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Stiffness of bio-based polyamide 11 reinforced with softwood stone ground-wood fibres as an alternative to polypropylene-glass fibre composites

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A B S T R A C T

Polyolefin had been successfully reinforced with glass fibres and applied in the industry during the last decades. However there are unsolved processability and recyclability problems due to its fragility. There are also concerns related with the human health. This had promoted the interest towards more environmentally friendly and healthier reinforcements such as natural fibres. In addition, the oil origin of polyolefin increases the interest in researching greener polymer alternatives. This work proposes polyamide 11 (PA11) as a promising alternative to polypropylene or other commodity polyolefin. This paper studies the behaviour of the Young's modulus of natural fibre reinforced PA11 composites at different fibre contents. The composites were prepared, injection molded and characterized to tensile modulus. Afterwards a micromechanical modelling was performed using two models: Hirsch's and Tsai-Pagano's. The results allow proposing natural fibre reinforced PA11 composites as a suitable replacement to glass fibre reinforced polypropylene composites.

1. Introduction

Stiffness has a big impact on designing structural applications; one of the main objectives during the design process is choosing materials that ensure the appropriate stiffness and strain during the use of the designed good [1]. Stiffness is related with the necessary strength to deform a material, and it is associated to the Young's modulus which represents the average slope in the elastic region of the strain-stress diagram. Experimentally, the Young's modulus is measured in the strain interval comprehended between 0.05 and 0.25% [2].

Composite materials are produced by combining two or more phases. The main objective of this mixture is obtaining materials with combined properties [3]. The chemical structure and intrinsic properties of both phases, the aspect ratio of the reinforcement and its orientation against the loads, the volume content of fibre and its dispersion inside the matrix have a remarkable importance on such final properties [2,4].

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Polyolefins, such as polypropylene (PP), polyethylene (PE) or polyvinylchloride (PVC), commonly considered commodities, when reinforced with glass fibres or natural fibres show a high enhancement of its stiffness and are, nowadays, widely used in industrial scale [5,6]. Nevertheless, these polymer matrices are commonly obtained from oil and in the near future it will be interesting searching for more sustainable biodegradables or bio-based matrices such as bio-polyamides (BioPA) alternatives [7–9]. Nonetheless one of the main drawbacks of such composites is its poor ability to sustain high deformation without breaking. This is specially visible in starch based composites [10,11]. Therefore, one of the objectives in the development of bio-based composites should be obtaining materials which could achieve stiffness values similar to glass fibre reinforced polyolefin composites.

BioPA are biotechnologically obtained polyamides (PA), produced through different processes and raw materials [12,13]. The natural resource contents can differ between different BioPAs, like polyamide 11 (PA11) which is 100% bio-based and polyamide 6.10 (PA6.10) that only has a 62% of bio-based carbon. However, their melting point, higher than the cellulose degradation temperature, made PAs difficult to reinforce with lignocellulosic fibres [14]. Nonetheless, adapting the processes, it is possible to reinforce these higher melting point PAs with natural fibres [15,16].

PA11 is produced using 11-aminoundecanoic acid derived from castor oil [12]. Castor oil is extracted from the *Ricinus communis*, a common plant in Asia. The variety of fatty acids contained in the oil, with the appropriate refinery process, lead to obtain a huge variety of products used in the industry [17,18]. PA11 shows good oil and water resistance [19], fair biocompatibility [20] and it is non degradable. Furthermore PA11 has a lower melting point than other PA (above 190 °C) which made it an interesting matrix to be reinforced with natural fibres [21,22]. Although PA11 is not degradable, it is bio-based and has mechanical properties comparable to PP. This converts PA11 in a greener alternative to PP, especially as composite matrix.

Glass fibres (GF) are, nowadays, one of the most extended polyolefin reinforcements. The main reason is its high capacity to improve the strength and stiffness of the composites. Nevertheless, this properties enhancement is accompanied by an acceptable diminution of the toughness of the composites. However, the main drawback of GF is related with its fragility, which reduces the number of recyclability cycles, as each process subjects the reinforcement to shrinkage. Other disadvantages of GF are related with the healthiness: dermatitis and respiratory problems have been reported, related with the manipulation of such material [23–25]. On the other hand, natural reinforcements based on lignocellulosic fibres have shown reasonable capacities to increase the mechanical properties in composites, regardless the polymer matrix used [26]. Its use is highly limited by the degradative temperature of the natural fibres. Despite performing a lower relative reinforcing effect than GF, lignocellulosic fibres have high specific properties, they are less abrasive, non-toxic, recyclable and easier to process [27–29]. Those advantages made natural fibres an attractive reinforcement for applications such as automotive [30], construction [31] and industrial goods [32,33].

Stone ground-wood pulp (SGW), a natural fibre, mechanically produced from *Pinus radiata*, with a yield of 98.5%, was choosed as reinforcement in that study. SGW has been commonly used in the paper industry [34]. Besides, SGW reinforced PP composites showed good stiffness compared to GF sized and GF coupled PP composites [35–37].

Considering the European Union environmental goals for 2025 and 2035 [38], the scientific community is doing an effort in the research of fully bio-based or biodegradables composites materials [39,40]. In a previous work, some of the authors studied the effect of the SGW reinforcement in the tensile strengths of the composites [40]. Significant increases of such property against the SGW content were obtained. Nonetheless, it is known that, commonly, increases on the strength of the materials drive to decreases on its toughness [41]. In this work, PA11-SGW composites with 20–60% of SGW contents were prepared and its Young's modulus was analysed and discussed. To better understand the effect of the reinforcement, some micromechanic properties of the Young's modulus were modelled.

2. Experimental

2.1. Materials

The composites were prepared using polyamide 11 (PA11) (Rilsan® BMNO TL), with a density of 1.03 g/cc and a melt volumetric index of 11 cc/10 min at 235 °C/2.16 kg. The PA11 was kindly provided by Arkema S.A (Colombes, France) as the polymer matrix. Stoneground wood (SGW) derived from softwood (*Pinus radiata*) was supplied by Zubialde, S.A. (Aizarnazabal, Spain) and was used as lignocellulosic reinforcement.

Dichloromethane (Extra Pure, stabilized with approx. 50 ppm of amylene, Pharmpur®) and Formic acid (Extra Pure, 98–100%), both supplied by Scharlau (Sentmenat, Spain) were used to dissolve the PA11 matrix and recover the fibres from the composites.

2.2. Methods

2.2.1. Compounding

Five different PA11-based composites, incorporating from 20 up to 60% of SGW reinforcement were prepared. The compounding was performed using a Gelimat kinetic mixer. The SGW and the polymer were added at a low speed (300 rpm).