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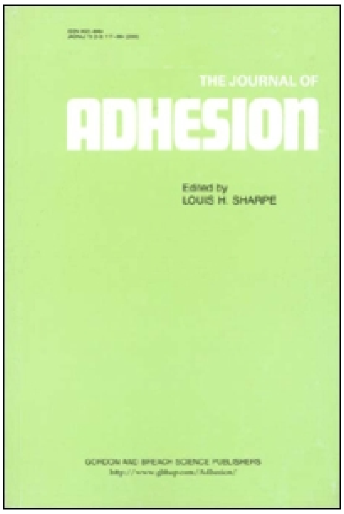

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Oxyfluorination of Wood-Fiber Reinforced Thermoplastic Composites to Improve Adhesion

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Oxyfluorination of Wood-Fiber Reinforced Thermoplastic Composites to Improve Adhesion

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Oxyfluorination was evaluated on a series of wood-fiber reinforced thermoplastic composite (WPCs) formulations as a means to improve the adhesion of a water-based acrylic coating. The oxyfluorination increased the acrylic coating peel load to WPCs by 179%, yielding adhesion levels higher than those obtained on control maple. For oxyfluorinated surfaces, the WPC formulation had a significant impact on the acrylic coating paint. Formulations without maleic anhydride polypropylene coupling agent developed better adhesion than formulations with the coupling agent. Formulations with polypropylene also performed better than formulations with high density polyethylene and so did formulations with pine compared with those with maple. Interestingly, the adhesion improvement imparted by oxyfluorination was higher for those formulations that were least amenable to bonding with the acrylic coating, i.e., those containing the coupling agent and high density polyethylene. Contact angle measurements and ATR-FTIR spectroscopy indicated that oxyfluorination improved wettability with polar liquids by generating new oxygenated groups on the surface. A moderate positive linear relationship ($r^2 = 0.5$) was established between the carbonyl/C-H stretch band intensity ratio $I_{1650cm^{-1}}/I_{2915cm^{-1}}$ in the infrared spectra of oxyfluorinated WPCs and the coating peel strength. It is, therefore, proposed that oxyfluorination improves the adhesion properties of WPCs by oxidizing the surface, and by increasing wettability with polar liquids, thus allowing the development of stronger interfacial forces.

Keywords: ATR-FTIR; Peel adhesion; Surface activation; Surface oxidation; Wettability; Wood plastic composites

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INTRODUCTION

In the last decade the market for wood-fiber reinforced thermoplastic polymer composites (WPCs) has experienced a large growth in the United States, mainly due to their use in decking and railing applications [1]. The implantation of WPCs in new applications such as siding, window, and door profiles could further fuel their market growth [1]. However, for WPCs to enter these new applications, some of the material attributes need to be improved. Indeed, although WPCs were first introduced as durable and maintenance-free materials, extended use in exterior environment has evidenced some weathering issues, in particular the loss of aesthetic qualities and mechanical performance [2,3]. For WPCs to perform adequately in new exterior applications their resistance to weathering needs to be improved.

One way to improve the weather resistance and the outdoors durability of WPCs is to protect them with coatings and paints. The ability to paint or coat WPCs is further advantageous in that it provides customers with the flexibility to choose and change the aesthetic of the WPCs over their lifetime. As a result, manufacturers and researchers have recently focused their attention on the surface and adhesion properties of WPCs [4–8]. Unfortunately, low adhesion levels have been repeatedly reported with coatings and adhesives [4,5,7]. Poor adhesion has been attributed to the surface concentration of polyolefins which produces an hydrophobic and low surface energy substrate [4,7,8]. On the other hand, the chemical heterogeneity and the surface roughness of WPCs appear to be favorable to adhesion and have been shown to directly relate to the adhesion strength in coated or bonded systems [4,5,7].

