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### Surface Activation and Adhesion Properties of Wood-Fiber Reinforced Thermoplastic Composites

Barun S. Gupta<sup>a</sup>; Marie-Pierre G. Laborie<sup>a</sup>

<sup>a</sup> Washington State University, Department of Civil and Environmental Engineering, Wood Materials and Engineering Laboratory, Pullman, Washington, USA

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## Surface Activation and Adhesion Properties of Wood-Fiber Reinforced Thermoplastic Composites

**Barun S. Gupta**  
**Marie-Pierre G. Laborie**

Washington State University, Department of Civil and Environmental Engineering, Wood Materials and Engineering Laboratory, Pullman, Washington, USA

*Four surface activation methods were evaluated on a series of wood-fiber reinforced thermoplastic composites (WPCs) as a means to improve the adhesion of a water-based acrylic coating. Treatments with chromic acid and oxygen plasma performed best, increasing the acrylic coating peel load to WPCs by 170 and 122%, respectively, and yielding adhesion levels equivalent to or higher than those obtained on wood. The benzophenone/ultraviolet and flame treatments also improved the coating adhesion by 100 and 64%, respectively, but did not reach the adhesion levels achieved on wood. For both the chromic acid and oxygen plasma treatments, the WPC formulation impacted the treatment efficacy. Profilometry and scanning electron microscopy (SEM) showed that the chromic acid treatment acted mainly by roughening WPC surfaces. While surface oxidation was not evident from attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR), the improved wettability of WPCs with water suggested that the oxygen plasma treatment oxidized WPCs.*

**Keywords:** Adhesion; Oxidation; Surface activation; Surface roughness; Wettability; Wood plastic composites

### INTRODUCTION

With the growing utilization of wood fiber reinforced thermoplastic polymer composites (WPCs) in exterior applications [1] and the durability issues associated with these materials [2–5], paints and coatings

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Current address of Barun S. Gupta is Department of Forest Resources, Pennsylvania State University, State College, PA 16804, USA.

Address correspondence to Marie-Pierre Laborie, Washington State University, Department of Civil and Environmental Engineering, Wood Materials and Engineering Laboratory, P.O. Box 641806, Pullman, WA 99164-1806, USA. E-mail: mlaborie@wsu.edu

are being considered as a means to improving their resistance to weathering [6]. Recent studies have, therefore, focused on the surface and adhesion characteristics of WPCs and low adhesion levels have been repeatedly reported with coatings and adhesives [6–8]. Poor adhesion has been attributed to the concentration of polyolefin on the surface which results in hydrophobic, low surface energy substrates [6–8]. In contrast, the chemical heterogeneity and surface roughness of WPCs have been reported to contribute to adhesion strength in coated or bonded systems [6–8]. For instance, the peel strength of a water-based acrylic coating on WPCs has been found to correlate linearly ( $R^2 = 0.89$ ) with the water wetting hysteresis, demonstrating the importance of surface heterogeneity [8]. In these systems, surface roughness was proposed to enhance intrinsic adhesion by providing greater interfacial area and favoring mechanical interlocking. In addition, surface roughness was proposed to change the stress distribution at the surface/coating interface, thereby altering the crack propagation path and augmenting the viscoelastic dissipation factor in the practical adhesion [8].

To overcome the low adhesion levels of adhesives and coatings on WPCs, researchers have turned to surface activation methods including corona, flame, and chromic acid treatments [6,7]. These treatments are well established on polyolefins and generally improve adhesion properties by oxidizing and/or roughening the substrate surface [9]. Furthermore, they increase the surface polarity and adhesion properties of bulk wood [10–12]. As expected, they have been demonstrated to effectively enhance the adhesion of adhesives and coatings on WPCs. For instance, corona treatment of compression molded wood fiber polyethylene composites improved the adhesion of a latex paint up to four fold by increasing wettability [6]. Evaluating the shear strength of epoxy bonds on a polypropylene (PP) based WPC, Gramlich *et al.* reported 97%, 67%, and 31% adhesion increases following treatments with chromic acid, flame, and water, respectively [7].

