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Reprocessing of wood flour reinforced polypropylene composites: Impact of particle size and coupling agent on composite and particle properties

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This work aims to understand the degradation induced by multiple injection molding cycles on numerous properties of wood flour reinforced polypropylene (PP) composites. The influence of the initial wood particle size was studied as well as the influence of the addition of polypropylene grafted with maleic anhydride (PPgma) as a coupling agent at a given rate. Biocomposite compounds (20wt% of wood flour) are produced by twin-screw extrusion. Then, multiple injection and grinding cycles were performed (up to 7 cycles) to obtain normalized samples. The evolution of the wood flour particle characteristics is first assessed by SEM observation, size measurements and nanoindentation experiments. Then, the evolution of the PP matrix microstructure is determined by SEC tests (average molecular weight measurements), rheometer tests and DSC (polymer crystallinity). Finally, material mechanical properties are measured at a macro-scale thanks to tensile tests. Our experimental results show that the composite mechanical properties remain quite stable after 7 processing cycles despite wood flour degradation and PP degradation.

1. Introduction

The use of vegetal fiber reinforced composites is growing since several years. These composites mainly concern thermoplastic polymers reinforced by wood fibers or flour. This trend is mainly fueled by the building and the automotive industries. One of the most widespread materials is wood flour reinforced polypropylene (PP) composite that is mainly prevalent in the construction market. Assessing its recycling capability is up to now a challenging economic and scientific goal [1].

Stark and Berger [2] investigated the effects of particle size on the properties of PP filled with wood flour. They concluded that tensile modulus and strength decrease with increasing particle size beyond a 250 μm average particle size. A previous work [3] also showed that fine flour filled composite presents a better strength and modulus and higher elongation than the coarse flour filled composite.

Another relevant parameter to consider is the fiber/matrix interface. Its quality is a prevalent topic of study because of its significance in the composite general properties. Given the poor adhesion between the natural fibers and the conventional polymer matrices, fiber surface treatments can be carried out. Among these, the addition of maleic anhydride grafted polypropylene (i.e. PPgma) is one of the most widespread. PPgma is able to bind PP macromolecular chains to hydroxyl groups present at the natural fiber surface thanks to ester bonds. In a wood sawdust flour reinforced polypropylene composite, tensile modulus and strength, flexural modulus and strength and impact strength were found to be improved by adding maleated PP (PPgma) [4]. Numerous works also show this tendency with various processing parameters, maleic anhydride contents and wood flour rates [5,6]. However, after a certain amount of this coupling agent, the tensile strength decreases because of its low molecular mass inducing a plasticization effect [7].

Thus, the effect of the wood particle size and the PPgma content on the properties is well known. However, these two factors are not studied during reprocessing cycles in order to simulate recycling in the case of wood flour reinforced PP.

Nevertheless, the reprocessing degradation of wood-fiber reinforced PP composites was studied by several authors among them

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Beg and Pickering [8]. They reported a gradual reduction of impact strength, tensile modulus and strength and an increase of the tensile elongation and crystallinity rate according to the successive processing cycles of composites. Bourmaud and Baley [9] compared thermal and mechanical properties of PP reinforced with hemp, sisal and glass fibers after reprocessing. SEM pictures display a length fiber reduction after reprocessing. After 7 processing cycles, they show that the tensile modulus decreases by 0.66% and by 10% for hemp and sisal fibers reinforced composites respectively and by 40% for the glass fiber reinforced composite. During processing, the natural fiber bundles are cut by their length but they also split into finer bundles and single fibers. The glass fibers only break by length and the diameter remains unchanged. Thus, the natural fiber aspect ratio (length/diameter L/D) is less affected than the glass fibers, and the mechanical performance is maintained while reprocessing natural fiber composites. The fiber length and the L/D ratio are two of the major key factors influencing the mechanical properties of a composite material [10]. Its decrease causes a lower rigidity and resistance. In case of a limited degradation of the matrix, the smaller fiber lengths may cause less fiber entanglement which leads to a more ductile composite material. The loss of impact resistance can be due to PP degradation by chain scission. Some rheological tests bring out a significant viscosity reduction, which can be mainly explained by PP chain scission [11–13].