To improve the adhesion properties of WPCs, researchers have evaluated the efficacy of surface activation methods that are known to improve the bondability of polyolefins *via* substrate oxidation and roughening [9]. Common surface activation methods that have been evaluated on WPCs include treatments with corona, flame, oxygen plasma, benzophenone/UV irradiation, and chromic acid. All the treatments were found to significantly increase the adhesion of adhesives and coatings to WPCs [4–6,8]. For example, a fourfold adhesion increase of a latex paint was noted after corona treatment of polyethylene-based composites [4]. Similarly, the shear bond strength of epoxies on polypropylene-based composites increased by 97%, 67%, and 31% following treatments with chromic acid, flame, and water, respectively [5]. Finally, the peel strength of a water-based acrylic coating on a series of WPCs improved significantly following surface treatments with chromic acid, oxygen plasma, flame, or benzophenone/UV [6]. For this series of WPCs, treatments with chromic acid and oxygen plasma performed best, increasing the acrylic coating adhesion to WPCs by 170% and 122%, respectively. In fact, the adhesion levels achieved by the coating following these surface treatments were similar to or higher than those achieved on control maple wood [6]. Surface characterization indicated that the chromic acid treatment essentially acted by roughening the surface, whereas the oxygen plasma treatment significantly improved the substrate wettability with polar liquids [6]. Common surface oxidation techniques are, therefore, also effective on WPCs as expected based on the treatments' performance on polyolefins [9] and the similarity in surface properties between these two classes of materials [7].

Another surface activation method well known for polyolefins [10–15] has recently been evaluated on polyolefin containing composites [16,17]. The surface activation method consists of subjecting the surface to gas atmospheres containing F_2 and O_2 with CO_2 or N_2 as a diluent, resulting in an oxyfluorination or surface functionalization with fluorine and oxygen [10,16–18]. Characterization by attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) and X-ray photoelectron spectroscopy (XPS) of polyolefins subjected to oxyfluorination has indicated incorporation of both oxygen and fluorine elements in functional groups such as ketones, carboxylic acids, aldehydes, and acid fluorides [10,11,13–15,19]. The oxidation follows a free radical mechanism. First, fluorine gas (F_2) abstracts a hydrogen atom from the polymer backbone creating a carbon radical. In a second step, oxygen reacts with the carbon radicals resulting in polar functional groups [19]. At the same time, crosslinking of the polymer can occur, locking the polar functional groups on the surface and providing permanency to the surface polarity [16]. As a result of oxyfluorination, the surface of polyolefins is oxidized and wettability with polar liquids is significantly improved [10,12,14,15]. For example, the critical surface tension of wetting of polyolefins increases from *ca.* 30 to $50\,\mathrm{mJ/m^2}$ after oxyfluorination, mainly because of changes in the polar components of the surface energy [12,14,15]. As a result, an excellent correlation between the acid component of the surface energy of treated PP fibers and their adhesion to a cementious matrix has been observed [12]. Oxyfluorination also appears to increase the surface roughness of polyolefins, but the change is minute and occurs at such a small scale (RMS changes from 4.2 to 5.0 nm after treating PP) that this effect has been disregarded as a potential mechanism for the significant adhesion improvement [10].

Considering the efficacy of oxyfluorination at improving wetting and adhesive properties of neat polyolefins and the similarity in surface attributes between neat polyolefins and WPCs [7], one may expect this treatment to also be effective on WPCs [6].

The objective of this work is, therefore, to evaluate the influence of oxyfluorination on the surface and adhesive properties of WPCs. As the formulation of WPC has a significant influence on the surface and adhesive properties of these materials [7] and on their response to surface activation methods [6], this study also aims at evaluating the impact of the formulation factor on the efficacy of oxyfluorination. This study, therefore, examines the peel adhesion of an acrylic coating on a series of WPC formulations before and after oxyfluorination. The wetting properties and surface chemistry of the treated surfaces are also characterized in order to gain some insight on the adhesion enhancement mechanisms of the fluorine treatment.

EXPERIMENTAL

Materials

Eight WPC formulations were produced according to a 2^3 factorial plan that used either pine (*Pinus spp.*) or maple (*Acer spp.*) flour, high density polyethylene (HDPE, Innovene Inc., Chicago, IL, USA), or isotactic polypropylene (PP, Equistar, Houston, TX, USA) and a maleic anhydride grafted polypropylene (MAPP, Honeywell, Morristown, NJ, USA) coupling agent or not (Table 1). More detailed information about the polymers used in this study is available in previous publications [6,7]. With this factorial design the influence of polymer selection (HDPE *vs.* PP), wood species selection (pine *vs.* maple), and coupling

TABLE 1 Design of Wood Plastic Composites Formulations. Lubricant (1% wt) and Talc (4%) were Added in all the Formulations

