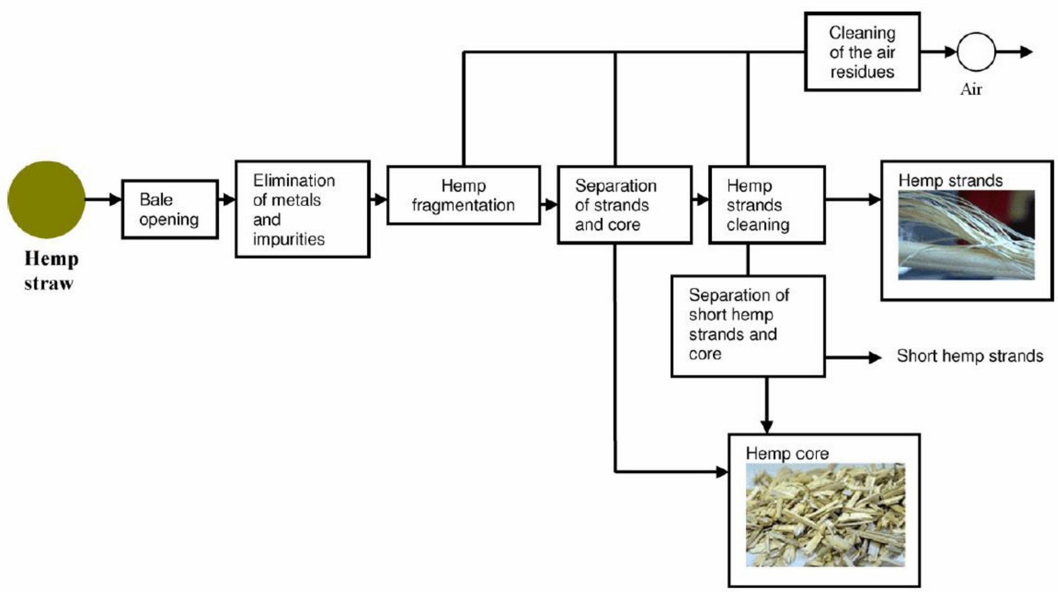

Figure 1: Hemp core straw treatment and separation[21]

RESULTS AND DISCUSSION

Table 1 shows the experimental values obtained after the strain strength tests were performed.

The composite strengths increased with the amount of fibre, leading to an increment of almost 100% with respect to the matrix for the 50% reinforced materials. At the same time, the elongation at break of the composite materials decreased, showing that the composite materials with higher fibre showed a more fragile behaviour. The work to fracture test supports this conclusion by the decrease of the energy that the materials are capable to absorb. The tensile strength increased linearly with the amount of reinforcement, showing a good dispersion of the fibres inside the composite and also a good fibre/matrix interphase. This fact supports the use of linear models to predict the composite strength behaviour, at least for up to 50 wt% reinforcement contents. One of the simplest, but more accepted models is the modified rule of mixtures (Eq. 1). Its formulation in the case of the tensile strength of a composite, and with all the experimental data available, allows computing the intrinsic tensile strength of the reinforcement, but a value for the compatibility factor must be proposed. In this study, a value of *fc*=0.2 was initially used, supposing a good to optimum interface. The obtained values were 553, 547, and 525 MPa for the 30 to 50 wt% composites, as the control composite was reinforced with 40% hemp content, the 547 MPa value was adopted to perform the following calculations. Then, a 15.4 MPa value for the the interfacial shear strength (τ) was computed in accordance with the presented methods (Eq. 3).

The matrix was dissolved and the fibers were obtained and analyzed. Figure 3 shows the fiber length distribution for the 40% composite. The fiber length distribution and the mean length and diameter were used to compute the 30 to 50% later calculations.

With all the available data, it was possible to apply the Kelly and Tyson equation (Eq. 2) to evaluate the theoretical strength of a fiber aligned reinforced composite (χ_1=1). The equation divides the fibres in two groups depending on their length: subcritical fibres, fibres that are under the critical length and are not totally loaded, and supercritical fibres, fibres that are longer than the critical length, and are totally loaded, representing a major role in the reinforcement. The critical length is defined by:

$$l_c^F = d^F \cdot \sigma_t^F / 2\tau \qquad (4)$$

The theoretical value of the tensile strength of the 30% HCF/PP aligned composite ($\sigma_t^{Cal,al}$) was calculated to be 146 MPa. Then, by calculating the ratio between $\sigma_t^C/\sigma_t^{Cal,al}$, it was possible to compute the theoretical value of the orientation angle: 0.356. The value is within the 0.25 to 0.4 range of expected values, and could be compared with very similar values obtained for other composite materials fabricated with the same equipment. If the relation $\chi_1=\cos^4(\alpha)$ is accepted, then the orientation angles for the composites are between 38º and 40º.

