Combined Surface Treatment of Wood Plastic Composites to Improve Adhesion

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To improve the adhesion properties, the surfaces of polyethylene wood plastic composites (WPCs) were treated by a combination of sanding then coating with a silane coupling agent, followed by plasma discharge. The surface properties of polyethylene WPCs were studied by assessing the contact angle and bonding strength, as well as implementing Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS). The results indicated that the roughness of the composites increased during the combined treatment, when compared with the untreated composites. The content of the oxygen elements on the surfaces of the combined treated composites also was found to increase. This indicated that there were polar groups formed, such as –OH, –C=O, and –O–C=O. The surface wettability of the composites improved after the combined treatment. At the same time, chemical bonding between the coupling agent and the wood fibers of the sanding-treated composites occurred. The surface properties of the polyethylene WPCs were changed by the combined treatment, which became favorable for adhesiveness. After the combined treatment, the shear strength and durability of the bonding joints of the composite increased significantly and displayed a synergistic effect from the surface treatment.

Keywords: Polyethylene wood plastic composites; Combined surface treatment; Adhesion; Surface property; Bonding strength

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INTRODUCTION

Polyethylene wood plastic composites (WPCs), which are made of wood powder and polyethylene by extruding or hot-pressing, have been widely used in the construction, automotive, packaging, and transport industries (Ashori 2008; Perisić et al. 2009). WPCs are desirable materials because of their high strength and wear resistance from both the wood and plastic elements. However, the widespread use of polyethylene WPCs is due more to the way in which they conveniently fit together. Traditionally, most polyethylene WPCs have been joined by a mechanical method. This is a convenient operation, but it has a negative influence on the appearance of the products because of the inability to achieve a seamless connection. Alternatively, bonding with an adhesive is a method used to reduce the weight and achieve a seamless connection for the products, making it useful for a wide range of applications (Özdemir and Mengeloglu 2008; Liu et al. 2010; Cheng et al. 2012a,b).

The polyethylene on the surface of polyethylene WPCs results in poor polarity, low surface energy, and difficult adhesion (Gupta et al. 2007; Gupta and Laborie 2007; Oporto et al. 2007). In recent years, several techniques have been investigated for solving the
adhesion problems of polyethylene WPCs. The plasma discharge surface treatment has the advantage of achieving a relatively high and fast bonding strength. Unfortunately, the stability and ageing of the plasma treatment, as well as the durability of the bonding joint for plasma-treated composites, have been found to be poor. This is especially true for durable performance in a wet environment (Tahara et al. 2003; Noeske et al. 2004; Wolkenhauer et al. 2008). In contrast, polyethylene WPCs that were sanded then coated with a coupling agent showed a high bonding strength and good durability. However, the processing of coating with a coupling agent requires a high-temperature heating procedure, causing a longer processing time (Wang et al. 2011; Di and Wang 2013; Kwona et al. 2014). In this study, the combined treatment for polyethylene WPCs of sanding then coating with a silane coupling agent, followed by plasma discharge, was utilized to achieve a fast treatment method and a satisfactory bonding performance.

Gramlich et al. (2006) combined flame and water surface treatments to treat the surface of WPCs. The experimental results showed that the combined treatment of the composites obtained a better bonding performance, and the combination of the two methods may appear as an unexpected combined action. Moghadamzadeh et al. (2011) employed several surface treatment methods, such as a flame, corona discharge, sanding, and a combination of sanding treatment followed by corona discharge treatment, to improve the bonding strength of WPCs. The strength of the bonded joints made with the combination of a sanding treatment followed by a corona discharge substantially increase when compared with that of the untreated composites. Previous research has shown that using combined processing methods to modify the surface of polyethylene WPC materials is more effective than using an individual processing method.

To further study the effects of the combined treatment of sanding then coating with a silane coupling agent, followed by plasma discharge, on the surface properties of polyethylene WPCs, and to test and analyze the bonding properties, a contact angle test, Fourier transform infrared (FTIR) spectroscopy, scanning electron microscope (SEM), and X-ray photoelectron spectroscopy (XPS) were used in this study.