Polyolefin (wt%)	Wood species (wt%)	Coupling agent (wt%)
HDPE (33.8)	Pine (59)	MAPP (2.3)
HDPE (33.8)	Maple (59)	MAPP (2.3)
PP (33.8)	Pine (59)	MAPP (2.3)
PP (33.8)	Maple (59)	MAPP (2.3)
HDPE (36.1)	Pine (59)	—
HDPE (36.1)	Maple (59)	—
PP (36.1)	Pine (59)	—
PP (36.1)	Maple (59)	—

agent could be evaluated. A commercial lubricant (OP100, Honeywell) and talc (Nicron 403, Luzenac America Inc., Centennial, CO, USA) were also included in all the formulations to represent commercial formulations. Finally, the coating used to assess the paint adhesion to WPCs was a water-based acrylic paint specifically formulated for wood plastic composites by Drew Paints, Inc. (Portland, OR, USA).

After dry blending, the formulations were fed into a 35 mm intermeshing twin screw extruder (Cincinnati Milacron, Cincinnati, OH, USA) operating at a 5–8 rpm screw speed, 3.45–5.52 MPa melt pressure, and equipped with a water-spray cooler. The barrel and die temperatures were 163 and 171°C for HDPE formulations and 185–193 and 185°C for PP formulations, respectively. Rectangular sections ($10 \times 38\,\text{mm}^2$) were, thus, extruded and specimens ($1 \times 9 \times 36\,\text{mm}^3$) were milled from the center of the WPC cross-sections to obtain homogeneous surfaces from the bulk. The specimen surfaces were refreshed as recommended in ASTM D2093 [20] prior to surface treatment or characterization in the case of untreated (control) samples. Sufficient material was prepared in order to obtain at least four specimens for surface characterization and for adhesion measurements with the acrylic coating. In addition, the longitudinal-radial surface of solid maple (*Acer spp.*) wood was used as a control surface [7].

Oxyfluorination Treatment

The surface treatment was performed by Inhance/Fluoro-Seal, Ltd., (Houston, TX, USA) using their proprietary oxyfluorination process. The process uses small amounts of elemental fluorine (<5% by wt) and elemental oxygen gas with a diluent gas, such as CO_2 or N_2, and is performed at room temperature [16,17]. After treatment, the samples were wrapped in aluminum foil and stored in a desiccator with calcium sulfate until the surface characterization and adhesion test were performed within approximately 1 week of the treatment.

Wetting Properties

Control and treated specimens were characterized on a dynamic contact angle analyzer (DCA, Cahn 322, Thermo Scientific, Waltham, MA, USA) using water as a probe liquid ($\gamma_L = 72.8\,\text{mJ/m}^2$) and a stage moving at speed of 194 μm/s. Advancing and receding contact angles, θ_a and θ_r, and wetting hysteresis, $\gamma_L(\cos\theta_r - \cos\theta_a)$, were measured.

Surface Chemistry

Fourier transform spectroscopy (FTIR) was conducted on the control and treated samples on a ThermoNicolet Avatar 370 FT-IR spectrometer (ThermoNicolet, Fitchburg, Germany) operating in the attenuated total reflection (ATR) mode (SmartPerformer, ZnSe crystal, Fitchburg, Germany). At least triplicate spectra consisting of 126 scans at a 4 cm^{-1} resolution were acquired. They were ATR and baseline corrected before averaging. Qualitative and quantitative spectral comparisons were made. Namely, the relative content in carbonyl and hydroxyl species was determined by normalizing the signal intensity of the functional group of interest to that of the C-H stretch of the polyolefin at 2915 cm^{-1} [21].

Adhesion Test

The acrylic coating was applied on the WPC surfaces using a wire-wound draw down bar (#32, Diversified Enterprises, Claremont, NH, USA) and a strip of gauze, 9 mm wide, was placed on the wet coated surface [22] after which the coating was cured at room temperature for 1 hr. A second layer of coating was then applied and cured at room temperature for another 48 hrs. The free end of the gauze was wrapped with a masking tape and placed into tensile grips on an Instron testing machine (model 4426, Norwood, MA, USA) to undergo a 180° adhesion test [23,24]. The peel test was conducted at a cross-head speed of 20 mm/min and peel load (N) was reported in Newton per meter of width [23].

Statistical Analyses

The data were analyzed in a randomized complete block design (CBD), using the eight formulations as a blocking factor. The effect of the treatment on the peel load and wetting parameters was detected with a one-way analysis of variance (ANOVA) using $\alpha = 0.05$. In addition, an ANOVA was also performed at $\alpha = 0.05$ to detect the impact of formulation factor on each measured property for the control WPCs and for the fluorine-treated WPCs.

