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From hydrophilic to hydrophobic wood using direct fluorination: A localized treatment

D'un bois hydrophile à un bois hydrophobe par fluoration directe : un traitement spatialement localisé

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ABSTRACT

When controlled by the treatment duration or the quantity of reactive molecules, direct fluorination using F_2 gas is efficient to decrease the hydrophilicity of wood both in the form of massive piece and powder. To prove that silver fir pieces and wood flour (mix of spruce and silver fir species) were investigated as representative examples. In both the cases, hydroxyl groups are converted into C–F bonds resulting in the decrease in affinity for water. Fluorination is mainly located in the outer parts of the wood cell, where the content of lignin is the highest, maintaining the inner ones nonmodified. Because the microstructure is maintained by this location of fluorination, the mechanical properties are conserved for silver fir pieces. The mechanical properties are even enhanced for composite containing fluorinated wood flour because of a better compatibility between the fluorinated fillers and the polyester matrix.

Mots-clés:
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RÉSUMÉ

Lorsque la durée de traitement ou la quantité de molécules réactives est contrôlée, la fluoration directe en utilisant le fluor moléculaire F_2 s'avère efficiente pour faire décroître l'hydrophilie du bois, à la fois sous forme de pièces massives et de poudre. Pour mettre en évidence cet effet, des morceaux de sapin et de la farine de bois ont été fluorés à titre d'exemples significatifs. Dans les deux cas, les groupements hydroxyles ont été remplacés par des liaisons C–F conduisant à la diminution de l'affinité du bois pour l'eau. Le greffage covalent d'atomes de fluor est principalement localisé sur la paroi externe des cellules, où la teneur en lignine est la plus forte. Comme la microstructure est globalement conservée grâce à cette fluoration spatialement localisée, les propriétés mécaniques sont maintenues pour le sapin. Celles-ci sont même améliorées pour des composites contenant de la farine de bois, grâce une meilleure compatibilité entre charge fluorée et matrice polyester.

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1. Introduction

Wood is considered as one of the main renewable materials used for a huge number of end products such as wooden frames, pulp and paper, wooden panels furniture, and so forth. Besides the ecological and economic aspects, which appear as an evidence, this raw material is light, stiff, and resistant and is available in large quantities and at low cost. All these advantages make wood a key material. However, its hygroscopic character results in high sensitivity to ambient humidity as well as changes in temperature. Swelling and shrinkage caused by water absorption and desorption result in cracks and volume deformation in the wood [1–3]. With the aim to decrease the wood's hydrophilic character, several studies and various treatments have been developed, for example, thermal treatment [4,5], electric discharge [6,7], or chemical treatment [8–14]. Nevertheless, most of them require toxic products and high energy costs because of their low yield or energy efficient aspects; the application at the industrial scale is then difficult. Wood pieces are not the only materials that can be used. Natural fibers and wood flour are increasingly used in bio-based composites. In the context of reduction of the amount of fossil carbon produced every day, the aim consists in the replacement of usual fillers, aramid fibers, carbonaceous materials, either fibrous or nanometric, or glass to reinforce the polymer matrix in composites. The main difficulty encountered when processing wood polymer composites is the lack of compatibility between the wood flour and the polymer matrix [15–17]. The intrinsic incompatibility between the hydrophobic polymer, which contains nonpolar groups, and the filler, which is hydrophilic with strongly polarized groups [18], does not favor good wettability of the filler in the matrix, that is, good adhesion, and, as a consequence, a homogeneous dispersion of the wood flour into the commonly used hydrophobic polymer [16]. This results in pores in the composite at the polymer/wood interface that alters the mechanical properties because of two main factors. On one hand, the mechanic strain is not efficiently transferred from the matrix to the fillers and, on the other hand, this porosity allows water absorption to occur; this latter effect is favored by the intrinsic hydrophilicity of the wood flour filler. Water is absorbed into the filler once incorporated into the polymer, leading to dimensional instability and thus to a degradation of the composite mechanical properties [19,20].

In this study, we propose to apply direct fluorination to both wood flour and massive wood pieces to broaden the application range of wood pieces, especially for outdoor uses and to enhance the properties of wood polyester composites. Considering wood as a complex biocomposite, involving hemicellulose and lignin polymer matrix and cellulose as the “filler”, a chemical treatment efficient to polymers may be considered: direct fluorination [21]; it 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 [22]; the best industrial process example is the surface treatment of petrol tanks to achieve barrier properties. Direct fluorination is also performed for the synthesis of fluorinated carbons [23]. To lower their hydrophilicity and enhance their adhesion to various polymers, fluorination has also been used to treat synthetic reinforcements, such as aramid fibers [24]. As a good indication that fluorination may be efficient for wood, some studies have been devoted to the surface treatment of paper; fluorination results in a significant decrease in the product's surface energy, that is, a gain in hydrophobicity [25].

2. Experimental section

2.1. Materials

Silver fir wood samples were selected from a French sawmill located in Auvergne. The logs processed by this sawmill come from plantations harvested in the sawmill proximity. The tested samples were selected randomly and their size reduced to $10 \times 1 \times 0.8$ cm to fit our experimental devices.

The wood flour under study was a mix of spruce and silver fir species obtained from sawmill coproducts 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 composites was unsaturated polyester Norsodyne G703, from Cray Valley, whose density was 1.17. Wood polyester composites with a reinforcement weight fraction of 45% (corresponding to a volume fraction of 40%) were processed by hot compression molding using an SATIM hot press. The wood/polyester mixture was poured into an aluminum mold of 100 mm × 100 mm × 2 mm size covered with 0.12 mm thick polytetrafluoroethylene sheets on each internal face (aimed at easing the final demolding). Then, the closed mold was placed in the press and kept under pressure of 60 kN and temperature of 80 °C for 2 h, so as to ensure the resin cross-linking. The cooling to ambient temperature was performed using pressurized air. Treated and untreated wood flour composites were processed in exactly the same way, without any precuring of the materials.

2.2. Fluorination

Fluorination by pure molecular fluorine was conducted in dynamic mode (continuous flux of reactive gas in an open reactor) or static mode (a defined amount of F_2 molecules is injected into a close reactor). Gaseous fluorine was purchased from Solvay Fluor (purity 98–99% v/v with HF max. 0.5% v/v and other gases, primarily O_2/N_2 at approximately 0.5% v/v). Before each fluorination whatever the mode, samples were outgassed overnight under primary vacuum (10^{-3}mbar) at 80 °C to eliminate physisorbed molecules on the particle surface or porosity. The reactor was flushed for 1 h with nitrogen gas to remove all traces of air and moisture. Whatever the means of fluorination, a passivated nickel reactor was used (covered with NiF_2).

About 5 g of wood flour was placed in a passivated nickel reactor. The thickness of the powder deposition was

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