**EXPERIMENTAL**

**Materials**

The polyethylene WPCs were provided by the Material Science and Engineering College of Northeast Forestry University of China. The manufacture method employed was extrusion molding. The weight percent of poplar flour (a mixture of wood powder with different particle size) was 60%, and the particle diameters range were 20 to 40 mesh (380 to 830 μm). Meanwhile, the weight percent of the high-density polyethylene (HDPE) with a density of 0.955 g/cm³ and a melt flow index of 0.35 g/10min under the temperature of 190 °C and the load of 2.16 Kg was 30%. In addition, the remaining components of the polyethylene WPCs were a maleic anhydride grafted polyethylene coupling agent. A γ-(2, 3-epoxy propoxy) propyl trimethoxy silane (KH-560) solution, which contains 95% ethanol and 5% silane coupling agent, was used for the surface coating treatment. An epoxy resin adhesive composed of bisphenol epoxy resin (E-51) and a polyamine curing agent were used to adhere the composites. The curing procedure was conducted at room temperature for 24 h and then at 50 °C for 4 h.
Surface Treatment

The surface treatment of the polyethylene WPCs was carried out following three steps, sequentially. Firstly, the sanding treatment of the surface of polyethylene WPCs with 180-mesh (80-μm) sandpaper was conducted. Secondly, coating of the surface of polyethylene WPCs by 5% wt silane coupling agent in absolute ethyl alcohol was conducted, after which the composites were left to stand for 10 min at room temperature. Finally, plasma discharge treatment of the polyethylene WPCs was carried out in a GSL-1100X-PJF-A low-temperature plasma apparatus (Shenyang KeJing Automation Equipment Co., Ltd., China). The specimens were positioned vertically under the plasma beam in the device. Ambient air at room temperature and atmospheric pressure was blown through the discharge gap of 30 mm between the specimens and the plasma beam current, and the specimens were treated for 30 s, which produced the best bonding adhesion strength.

Tests and Analysis

A JC2000A goniometer, provided by Shanghai ZhongChen Digital Technique Equipment Co. Ltd. of China, was used to calculate the contact angle at 25 °C and used for measurements of untreated and surface-treated specimens using distilled water and glycerol, respectively. The contact angle was measured for at least five different locations by single drops (2 μL) of the test liquid per specimen. The FTIR spectral analysis with an ATR mode was conducted on a Magna-IR 560 Fourier transform infrared spectrooscope provided by Nicolet Co., Ltd. (USA), to measure the functional groups on the surfaces of untreated and surface-treated specimens. The resolution of the device is 4 cm⁻¹, and the scanning range is 4000 to 400 cm⁻¹. SEM images of the surfaces of untreated and surface-treated polyethylene WPCs were acquired using a Quanta200 Scanning Electron Microscope provided by FEI Co., Ltd. (USA) with an accelerated voltage of 12.5 KV and a magnification factor of 400. The XPS spectra of the untreated and surface-treated specimens were obtained using K-Alpha X-Ray Photoelectron Spectra equipment provided by Thermo Fisher Scientific Co., Ltd. (USA) with a vacuum chamber pressure of 5×10⁻⁷ Pa. The energy scale using the energy of the C1s peak of adventitious aliphatic carbon (285.00 eV) was calibrated as the reference. When the XPS spectra results were recorded in the energy range from 0 to 1000 eV, the pass energy was 50 eV and the step size was 0.1 eV. During the curve fitting, the shape of the fitting curves was determined by the Gaussian and Lorentzian distributions, in which the Gaussian distribution ratio was not less than 80%. The shear bonding strength measurements of untreated and surface-treated specimens that were bonded with the epoxy resin adhesive were conducted on a CMT 5504 Universal Mechanical Testing Machine provided by Shenzhen XinSanSi Co., Ltd. of China according to ASTM D905-08 (2013), and the rate of testing was 5 mm/min.

RESULTS AND DISCUSSION

Contact Angle

Table 1 shows the contact angle values, and the corresponding standard deviations, of the distilled water and glycerol on the surface of untreated, sanding-treated, and combined treated polyethylene WPCs for 60 s. From Table 1, it can be seen that the contact angle values in the table for both water and glycerol increased over that of the untreated...
specimen after sanding treatment. The reason may be that the test liquid could not spread on the surface of the specimen in a short time because of the rough surface excessively (Wenzel 1936). After the combined treatment, the contact angle of the surface of the polyethylene WPCs clearly decreased when compared with the sanding treatment, which attribute to the polarity oxygen-containing groups were introduced on the surface of the polyethylene WPCs by the plasma discharge. And it can be seen that the wettability is concerned with the elemental composition and the molecules polarity of the surface besides the roughness of the surface. It is important to note that combined treatment resulted in a greater change in the surface properties of the polyethylene WPCs.

### Table 1. Contact Angles and their Standard Deviations (SD) for WPCs Treated by Various Methods

<table>
<thead>
<tr>
<th></th>
<th>Untreated</th>
<th>Sanding-treated</th>
<th>Combined treated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Distilled water</td>
<td>Glycerol</td>
<td>Distilled water</td>
</tr>
<tr>
<td>Contact angle (*)</td>
<td>94.6</td>
<td>78.6</td>
<td>106.9</td>
</tr>
<tr>
<td>SD</td>
<td>1.7</td>
<td>3.7</td>
<td>6.8</td>
</tr>
</tbody>
</table>

### FTIR Analysis

Figure 1 shows the infrared spectra of the surface of untreated, sanding-treated, and combined treated polyethylene WPCs. The infrared spectra show that the surface of the untreated polyethylene WPCs contains a great deal of CH2– symmetric and anti-symmetric stretching vibration absorption peaks (2913 and 2846 cm\(^{-1}\)), C–H in-plane bending vibration absorption peaks (1472 cm\(^{-1}\)), and CH2– swaying in-plane vibration absorption peaks (715 cm\(^{-1}\)). This confirms that the polyethylene was concentrated on the surface of the polyethylene WPCs. After the sanding treatment, the specimen surface appeared to have many characteristic absorption peaks of cellulose, hemicelluloses, and lignin. The peak at 3324 cm\(^{-1}\) can be attributed to the stretching vibration absorption peak for –OH. The peak at 1734 and 1648 cm\(^{-1}\) can be attributed to the stretching vibration absorption peak for C=O (Nicole and Laurent 2004). The peaks at 1596 and 1239 cm\(^{-1}\) can be attributed to the benzene ring carbon skeleton vibration of lignin and oxygen stretching vibration. Lastly, the peak at 1030 cm\(^{-1}\) can be attributed to the stretching vibration absorption peak for C–O. This is due to the sanding treatment, which removed the polyethylene on the surface of polyethylene WPCs, and also due to the internal wood powder, which contained exposed cellulose, hemicellulose and lignin.

After the combined treatment of sanding then coating with a silane coupling agent followed by plasma discharge, the specimen surface appeared to have a Si–O stretching vibration absorption peak (1109 cm\(^{-1}\)), which indicated persuasively that the coupling agent reacted with the hydroxyl group of the wood powder (Abdelmouleh et al. 2002), leading to a decrease in the amount of –OH. However, the plasma discharge increased the number of polar groups, such as –OH, C=O, and C–O; therefore, the specimen surface could be expressed finally by an increase in the amount of –OH, C=O and C–O. These newly generated polar groups would be a great benefit for the wettability and adhesion of the polyethylene WPCs.
Fig. 1. Infrared spectra of the surface of polyethylene WPCs: 1-untreated; 2-sanding-treated; 3-combined treated

**SEM Analysis**

Figure 2 shows the surface morphologies of untreated, sanding-treated, and combined treated specimens. It can be seen that the untreated polyethylene WPCs have a relatively smooth surface, and the slight scratch was caused by the molding process. In comparison with the untreated composite, the surface roughness of the sanding-treated composites increased evidently. The reason is that the sanding treatment wiped off the polyethylene from the surface of the material, thereby revealing the internal wood fibers. After the combined treatment, the surface roughness of the composite materials decreased slightly compared with the results of the sanding treatment. This is due to the plasma discharge on the surface of the materials. Compared with the untreated specimen, the surface roughness of the combined treated composite increased, which is beneficial for the wettability and adhesion of the polyethylene WPCs.

Fig. 2. SEM micrographs of the surface of polyethylene WPCs: 1-untreated; 2-sanding-treated; 3-combined treated
XPS Analysis

Analysis of the content of surface elements of polyethylene WPCs

Table 2 illustrates the content change in the surface elements for untreated, sanding-treated, and combined treated polyethylene WPCs. The content of the carbon element decreased and the oxygen element content increased after sanding treatment, and this trend is even more apparent after the combined treatment. Accordingly, the O/C value increased. It can also be seen that the silicon element and the nitrogen element were generated after the combined treatment. The generation of the former element showed that chemical bonds between the coupling agent and the materials were formed. The generation of the latter element was due to the plasma discharge on the surface of the polyethylene WPCs in air. The results illustrated that the surface of polyethylene WPCs was oxidized during the plasma discharge treatment, which is consistent with the results of the FTIR analysis.

Table 2. Elemental Content of the Surface of Polyethylene WPCs

<table>
<thead>
<tr>
<th>Treatment</th>
<th>C (%)</th>
<th>O (%)</th>
<th>Si (%)</th>
<th>N (%)</th>
<th>O/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>92.70</td>
<td>7.30</td>
<td>-</td>
<td>-</td>
<td>0.079</td>
</tr>
<tr>
<td>Sanding-treated</td>
<td>89.36</td>
<td>10.63</td>
<td>-</td>
<td>-</td>
<td>0.119</td>
</tr>
<tr>
<td>Combined treated</td>
<td>74.65</td>
<td>21.35</td>
<td>1.67</td>
<td>2.33</td>
<td>0.286</td>
</tr>
</tbody>
</table>

Analysis of C spectrum

Figure 3.1 shows the curves for the peak fitting the C1s peak on the surface of untreated polyethylene WPCs. The C1s peak can be fitted into three peaks (Nicole and Laurent 2004). For example, the C1s A peak, with a binding energy of 285.00 eV, corresponds to –C–C– and –C–H bonds, which are mostly involved in the formation of polyethylene, with a relative content of 80.1%. The C1s B peak, with a binding energy of 286.61 eV, corresponds to the –C–O– bond, with a relative content of 10.0%. The appearance of the –C–O– bond was due to the small amount of wood powder contained within the surface of the polyethylene WPCs, and the cellulose and the hemicelluloses in the wood powder contained a large amount of –C–O– bonds. The C1s C peak, with a binding energy of 288.40 eV, corresponds to –C=O and –O–C–O– bonds, and with a low relative content of only 2.6%. The appearance of the –C=O and –O–C–O– bonds was due to the lignin, which contained some aldehyde and keto groups within the wood powder, and slight oxidation by the air on the surface of the polyethylene WPCs.

Figure 3.2 shows the curves for the peak fitting of the C1s peak on the surface of the sanding-treated polyethylene WPCs. The C1s peak can be fitted into four peaks. The peaks for C1s A-D correspond to –C–C– and –C–H bonds, –C–O– bond, –C=O– and –O–C–O– bonds, and –O=O–C–O– bond respectively (Nicole and Laurent 2004). When compared with Fig. 3.1, it can be seen that the content of the C1s A peak decreased noticeably, while the content of the C1s B and C1s C peaks increased and the C1s D peak was generated. This is due to the polyethylene being removed from the surface and the internal lignocelluloses being exposed after the sanding treatment. Also, the large amount of polar oxygen-containing groups in the wood fibers resulted in an increase in the content of oxygen-containing groups on the surface of the polyethylene WPCs.

Figure 3.3 shows the curves for the peak fitting of the C1s peak on the surface of the combined treated polyethylene WPCs. The C1s peak can be fitted into five peaks. The peaks for C1s A-E correspond to –C–C– and –C–H bonds, –C=O– and –O–C–O– bonds, –C=O– and –O–C–O– bonds, –O=O–C–O– bond and –C–O–Si bond, respectively (Abdelmouleh et al. 2002; Nicole and Laurent 2004). The binding energies of the C1s A,
C1s B, C1s C, and C1s D peaks shown in Fig. 3.3 were different from those in Fig. 3.2. This is due to the insulation property of the polyethylene WPCs. During testing, there was a cumulative charge on the surface of the sample, which led to a shift in the binding energy. Following the combined treatment of sanding then coating with a silane coupling agent and discharge plasma, the C1s B, C1s C, and C1s D peak contents increased, while that of the C1s A peak decreased and the C1s E peak was generated. These results illustrate that the surface properties of the polyethylene WPCs were changed after the combined treatment, which was evident in the generation of oxygen-containing groups such as –C–O–, –C=O, and –O–C=O. Oxidation occurred in the process of the plasma discharge, and the generation of the –C–O–Si– group because of the chemical bonding between the coupling agent and the surface of the composites led to a decrease in the content of –C–C– and –C–H– bonds.

Fig. 3. C spectrum analysis of the surface of polyethylene WPCs: 1-untreated; 2-sanding-treated; 3-combined treated

Shear Bonding Strength Test

Table 3 describes the results of the shear bonding strength tests for the polyethylene WPCs. Compared with untreated specimens and specimens treated by other methods, the combined treated samples bonded with the epoxy resin adhesive exhibited a distinct increase in shear bonding strength, which reached the highest strength of 16.6 MPa. In the shear strength test, the fracture mode of the untreated bonded samples was interfacial failure. The fracture modes of the bonded samples treated by other methods were partial...
bulk failures, while the fracture modes of the combined treated bonded samples were bulk failures of the entire composites. From Table 3, it also can be seen that the combined treated samples showed an excellent bonding durability in water environment conditions, especially in a boiling water environment, when compared with sanding-treated samples, as well as the untreated samples. These results indicated that the combined treatment on the surface of the polyethylene WPCs effectively improved the adhesion properties of the composites.