RESULTS AND DISCUSSION

Impact of Oxyfluorination on the Adhesion of the Acrylic Coating

Table 2 presents the peel strength of the acrylic coating on each WPC formulation before and after the surface treatment. The surface

TABLE 2 Peel Load (N/m) of the Acrylic Coating on WPC Surfaces Before and After Oxyfluorination. Values are Averages of 4 Replicates and the Significant Formulation Factors are Identified

Formulation	Untreated	Oxyfluorinated
HDPE/Pine/MAPP	177 ± 21	589 ± 41
HDPE/Maple/MAPP	168 ± 13	526 ± 44
PP/Pine/MAPP	232 ± 9	709 ± 96
PP/Maple/MAPP	249 ± 9	605 ± 60
HDPE/Pine	218 ± 16	677 ± 41
HDPE/Maple	217 ± 23	605 ± 74
PP/Pine	290 ± 24	708 ± 56
PP/Maple	309 ± 20	752 ± 113
Average[a]	232 ± 46	646 ± 95
Significant factors (level giving the highest value)	PP No MAPP	PP No MAPP Pine

[a] For comparison, peel load on maple and HDPE averaged 524 ± 64 N/m, respectively [7]. Chromic acid treatment on a similar series of WPCs has increased the average peel load to 637 ± 88 N/m [6].

treatment significantly improves the adhesion of the acrylic coating to WPCs; the peel load for treated samples averages (646 ± 95 N/m), which is well above that measured on untreated WPC surfaces (232 ± 46 N/m). Moreover, note that the coating adhesion to the oxyfluorinated WPC formulations is similar, or higher than that observed on control maple at (524 ± 64 N/m). A large improvement in the adhesion strength of a polar coating on WPCs following oxyfluorination is expected considering that the physical and chemical characteristics of WPCs have been found to be similar to those of the neat plastics [7] and that this treatment oxidizes neat polyolefins [16,18,19]. The efficacy of surface activation is also consistent with previous observations on a similar series of WPCs [6]. However, oxyfluorination is at least as effective as common surface activation methods that were previously evaluated on this WPCs series including treatments with chromic acid (637 ± 88 N/m), oxygen plasma (526 ± 116 N/m), flame (381 ± 94 N/m), and benzophenone coupled with UV irradiation (466 ± 107 N/m) [6]. In fact, the percent increase in the coating peel load induced by oxyfluorination is approximately 179% which compares favorably with the adhesion improvement previously reported following treatments with chromic acid at 175% and oxygen plasma at 122% [6]. Oxyfluorination is, therefore, a method of choice for improving the adhesion of a water-based acrylic coating on WPCs.

An earlier study on the surface and adhesion properties of the same series of WPCs to the same acrylic coating demonstrated that these properties were formulation dependent [7]. In particular, the peel strength of the coating to WPCs was shown to be higher when no MAPP was included in the formulation and when the thermoplastic polymer was PP (Table 2) [7]. While the higher peel strength on the MAPP-devoid formulations could be ascribed to the greater surface roughness in these formulations, higher peel strength in PP formulations possibly related to the higher proportion of wood and polarity observed on the surface of PP-based formulations [7].

In the case of oxyfluorinated WPCs, a formulation dependence of adhesion strength may, therefore, also exist. To evaluate the impact of WPC formulation factors on the adhesion strength of oxyfluorinated WPCs, an ANOVA was conducted using α level of 0.05 (Table 2). For oxyfluorinated WPCs, the adhesion that developed between the acrylic coating and the composites was significantly influenced by the formulation (Table 2). That is, formulations without MAPP developed higher peel loads to the acrylic coating than formulations containing MAPP and so did formulations with PP compared with those with HDPE. This formulation effect was also observed in the control WPCs (Table 2). Besides, the wood species also appeared to influence the adhesion of oxyfluorinated WPCs, an effect that was not evidenced in control WPCs (Table 2). After treatment, the WPC formulations with pine developed higher adhesion levels than the ones with maple. This additional species dependence of the coating adhesion on oxyfluorinated WPCs suggests that oxyfluorination may distinctively enhance the adhesive properties of selected WPC formulations.

