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Macro and micro-mechanics behavior of stifness in alkaline treated hemp core fibres polypropylene-based composites

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ABSTRACT

Traditionally, glass fibre has been used as plastic reinforcement whenever mechanical properties of a matrix, like stiffness, do not meet the specifications. However, current tendencies try to replace glass fibres by more sustainable fibres to obtain eco-friendlier products. Natural fibres show comparatively good physical and mechanical properties and, unlike glass fibres, come from renewable resources and are recyclable and sustainable. In this work, hemp straw discarded from hemp manufacturing was used as reinforcement in polypropylene composites. One drawback associated to hemp straw is its high lignin content that reduces its reinforcing potential. Therefore, a soft alkaline treatment was employed to adjust the lignin contents. In this work, the evolution of the Young's modulus with the NaOH treatment is assessed and discussed. Intrinsic Young's moduli of hemp straw fibres at different alkaline conditions were determined by Hirsch model. Finally, Tsai-Pagano and Halpin-Tsai equations allowed the prediction of the theoretical Young's modulus of the composites. The results showed the competitiveness of a by-product reinforced composite in front of commodity materials.

1. Introduction

The concern of the society towards the environment is nowadays promoting the development of eco-friendly materials [1–4]. In recent times, therefore, the use of natural fibres to substitute synthetic reinforcements like glass fibres has gained importance in the composites field [5–7].

The present work is part of a comprehensive study where hemp straw is being exploited as raw material to produce composites with significant tensile and flexural moduli, notable strength, and relevant acoustic and thermal properties. Hemp is an agricultural commodity crop applicable to a wide variety of uses like textiles, paper, building materials, foods … The global production of hemp was170.000 tons in 2014 [8]. Nonetheless, its production changes noticeably year to year, being 85.000 and 113.000 tons in 2013 and 2014, respectively in Refs. [8,9]. Once the hemp plants are treated to extract the bast fibers, 50–55% of the outputs are hemp core, considered as waste with little value. This hemp core is usually devoted to bedding for livestock, due to its high capacity to liquid abortion [1].

In the literature, there are examples of the integral exploitation of hemp straw used as filler for composite materials, but such materials showed uncompetitive mechanical properties despite the use of coupling agents. Good example for this is Vallejos et al. work [10] who reported that PP composites with 40 wt/wt% of hemp straw, in presence of maleated-polypropylene, improved by 20% the tensile strength of the polymeric matrix. This improvement can be defined as weak and the literature shows higher increments for natural-fiber or by-product fibres reinforced composites [11,12]. However, if hemp core is treated in alkaline conditions and defibrated, a byproduct turns into a valuable source of papermaking or reinforcing fibers. This is the case of a recent work by some of the authors [1] where PP composites reinforced with hemp core fibres gave significant improvements for matrix tensile strength. Moreover, these treatments agreed with the principles of green chemistry to minimize waste generation [13].

Nonetheless, stiffness is one of the most significant characteristics to attain competitive composites for structural and semi structural applications [14]. The stiffness evaluates the resistance of a body to deform under loads. More specifically, this property is related to the Young's

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modulus or modulus of elasticity, which is a numerical quantification of the stress increment over an increment of strain in the elastic region of the material. From an engineering point of view, a design has to sustain reasonable deformations under working conditions. However, a high percentage of polyolefin matrices show comparatively low rigidity, explaining the need to reinforce them with fibrous materials.

Industries like automobile and building are two examples where lignocellulosic fibres can be used as polymer reinforcements. Automobile applications include door panels, package trays, car roofs or load floors. The building sector uses lignocellulosic reinforced polymers for decking, railing, fencing, windows and doors [4,15–17]. In these products, the rigidity is more relevant than its ultimate strength. Therefore, the stiffness of the hemp core fibre reinforced polypropylene composite materials, where a by-product can replace a raw material, is worth studying. To the best of our knowledge, this has not yet been investigated.

Natural fibres show high standard deviations in the value of their intrinsic modulus of elasticity [18,19]. Moreover, the experimental quantification of the Young's modulus in short fibres, such as hemp core fibres, is difficult, and due to its variability must be based in a large number of experiments. Besides, some researchers declare that the intrinsic properties of a single fibre outside and inside a composite can vary noticeably [20]. Nevertheless, the intrinsic elastic modulus of the fibres is an essential parameter to predict the stiffness behaviour of the composite material. This study proposes a specific methodology to analyse the Young's modulus of short-fibre reinforced composites. Such methodology is based on the use of Hirsch [21,22], Cox-Krenchel [23,24] and Tsai-Pagano [25,26] models to solve the modified rule of mixtures (mRoM). The method has been used previously and has proved its usefulness to establish the intrinsic Young's modulus of the fibres and to predict the Young's modulus of the composites [12,27–31]. These models have allowed the determination of the intrinsic modulus of the fibres, the efficiency factor, orientation factor, length factor or the influence of the aspect ratio in the final properties of the composite.