Once the micromechanical properties for the 40% composite were known, it was possible to compute the theoretical tensile strength of the 30 and 50% composites. Table 2 shows the obtained values under the row σ_t^{Cal}.

One of the hypotheses that could be enunciated is that the difference between the theoretical values and the experimental ones is mainly due to the orientation of the fibers inside the composite. Then, it is supposed that the interfacial shear strength, the length distribution, and the intrinsic strength remain approximately the same. Therefore, the division between the experimental values and the theoretical ones will determine the orientation factor. Table 1 shows the computed values. These values are within the 0.25 to 0.4 expected range, and could be compared with very similar values obtained for other composite materials fabricated with the same equipment. If the relation $\chi_1=\cos^4(\alpha)$ is accepted, then the orientation angles for the composites are between 38º and 40º.

The usefulness of the methodology is clearer when only one of the reinforcement percentages is experimentally characterized, and the data are used to predict the theoretical values of other reinforcement percentages.

Table 1
Experimental data of the tensile strength characterization of the materials

Hemp (wt%)	V^f (%)	σ_t^C (MPa)	ε_t^C (%)	W_F (MJ/m^3)
0	0	27.60±0.50	9.30±0.2	158.51±9.13
30	0.217	44.70±1.24	4.71±0.2	59.77±1.79
40	0.301	49.86±1.86	3.40±0.2	40.60±2.39
50	0.393	54.80±1.77	2.69±0.2	25.43±0.97

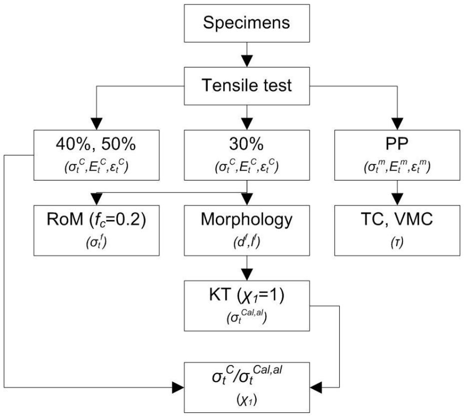

Figure 2: Methodology flowchart

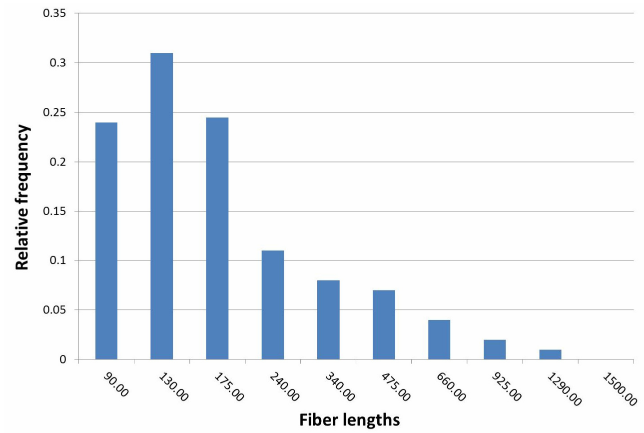

Figure 3: Fiber length distribution of fibers inside the composite

Table 2
Computed mechanical and micromechanical values

% Fiber	V^f	σ_t^{m*} (MPa)	σ_t^f (mROM)	τ (MPa)	σ_t^{Cal} (MPa)	χ_1	L_c (μm)
30	0.217	26.5	542	15.4	113.4	0.39	315
40	0.301	24.2	542	15.4	141.4	0.35	322
50	0.393	22.2	542	15.4	166.2	0.34	319

CONCLUSION

The proposed method returned useful results, in line with the experimental ones obtained in past works.

The hypotheses imply good interfaces and the use of linear models, and thus should not be applied if the experimental values show non-linear patterns.

The correlation between the experimental tensile stress and the theoretical tensile stress for an aligned fiber composite is almost perfect.

The method could be applied to make a rough estimation of some of the micromechanical characteristics of composites, allowing to avoid expensive and time-consuming methods. Nonetheless, the methodology does not substitute experimental methods to fully calculate the properties, but could be used to discard cases and better experiment scheduling.

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