To further evaluate the formulation dependency of the fluorine treatment efficacy, the % peel load increase was also examined for each formulation. In Figure 1, the % increase in peel load is shown for each WPC formulation. It is clear that formulations with HDPE experienced a higher peel load increase than the equivalent formulations using PP. Similarly, formulations with MAPP underwent a higher adhesion improvement than the equivalent formulations free of MAPP. Pine formulations also experienced, on average, a higher peel load increase than the corresponding formulations using maple, thereby explaining the noted species dependence of coating adhesion for fluoro-oxidized WPCs. The reason for this species dependency is not known nor was it further investigated. It is interesting, however, to recall that in the untreated WPCs, formulations with HDPE and

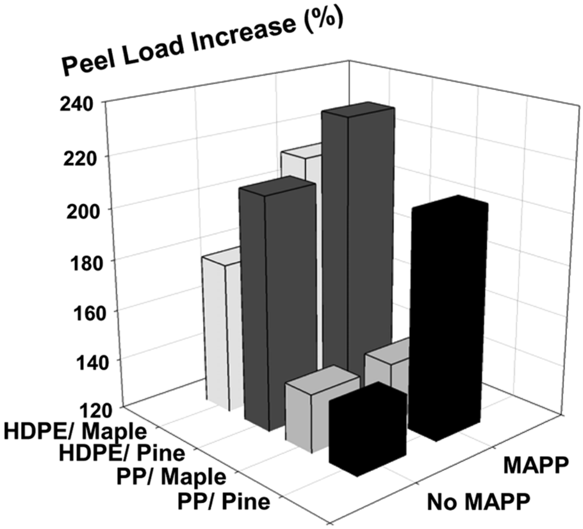


FIGURE 1 Impact of formulation factor on the adhesion increase imparted by oxyfluorination of WPCs.

with MAPP were the least prone to bonding (Table 2) and developed the lowest adhesion level with the acrylic coating. The preferential improvement in adhesion observed in formulations containing HDPE and MAPP suggests that oxyfluorination may be particularly well suited for WPC surfaces that are the most challenging to bond.

Impact of Oxyfluorination on the Surface Chemistry of WPCs

It has been repeatedly noted that oxyfluorination of polyolefins causes the incorporation of oxygen and fluorine in functional groups such as ketones, carboxylic acids, aldehydes, and acid fluorides [10,11,13–15,19]. To evaluate whether surface oxidation also occurred on WPCs, the ATR-FTIR spectra of the control and treated WPC formulations were compared (Figure 2). In the ATR-FTIR spectrum of treated WPC, one first notes the absence of new C-F bands (1000 to 1200 cm^{-1}) and of the acid fluoride band (C-OF at 1850 cm^{-1}) suggesting that fluorine is not significantly incorporated on the WPC surface. This is in contrast to previous observations on polyolefins [10,13–15]. On the other hand, the hydroxyl region is clearly altered as a result of the oxyfluorination treatment. The broad OH stretching vibration of control WPC at 3345 cm^{-1} which originates

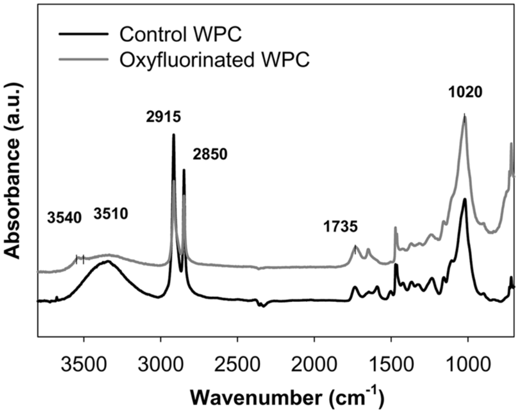


FIGURE 2 ATR-FTIR spectra of untreated and oxyfluorinated WPC showing significant changes in the hydroxyl and in the carbonyl regions of the WPC surfaces after oxyfluorination.

