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

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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 ^{19}F 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.

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, Balatinecz, & Matuana, 1999; Klason, Kubát, & Strömvall, 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; Dányádi, Móczó, & Pukánszky, 2010; Dominkovics, Dányádi, & Pukánszky, 2007; Ichazo, Albano, González, & 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 CF_4 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 F_2 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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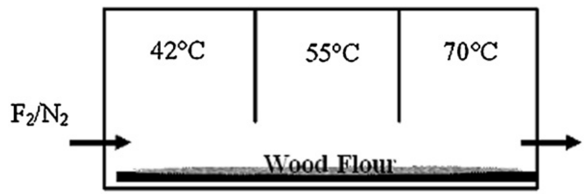

Fig. 1. Direct fluorination system.

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 ($MgCl_2$,·$6H_2O$)	33
Sodium bromide (NaBr)	59
Sodium chloride (NaCl)	75
Potassium sulphate (K_2SO_4)	98

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 was performed in attenuated total reflectance (ATR) mode using a SHIMADZU FT-IR 8300 spectrometer. The spectra were recorded in the mid infrared region (4000–400 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}F–^{19}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 °C/min. Then the sample was cooled to 35 °C with a cooling rate of 50 °C/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

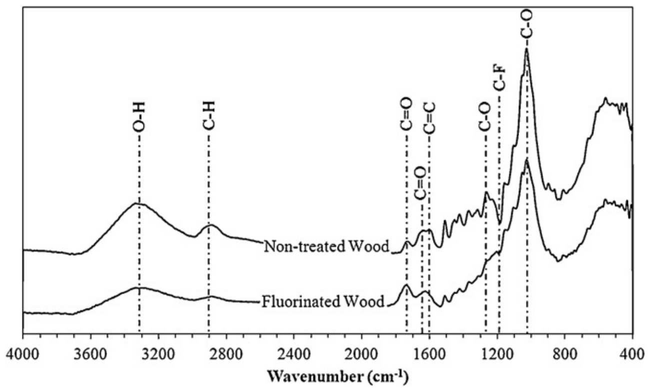

Fig. 2. FT-IR spectra of non-treated and fluorinated wood flours.

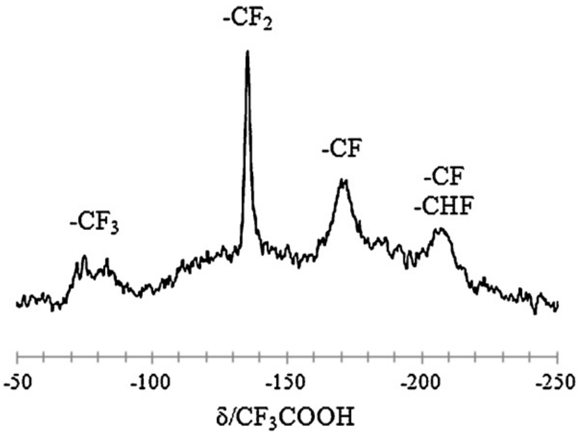

Fig. 3. ^{19}F NMR spectrum of fluorinated wood flour.

bonds of the wood components (Müller, Rätzsch, Schwanninger, Steiner, & Zöbl, 2003; Popescu, Froidevaux, Navi, & Popescu, 2013; Schwanninger, Rodrigues, Pereira, & Hinterstoisser, 2004). The broad peak around 3320 cm^{-1} is due to the —OH hydroxyl groups in cellulose whereas the peak around 2900 cm^{-1} is ascribed to the asymmetric and symmetric mode of hydrocarbon (C—H) stretching. The C═O stretching vibration of carbonyl, carboxyl and acetyl groups appears at 1740 cm^{-1}. The band at 1640 cm^{-1} is due to C═O stretch of aromatic ketones. The band at 1600 cm^{-1} corresponds to the C═C stretching of aromatic skeletal in lignin. C—O stretching in lignin is observed at 1260 cm^{-1}and the large peak at 1020 cm^{-1} is attributed to C—O stretching vibration.

It is well known that wood hydrophilia is essentially due to the hydroxyl groups (—OH) of both the cellulose and hemicelluloses. Indeed, these hydroxyl groups have the property of absorbing water molecules, forming hydrogen bonds. The FT-IR spectroscopy analysis of fluorinated wood flour reveals a significant decrease in the number of hydroxyl bonds (3320 cm^{-1} in Fig. 2). As there are fewer sites for hydrogen bonding, the fluorinated wood particles should adsorb less water. In other words, the decrease in the number of —OH groups in the wood flour was one of the first proofs of the weakening of its hydrophilia.