The success of these activation methods prompts a comprehensive evaluation of the most efficient surface activation techniques that have been developed for polyolefins on WPCs. For both polyethylene and PP, the most efficient activation methods that can be easily implemented on profiled samples include flame and oxygen plasma treatments, but also treatments with chromic acid or with benzophenone (BP) in combination with ultra-violet (UV) radiation [9]. Furthermore, as the plastic selection and the addition of a coupling agent in the WPC formulation impact the surface and adhesion properties of WPCs, it is possible that surface treatments perform differently on distinct formulations [8]. A comprehensive evaluation of surface

activation techniques for WPCs, therefore, requires considering a series of WPC formulations.

The overall objective of this research is to develop a comprehensive evaluation of common surface activation methods for improving the adhesion of an acrylic coating on WPCs. In particular this study is designed to:

1. Determine the best surface treatments at improving the adhesion of a water-based acrylic coating across a series of WPC formulations.
2. Evaluate the impact of WPC formulation on the treatments' efficacy.
3. Gain insight on the adhesion mechanisms favored by the most effective surface activation techniques.

In these objectives, this study examines the peel adhesion of an acrylic coating on a series of WPC formulations before and after treatment with flame, oxygen plasma, chromic acid, and BP/UV. The surface chemistry, wettability, and topography of treated surfaces are then characterized in order to shed light on the adhesion mechanisms that are taking place between the WPC substrate and the acrylic coating.

## EXPERIMENTAL

### Materials

The manufacture of WPCs has been described in detail in a previous publication [8]. Briefly, a  $2^3$  factorial design was used to design eight WPC formulations including either pine (*Pinus spp.*) or maple (*Acer spp.*), either high density polyethylene (HDPE, Innovene Inc., Chicago, IL) or isotactic PP (Equistar, Houston, TX, USA), and either a maleic anhydride grafted polypropylene (MAPP, Honeywell, Morristown, NJ, USA) coupling agent or not (Table 1). This factorial design was developed so that the impact of polymer selection (HDPE vs. PP), wood species selection (pine vs. maple), and coupling agent could be evaluated. The formulations also comprised a commercial lubricant (OP100, Honeywell, Morristown, NJ, USA) and talc (Nicon 403, from Luzenac America Inc., Centennial, CO, USA), respectively. A water-based white acrylic coating (Raykote 2000, sp. gravity 10.57 and coating VOC 132.67) was supplied by Drew Paints, Inc. (Portland, OR, USA) for testing the paint adhesion to WPCs.

All the formulation components were first dry blended and then fed into a 35 mm intermeshing twin screw extruder (Cincinnati Milacron,

**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)	—

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°C and 171°C for HDPE formulations and 185–193°C 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 [13] prior to surface treatments or characterization in the case of untreated (control) samples. Sufficient material was prepared in order to obtain at least four specimens for each of the surface characterization techniques and for adhesion measurements with the acrylic coating. In addition, solid maple (*Acer spp.*) wood was used as a control surface [8].

## Surface Treatments

The four surface activation methods evaluated consisted of treatments with oxygen plasma, flame, chromic acid, and benzophenone/UV (BP/UV) irradiation. The oxygen plasma was generated in a cylindrical reactor [14] with a coil operating at a radio frequency of 13.56 MHz [15], room temperature and base pressure between  $0.2 \times 10^{-6}$ – $2.1 \times 10^{-6}$  MPa. Four replicates were placed in the center of the coil and treated in a single run. HDPE formulations were treated for 30 minutes at  $0.013 \times 10^{-3}$  MPa pressure, 52 sccm oxygen flow rate [14], while PP formulations were treated at  $0.011 \times 10^{-3}$  MPa pressure, 10 sccm oxygen flow rate for 10 minutes [16].

The chromic acid treatment consisted of a 2 minute immersion in a fresh chromic acid solution kept at 70°C under constant stirring

according to ASTM D2093–03 [13] after which the specimens were washed in distilled water and dried in an oven at 40°C for 1 hr.

The flame treatment was performed on a flame generator from Ensign Ribbon Burners LLC (Pelham Manor, NY, USA). Air (2.9 kPa) and natural gas (3.7 scfm) were mixed in a venturi-tube to generate a flame from a ‘T’ type utility ribbon burner. Specimens were manually moved under the flame, at a 12 mm distance from the burner edge, at an approximate speed of  $\sim 0.3$  m/s [17].