In the present work, hemp straw was submitted to a chemo thermomechanical treatment under alkaline conditions to obtain hemp core fibres. Hemp core fibres/polypropylene composites were then prepared and their Young's modulus characterized. The composite materials were produced with percentages of reinforcement in the range from 20% to 50% wt%. A coupling agent was also added in some cases. The effect of alkaline treatments on the Kappa number and on morphological properties of the fibres is reported and discussed.

2. Experimental

2.1. Materials

Hemp straw of *Cannabis Sativa* was kindly provided by Agrofibra S.L. (Puigreig, Spain). The matrix was polypropylene (PP) ISPLEN® 090 G2M kindly provided by Repsol-YPF (Tarragona, Spain). Maleic-grafted polypropylene (MAPP) Epolene® G30 15, with an acid number of 15 mg KOH/g and Mn of 24800 Da, which was acquired from Eastman Chemical Products (Middelburg, The Netherlands) was used as coupling agent where necessary.

Chemical reagents, sodium hydroxide (NaOH) and anthraquinone (AQ), both were supplied by BASF (Tarragona, Spain), were used for fibres digestion. Decahydronaphtalene (decalin), provided by Sharlab S.L. (Sentmenat, Spain), was employed to dissolve the polymeric matrix in the fibre extraction process. All the reactants were used as received.

2.2. Preparation of hemp core fibres

The hemp core straw was submitted to a chemo thermomechanical process during 30 min at 160 °C in a 15 L batch reactor. Three different digestions, containing 5%, 7.5% and 10% of NaOH based on the fibre content (wt%), were produced. The liquid/solid ratio was set at 10. A 0,1% of AQ based on the fibre amount was added to catalyse the cooking process. Following, the resulting treated hemp straw was water rinsed and passed through a Sprout-Waldron equipment to obtain defibrated fibres from the hemp core bundles. Finally, the slurry was filtered and dried for at least 24 h at 80ºC in a Dycometal oven (Viladecans, Spain) to obtain dry hemp core fibres.

2.3. Compounding and injection moulding

PP composites comprising 20–50% wt% hemp core fibres (HCF) contents were compounded in a Gelimat multikinetic mixer model G5S by Draiswerke (Mahaw, New Jersey, USA). The process parameters were 2500 rpm for 2 min until a discharge temperature of 210ºC was reached. Previous researches showed that the fibre length remained longer with Gelimat multikinetic mixer than with other mixing processes like twin screw extruders or Brabender mixers. Longer lengths promote better strengthening capabilities to the fibres and improve the final tensile properties of the composites [32].

The resulting blends were ground in pellet shape by means of blade mill equipment and, dried and stored for at least 24 h at 80 °C in a Dycometal oven (Viladecans, Spain) before processing.

The standardized samples for stress-strain test were prepared with a Meteor 40 injection-moulding machine Mateu & Solé (Barcelona, Spain). The processing temperatures of the three heating zones were 175, 175, and 190 °C, respectively. The first and the second pressures were 120 and 37.5 kgf/cm^2, respectively. Normalized samples (approximately 160 × 13.3 × 3.2 mm) in accordance with ASTM D638 were produced.

2.4. Mechanical characterization

The specimens were conditioned during 48 h at 23 °C and 50% of relative humidity as required by ASTM D618 standard. Following, the specimens were tensile tested using a universal testing machine DTC-10 supplied by IDMtest (San Sebastian, Spain), fitted with a loading cell charge of 5 kN and working at a speed rate of 2 mm/min. Results were obtained from the average of at least 5 samples. An extensometer MFA2 (Velbert, Germany) was used in agreement with ASTM D638.

2.5. Kappa number determination

Kappa number is a method used to determine the lignin content in a sample of pulp. The Kappa number determination of hemp core fibres was realized in line with the standard ISO 302:2004-Determination of Kappa number.

2.6. Fibres extraction and morphological characterization

Reinforcing fibres were extracted from the composites by polymeric matrix dissolution using a Soxhlet equipment. Decalin was employed as solvent. Small portions of material were cut and introduced into a specific cellulose filter and placed inside the Soxhlet apparatus. The fibre extraction was finished after 24 h. Then, the extracted fibres were cleaned with acetone and water to eliminate the residual solvent. Lastly, the extracted fibres were dried at 105 °C for 24 h.

Fibre morphological properties were determined and characterized by Morfi Compact analyser by Techpap SAS (Grenoble, France). Length and diameter distributions were achieved processing close to 30000 images. A minimum of 4 samples were analysed for every test.

2.7. Density measurement

The density determination of the composites (ρ^c) was performed using a pycnometer. The temperature conditions were 23 °C and distilled water was utilized as reference liquid. The method followed was the ISO 1183-1. The identity used to calculate the density of the