**Table 3. Shear Strength of Polyethylene WPCs Bonded with Epoxy Resin Adhesive (MPa)**

<table>
<thead>
<tr>
<th>Soaking time</th>
<th>Untreated</th>
<th>Sanding</th>
<th>Combined treated</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.3</td>
<td>6.8</td>
<td>16.6</td>
</tr>
<tr>
<td>100 h/25 °C</td>
<td>0.3</td>
<td>5.7</td>
<td>15.0</td>
</tr>
<tr>
<td>100 h/100 °C</td>
<td>n</td>
<td>n</td>
<td>12.3</td>
</tr>
</tbody>
</table>

Note: n means the bonding joint was destroyed and the bonding strength could not be measured.

**Analysis and Discussion**

Polyethylene was located on the surface of the polyethylene WPCs throughout the molding process. Adhesion was difficult because of the poor polarity and low surface energy of the polyethylene ingredient. Only when the surface of the composites was modified could the adhesion be improved. In addition to the poor adhesion caused by the polyethylene on the surface of the composites, the wood components of polyethylene WPCs also had a great influence on the water resistance of the bonding joint because of the absorption of water (Di and Wang 2013).

As mentioned above, the sanding treatment of the composites only removed the polyethylene on the surface of the composites and revealed the wood components of the composites. This did not change the surface properties of polyethylene or wood components in the composites radically. The plasma discharge treatment of the composites was primarily aimed at the polyethylene in the polyethylene WPCs, to increase the polarity and the surface energy. The surface wettability and adhesion properties of the composites improved accordingly (Liu et al. 2010). Coating with a silane coupling agent on the surface of sanding-treated composites was mostly aimed at the wood components in the polyethylene WPCs, to achieve chemical bonding between the coupling agent and –OH groups of the wood fibers (Abdelmoulel et al. 2002). This resulted in chemical bonding between the epoxy resin adhesive and the surface of the composites through the silane coupling agent, increasing the bonding strength and improving the water resistance of the bonding joint by reducing the amount of hydrophilic groups (Kwona et al. 2014; Wang et al. 2011).

As mentioned previously, an individual surface treatment could not change the characteristics of the polyethylene and woody ingredients simultaneously. Therefore, the individual surface treatment could not simultaneously achieve the satisfactory bonding strength and durability. In contrast, the combined surface treatment of sanding then coating with a silane coupling agent, followed by plasma discharge, could modify the properties of both the polyethylene and wood fibers within the composites, in which polar groups such as –OH, C=O, and C–O were introduced on the surface of the polyethylene by plasma discharge (Noeske et al. 2004; Wolkenhauer et al. 2008). Chemical bonding between the coupling agent and the surface of the wood fibers was promoted and formed under the
plasma discharge. The formation of the polar groups on the surface of the polyethylene, and the chemical bonding of the silane coupling agent on the surface of the wood fibers, would cause an increase in the bonding strength of the composites. Meanwhile, the reduction of the hydrophilic hydroxyl groups, and the chemical bonding of the hydroxyl groups and the silane coupling agent, would help improve the water resistance of the composites’ bonding joints.

Furthermore, the combined surface treatment of sanding then coating with a silane coupling agent, followed by plasma discharge, could also maintain the characteristics of a rapid and efficient treatment effect of the plasma discharge, as well as overcome the drawback of heating the coupling agent for a long length of time at high temperature. The combined surface treatment of sanding then coating with a silane coupling agent, followed by plasma discharge, led to good results by improving both the strength and durability of the bonding joints, which showed a synergistic effect for the surface treatment.

CONCLUSIONS

1. The combined treatment of polyethylene WPCs by sanding then coating with a silane coupling agent, followed by plasma discharge, reduced the contact angle, introduced polar groups such as –OH, –C=O, and –O–C=O, and increased the surface roughness of the composites.

2. Following the combined treatment, the content of oxygen elements on the surface of the polyethylene WPCs increased, carbon elements decreased, and the O/C also increased. Meanwhile, chemical bonding between the coupling agent and the surface of the composites occurred after the combined treatment.

3. The surface properties of polyethylene WPCs were changed by the combined treatment, which proved favorable with respect to wettability and adhesion.

4. Following the combined treatment, the shear bonding strength and durability of the bonding joints of polyethylene WPCs improved considerable, which showed a synergistic effect for the surface treatment.

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REFERENCES CITED


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