Improvement of wood polymer composite mechanical properties by direct fluorination

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ABSTRACT

Direct fluorination was applied to wood flour to enhance the mechanical properties of wood polyester composites by acting on the wood/polymer interfaces. X-ray tomography showed that this treatment decreased the quantity of pores within the composites. Tensile and flexural tests revealed an improvement of the composite properties through fluorination of the reinforcements. Both the elastic modulus and the strength were increased. The treatment also improved the creep properties of the wood–polyester composites, making them less sensitive to temperature. Furthermore, the composite surface energy and its hydrophilicity were decreased after the treatment of the wood reinforcements.

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1. Introduction

Natural fibers, including wood, are increasingly used in order to replace usual aramid, carbon or glass reinforcements in composites, and to reduce the amount of fossil carbon produced every day. The most common application fields of wood polymer composites are building (decking for outdoor, doors, windows, *etc.*) and automotive industries (in door panels, dashboards, interior liners, *etc.*). Wood polymer composites are also used in other areas such as furniture industries (kitchen worktops, wardrobes, tables, *etc.*) or packaging (pallets, container floors, *etc.*). These composites give added value to a relatively abundant and cheap raw material, *i.e.* co-products of wood transformation. Nevertheless, their use is restricted to non-structural applications because of the lack of compatibility between the hydrophilic wood reinforcements and the hydrophobic polymer matrix, which generates porosity and low ability to transfer load at the interface, leading to poor composite mechanical properties. Therefore, a pre-treatment of the wood reinforcements is often necessary before processing these composites. During the last few years, various treatments have been developed to decrease wood's hydrophilic character and make it more compatible with polymer matrices. However, none of them is really convincing at the industrial scale in the case of

wood based composites: chemical treatments based on maleated polypropylene [1], maleated polyethylene [2], benzyl chloride [3], acetic or propionic anhydrides [4], isocyanate [5], silane [6] or ketene [7] are environmentally harmful and their durability is often limited; alkali treatment [8] lowers composite water absorption but also its stiffness [9]; high temperature treatments [10–12] are highly energy-consuming and lead to a degradation of the wood's mechanical properties [13]; treatments using corona discharge [14] or cold plasma [15] turn out to be very costly and species specific.

In this study, we propose to apply direct fluorination to wood flour so as to enhance the properties of wood polyester composites. Direct fluorination [16] is commonly used to treat the surface of polymers to improve their barrier properties against oil, increase their resistance to chemical solvents attack, and make them more hydrophobic [17]. It is already an industrial process for the surface treatment of petrol tanks in order to achieve barrier properties, and for the synthesis of fluorinated carbons [18]. It has also been used to treat synthetic reinforcements, such as aramid fibers [19], in order to lower their hydrophilicity and enhance their adhesion to various polymers. In addition, some studies have been carried out on the application of the direct fluorination to paper, and a significant decrease in the product's surface energy has been obtained [20].

In a previous article, we studied the effect of direct fluorination on the wood flour properties [21]. An efficient decrease in the wood's water content was observed without displaying damage to the particles' physical structure. We would thus expect better

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compatibility of the wood particles with polymers after this treatment, and hence better mechanical properties. Based on these promising initial results, work was carried out at the composite scale, aiming at determining the effect of direct fluorination of the wood flour on the derived composite mechanical properties. To the authors' best knowledge, the use of fluorine chemistry to enhance the properties of wood based composites has never been studied before.

First, pores within the treated and non-treated wood composites were revealed by X-ray tomography. Then, tensile, flexural and creep tests were performed on unsaturated polyester reinforced with non-treated or fluorinated wood flours. The effect of the treatment of the reinforcements on the composite surface energy was also studied by contact angle measurements. Finally, the effect of humidity was investigated by testing composites that had been stored several days at normal or high relative humidity.

2. Materials and methods

2.1. Materials

The wood flour under study was a mix of spruce and Douglas species obtained from sawmill co-products in Auvergne, France. Its density was measured by the solvent method using xylene and toluene and was found equal to 1.41 ± 0.17. The flour was sifted so that its grading was smaller than 250 μm. The polymer used to process the derived composites was unsaturated polyester Norsodyne G703, from Cray Valley, whose density was given equal to 1.17.

