



Direct fluorination applied to wood flour used as a reinforcement for polymers

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ARTICLE INFO

Article history:

Received 18 December 2012

Received in revised form 16 January 2013

Accepted 21 January 2013

Available online 1 February 2013

Keywords:

Wood flour

Direct fluorination

Water content

ABSTRACT

Direct fluorination was applied to wood flour in order to improve its compatibility with polymers and thus enhance the properties of wood–polymer composites. Fourier–transform infrared spectra and ¹⁹F solid-state nuclear magnetic resonance results underlined a successful covalent grafting of fluorine atoms onto the wood chemical structure. No physical damage of the wood particles was observed during scanning electron microscopy analysis. The thermal behaviour of the wood flour was also studied by thermogravimetric analysis. The hydrophilic property changes of wood flour were examined by evaluating the water content and the rate of water uptake of samples under different relative humidity conditions. A decrease in the wood flour water content was noted after fluorination. All these studies tend to prove the efficiency of this treatment on wood hydrophilia.

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1. Introduction

The major difficulty encountered when processing wood–polymer composites (WPC) is the lack of compatibility between the wood flour and the polymer matrix (Chotirat, Chaochanchaikul, & Sombatsompop, 2007; Kazayawoko, Balatincez, & Matuana, 1999; Klason, Kub  t, & Str  mvall, 1984). In point of fact, the former is highly hydrophilic while the latter is generally hydrophobic. This incompatibility results in poor adhesion between the matrix and the reinforcements, and leads to a poor ability to transfer load at the interface, reducing the interest of WPC. In recent years, various treatments have been developed and used in order to reduce the hydrophilic character of wood and make it compatible with polymers (Cui, Lee, Noruziaan, Cheung, & Tao, 2008; D  ny  di, M  cz  , & Puk  nszky, 2010; Dominkovics, D  ny  di, & Puk  nszky, 2007; Ichazo, Albano, Gonz  lez, & Perera, 2001). However, none of these approaches is really convincing at the industrial scale.

On the other hand, direct fluorination is currently used to treat the surface of polymers, in order to enhance their barrier property against multiatomic molecules, e.g. hydrocarbons, and improve their chemical resistance to solvent attack (Kharitonov et al., 2005; Kharitonov, 2008). It is known to decrease the permeability of materials such as polyvinyl chloride, thermosetting

resins, polyurethane, or polypropylene. The application of direct fluorination to synthetic fibres, such as aramid fibres, has also been analysed, evincing a clear impact on material surface energy (Maity, Jacob, Das, Alam, & Singh, 2008). In particular, direct fluorination has been developed in the treatment of carbon fibres, and an increase in fibre hydrophobicity has been observed by contact angle measurements (Bismarck et al., 1997; Ho, Beamson, Shia, Polyakova, & Bismarck, 2007).

The application of direct fluorination to lignocellulosic products has been studied in the past with the intention of making Kraft paper waterproof (Sapieha, Verreault, Klemberg-Sapieha, Sacher, & Wertheimer, 1990). Then the surface fluorination of paper was developed using the CF₄ radio-frequency plasma technique (Sahin, Manolache, Young, & Denes, 2002). In both studies, the published results reported a significant increase in the paper contact angle (i.e. a decrease in the hydrophilic character) after fluorination.

These findings suggest that direct fluorination could be applied in the treatment of wood fibres used as reinforcements for polymer matrices. This work focuses on the direct fluorination of wood flour in order to reduce its hydrophilic character and then improve its compatibility with unsaturated polyester. Changes in the chemical structure of the wood and the impact on its surface properties are observed and discussed, in order to verify the validity of this method to produce good quality WPC. The main difficulty and, at the same time, the main advantage, is the high reactivity of molecular fluorine F₂ towards wood. With such a reactive sample, fluorination, i.e. the formation of C–F covalent bonds, competes with wood decomposition; when the fluorination is not controlled,

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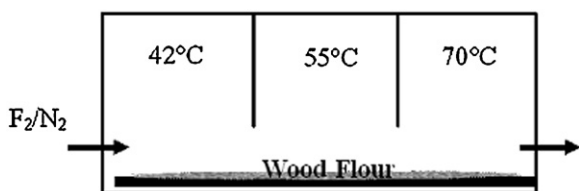


Fig. 1. Direct fluorination system.

the wood may react with fluorine gas to form volatile perfluorinated groups (such as CF_4 , C_2F_6). In other words, the wood may burn in the fluorine atmosphere as it does in air at high temperature. The first objective was therefore the perfect control of the fluorination conditions in order to treat only the surface of the wood. Once the fluorination parameters were optimised, both the non-treated and fluorinated wood flours were characterized by Fourier transform infrared (FT-IR) spectroscopy, ^{19}F solid-state nuclear magnetic resonance (^{19}F NMR) spectroscopy, scanning electron microscopy (SEM), thermogravimetric analysis (TGA), and hygroscopic analysis in order to highlight the effects of the treatment.