from aliphatic and phenolic OH of wood polymers is augmented by two sharp shoulders centered at 3540 and 3510 cm^{-1}. Bands within this frequency have been assigned to the OH stretching of free hydroxyl groups of cellulose [25]; however, free hydroxyl groups are unlikely to exist in solid cellulose. A more likely assignment for these bands is intramolecularly hydrogen bonded OH groups in lignin phenolic units, which may arise from lignin modification during the treatment [26]. Further information on the chemical modification imparted by oxyfluorination can be noted from the 1500–1800 cm^{-1} spectral region. In the control WPC, a band at 1735 cm^{-1} arising from the C=O stretching in ketones, carboxylic acid, and ester groups [27,28] increases and broadens after treatment (Figure 3). A band at 1650 cm^{-1} is also present in the control WPC and has been ascribed to the C=O stretching of p-substituted aryl ketones originating from lignin [26,28,29]. It also increases and sharpens after oxyfluorination. The intensity increase of the 1735 cm^{-1} and the 1650 cm^{-1} bands indicate that oxyfluorination generates C=O groups on the surface of WPCs. The increase in the 1650 cm^{-1} band could also originate from the formation of C=C groups since the stretching vibration for vinyl coincides with this region in wood; however, this possibility was discarded due to the absence of other characteristic vinyl vibrations such as the out-of-plane C-H bending and the $=CH_2$ wagging in the 1000 to 650 cm^{-1} region. Finally, the bands at 1590 cm^{-1} and at 1505 cm^{-1} arising from lignin C=C and C=C aromatic skeletal vibrations, respectively, disappear into a shoulder in

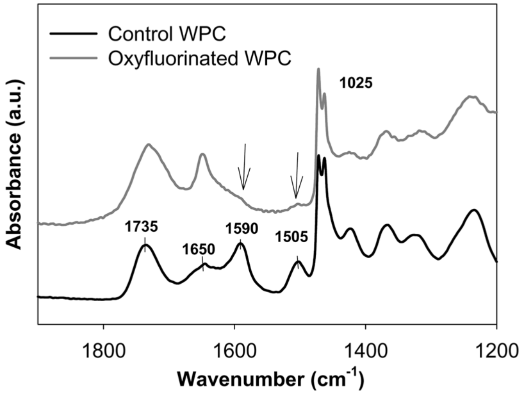


FIGURE 3 ATR-FTIR spectra of untreated and oxyfluorinated WPC showing significant changes in the hydroxyl and in the carbonyl regions of the WPC surfaces after oxyfluorination.

treated WPCs. Altogether, the increase of the C=O vibrations at 1735 cm^{-1} and at 1650 cm^{-1} along with the perturbation of lignin aromatic skeletal vibrations suggest that lignin is being oxidized during the treatment. Indeed, lignin can oxidize by cleavage of β-aryl ether linkages generating acid derivatives and quinoid structures [30], a mechanism that is consistent with the appearance of the new carbonyl and hydroxyl groups observed in the FTIR spectra.

In order to quantify the degree of oxidation, the intensities (areas) of the two carbonyl bands at 1735 cm^{-1} and 1650 cm^{-1} and of the OH band between 3000–3650 cm^{-1} were normalized to the polyolefin C-H stretching vibration at 2915 cm^{-1} [21]. Correlations between the intensity of each functional group and the coating peel load were then evaluated. A moderate linear trend was found between the $I_{1650\text{cm}^{-1}}/I_{2915\text{cm}^{-1}}$ band ratio and the acrylic peel load with $r^2 = 0.5$ (Figure 4). Other band ratios displayed very poor correlations with the acrylic peel load. This correlation indicated that 50% of the variation in peel load among the treated WPCs could be explained by the variation in the surface α-aryl ketone groups in lignin. Therefore, the increase in WPC surface polar groups actively participated in the adhesion enhancement mechanisms of WPC oxyfluorination, although it did not fully explain the adhesion improvement. With more polar groups on the surface, a better wettability with a water-based acrylic resin is expected along with stronger interfacial adhesion forces brought about by polar forces and secondary interactions.

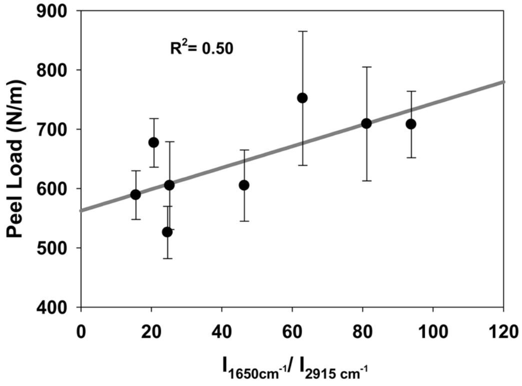


FIGURE 4 Evaluation of relationships between the surface C=O band intensity measured by ATR-FTIR and the coating adhesion strength on oxyfluorinated WPCs.