2.2. Treatment of the wood flour

The process of direct fluorination using F_2 gas has been described in a preceding article [21]. It has been optimized in order to obtain non-degraded but well fluorine-coated and less hydrophilic wood particles. About 5 g of wood flour were scattered on a tray, placed in a nickel reactor, and outgassed under vacuum at 150 °C for 2 h to remove all traces of absorbed water. Actually, water may react with F_2 gas to form HF molecules, which are known to act as catalysts during the fluorination and may induce inhomogeneous grafting. Then, the sample was exposed to a fluorine atmosphere (F_2/N_2) for 3 h under the following temperature gradient: 42 °C on the left of the oven, 55 °C in the middle and 70 °C on the right. The temperature was used to control the reaction and create an homogeneous treatment. The F_2 molecules that did not react with the wood surfaces were removed by a N_2 gas flow for 2 h. Finally, after 11 h at ambient temperature, the treated wood flour was heated once again to 150 °C under a flow of N_2 gas for 1 h to remove non-grafted fluorinated species such as F_2, HF, CF_4 and C_2F_6. The presence of covalent C–F bonds onto the wood flour surface (i.e. the covalent grafting of the fluorine atoms) has been previously underlined using infra-red spectroscopy and ^{19}F solid state NMR [21].

2.3. Wood–polyester composite processing

Wood polyester composites with a reinforcement weight fraction of 45% (corresponding to a volume fraction of 40%) were processed by hot compression molding, using a SATIM hot press. The wood polyester mixture was poured into an aluminum mold of 100 mm × 100 mm × 2 mm covered with 0.12 mm thick PTFE sheets on each internal face (aimed at easing the final demolding). Then, the closed mold was placed in the press and kept under a pressure of 60 kN and a temperature of 80 °C for 2 h, so as to ensure the resin cross-linking. The cooling to ambient temperature

was performed using air under pressure. Treated and non-treated wood flour composites were processed in exactly the same way, without any pre-curing of the materials. Samples for the mechanical tests were taken from the plates thus obtained; their width was 10 mm and their thickness was 1.76 mm.

2.4. X-ray tomography

Wood polyester composites were analyzed by X-ray tomography in order to determine the amount of pores present within the volume of the sample and to compare these amounts according to the applied treatment. The device used, a compact SkyScan 1174, enables the 3D reconstruction of the composite with a resolution of 30 μm under 50 kV, which means that the micro-porosity cannot be visualized. Therefore, this may give an idea of the potential improvement of the fiber/matrix compatibility. The dimensions of the observed composites were 10 mm × 10 mm × 1.76 mm.

2.5. Mechanical characterization

2.5.1. Tensile tests
The tensile tests were performed on a Zwick/Roell Zmart Pro test machine, with a prescribed crosshead displacement rate of 1 mm/min and a gage length of 50 mm, until the rupture of the sample. The initial length of the samples was 70 mm, adapted from the standard NF EN ISO 527-3 [22]. The tests were conducted at room temperature (about 23 °C) and relative humidity (about 40%). The longitudinal stress (σ) and strain (ε) of the sample were calculated from the measured force (F), the sample elongation (ΔL), the sample section S_0 (supposed to be constant), and the gage length L_0 as follows:

$$\sigma = F/S_0 \tag{1}$$

$$\varepsilon = \Delta L/L_0 \tag{2}$$

2.5.2. Flexural tests
Three point bending tests were performed on an Instron 5543 test machine equipped with a 500 N load cell, at room temperature (about 23 °C) and relative humidity (about 40%). The length of the sample was 35 mm and the distance between the supporting pins was set to 28 mm, following the standard NF EN ISO 178 [23]. The samples were tested at a crosshead displacement rate of 1 mm/min with the load applied at mid-span. The flexural strain (ε) and stress (σ) at the middle of the sample were calculated from the deflection (Y, corresponding to the crosshead displacement) and the force (F). Considering the material as homogeneous, we had:

$$\varepsilon = 6hY/L_0^2 \tag{3}$$

$$\sigma = 3FL_0/2bh^2 \tag{4}$$

where L_0 is the span, b and h respectively the width and the thickness of the samples.

2.5.3. Creep tests
The composite creep behavior was studied by tensile creep tests, following the standard NF EN ISO 899-1 [24]. The tests were performed on a viscoanalyser Metravib VA 2000 equipped with a 150 N load cell. The initial sample length, restricted by the volume of the viscoanalyser, was 50 mm and the gage length was set to 40 mm. The samples were tested under a constant tensile force of 30 N (corresponding to 1.7 MPa) and a constant temperature (20, 45 or 60 °C) for 4000 s. The frequency of acquisition of the