For the BP/UV irradiation treatment, specimens were first immersed for 1 minute in a 5% weight solution of BP in acetone, and after solvent evaporation, they were irradiated for 2 minutes under a metal halogenide lamp (Heraeus 380 watt, Hanau, Germany) using a 20 cm substrate-to-source distance [18]. The specimens were washed with acetone (to remove extra BP) and kept in glass vials wrapped with aluminum foil to avoid further exposure to light until characterization.

## Surface Characterization

Control and treated specimens were characterized to evaluate the changes in surface chemistry, wettability, and topography upon surface treatment.

The surface chemistry was first characterized with attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) using a ZnSe crystal (Thermo Nicolet Continuum model, Fitchburg, Germany, MCT-A detector, incident angle of  $45 \pm 5^\circ$ ). For each specimen, 560 scans were acquired at a  $4 \text{ cm}^{-1}$  resolution. A surface wood index, OH/CH, was obtained by normalizing the cellulosic hydroxyl peak intensity at  $1023 \text{ cm}^{-1}$  to the polyolefinic C–H stretching peak intensity at  $2912 \text{ cm}^{-1}$  [19].

Contact angle measurements were then performed 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  $194 \mu\text{m/s}$ . Advancing and receding contact angles,  $\theta_a$  and  $\theta_r$ , were thus measured along with the wetting hysteresis,  $\gamma_L(\cos \theta_r - \cos \theta_a)$ .

The surface topography of the HDPE/Pine/MAPP formulation was also evaluated with a diamond stylus profilometer (SPN Technology Inc., Goleta, CA, USA) using a force of  $9.8 \cdot 10^{-6} \text{ N}$  and a scanning rate of  $0.4 \text{ mm/sec}$  on  $10 \text{ mm}$  long scan. Finally, these samples were imaged on a Hitachi scanning electron microscope (SEM, Tokyo, Japan) after gold coating (20 kV).

## 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 [20] 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 in tensile grips on an Instron testing machine (model 4426, Norwood, MA, USA) to undergo a 180° adhesion test [21]. The peel test was conducted at a crosshead speed of 20 mm/min [22]. Peel load (N) was normalized to a specimen width of 10<sup>3</sup> mm according to the ASTM [22].

## Statistical Analyses

The data were analyzed in a randomized complete block design (CBD), using the eight formulations as a blocking factor. The effect of treatments on all the measured properties was detected with a one-way analysis of variance (ANOVA) and Duncan's multiple test using  $\alpha = 0.05$ . For the peel load only, an ANOVA was also performed within each treatment dataset at  $\alpha = 0.1$  to detect the impact of formulation factor on the peel load. Finally, qualitative comparison of SEM images and topographic profiles before and after treatments was performed for the HDPE/Pine/MAPP formulation.

## RESULTS AND DISCUSSION

### Impact of Surface Treatments on the Adhesion of an Acrylic Coating

Table 2 summarizes the peel strength of the acrylic coating on WPCs before and after the surface treatments. When evaluated across all formulations, all four treatments significantly improve the adhesion of the acrylic coating to WPCs, as previously observed in other systems [6,7]. However, there are significant differences in the efficacy of the various surface activation methods. Overall, the chromic acid treatment is the most effective ( $637 \pm 88$  N/m), followed by the oxygen plasma treatment ( $516 \pm 116$  N/m), and then the BP/UV treatment ( $466 \pm 107$  N/m). The flame treatment ( $381 \pm 94$  N/m) is the least effective of all treatments. Except for the flame treatment, the treatments more than double the adhesion strength of the acrylic coating to WPCs as compared with that on control WPCs ( $232 \pm 56$  N/m).