Impact of Oxyfluorination on the Dynamic Wettability of WPCs

For polyolefins, another consequence of oxyfluorination is an increase in the surface wettability with polar liquids brought about by surface oxidation [10,19]. To evaluate whether a similar mechanism was taking place on WPCs, dynamic contact angles were measured on the treated WPC surfaces using water as a liquid probe. Average θ_a, θ_r, and wetting hysteresis measured before and after the fluorine treatments for all WPC formulations are summarized in Table 3. While the advancing water contact angle particularly probes the hydrophobic component of heterogeneous surfaces such as WPCs, the receding water contact angle is more sensitive to the polar or hydrophilic component of heterogeneous surfaces [7,31,32]. The large θ_a ($100 \pm 7^\circ$) of the untreated WPCs, therefore, reflects the surface hydrophobicity similar to that measured on neat polyolefins, whereas the lower receding contact angle ($27 \pm 14^\circ$) in the untreated WPCs suggests some fraction of hydrophilicity likely arising from the wood component [7]. Following oxyfluorination, a significant reduction in the water advancing contact angle is observed from an average $100 \pm 7^\circ$ to $30 \pm 10^\circ$. Wettability with polar liquids is, therefore, largely improved by the surface treatment likely due to the development of polar functional groups on WPC surfaces [10,19]. The water θ_r also decreased after the fluorine treatment (Table 3), further supporting the observation that WPCs become more hydrophilic. The increased hydrophilicity and wettability of WPCs with polar liquids after the

TABLE 3 Water Advancing (θ_a) and Receding Contact Angles (θ_r) and Wetting Hysteresis on WPC Surfaces Before and After Oxyfluorination. Values are Averages of 4 Replicates and the Significant Formulation Factors are Identified

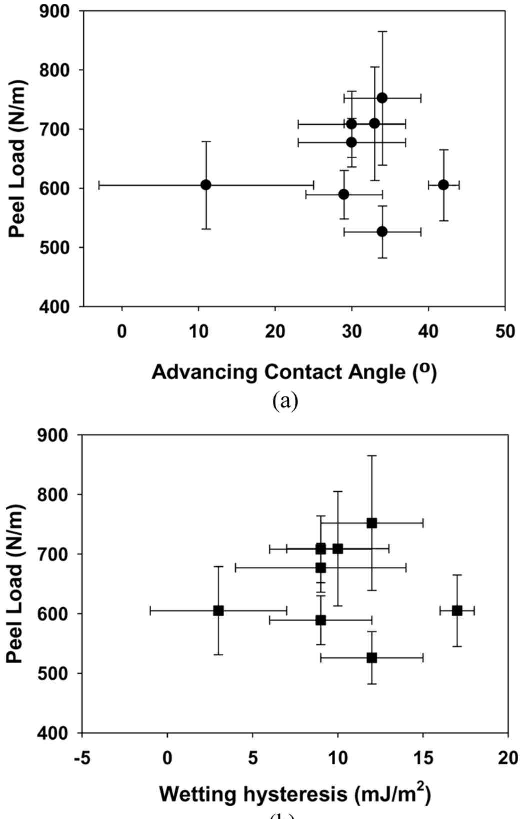
	Untreated			Oxyfluorination		
Formulation	θ_a (°)	θ_r (°)	Wetting hysteresis (mJ/m^2)	θ_a (°)	θ_r (°)	Wetting hysteresis (mJ/m^2)
HDPE/Pine/MAPP	95 ± 5	41 ± 3	67 ± 15	29 ± 5	3 ± 3	9 ± 3
HDPE/Maple/MAPP	95 ± 5	35 ± 8	63 ± 9	34 ± 5	2 ± 2	12 ± 3
PP/Pine/MAPP	102 ± 6	30 ± 9	82 ± 16	33 ± 4	11 ± 8	10 ± 3
PP/Maple/MAPP	101 ± 4	24 ± 8	80 ± 8	42 ± 2	12 ± 3	17 ± 1
HDPE/Pine	99 ± 3	22 ± 7	79 ± 2	30 ± 7	5 ± 5	9 ± 5
HDPE/Maple	98 ± 3	20 ± 2	78 ± 3	11 ± 14	0 ± 0	3 ± 4
PP/Pine	99 ± 2	24 ± 13	85 ± 12	30 ± 7	4 ± 4	9 ± 3
PP/Maple	105 ± 1	18 ± 9	90 ± 2	34 ± 5	0 ± 0	12 ± 3
Average	100 ± 7[b]	27 ± 14	78 ± 12	30 ± 10	5 ± 7	10 ± 5
Significant factors (level giving the highest value)	PP	HDPE MAPP	PP No MAPP	PP MAPP	PP MAPP	PP MAPP