Fluorination also induces the substitution of certain specific atoms in the treated material by fluorine atoms. Hydrogen atoms in hydrocarbon groups on the wood surface are expected to be replaced by fluorine, because of both the weakness of C—H bonds and the reactivity of molecular fluorine. In fact, the substitution of C—H bonds (2900 cm^{-1}) by carbon–fluorine (C—F) bonds (1180 cm^{-1}) was observed after the fluorination of the wood flour. This latter band corresponds to covalent C—F bonds (Kharitonov, 2008). Even with weak intensity, its presence underlines the formation of C—F bonds onto the wood components. Moreover, the fact that samples taken at various distances from the gas inlet of the reactor showed similar spectra confirms that the temperature gradient ensured the homogeneity of the fluorine grafting onto the wood.

The ^{19}F NMR measurements were used to confirm both the covalent grafting of fluorine atoms and the nature of the fluorinated groups, i.e. —CF, —CF$_2$ or —CF$_3$ (Aimi & Ando, 2004; Calleja et al., 2011; Harris, Monti, & Holstein, 1998; Isbester, Kestner, & Munson, 1997; Varcoe et al., 2007; Zhang et al., 2010). An example of the ^{19}F MAS NMR spectrum of fluorinated wood flour is presented in Fig. 3. It is typical of the samples, whatever their location in the reactor. The resonances are attributable to the different groups, namely —CF, —CF$_2$ or —CF$_3$. The broad signal at −135 ppm *vs.* CFCl$_3$ matches —CF$_2$ groups, while the signal at −182 ppm corresponds to C—F bonds and the signals at −74 and −83 ppm are both attributed to —CF$_3$ groups with different neighbours. Finally, the signal at −207 ppm is due to an aromatic —CF bond or —CHF bond. Bearing out the evidence of IR spectroscopy, NMR unambiguously highlights the presence of both fluorinated and perfluorinated groups on the wood surface.

The electronegativity of the fluorine atom, the highest in the periodic table, confers a strong polarity to the carbon–fluorine bonds, which creates a polar hydrophobicity of the fluorinated compounds. For this reason, the presence of fluorine atoms on the wood surface should imply a decrease in the hydrophilic character of the resulting samples. This decrease has to be confirmed by hygroscopic characterisation.

3.2. Decrease of the wood hydrophilic character

Through the adsorption effect, the water content of the wood moves towards an equilibrium state according to the ambient relative humidity. Thus, when the wood flour was conditioned in a humidity-controlled chamber after drying, the water content increased to match the conditions of the enclosure. Continuous measurements of the sample weight allowed the evolution of the water content for each relative humidity value to be monitored, from the anhydrous state to the equilibrium point. The adsorption curves of untreated and fluorinated wood flours are given in Fig. 4. The hygroscopic analysis of the non-treated wood flour was performed both to validate the method and to make a reference to check the effect of direct fluorination on the hygroscopic behaviour of wood flour. The experimental results corresponded with previous studies found in the literature in terms of water content (Stamm, 1964). For example, the water content of wood after equilibrium is known to be about 11% for a relative humidity of 60% at 20 °C, and the wood flour studied here contained 10.5% of water under 59% relative humidity at the same temperature.

After fluorination, an increase in the adsorption rate was observed. For instance, in the case of a relative humidity equal to 75%, the water content of fluorinated wood flour was stabilized in 5 h, compared to 24 h for the non-treated wood flour. Hygroscopic analysis also underlined the decrease in the equilibrium water content of the wood flour after fluorination. The water content of both non-treated and fluorinated wood flours under the different relative humidity conditions are listed in Table 2. An average decrease of 2 points in the water content of the wood flour after treatment can be observed, representing a drop of 10%–30% in the water content.