2. Materials and methods

2.1. Material and preparation of the wood flour

The wood used was a mix of Spruce and Douglas species, coming from sawmill co-products of the Auvergne Region in France. It was ground with a GRINDOMIX GM 200 knife mill, and sifted with a filter screen in order to obtain a powder with grading smaller than 250 μm .

2.2. Direct fluorination

About 5 g of wood flour was scattered on a tray of 45 cm length by 3 cm width, and then placed in a nickel reactor, which was passivated by a covering NiF_2 layer. The thickness of the powder deposition was less than 2 mm in order to favour the diffusion of fluorine gas in the whole volume. The gas inlet was located to the left of the sample. The entire sample was first outgassed under a dynamic vacuum (-960 mb) at 150°C for 2 h in order to remove all traces of water. This was because water molecules may be adsorbed on the surface of the wood flour and can react with fluorine gas (pure F_2) to form HF molecules, which may act as a catalyst for fluorination, leading to the inhomogeneity of the treatment. The reaction oven was divided into three parts; it was set at 42°C on the left, 55°C in the middle and 70°C on the right, as shown in Fig. 1. Such a temperature gradient is necessary to avoid a high fluorination rate near to the gas inlet of the oven. This variation allows then the control of the fluorination process and a homogenous treatment. A partial vacuum was applied to the closed reactor (-20 mb) and F_2 gas was injected in addition to N_2 gas to reach 1 atm. The total pressure inside the closed reactor was maintained constant for 3 h, and five additions of fluorine were performed in order to compensate for the consumption of molecular fluorine because of the reaction. Finally, after the removal of all the F_2 molecules over a period of 2 h thanks to a flow of N_2 gas at 150°C and then cooling to ambient temperature for 11 h, the flour was heated again to 150°C with a flow of N_2 gas for 1 h to eliminate traces of adsorbed F_2 , HF and CF_4 molecules.

2.3. FT-IR and NMR spectroscopy

Samples of fluorinated wood flour were taken at different locations in the reactor in order to check the homogeneity of the treatment using FT-IR and ^{19}F NMR analyses. FT-IR spectroscopy

Table 1

Saturated salt solutions and corresponding relative humidity.

Saturated aqueous salt solutions	Relative humidity at 20°C (%)
Potassium hydroxide (KOH)	9
Magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$)	33
Sodium bromide (NaBr)	59
Sodium chloride (NaCl)	75
Potassium sulphate (K_2SO_4)	98

was performed in attenuated total reflectance (ATR) mode using a SHIMADZU FT-IR 8300 spectrometer. The spectra were recorded in the mid infrared region ($4000\text{--}400\text{ cm}^{-1}$), and 64 co-added scans were collected for each sample.

^{19}F NMR experiments were carried out using a Bruker Avance spectrometer, with working frequencies of 282.2 MHz. For magic angle spinning (MAS), a Bruker probe operating with 2.5 mm rotors was used. A simple sequence was performed with a single $\pi/2$ pulse length of 4.0 μs . 128 scans were recorded. The MAS spinning speed was set to 34 kHz, high enough to significantly average and weaken the $^{19}\text{F}\text{--}^{19}\text{F}$ homonuclear coupling, which is the main interaction. ^{19}F chemical shifts were externally referenced to CFCl_3 .

2.4. SEM analysis

The surface morphology of the wood particles before and after fluorination was observed by SEM analysis, performed with a PHENOM FEI microscope.

2.5. TGA

The thermogravimetric analysis was performed under a nitrogen atmosphere of 0.9 bars, using a PerkinElmer TGA 4000 analyser. About 10 mg of wood flour was heated from 35°C to 450°C with a heating rate of $5^\circ\text{C}/\text{min}$. Then the sample was cooled to 35°C with a cooling rate of $50^\circ\text{C}/\text{min}$.

2.6. Hygroscopic characterisation

Humidity-controlled chambers were created following the NF EN ISO 483 standard, so as to study the hygroscopic behaviour of the wood flour under different relative humidity (RH) conditions (9%, 33%, 59% 75% and 98% RH). Hermetic jars were filled with diverse saturated salt solutions, which are listed in Table 1. A plastic tube and an iron grid were used to maintain the sample 3 cm above the solution and thus prevent direct contact with water.

The wood flour was placed in plastic caps and dried in an oven at 90°C for 48 h to attain the anhydrous state. Then each sample was conditioned in the humidity-controlled chambers until its weight was stabilized. Hygroscopic characterization was carried out by measuring the weight variation of the wood samples throughout the conditioning procedure for each relative humidity. Finally, the water content of the wood was evaluated using the following formula, where m is the sample weight at the considered time and m_0 the weight at the anhydrous state: $x = (m - m_0)/m_0$.

For each relative humidity value, five samples of non-treated and fluorinated wood flour were analysed. The weight was measured with a KERN ABJ weighing scale.

3. Results and discussion

3.1. Covalent grafting of fluorine chains onto wood particles

The ATR FT-IR spectra of the wood flour before and after direct fluorination are given in Fig. 2. The absorbance peaks in the non-treated wood flour spectrum correspond to the main

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