[b] For comparison, advancing contact angle on PP and on HDPE is 95° and 87°, respectively [7].

oxyfluorination, therefore, clearly contribute to the treatment efficacy at improving adhesion with a water-based acrylic coating. Interestingly, the dynamic contact angles in the oxyfluorinated surfaces are still influenced by the WPC composition (Table 3). That is, formulations with PP and formulations with MAPP display significantly higher advancing contact angles than the respective formulations containing HDPE and devoid of MAPP. In other words, after oxyfluorination the wettability of PP- and MAPP-containing formulations is lower than that of HDPE and MAPP-devoid formulations. The formulation dependency of the advancing contact angle with water is somewhat different from that of the control WPCs where only the matrix choice affected the contact angle (Table 3).

In order to evaluate whether the adhesion enhancement imparted by the treatment was a direct consequence of the changes in wettability, correlations between wetting parameters and peel load were sought (Figure 2). Indeed, water wetting hysteresis has previously been found to correlate linearly ($R^2 = 0.89$) with the adhesion strength of the acrylic coating on the same series of untreated WPCs [7].

In oxyfluorinated WPCs, however, no clear relationship could be established between the adhesion of the acrylic coating and the wetting parameters, advancing contact angle, or wetting hysteresis (Figure 5). It might be that other parameters relevant to wettability such as the critical surface tension of wetting and/or its various components relate better to the adhesion improvement imparted by oxyfluorination as observed in other systems [12–14]. Additionally, it is clear that other factors, such as surface chemical group concentration, compound the contribution of surface wettability [12–14]. One might also speculate that the WPCs surface roughness is increased by oxyfluorination, thus participating in the adhesion properties of treated WPCs [7]. However, previous research on polyolefins indicates that



(a)

(b)

FIGURE 5 Evaluation of relationships between wetting properties and coating adhesion on oxyfluorinated WPCs.

oxyfluorination does not significantly increase the surface roughness of polyolefins. Besides, roughening occurs at a much smaller scale (nm) than the known surface roughness of WPCs (μm) [7,10]. If roughening also occurs on WPCs, it is, therefore, likely not a major contributor to the large adhesion improvement observed in these materials. As a conclusion, multiple adhesion enhancement mechanisms participate in the adhesion enhancement of oxyfluorinated WPCs. The numerous polar groups generated on WPC surface by wood polymer oxidation, and lignin in particular, may increase the potential for polar interactions at the coating/WPC interface. The improvement of wettability with polar liquids also clearly contributes to the adhesion improvement of the acrylic coating on oxyfluorinated WPCs.

CONCLUSIONS

Eight formulations of WPCs were subjected to oxyfluorination in order to improve their adhesion properties with a water-based acrylic coating. The coating adhesion was measured using an 180° peel test while dynamic wettability was characterized by dynamic contact angle measurements with water and changes in surface chemistry were monitored with ATR-FTIR.

On average, the coating adhesion to WPCs increased by 179% after oxyfluorination leading to higher adhesion levels than on control maple. For oxyfluorinated WPCs, formulations without MAPP coupling agent and formulations with polypropylene developed higher adhesion levels than formulations having a coupling agent or high density polyethylene. Pine formulations also demonstrated higher adhesion levels than maple formulations. Interestingly, the treatment improved more effectively the adhesion of formulations that were initially least amenable to bonding. The improvement in adhesion could be ascribed to changes in surface chemistry and in surface wettability. Upon oxyfluorination, the WPC surfaces exhibited increases in the FTIR carbonyl and hydroxyl absorption bands revealing surface oxidation of the lignin component in particular. A moderate linear correlation was detected between the normalized α-aryl ketones FTIR band intensity of WPCs and the coating adhesion strength. Improved wettability with water was also observed after treatment although no direct relationship could be established with the adhesive strength in this case. It is, thus, proposed that oxyfluorination enhances the adhesion properties of WPCs by generating polar groups on the surface which, in turn, improve wettability, thus allowing for greater polar forces at the coating/WPC interface. This study therefore suggests that oxyfluorination may be a surface treatment of choice to improve the adhesion of polar adhesives and coatings on WPCs.

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