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Bio-polyethylene reinforced with thermomechanical pulp fibers: Mechanical and micromechanical characterization and its application in 3D-printing by fused deposition modelling

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ABSTRACT

Two biobased polyethylenes (BioPE) and thermomechanical pulp (TMP) fibers were used to produce biocomposites. The impact of TMP fibers on the mechanical properties was assessed in detail. An increase on the viscosity of the melted biocomposites was quantified and was related to the incorporation of the TMP fibers (0–30% w/w). The impact of polyethylene functionalized with maleic anhydride (MAPE) on the mechanical properties was quantified. Compared to neat BioPEs, a maximum increase of tensile strength between 115 and 127% was obtained, for the biocomposites containing 6% w/w of MAPE and 30% w/w TMP fibers. The formulated biocomposites containing 10 and 20% TMP fibers were three-dimensional (3D) printed, by fused deposition modelling. We confirmed that TMP fibers facilitated the 3D printing and correspondingly improved the mechanical properties of the biocomposite materials.

1. Introduction

During the last years, composite materials with natural fiber reinforcement, commonly called wood-plastic composites (WPCs), have received considerable attention [1–4]. Additionally, the term "biocomposite" has been adopted to classify the materials that are composed of, at least, one bio-based component, e.g. bioplastics, natural fibers, nanocellulose. Biocomposites offer the possibility to produce products with adequate properties for a range of applications [5,6], and with a good environmental performance [7].

Biocomposites based on natural fibers and conventional plastic polymers do not solve completely environmental problems associated with the use of fossil-based materials (using e.g. polypropylene (PP), polyethylene (PE)). Usually, the content of natural fibers is in the range from 10 to 50% w/w [8,9]. Thus, at least 50% w/w of biocomposite material is commonly fossil-based. The use of biobased plastics (bioplastics) can potentially contribute to improve the environmental performance of future plastic products. Specifically, biobased polyethylene (BioPE) is industrially available and can be manufactured from biomass, e.g. sugarcane [10]. BioPE is a chemically identical alternative to polyethylene from petrochemical feedstock. Nowadays, the production of bioplastics is comparatively expensive [11]. Therefore, the addition of natural fibers would be highly beneficial from a point of view of costs and mechanical properties.

The use of natural fiber-based biocomposites is presented as an opportunity for applications in automotive industry where lightweight construction is an important factor. Nowadays, automotive companies are attempting to reduce the use of man-made fibers by the addition of natural fibers in the non-structural plastic parts of vehicles. The eco-awareness of actual society and the incipient legislative actions from governments promote the study and use of biobased materials. In this sense, biocomposites from biobased matrices like natural fibers are emerging as new materials [12].

However, natural fibers have some limitations, e.g. i) processing temperatures below 220 °C [13] and ii) incompatibility between hydrophilic fibers and commonly hydrophobic polymer matrices [14]. The use of maleated polyethylene as coupling agent is a rather attractive method because it avoids the use of expensive and toxic reagents [15]. The improvement of the interfacial adhesion between fibers and matrix can lead to improved physical and mechanical properties of the biocomposite materials [14,16].

Three-dimensional (3D) printing has appeared as a new technology

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to produce customized and complex structures [17], which can be difficult to produce by conventional methods such as extrusion and injection molding. Fused deposition modelling (FDM) is one of the most used 3D printing methods because this enables quick and easy manufacturing of complex shapes [18]. The FDM method applies a nozzle that deposits material layer by layer [19]. Moreover, FDM can be used in rapid-prototyping or tailor-made manufacturing for specific workpieces [20]. Advances in the 3D printing of biocomposites have been reported recently [20,21], focusing on the use of poly-lactic acid (PLA) as a matrix material, reinforced with wood fibers.

This work advances our previous study [22] and focuses on the evolution of the mechanical properties of biocomposite materials produced with two different biobased polyethylenes (BioPE), reinforced with thermo-mechanical pulp (TMP) fibers. PE is a semi-crystalline polymer, which shrinks and warps during solidification. Such characteristics affect negatively the 3D performance of PE. Therefore, there are no commercial PE filaments that guarantee printability by FDM [22]. Hence, in this study we provide additional data that TMP-reinforced BioPE can be manufactured with adequate mechanical performance for injection molding. Additionally, we demonstrate and confirm that the biocomposites are suitable for manufacturing printable filaments, for fused deposition modelling (FDM).

2. Materials and methods

2.1. Materials

TMP fibers were kindly provided by Norske Skog Saugbrugs in granule form with approx. diameter of 8 mm. The TMP fibers were collected from a reject press. The fibers were granulated and dried by Norske Skog Saugbrugs. More details about the TMP fibers used in this study can be found in the literature [21,22].