**TABLE 2** Peel Load (N/m) of An Acrylic Coating on Eight WPC Formulations Before and After Surface Treatments

Formulation	Control	Flame	Chromic	BP/UV	O <sub>2</sub> Plasma
HDPE/Pine/MAPP	177 ± 21	317 ± 50	667 ± 74	462 ± 96	454 ± 89
HDPE/Maple/MAPP	168 ± 13	356 ± 12	631 ± 79	516 ± 14	502 ± 109
PP/Pine/MAPP	232 ± 9	483 ± 214	707 ± 67	460 ± 130	460 ± 71
PP/Maple/MAPP	249 ± 9	362 ± 30	711 ± 77	389 ± 124	478 ± 160
HDPE/Pine	218 ± 16	372 ± 37	583 ± 26	429 ± 96	549 ± 164
HDPE/Maple	217 ± 23	412 ± 94	639 ± 57	449 ± 67	430 ± 62
PP/Pine	290 ± 24	336 ± 71	642 ± 71	461 ± 65	646 ± 20
PP/Maple	309 ± 20	410 ± 7	514 ± 100	561 ± 183	609 ± 8
Maple	524 ± 64	—	—	—	—
PP	126 ± 35	—	—	—	—
HDPE	48 ± 1	—	—	—	—
Average*	232 ± 56 (E)	381 ± 94 (D)	637 ± 88 (A)	466 ± 107 (C)	516 ± 116 (B)
Significant factors (level giving the highest peel load is noted)	No MAPP PP	—	MAPP	—	No MAPP PP

\*Average across all WPC formulations. Letter indicates grouping from the Tukey-test from high (A) to low (E) values.



Specifically, the chromic acid, oxygen plasma, and BP/UV increase the average peel load by 175%, 122%, and 100%, respectively. The flame treatment only increases the peel load by 64%. Moreover, note that the coating adhesion to chromic acid or plasma treated WPCs is in the same range as that to maple ( $524 \pm 64$  N/m) and well above that of neat plastic (48–126 N/m) [8]. It is, therefore, evident that the surface treatments that are normally effective for polyolefins are also effective for WPCs. Moreover, following treatment with chromic acid or oxygen plasma, WPCs can be coated more or equally efficiently as maple. The efficacy of the surface treatments on WPCs is not a surprise considering that the surface properties of WPCs and wettability in particular have been found to resemble those of the neat plastics [8]. Furthermore, these results are consistent with a previous report that the chromic acid and flame treatments improved the shear strength of an epoxy coating by 97% and 67%, respectively [7].

Using the same acrylic coating on neat WPCs, it has been previously established that distinct WPC formulations performed differently in terms of surface and adhesion properties [8]. In particular, formulations without MAPP coupling agent were more effectively coated than formulations with MAPP. Higher peel strength on MAPP-devoid formulations correlated with greater surface roughness which favorably impacted adhesion. Similarly, PP formulations developed higher peel loads than HDPE formulations, possibly due to the higher surface wood index and polarity observed in the PP formulations. To further evaluate the impact of WPC formulation factors on the efficacy of each treatment, ANOVA was conducted within each dataset (Table 2). For the plasma treatment, the impact of formulation factors on the acrylic peel load was similar to that in control WPCs. That is, formulations without MAPP developed higher peel loads to the acrylic coating and so did formulations with PP compared with HDPE. This suggested that the plasma treatment did not differentially improve the surface and adhesion properties of WPC formulations. In contrast, following the chromic acid treatment, formulations that contained MAPP developed higher peel loads than formulations without MAPP (Table 2). This differed with the adhesion properties of control WPCs, indicating that the chromic acid treatment most effectively improved the adhesion of formulations containing MAPP. Interestingly, both the BP/UV and the flame treatments eliminated the formulation dependency of the peel load. In other words, following the BP/UV and flame treatments, all formulations could be equally bonded by the acrylic coating.

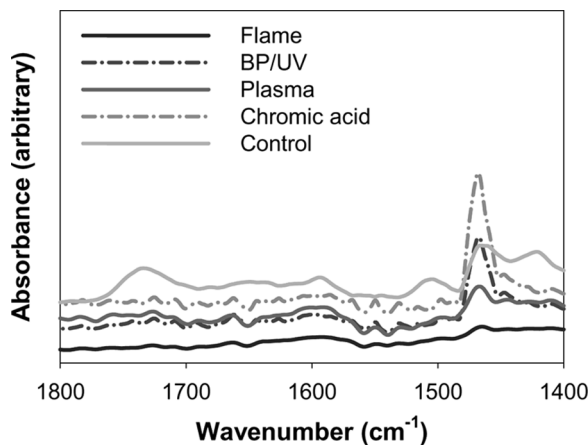
To conclude, although all four treatments were effective at improving the coating adhesion to WPCs, their efficacy varied largely and

also depended on the WPC formulation. The differential effects of the four treatments on WPC formulations suggested that different adhesion mechanisms may be acting. To shed light on the mechanisms by which each treatment improved the coating adhesion, the surface properties of the treated WPCs were evaluated.

### Impact of Surface Treatments on WPC Surface Chemistry

All the surface treatments are expected to oxidize the substrates, improving both their polarity and wettability [9]. However the ATR-FTIR spectra of all the WPCs after treatment did not clearly reveal surface oxidation, at least when considering the carbonyl region in the  $1530\text{--}1840\text{ cm}^{-1}$  region (Figure 1). In fact, a carbonyl band is observed at  $1725\text{ cm}^{-1}$  in the untreated sample only and is likely due to lignin, suggesting that the treatments may have induced a loss of wood component on the surface. In a study of chromic acid etching of polyolefins, Blais et al. noted that ATR-FTIR was not very effective at detecting carbonyl species on polyolefins other than low density polyethylene for which large amount of oxidation occurs [23,24]. Perhaps, oxidation also occurs in WPCs, but it is not significant enough to be observed with ATR-FTIR.

On the other hand, the OH/CH ratio or wood index was clearly altered by most surface treatments (Table 3). Specifically, treatments with chromic acid, BP/UV and, to a lesser extent, with flame



**FIGURE 1** ATR-FTIR spectra of the HDPE/Pine/MAPP formulation before and after surface treatments.

**TABLE 3** Comparison of the Surface Properties and Coating Adhesion of WPC Surfaces Before and After Surface Treatments. Values are Averages of All the Formulations

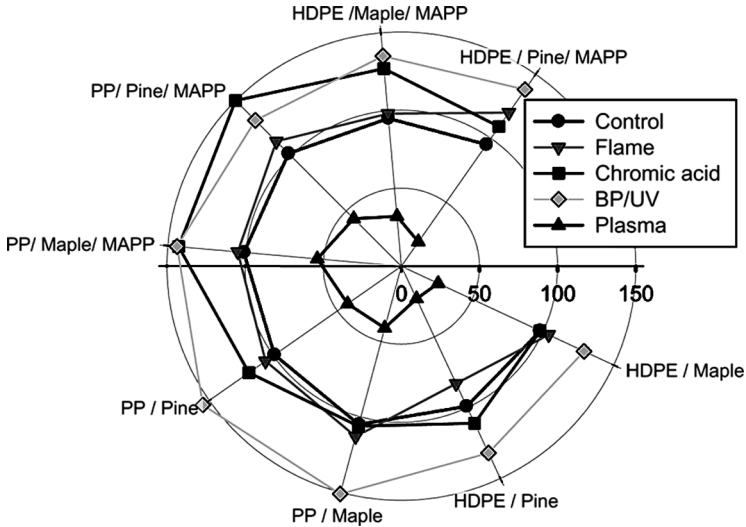
Treatment	O–H/C–H	$\theta_a(^{\circ})$	$\theta_r(^{\circ})$	Wetting hysteresis (mJ/m <sup>2</sup> )
Control	2.11 ± 0.77(A)*	100 ± 7 (C)	23 ± 14 (A)	78 ± 12 (D)
Flame	1.70 ± 0.56(B)	104 ± 14 (C)	0	90 ± 17 (C)
Chromic	1.01 ± 0.46 (C)	120 ± 19 (B)	0	107 ± 20 (B)
BP/UV	1.25 ± 0.69(C)	140 ± 10 (A)	0	128 ± 8 (A)
O <sub>2</sub> Plasma	1.97 ± 0.91 (A)	35 ± 14 (D)	0	71 ± 11 (E)

\*Letter indicates grouping from the Tukey-test from high (A) to low (E) values.

decreased the surface wood index or increased the concentration of plastic on the first few microns of the surface as probed by ATR-FTIR. The lowering of the wood index following these treatments may have been caused by preferential etching of the wood components or by temperature induced migration to the surface of the C-H rich components, such as the polyolefin and the lubricant. Perhaps the change in the surface composition of WPCs further obscured the spectroscopic detection of oxidation that is expected as a result of the treatments.

### Impact of Surface Treatments on WPC Surface Wettability

Average  $\theta_a$ ,  $\theta_r$ , and wetting hysteresis measured before and after surface treatments are summarized in Table 3 along with their grouping according to the Tukey-test. The first striking feature in considering  $\theta_a$  is the large reduction induced by the oxygen plasma treatment from 100 ± 7° to 35 ± 14° indicating improved wettability (Table 3). In fact, the water  $\theta_a$  was consistently reduced for all formulations after the plasma treatment (Figure 2). The reduction in the water  $\theta_a$  following the plasma treatment may have been induced by a decrease in the substrate hydrophobicity or roughness [25,26]. The water  $\theta_r$  also decreased after the plasma treatment (Table 3) further supporting the enhanced substrate hydrophilicity. Indeed, for heterogeneous surfaces having both an hydrophobic and hydrophilic component, the advancing contact angle reflects the hydrophobic component, whereas the receding contact angle is dictated by the hydrophilic component [26]. Improved water wettability in oxygen plasma treated WPCs could be due to surface oxidation although it was not clearly detected from the ATR-FTIR. The improved wettability of WPCs with polar



**FIGURE 2** Advancing contact angle of WPC formulations before and after surface treatments.

liquids after the plasma treatment likely contributed to its success at improving adhesion with a water-based acrylic coating.

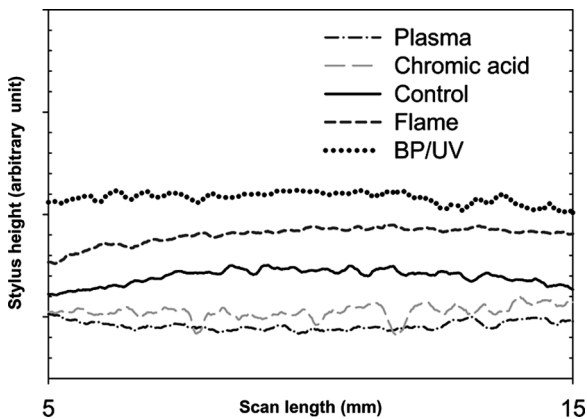
In contrast, the BP/UV ( $140 \pm 10^\circ$ ) and the chromic acid treatments ( $120 \pm 19^\circ$ ) actually increased the  $\theta_a$  compared with the control WPCs ( $100 \pm 7^\circ$ ), suggesting a more hydrophobic surface and lower wettability (Table 3). The flame treatment did not alter the advancing contact angle. Again, these changes in  $\theta_a$  with surface treatments were consistently observed for all the formulations (Figure 2). For all the treatments,  $\theta_r$  also decreased to 0 (Table 3). A similar behavior has been observed when PP was treated with chromic acid and this was mainly ascribed to surface roughening [27]. Indeed, for hydrophobic surfaces such as WPCs, surface roughening increases  $\theta_a$  upon wetting but also decreases  $\theta_r$  upon dewetting as water gets trapped in the surface asperities [25]. The trends in dynamic contact angles observed after the treatments with chromic acid and BP/UV are, thus, consistent with a surface roughening induced by treatments. Furthermore, surface roughening is expected from the etching process with chromic acid [27] and has been previously noted on a PP-based WPC formulation [7]. The effectiveness of the chromic acid and BP/UV treatments at improving coating adhesion to WPCs may then be related in large part to their effects on the substrate topography.