In most processing studies, general properties of the composites are measured but not the evolution of the mechanical properties of the particles themselves. Wood flour is particles which are sensitive to the high temperatures in extrusion and injection processes. The measurement by nanoindentation of elastic modulus is proposed to assess the evolution of the wood flour particles properties (hardness and elastic modulus) through the successive processing cycles. The nanoindentation showed a considerable potential for in-situ and comparative analysis to obtain local mechanical information from the different constituting layers on plant cell walls. Nanoindentation tests are performed with a Berkovich-type indenter loading the wall at an angle of approximately 25°. Consequently, the resulting three-dimensional stress is not only a result of the deformations and thus modulus in longitudinal direction, but is also affected by the transverse and shear moduli (together microfibril angle and Poisson ratios) [14]. Thus owing to very different scales and solicitation modes, the average modulus of fibers measured by nanoindentation in longitudinal direction is low compared to the modulus obtained with conventional tensile tests [15,16]. In literature, nanoindentation was used for comparative studies in hair [17,18], wood [19,20] or bamboo cell walls [21]. Moreover, it is a suitable tool to estimate the decrease of cell wall mechanical properties induced by processing [15].

Thus, this paper aims to evaluate the influence of the wood particle size and of a PPgma coupling agent on the degradation of spruce wood flour reinforced PP composites after grinding and injection molding cycles (up to 7 cycles). The evolution of the wood flour particle characteristics is first assessed by SEM observation, size measurements and nanoindentation experiments. Then, the evolution of the PP matrix microstructure is determined by SEC tests (average molecular weight measurements), rheometer tests and DSC (polymer crystallinity). Finally, material mechanical properties are measured at a macro-scale thanks to tensile tests.

2. Materials & methods

2.1. Materials

The matrix polymer was a standard homopolymer PP H733-07 grade supplied by Braskem Co. (Brazil) with a melt flow rate of 7.5 g/10 min (230 °C, 2.16 kg) according to the ISO1133 standard. PPgma (Orevac® CA100) provided by Arkema Co. (France) was used as coupling agent with a 1%w/w grafting rate and was dry-mixed before processing at 5%w/w of the PP part. The wood flour is based on spruce wood and is obtained from AFT Plasturgie Co. (France). Some characterizations of the initial wood particles are presented in section 3.1. Two wood particle sizes were considered noted G1 and G2. Both wood flours were added at a content of 20% by weight in PP. Table 1 sums up the composition of the studied materials regarding the content by weight.

The processing methodology is summarized in Fig. 1 and the successive stages are detailed below.

2.2. Compounding

Prior to extrusion, the polymer granules have been dried at least 4 h at 80 °C and the wood flour, 15 h at 80 °C. Table 2 reveals that these drying conditions induce a decrease of WF moisture content from around 4.8%–0.4% using a Karl Fisher method with a sample heated at 150 °C.

In the subsequent phase, the PP matrix and the wood particles were mixed together in a BC21 Clextral co-rotating twin-screw extruder (step ①). Its L/D ratio is 36 with a 25 mm screw diameter and a 900 mm screw length. The heating barrel is composed of 12 modules. Polymer pellets were fed in module 1 and the fiber incorporation was made through a feeding hopper located on module 5. Temperature was set at 180 °C along the barrel. The screw speed was arbitrarily fixed at 300 rpm, with a total feeding rate of 4 kg/h.

Extruded compound rods were cooled into water and rapidly dried by air pulsing before the granulating step. Pellets were kept overnight at 80 °C in a vacuum oven beforehand to remove the residual humidity (step ②).

2.3. Injection molding and grinding cycles

The pellets were injection molded on a Krauss Maffei KM50-T180CX. The temperature was fixed at 210 °C along the barrel. The mold was kept at 25 °C by a water cooling system. The plastification and injection speeds were set respectively at 120 rpm and 60 $cm^3 s^{-1}$. The samples were injected to obtain dog-bone samples ISO 1A according to ISO 527-2 (step ③). Some of them were grinded and injected multiple times (step ④) while a set was characterized (step ⑤).

The grinding process was performed in a RETSCH SM300 cutter mill to obtain flakes. The grinding process was carried out at 700 rpm at room temperature with an 8 mm sieve. The flakes were stored at room temperature and vacuum dried overnight at 80 °C before injection molding. This protocol was accomplished 1, 3, 5 and 7 times in order to purvey samples called P1, P3, P5 and P7 according to the number of passes they underwent (step ⑥).

2.4. Wood flour characterizations

2.4.1. TGA

To determine the process temperature effect on wood particles, wood flour was tested by thermo-gravimetric analysis (TGA) using

Table 1
Composition of the studied materials.

	Wood flour content	PPgma content on the PP part
Neat PP	–	–
PP/WF G1	20%w/w	–
PP/WF G2	20%w/w	–
PP/PPgma/WF G2	20%w/w	5%w/w