This analysis shows that direct fluorination efficiently lowers the water content in wood flour. This decrease can be explained by the reduction in the number of sites for hydrogen

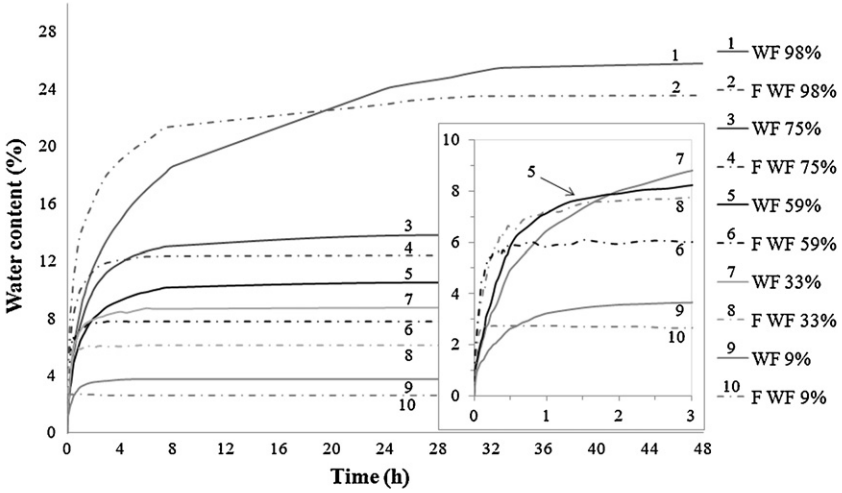

Fig. 4. Adsorption curves of the wood flour before (WF) and after (F WF) fluorination for various relative humidity conditions.

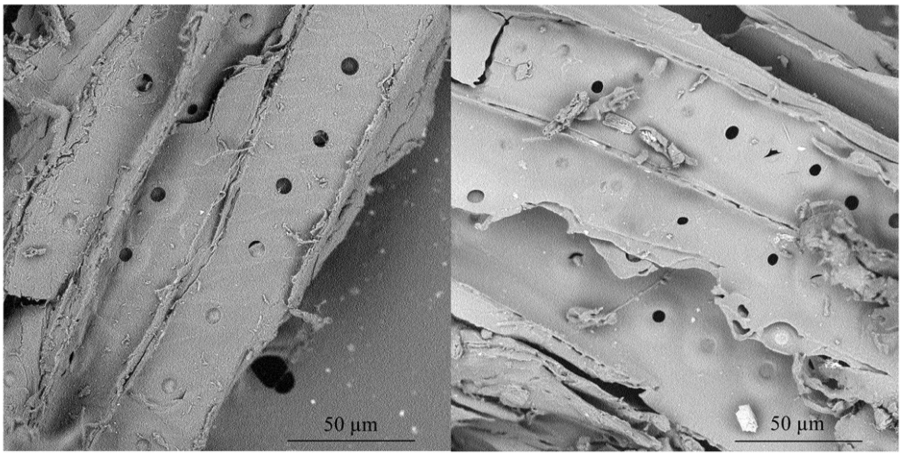

Fig. 5. Scanning electron micrographs of an untreated wood particle (left) and a fluorinated wood particle (right) (magnification: 1380×).

bonding. In addition, the fluorinated wood flour reaches its water equilibrium point faster than the non-treated wood flour. The presence of electronegative fluorine in the constitution of the fluorinated wood increases the attractiveness of its surface and accelerates its reaction with water.

3.3. *Preservation of the physical structure of the wood*

Excessive fluorination may cause important damage to a material surface because of the formation of volatile species such as CF_4 and C_2F_6. In order to verify that the treatment does not damage the wood texture, a SEM analysis was performed. The SEM images of a non-treated wood particle and a fluorinated wood particle are represented in Fig. 5. The tracheid physical structure appears preserved after direct fluorination; even the wood pits were maintained intact.

3.4. *Analysis of the thermal behaviour of wood flour*

TGA was performed on raw and fluorinated wood flours. The curves obtained are presented in Fig. 6. The first weight loss in the curves corresponds to water desorption, which occurred before 100 °C due to the pressure and the N_2 atmosphere. The weight loss for the fluorinated sample between 140 °C and 220 °C is due to the decomposition of carbon–fluorine bonds. It corresponds to about 5% of the sample weight. Wood degradation was noticed from 220 °C, in good agreement with recent studies on wood thermal degradation (Jeske, Schirp, & Cornelius, 2012; Poletto, Zattera, Forte, & Santana, 2012). The TGA data underline that the treatment is effective up to 100 °C. Since the unsaturated polyester resin is usually polymerized at 80 °C, the direct fluorination of wood flour appears to be an efficient treatment for wood flour used as a polyester composite reinforcement.

Table 2
Water content of the fluorinated and non-treated wood flours under various relative humidity conditions.

Relative humidity		9%	33%	59%	75%	98%
Water content (%)	Non-treated wood	3.76 ± 0.17	8.72 ± 0.31	10.46 ± 0.37	13.76 ± 0.25	25.79 ± 0.80
	Fluorinated wood	2.65 ± 0.28	6.10 ± 0.46	7.76 ± 0.15	12.39 ± 0.16	23.58 ± 0.15
Loss of water content		30%	30%	26%	10%	9%

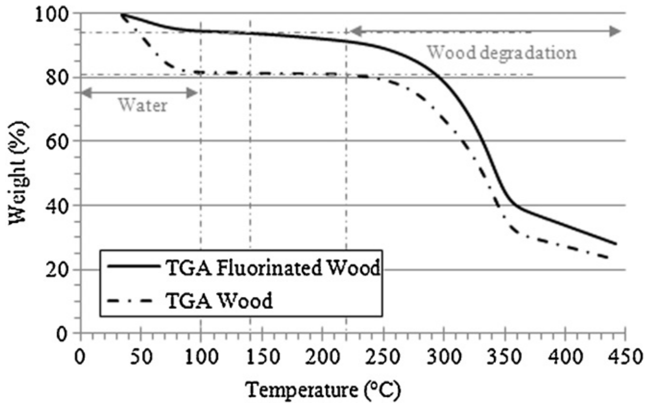

Fig. 6. TGA curves of non-treated wood flour (W) and fluorinated wood flour (FW).

4. Conclusions

A decrease in the hydrophilic character of wood flour was obtained by direct fluorination using molecular fluorine F_2. This can be explained by the formation of C—F bonds onto the surface of the wood flour particles and the decrease in the number of —OH groups in the wood, observed using FT-IR and ^{19}F RMN spectroscopy, and confirmed by hygroscopic characterisation. Moreover, SEM analysis showed that the treatment did not damage the physical structure of the wood. The thermal behaviour of wood flour remained stable under 100 °C after direct fluorination, which enables its use as a reinforcement for unsaturated polyester or other resins with low-temperature manufacturing characteristics.

Further studies will focus on the impact of wood flour direct fluorination on the mechanical properties of composites with a polyester matrix and wood flour reinforcements, in order to verify the improvement in wood–polyester compatibility.

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References

Aimi, K., & Ando, S. (2004). Conformation analysis and molecular mobility of ethylene and tetrafluoroethylene copolymer using solid-state ^{19}F MAS and 1H → ^{19}F CP/MAS NMR spectroscopy. *Magnetic Resonance in Chemistry*, *42*, 577–588.

Bismarck, A., Tahhan, R., Springer, J., Schulz, A., Klapötke, T. M., Zeil, H., & Michaeli, W. (1997). Influence of fluorination on the properties of carbon fibres. *Journal of fluorine chemistry*, *84*, 127–134.

Calleja, G., Houdayer, A., Etienne-calas, S., Bourgogne, D., Flaud, V., Silly, G., Shibahara, S., et al. (2011). Conversion of poly(ethylene-alt-tetrafluoroethylene) copolymers into polytetrafluoroethylene by direct fluorination: a convenient approach to access new properties at the ETFE surface. *Journal of Polymer Science Part A: Polymer Chemistry*, *49*, 1517–1527.

Chotirat, J., Chaochanchaikul, K., & Sombatsompop, N. (2007). On adhesion mechanisms and interfacial strength in acrylonitrile-butadiene-styrene/wood sawdust composites. *International Journal of Adhesion and Adhesives*, *27*, 669–678.

Cui, Y., Lee, S., Noruziaan, B., Cheung, M., & Tao, J. (2008). Fabrication and interfacial modification of wood/recycled plastic composite materials. *Composites Part A: Applied Science and Manufacturing*, *39*, 655–661.

Dányádi, L., Móczó, J., & Pukánszky, B. (2010). Effect of various surface modifications of wood flour on the properties of PP/wood composites. *Composites Part A: Applied Science and Manufacturing*, *41*, 199–206.

Dominkovics, Z., Dányádi, L., & Pukánszky, B. (2007). Surface modification of wood flour and its effect on the properties of PP/wood composites. *Composites Part A: Applied Science and Manufacturing*, *38*, 1893–1901.

Harris, R. K., Monti, G. A., & Holstein, P. (1998). Chapter 6.6: ^{19}F NMR. In I. Ando, & T. Asakura (Eds.), *Studies in physical and theoretical chemistry* (pp. 253–266). Elsevier (1998).

Ho, K. K. C., Beamson, G., Shia, G., Polyakova, N. V., & Bismarck, A. (2007). Surface and bulk properties of severely fluorinated carbon fibres. *Journal of Fluorine Chemistry*, *128*, 1359–1368.

Ichazo, M. N., Albano, C., González, J., & Perera, R. (2001). Polypropylene/wood flour composites: treatments and properties. *Composite Structures*, *54*, 207–214.

Isbester, P. K., Kestner, T. A., & Munson, E. J. (1997). High-resolution variable-temperature MAS ^{19}F NMR spectroscopy of fluorocarbon polymers. *Macromolecules*, *30*, 2800–2801.

Jeske, H., Schirp, A., & Cornelius, F. (2012). Development of a thermogravimetric analysis (TGA) method for quantitative analysis of wood flour and polypropylene in wood plastic composites (WPC). *Thermochimica Acta*, *543*(0), 165–171.

Kazayawoko, M., Balatinecz, J. J., & Matuana, L. M. (1999). Surface modification and adhesion mechanisms in wood fiber-polypropylene composites. *SpringerLink – Journal of Materials Science*, *34*, 6189–6199.

Kharitonov, A. P. (2008). *Direct fluorination of polymers*. Nova Publishers.

Kharitonov, A. P., Taege, R., Ferrier, G., Teplyakov, V. V., Syrtsova, D. A., & Koops, G.-H. (2005). Direct fluorination–useful tool to enhance commercial properties of polymer articles. *Journal of Fluorine Chemistry*, *126*, 251–263.

Klason, C., Kubát, J., & Strömvall, H.-E. (1984). The Efficiency of cellulosic fillers in common thermoplastics, Part 1. filling without processing aids or coupling agents. *International Journal of Polymeric Materials*, *10*, 159–187.

Maity, J., Jacob, C., Das, C. K., Alam, S., & Singh, R. P. (2008). Direct fluorination of Twaron fiber and the mechanical, thermal and crystallization behaviour of short Twaron fiber reinforced polypropylene composites. *Composites Part A: Applied Science and Manufacturing*, *39*, 825–833.

Müller, U., Rätzsch, M., Schwanninger, M., Steiner, M., & Zöbl, H. (2003). Yellowing and IR-changes of spruce wood as result of UV-irradiation. *Journal of Photochemistry and Photobiology B: Biology*, *69*, 97–105.

Poletto, M., Zattera, A. J., Forte, M. M. C., & Santana, R. M. C. (2012). Thermal decomposition of wood: influence of wood components and cellulose crystallite size. *Bioresource Technology*, *109*, 148–153.

Popescu, M.-C., Froidevaux, J., Navi, P., & Popescu, C.-M. (2013). Structural modifications of Tilia cordata wood during heat treatment investigated by FT-IR and 2D IR correlation spectroscopy. *Journal of Molecular Structure*, *1033*, 176–186.

Sahin, H. T., Manolache, S., Young, R. A., & Denes, F. (2002). Surface fluorination of paper in CF_4-RF plasma environments. *Cellulose*, *9*, 171–181.

Sapieha, S., Verreault, M., Klemberg-Sapieha, J. E., Sacher, E., & Wertheimer, M. R. (1990). X-Ray photoelectron study of the plasma fluorination of lignocellulose. *Applied Surface Science*, *44*, 165–169.

Stamm, A. J. (1964). *Wood and cellulose science*. New York: Ronald press.

Schwanninger, M., Rodrigues, J. C., Pereira, H., & Hinterstoisser, B. (2004). Effects of short-time vibratory ball milling on the shape of FT-IR spectra of wood and cellulose. *Vibrational Spectroscopy*, *36*, 23–40.

Varcoe, J. R., Slade, R. C. T., Lam How Yee, E., Poynton, S. D., Driscoll, D. J., & Apperley, D. C. (2007). Poly(ethylene-co-tetrafluoroethylene)-derived radiation-grafted anion-exchange membrane with properties specifically tailored for application in metal-cation-free alkaline polymer electrolyte fuel cells. *Chemistry of Materials*, *19*, 2686–2693.

Zhang, W., Dubois, M., Guérin, K., Bonnet, P., Kharbache, H., Masin, F., Kharitonov, A. P., et al. (2010). Effect of curvature on C—F bonding in fluorinated carbons: from fullerene and derivatives to graphite. *Physical Chemistry Chemical Physics*, *12*, 1388–1398.