## Impact of Surface Treatments on WPC Surface Topography

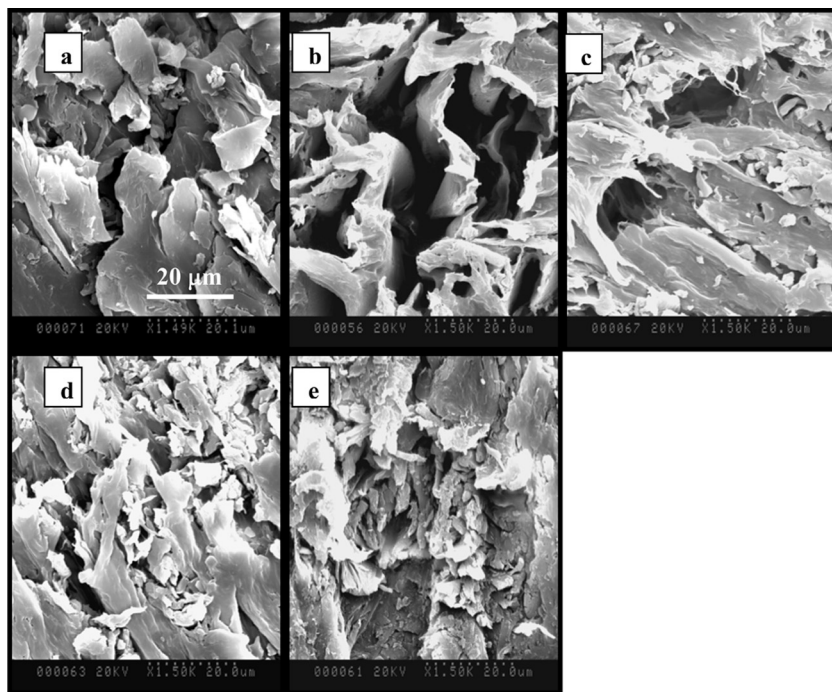
To further test whether the treatments had affected surface roughness, the topography of HDPE/Pine/MAPP formulation before and after treatments was qualitatively compared using both profilometry and SEM. The chromic treated WPC clearly displayed larger variations in topography, *i.e.* indicating higher surface roughness than all the other surfaces (Figure 3). After treatments with BP/UV, plasma, and flame the topographies were similar to those of the untreated WPCs (Figure 3). SEM images of the samples before and after treatments confirmed the observations from the profilometry (Figure 4). Namely, large crevasses formed on the WPC surface as a result of the chromic acid treatment; crevasses that are not observed after the other treatments. Although qualitative, these images are consistent with the hypothesis that a major mechanism of adhesion enhancement of the chromic acid treatment involved roughening.

## Adhesion Mechanisms of Surface Treatments

Because surface roughness, chemical heterogeneity, and viscoelastic energy dissipation mechanisms all contribute to both wetting hysteresis and adhesion, a strong correlation ( $r^2 = 0.89$ ) between the water wetting hysteresis and the adhesion of a water-based acrylic coating on WPCs exists [8]. In this study, all but the plasma treatment significantly increased the wetting hysteresis of WPCs (Table 3). The BP/UV



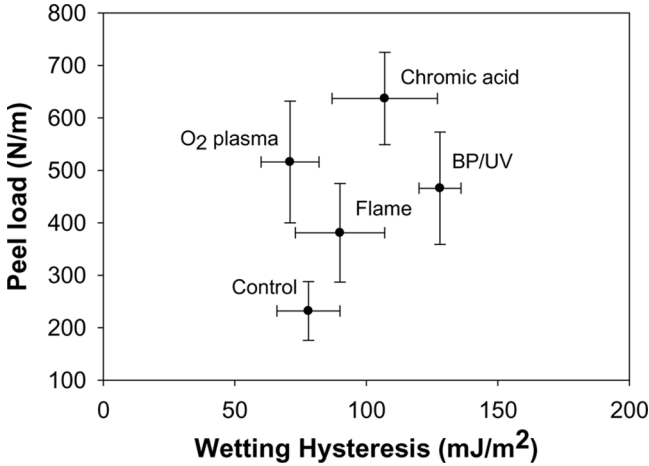
**FIGURE 3** Surface topography of the HDPE/Pine/MAPP formulation before and after surface treatments.



**FIGURE 4** SEM (1.5 K magnification) images of the HDPE/Pine/MAPP formulation a) before treatment, and after treatments with b) chromic acid, c) flame, d) BP/UV, and e) oxygen plasma.

treatment ( $128 \pm 8 \text{ mJ/m}^2$ ) increased the wetting hysteresis most, followed by the chromic acid treatment ( $107 \pm 20 \text{ mJ/m}^2$ ), and finally the flame treatment ( $90 \pm 17 \text{ mJ/m}^2$ ) (Table 3). The increase in wetting hysteresis for all treatments but the plasma treatment is, therefore, consistent with the improved adhesion of the coating following these surface treatments.

To comprehend further the adhesion mechanisms in place following the surface treatments, relationships between peel load and surface wood content (O–H/C–H), contact angle ( $\theta_a$ ) and wetting hysteresis were evaluated as previously done in a series of WPCs [8]. In the case of treated WPCs, no distinct relationships could be established between the peel load and any surface properties. At the most an ascending trend of peel load with wetting hysteresis may be suggested (Figure 5). The lack of distinct relationship likely reflected the greater complexity and diversity of adhesion mechanisms in action with the various surface treatments. Indeed, for the most efficient surface



**FIGURE 5** Dependency of peel load (N/m) on wetting hysteresis across WPC formulations.

treatments, distinct factors and possibly adhesion mechanisms appeared to predominantly contribute to the treatment efficacy.

The chromic acid and oxygen plasma were the most efficient treatments for improving the adhesion of an acrylic coating on WPCs. With the chromic acid treatment, the surface roughness of WPC was found to increase as large crevasses formed on the surface. Gramlich *et al.* demonstrated that surface roughening in PP based composites was indeed apparent after water treatment and this was ascribed to preferential swelling of wood [7]. Surface oxidation was also proposed although not demonstrated as a surface activation mechanism. In the present study, surface roughening was accompanied by a decrease in the surface wood index suggesting that the chromic acid may have preferentially etched the wood components. In any case, the increase in surface roughness induced by the chromic acid treatment results in a higher interfacial area for bonding and possibly greater energy dissipation mechanisms for plastics. In addition, greater surface roughness may also contribute mechanical interlocking at the interface and change the stress distribution as previously discussed for wood plastic composites [8]. These may be the main adhesion mechanisms in place in the case of chromic acid treated WPC. It is also possible that surface oxidation occurred as a result of the chromic acid treatment as expected on polyolefins [23,24], but it was not detected with ATR-FTIR.

In the case of plasma treated WPCs water wettability was improved, suggesting higher hydrophilicity of the surface possibly imparted by the oxidizing effect of the oxygen plasma treatment although it could not be detected with the limited techniques used in this study. In this case, oxygen containing functional groups on the surface can give rise to polar interactions with the acrylic coating, whether these involve primary bonding or secondary interactions such as H-bonding. Enhanced wettability is also important to achieve molecular contact between the substrate and the liquid coating upon application. Higher surface polarity and greater wettability would, therefore, explain the high efficacy of the oxygen plasma treatment on WPCs. Moreover, considering that the chromic acid treatment and the oxygen plasma treatment enhance coating adhesion *via* distinct mechanisms, one may speculate that successive implementation of each treatment could further improve the coating adhesion to WPCs.

## CONCLUSIONS

Eight formulations of WPCs were treated with chromic acid, oxygen plasma, flame, and BP/UV treatments to improve their adhesion properties with an acrylic coating. The acrylic coating adhesion to WPCs was measured using an 180° peel test. The surface chemistry, wettability, and topography of the treated WPCs were evaluated by ATR-FTIR spectroscopy, dynamic contact angle measurements, and profilometry combined with scanning electron microscopy.

Overall, the surface treatments increased the acrylic coating adhesion to WPCs by 1.5–2.5 fold. The chromic acid treatment performed best followed by the oxygen plasma treatment, achieving coating adhesion superior or equal to that obtained on untreated maple. For these two treatments, the selection of the WPC formulation impacted the coating peel load. However, both treatments acted differently on the surface and adhesion properties of WPCs. The chromic acid treatment primarily increased the surface roughness, yielding greater wetting hysteresis and interfacial adhesion. In contrast, the oxygen plasma treatment likely oxidized the surface of WPCs resulting in a large improvement in wettability and thus adhesion. The efficacies and the adhesion enhancement mechanisms of the chromic acid and the plasma treatments suggest that greater adhesion properties may be obtained by successively applying both treatments to WPCs. In any case, both treatments allow adhesion levels to WPCs that are greater than those to wood, confirming the ability of WPCs to be properly painted or coated. These results are of particular interest to



the WPC industry, as the application of protective coatings can improve the durability and aesthetics of WPCs.

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