The polymer matrices were two biopolyethylene (BioPE) grades for injection molding. The BioPEs had a relatively high and low melt flow index (MFI) and were coded as BioPE1 and BioPE2, respectively. The BioPE grades were kindly provided by Braskem (Sao Paulo, Brazil) and had a molecular weight of 61.9 g/mol and 92.9 g/mol for BioPE1 and BioPE2, respectively. In order to improve the compatibility between the fibers and the BioPE, polyethylene functionalized with maleic anhydride (MAPE) was used as coupling agent (Fusabond MB100D, 0.9%, Eastman Chemical Products, San Roque, Spain).

Reagents used for fiber characterization were bought from Scharlab Spain (Barcelona, Spain) and used without further purification.

2.2. Assessment of TMP fibers

The morphological characteristics (length and width) of the raw TMP fibers and the TMP fibers extracted from the biocomposites were assessed with a MorFI compact analyzer (TechPap, France). After compounding, the TMP fibers were extracted from the biocomposites by BioPE solubilisation. The extraction of fibers was performed using a Soxhlet equipment and Decalin as solvent of small pieces of the biocomposites. A cellulose filter was used and the extraction was carried out during 24 h. Finally, the extracted fibers were rinsed with acetone and distillated water, and dried in an oven at 105 °C, 24 h.

2.3. Biocomposite processing

TMP fibers, together with BioPE and MAPE, were mixed at different percentages (w/w) by using an intensive kinetic Gelimat mixer (Fig. 1).

Initially, the fiber amount was introduced at 300 rpm for its disaggregation. BioPE together with MAPE were added at 300 rpm. Finally, the mixing process was carried out during 2 min at 3000 rpm and the blends were discharged when a temperature of approximately 210 °C was reached. In order to study the impact of MAPE contents on the tensile strength of the composites, the materials with a 20% of reinforcement were coupled with 0–8% w/w of MAPE (with regard to the fiber content). Once the percentage of coupling agent needed to obtain the best tensile strength was established, the rest of coupled biocomposites added this amount of MAPE. Coupled and uncoupled biocomposite blends containing 10 to 30 wt % of TMP were prepared. The obtained blends were ground to relatively small granules (diameter ~10 mm). The granules were dried and stored at 80 °C during 24 h. For comparison purposes, the same process was applied to produce biocomposites with a high density fossil PE matrix (INEOS Polyolefins, Europe) and TMP fibers. The biocomposite granules were used for injection molding. Additionally, the BioPE-based biocomposites were tested for filament extrusion and for 3D-printing, by FDM.

2.4. Injection molding

The biocomposite specimens were injection-molded in a 220 M 350-90U injection machine (Aurburg, Germany). The injection molding process was carried out at 180, 190, 200 and 210 °C. The first and second pressures during injection molding were 120 and 37.5 kg.cm-2, respectively.

2.5. Filament extrusion and 3D printing

Filaments for 3D printing were manufactured based on the techniques described by Filgueira et al. [21,22]. A Noztek filament extruder was used. The applied temperatures in the Noztek extruder were 180, 190 and 200 °C. The filaments were used for 3D printing in an Original Prusa i3. Standard dog bone specimens for mechanical testing were 3D printed.

2.6. Physical characterization

Melt flow index (MFI) measurements were carried out in a plastometer CEAST (Pianezza, Italy). The plastometer was equipped with two independent thermal resistances heating a capillary. The MFI value indicates the amount of biocomposite melted and delivered, at constant temperature and load, during 10 min.

2.7. Mechanical characterization

Test specimens were placed in a climatic chamber (Dycometal, Spain) at 50% of relative humidity and 23 °C during at least 48 h before testing, according with ASTM D618. Tensile properties were assessed using an Universal testing machine Instron TM 1122, with a 5 kN load cell. An extensometer MFA2 was used for more precise measurements of deformation. The tensile tests were carried out at a speed rate of 2 mm/min following ASTM D790 standard.

2.8. Micromechanical analysis of tensile strength

The quality of the interface between the matrix and fibers in the biocomposites was verified through the use of three models. The first model was a modified Rule of Mixtures (mRoM) for the tensile strength of biocomposite materials:

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

Where, σ_t^C is the composite tensile strength, f_c is the compatibility factor, σ_t^f is the intrinsic tensile strength of the fibers, V^f is the volume fraction of the reinforcement and $\sigma_t^{m^*}$ is the matrix tensile strength at the composite failure point.

The second model, a modified Kelly and Tyson equation, was used to divide the fiber contribution on the composite tensile strength in two groups, the supercritical and the subcritical fibers [23,24]: