

PROOF COVER SHEET

Author(s): José Miguel Martín-Martínez

Article title: Surface modification and adhesion of wood-plastic composite (WPC) treated with UV/ozone

Article no: TCOI 1340042

Enclosures: 1) Query sheet
2) Article proofs

Dear Author,

Please find attached the proofs for your article.

1. Please check these proofs carefully. It is the responsibility of the corresponding author to check these and approve or amend them. A second proof is not normally provided. Taylor & Francis cannot be held responsible for uncorrected errors, even if introduced during the production process. Once your corrections have been added to the article, it will be considered ready for publication

Please limit changes at this stage to the correction of errors. You should not make trivial changes, improve prose style, add new material, or delete existing material at this stage. You may be charged if your corrections are excessive (we would not expect corrections to exceed 30 changes).

For detailed guidance on how to check your proofs, please paste this address into a new browser window: <http://journalauthors.tandf.co.uk/production/checkingproofs.asp>

Your PDF proof file has been enabled so that you can comment on the proof directly using Adobe Acrobat. If you wish to do this, please save the file to your hard disk first. For further information on marking corrections using Acrobat, please paste this address into a new browser window: <http://journalauthors.tandf.co.uk/production/acrobat.asp>

2. Please review the table of contributors below and confirm that the first and last names are structured correctly and that the authors are listed in the correct order of contribution. This check is to ensure that your names will appear correctly online and when the article is indexed.

Sequence	Prefix	Given name(s)	Surname	Suffix
1		Andrés Jesús	Yáñez-Pacios	
2		José Miguel	Martín-Martínez	

Queries are marked in the margins of the proofs, and you can also click the hyperlinks below.

Content changes made during copy-editing are shown as tracked changes. Inserted text is in **red font** and revisions have a **blue** indicator [^]. Changes can also be viewed using the list comments function. To correct the proofs, you should insert or delete text following the instructions below, but **do not add comments to the existing tracked changes**.

AUTHOR QUERIES

General points:

- 1. Permissions:** You have warranted that you have secured the necessary written permission from the appropriate copyright owner for the reproduction of any text, illustration, or other material in your article. For further guidance on this topic please see: <http://journalauthors.tandf.co.uk/copyright/usingThirdPartyMaterial.asp>
- 2. Third-party material:** If there is material in your article that is owned by a third party, please check that the necessary details of the copyright/rights owner are shown correctly.
- 3. Affiliation:** The corresponding author is responsible for ensuring that address and email details are correct for all the co-authors. Affiliations given in the article should be the affiliation at the time the research was conducted. For further guidance on this topic please see: <http://journalauthors.tandf.co.uk/preparation/writing.asp>.
- 4. Funding:** Was your research for this article funded by a funding agency? If so, please insert ‘This work was supported by <insert the name of the funding agency in full>’, followed by the grant number in square brackets ‘[grant number xxxx]’.
- 5. Supplemental data and underlying research materials:** Do you wish to include the location of the underlying research materials (e.g. data, samples or models) for your article? If so, please insert this sentence before the reference section: ‘The underlying research materials for this article can be accessed at <full link>/ description of location [author to complete]’. If your article includes supplemental data, the link will also be provided in this paragraph. See <http://journalauthors.tandf.co.uk/preparation/multimedia.asp> for further explanation of supplemental data and underlying research materials.
- 6. The CrossRef database** (www.crossref.org/) has been used to validate the references. Changes resulting from mismatches are tracked in **red font**.

AQ1	The ORCID information has been imported from data supplied with the original manuscript. Please revise if incorrect.
AQ2	Please check whether the funding has been set correctly.
AQ3	The disclosure statement has been inserted. Please correct if this is inaccurate.
AQ4	The CrossRef database (www.crossref.org/) has been used to validate the references. Mismatches between the original manuscript and CrossRef are tracked in red font. Please provide a revision if the change is incorrect. Do not comment on correct changes.
AQ5	If Ref. [18] has been published, please give details for references list following journal style.
AQ6	Please provide missing caption for Scheme 1.

How to make corrections to your proofs using Adobe Acrobat/Reader

Taylor & Francis offers you a choice of options to help you make corrections to your proofs. Your PDF proof file has been enabled so that you can mark up the proof directly using Adobe Acrobat/Reader. This is the simplest and best way for you to ensure that your corrections will be incorporated. If you wish to do this, please follow these instructions:

1. Save the file to your hard disk.
2. Check which version of Adobe Acrobat/Reader you have on your computer. You can do this by clicking on the “Help” tab, and then “About”.

If Adobe Reader is not installed, you can get the latest version free from <http://get.adobe.com/reader/>.

3. If you have Adobe Acrobat/Reader 10 or a later version, click on the “Comment” link at the right-hand side to view the Comments pane.
4. You can then select any text and mark it up for deletion or replacement, or insert new text as needed. Please note that these will clearly be displayed in the Comments pane and secondary annotation is not needed to draw attention to your corrections. If you need to include new sections of text, it is also possible to add a comment to the proofs. To do this, use the Sticky Note tool in the task bar. Please also see our FAQs here: <http://journalauthors.tandf.co.uk/production/index.asp>.
5. Make sure that you save the file when you close the document before uploading it to CATS using the “Upload File” button on the online correction form. If you have more than one file, please zip them together and then upload the zip file.

If you prefer, you can make your corrections using the CATS online correction form.

Troubleshooting

Acrobat help:<http://helpx.adobe.com/acrobat.html>

Reader help:<http://helpx.adobe.com/reader.html>

Please note that full user guides for earlier versions of these programs are available from the Adobe Help pages by clicking on the link “Previous versions” under the “Help and tutorials” heading from the relevant link above. Commenting functionality is available from Adobe Reader 8.0 onwards and from Adobe Acrobat 7.0 onwards.

Firefox users: Firefox’s inbuilt PDF Viewer is set to the default; please see the following for instructions on how to use this and download the PDF to your hard drive:

http://support.mozilla.org/en-US/kb/view-pdf-files-firefox-without-downloading-them#w_using-a-pdf-reader-plugin



Surface modification and adhesion of wood-plastic composite (WPC) treated with UV/ozone

Andrés Jesús Yáñez-Pacios and José Miguel Martín-Martínez

AQ1

5 Adhesion and Adhesives Laboratory, Department of Inorganic Chemistry, University of Alicante, Alicante, Spain

ABSTRACT

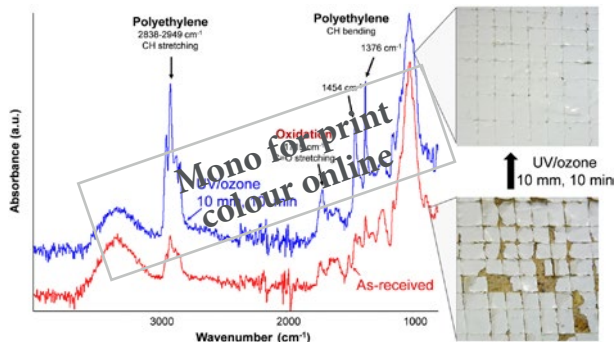
Because of the surfaces of wood-plastic composite (WPC) materials are enriched in polymers of low surface energy, they exhibit low adhesion properties. UV/ozone is proposed as surface treatment for increasing the surface energy and adhesion of WPC materials made with different polymers (polyethylene, polypropylene and polyvinyl chloride). UV lamp-WPC surface distance and time of UV exposure were varied for optimizing UV/ozone treatment of WPC, and UV dose used ranged between 2.02×10^{-14} and 5.05×10^{-12} J-s/m². UV/ozone treatment created new carbon-oxygen polar groups in WPC surfaces and increased their surface energy, mainly their polar component. Furthermore, ablation of the outermost WPC surface was produced, more noticeably by reducing the distance between WPC surface and UV lamp and by increasing the duration of the treatment. Noticeable increase in 180° peel adhesion was obtained in the joints made with UV/ozone treated WPC at 10–30 mm distance during 1–5 min (i.e., UV dose between 5.61×10^{-14} and 2.53×10^{-12} J-s/m²). Although 180° peel strength of joints made with acrylic adhesive tape and UV/ozone treated WPC for 10 min and 10 mm distance (UV dose: 5.05×10^{-12} J-s/m²) was not increased because of dominant effect of ablation over creation of polar groups, the cross-hatch adhesion to different coatings was highly improved, irrespective of the polymer used and the wood content of WPC; however, the surface modifications and adhesion of UV/ozone treated WPC were more marked when its wood content was higher and by using UV dose between 0.10×10^{-12} and 2.53×10^{-12} J-s/m².

ARTICLE HISTORY

Received 29 April 2017
Accepted 6 June 2017

KEYWORDS

Wood-plastic composite (WPC); UV/ozone surface treatment; surface energy; adhesion; coating



1. Introduction

Wood-plastic composite (WPC) is prepared by mixing wood fibers or flour, polymer and several processing additives (biocides, lubricants, etc.) [1]. WPC materials are widely used in building and furniture industry as materials for decking, railing, siding and paneling, and in applications requiring high outdoor resistance. Due to the similar appearance of wood and WPC, WPC is a good alternative material with improved properties (higher stiffness, higher mechanical strength and lower biodegradability) which are imparted by the polymer used in its manufacturing. In general, the polymer constitutes 30–70 wt% of the WPC mass, and most used polymers are polyethylene (PE), polypropylene (PP) and poly (vinyl chloride) (PVC). Due to processing the surface and the bulk properties of WPC materials are different because the external surface is covered with polymer of low surface energy. In fact, WPC has the same surface properties than the polymer in its composition, and thus WPC materials made with PE and PP show low surface energies due to their non-polar character, they are difficult to paint, coat and bond. Currently, WPC materials are joined by mechanical interlocking by means of nails or by attaching complemented extruded shapes [2]. As an alternative, for improving the surface energy and adhesion of WPC, several surface treatments have been proposed in the literature.

The treatment of different WPC materials with surface treatments including flame, sanding, chromic acid treatment and corona discharge, have been proposed elsewhere [1,3]. The application of these surface treatments showed notable improvement of surface energy and adhesion of WPC. Laborie et al. [4] proposed oxy-fluorination of WPC materials made with PE and PP for increasing adhesion and wettability. In more recent study [5], four environmentally friendly surface treatments (hot air, flame, hydrogen peroxide solution and halogen heating lamps) to improve adhesion of WPC were proposed, and an improvement of 37–44% in adhesion was obtained. A comparison of the effectiveness of several surface treatments (flame, mechanical abrasion, corona discharge) of WPC was also carried out by Moghadamzadeh et al. [6] and they obtained notable improvement in pull-off strength which was ascribed to surface roughness and chemical modifications of WPC. Other studies considered the surface modifications of WPC treated with corona discharge [7–10] which consisted in the creation of surface roughness and chemical modifications. Gupta et al. [11] proposed the surface activation of different WPC materials by flame, chromic acid and oxygen low-pressure plasma, concluding that the surface treatment with oxygen low-pressure plasma improved notably wettability and adhesion. Constantinescu et al. [12] treated WPC with air low-pressure plasma but the adhesion properties were not characterized. More recently, the treatment with dielectric barrier discharge (DBD) have been proposed for improving adhesion and increase the surface energy of WPC both were independent on the system configuration [13–15]. In addition, atmospheric pressure plasma treatments have been proposed for improving wettability and adhesion of WPC made with PP [16–18]. In general, the improved properties of WPC treated with low-pressure or atmospheric pressure plasmas have been ascribed to increase in surface polarity and modification of roughness.

The surface treatments of WPC proposed up to date show some limitations. For example, the surface treatment with corona discharge is difficult for treating three-dimensional WPC pieces, and the surface treatment with low-pressure plasmas is discontinuous and limited to small pieces. In this study, UV/ozone surface treatment of WPC is proposed because of it is simple and fast, and can be used for treatment of three-dimensional and small or large

WPC pieces. It has been shown elsewhere [19–21] that UV/ozone treatment is effective in improving the polarity and adhesion of different polyolefins and rubbers. More precisely, some literature has shown that the combined treatment of UV radiation with ozone produced oxidation of polypropylene, polyethylene terephthalate and polyethylene surfaces [19,22,23] leading to increased adhesion.

There are few references [11,24–26] on the influence of UV radiation on the properties of WPC. The prolonged exposure to UV radiation on ageing of WPC has been studied [24–26] and surface oxidation and changes in morphology were produced leading to increased moisture absorption and worsened mechanical properties. On the other hand, UV radiation exposure of WPC surface treated with benzophenone derivative has been proposed for improving adhesion but small increase was obtained [11]. To the best of our knowledge, there are no previous studies on the surface treatment of WPC with UV/ozone for improving adhesion, and in this study the optimization of UV/ozone surface treatment for improving surface energy and adhesion of several WPC materials made with different polymers and the characterization of the surface modifications produced by the treatment have been carried out.

2. Experimental

2.1. Materials

Three different commercial WPC materials were used [18] to compare the influence of the polymer in their composition on the effectiveness of UV/ozone surface treatment: (i) PE-WPC composite prepared with wood flour and high density polyethylene (HDPE) was supplied by Condepols Company (Jaén, Spain); (ii) PP-WPC is wood filled polypropylene composite supplied by SCT-Straw (Barcelona, Spain); and (iii) PVC-WPC composite prepared with vegetable fibres, poly(vinyl chloride) and mineral inorganic fillers was supplied by Plásticos Viters S.A. (Valencia, Spain). PE-WPC and PVC-WPC composites were received in the form of alveolar boards which were cut into pieces of $30 \times 70 \text{ mm}^2$, and PP-WPC composite was received as solid profiles that were cut into pieces of $40 \times 40 \text{ mm}^2$ for characterization, surface modification and adhesion tests.

2.2. Surface treatment with UV/ozone

UV/ozone treatment unit is composed of box made of UV resistant polycarbonate inside which low-pressure vapor grid mercury lamp is placed (Figure 1). Exhaust fan is located in one side of the treatment unit to avoid the over-heating of the UV lamp and for maintaining constant the concentration of ozone during surface treatment. Ozone generator is not used but is produced by the wavelength of 184.9 nm of UV lamp. Several open holes on the upper part of the treatment unit allow continuous air inlet into the chamber for ozone formation. Ozone concentration is controlled by continuous operation of the exhaust fan which is able to evacuate $625 \text{ m}^3/\text{h}$ air, i.e., the flow of the inlet air is controlled by the exhaust fan which is removing ozone and, at the same time, allow new air introduction into the chamber for ozone formation. WPC surface-UV lamp distance was varied by means of rotating screw operated by manual handle. In this study, the distance between the WPC surface and the

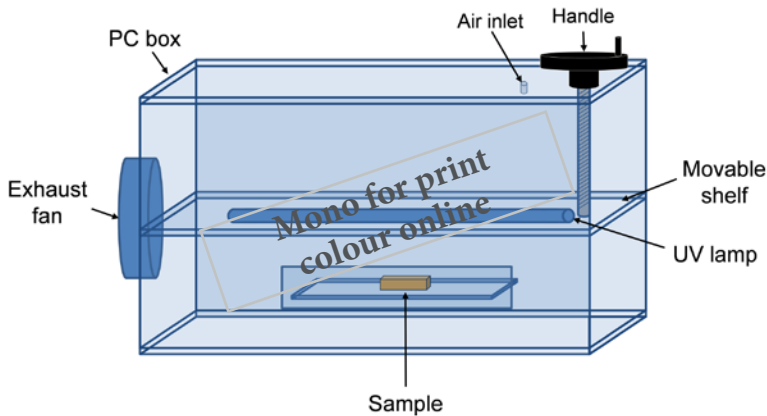


Figure 1. Scheme of UV/ozone equipment.

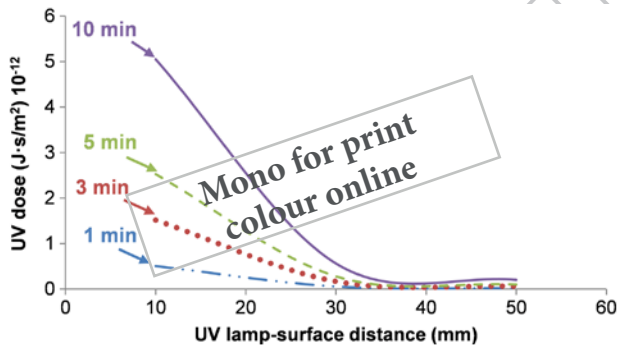


Figure 2. Variation of the UV dose as a function of UV lamp-WPC surface distance at different treatment times.

UV lamp was varied from 10 to 50 mm and the duration of the UV/ozone surface treatment was varied between 1 and 10 min.

UV lamp was manufactured by American Ultraviolet (Lebanon, IN, USA) and has two main emissions, 20% at wavelength of 184.9 nm and 80% at wavelength of 253.7 nm. The energy (E) provided by UV lamp was calculated by using Equation (1):

$$E = hc/\lambda \quad (1)$$

where h is Planck's constant ($6.626 \cdot 10^{-34}$ J·s), c is the light speed ($3 \cdot 10^8$ m/s), and λ is the wavelength of the UV lamp calculated by assuming that 20% of the energy is produced at 184.9 nm and 80% at 253.7 nm. The energy of the UV lamp used in this study is 8.42×10^{-19} J.

UV dose applied to WPC surface will vary with the treatment time and the UV lamp-WPC surface distance. UV dose was calculated by multiplying the energy of the UV lamp by the time of treatment in seconds and by dividing by the square of the UV lamp-WPC surface in meters, and therefore it was expressed as $\text{J} \cdot \text{s} / \text{m}^2$. Figure 2 shows the variation of UV dose as a function of the UV lamp-WPC surface distance for different treatment times.

As expected, UV dose increases by increasing the treatment time and by decreasing the UV lamp-WPC surface distance. However, UV dose is somewhat similar for UV lamp-WPC

surface distances of 30 mm or higher (2.81×10^{-13} to 2.02×10^{-14} J·s/m²), irrespective of the treatment time.

2.3. Experimental techniques

2.3.1. Attenuated total reflectance infrared spectroscopy

5 The chemical modifications of WPC surface treated with UV/ozone were determined by infrared spectroscopy operating in attenuated total reflectance mode (Attenuated total reflectance infrared [ATR-IR] spectroscopy). ATR-IR spectra were obtained in Tensor 27 spectrometer (Bruker Optiks, Ettlingen, Germany) and diamond prism was used. The incidence angle of the IR beam was 45°, and 60 scans with a resolution of 4 cm⁻¹ were recorded
10 and averaged. Under these experimental conditions, the depth of the WPC surface analyzed was about 10–15 µm.

2.3.2. Thermal gravimetric analysis

The thermal stability and the chemical composition of WPC materials were obtained by thermal gravimetric analysis (TGA). 10 mg of WPC sample were placed in platinum crucible
15 of TGA TA Q500 equipment (TA instruments, New Castle, DE, USA) and the sample was heated up under nitrogen atmosphere (flow: 60 ml/min) from room temperature to 800 °C by using a heating rate of 10 °C/min. For determining the existence of inorganic fillers in WPC, at the end of the TGA experiment the nitrogen was changed onto air (flow: 60 ml/min) and heated at 800 °C during 15 min.

2.3.3. Contact angle measurements

20 Contact angles were measured at 25 °C in Ramé-Hart 100 goniometer (Netcong, NJ, USA) and different test liquids were used. 4 µl drops of bidistilled and deionized water (polar liquid) or diiodomethane (non-polar liquid) were placed on the WPC surface, and the contact angle values were measured immediately after drop deposition. The advancing and
25 receding contact angles were measured by using the tilting-plate technique. A minimum of five drops of the same test liquid were placed on different locations of WPC surface and the measured contact angle values were averaged. Furthermore, the contact angles on the WPC surface were measured by using the sessile drop method and the static contact angles obtained were similar to the advancing contact angle values.

30 The surface energy (γ_s), and their polar (γ_s^p) and dispersive (γ_s^d) components of as-received and UV/ozone treated WPC were obtained from the water and diiodomethane advancing contact angle values. Assuming that $\gamma_s = \gamma_s^p + \gamma_s^d$, the calculation of the polar and dispersive components of the surface energy of WPC was carried out by using Owens-Wendt approach – Equation (2):

35

$$(1 + \cos_i)(\gamma_i^d + \gamma_i^p) = 2 \left(\sqrt{\gamma_i^d \gamma_s^d} + \sqrt{\gamma_i^p \gamma_s^p} \right) \quad (2)$$

where γ_i is the surface tension of the test liquid, θ_i is the advancing contact angle value, and the superscripts p and d correspond to the polar and dispersive components respectively of the surface tension of the test liquids or the surface energy of WPC. The components of

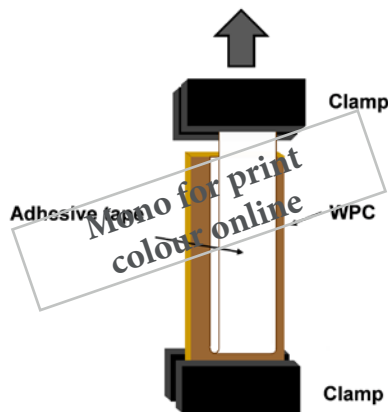


Figure 3. Scheme of 180° peel adhesion test.

the surface tension of water were $\gamma_{\text{water}}^p = 51$ mN/m and $\gamma_{\text{water}}^d = 21.8$ mN/m, and the ones for diiodomethane were $\gamma_{\text{CH}_2\text{I}_2}^p = 0$ mN/m and $\gamma_{\text{CH}_2\text{I}_2}^d = 50.8$ mN/m.

2.3.4. Scanning electron microscopy

The changes in the surface topography of WPC after UV/ozone treatment were assessed by Scanning electron microscopy (SEM) in Jeol JSM-840 microscope (Jeol Ltd., Tokyo, Japan) working at 15 kV. In order to improve the contrast of the SEM micrographs, WPC surfaces were gold coated in Au/Pd Balzers metallizer SCD 004 (Oerlikon Surface Solutions, Balzers, Liechtenstein).

2.3.5. Adhesion measurements

The intrinsic adhesion of the as-received and UV/ozone treated WPC were assessed by using 180° peel tests of WPC/acrylic adhesive tape joints (Figure 3) in TA-XT2i texture analyser (Stable Micro Systems, Godalming, UK); a peeling rate of 10 mm/s was used. Acrylic adhesive tape of 19 mm width – Magic Scotch[®] tape (3 M, MN, USA) – was used for avoiding the influence of the solvents and the chemical characteristics of the adhesives or coatings on adhesion, as they may hinder the influence of the surface modifications of WPC on adhesive strength [18]. For preparing the joints, pieces of 180 mm length of the adhesive tape were placed on the WPC surface and, then, 30 consecutive passes with a rubber roller of 1 kg weight were carried out in order to create an intimate contact between WPC surface and adhesive tape. For facilitating the attachment of the adhesive joint to the upper clamp during adhesion test, about 110 mm length of the adhesive tape was not joined to the WPC. For adhesion test, the WPC specimen was attached to the lower clamp and the adhesive tape was attached to the upper clamp (Figure 3).

To evaluate the adhesion of WPC to different coatings, the cross-hatch adhesion test according to ASTM D3359 standard was used. The cross-hatch adhesion test consists in making 6 parallel cuts over the coated WPC surface by using multi-blade cutting device 0302001 (Neurtek Instruments S.A. Eibar, Spain). Then, standard Tesa[®] adhesive tape was placed on the coated WPC surface and detached. The number of squares of the coating adhered to the tape were recorded and the adhesion values were obtained according to the

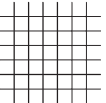
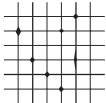
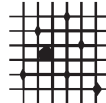



Surface cross-cut area from which flaking has occurred (6 parallel cuts)						
Classification	5B (0%)	4B (<5%)	3B (5-15%)	2B (15-35%)	1B (35-65%)	0B (>65%)

Figure 4. Cross-hatch adhesion scale according to ASTM D3359 standard.

scale given in Figure 4, i.e., cross-hatch adhesion value of 5B (no squares of the coating adhere to the tape) means excellent adhesion, and cross-hatch adhesion value of 0B (the most squares of the coatings adhere to the tape) means poor adhesion [18].

Two commercial liquid coatings of different chemical nature and composition were used, modified silane polyurethane Sintex MS-35 Plus (Quilosa-Selena Iberia, Madrid, Spain) and polyvinyl acetate Caryal R-1 (Paniker S.L., Barcelona, Spain). The liquid coatings were applied over the WPC surface and the thickness was controlled by using 200 μm metering rod. The curing of the polyurethane coating was carried out at 25 $^{\circ}\text{C}$ for 4 weeks and the polyvinyl acetate coating was cured at 25 $^{\circ}\text{C}$ for 24 h. The coated WPC pieces were kept at 23 $^{\circ}\text{C}$ and 50% relative humidity for a minimum of 24 h before adhesion measurement. Although three to five replicates are generally recommended for measuring adhesion, because of the high reproducibility of the results obtained in this study only two replicates were carried out and the cross-hatch adhesion values were averaged.

3. Results and discussion

3.1. Characterization of as-received WPCs

All WPC materials were commercial products and their surface and structural properties were characterized to understand the modifications produced by surface treatment with UV/ ozone. The ATR-IR spectrum of PP-WPC is shown, as typical example, in Figure 5. Typical bands due to lignocellulosic material – broad stretching band of OH groups at 3340 cm^{-1} , stretching C=O band at 1633 and 1740 cm^{-1} , hydroxyl group band at 1023 cm^{-1} (the most intense) – and polymer – CH stretching bands at 2842–2950 cm^{-1} , CH bending bands at 1375 and 1455 cm^{-1} – can be distinguished [27–29].

According to Stark et al. [29], IR spectroscopy is useful to determine the so-called ‘wood index’ that is related to the wood content of the WPC. The wood index values of the WPC materials used in this study were calculated as the ratio of the intensities between the bands of hydroxyl groups at 1023 cm^{-1} (I_{1023}) and methylene groups at 2912 cm^{-1} (I_{2912}) – Equation (3):

$$\text{Wood Index} = \frac{I_{1023}}{I_{2912}} \times 100 \quad (3)$$

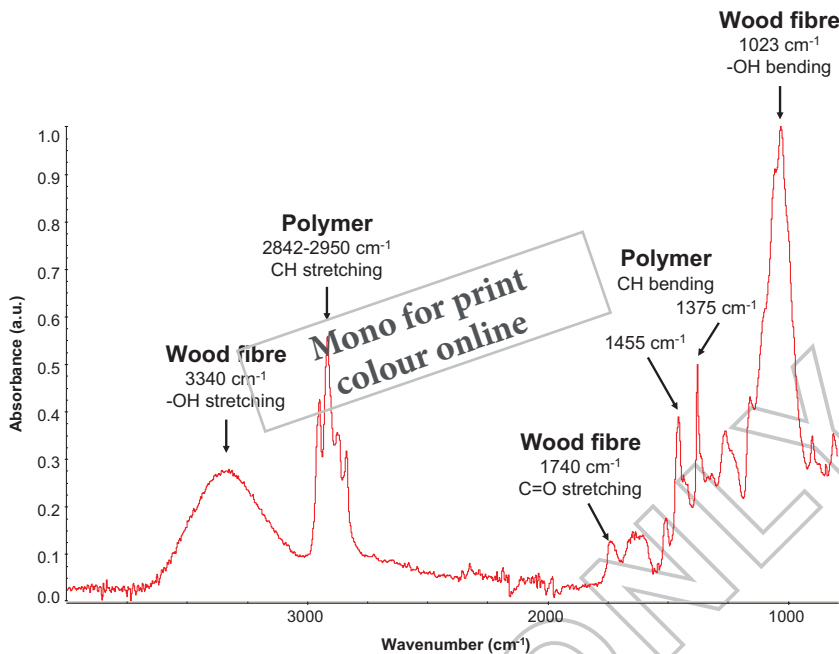


Figure 5. ATR-IR spectrum of as-received PP-WPC.

Table 1. Wood index values of WPC materials.

WPC	Wood index
PE-WPC	332
PP-WPC	179
PVC-WPC	60

The wood index values of the WPC materials are shown in Table 1. PE-WPC composite has the highest wood content, and the lowest one corresponds to PVC-WPC.

The composition and thermal stability of as-received WPC materials were analyzed by TGA. Figure 6 shows, as typical example, the variation of the weight as a function of the temperature for PP-WPC. Three different thermal decompositions can be distinguished in PP-WPC due to water removal (maximum temperature of decomposition at 159 °C), decomposition of the lignocellulosic material (maximum temperature of decomposition at 328 °C), and decomposition of the polymer (maximum temperature of decomposition at 454 °C). The temperatures and weight losses of the different thermal decompositions of all WPC materials are given in Table 2. PE-WPC and PP-WPC composites show practically the same weight losses indicating very similar composition, but the temperatures of maximum decomposition of water and lignocellulosic material are different likely due to the different nature of the wood material used in their preparation. The amount of wood component in PE-WPC and PP-WPC obtained from TGA experiment and ATR-IR spectra (Tables 1 and 2, respectively) are not similar. TGA provides information on the composition of the bulk WPC whereas ATR-IR spectroscopy gives information on about 10–15 μm surface depth. Because of UV/ozone treatment is restricted to the surface, in this study the values of Table

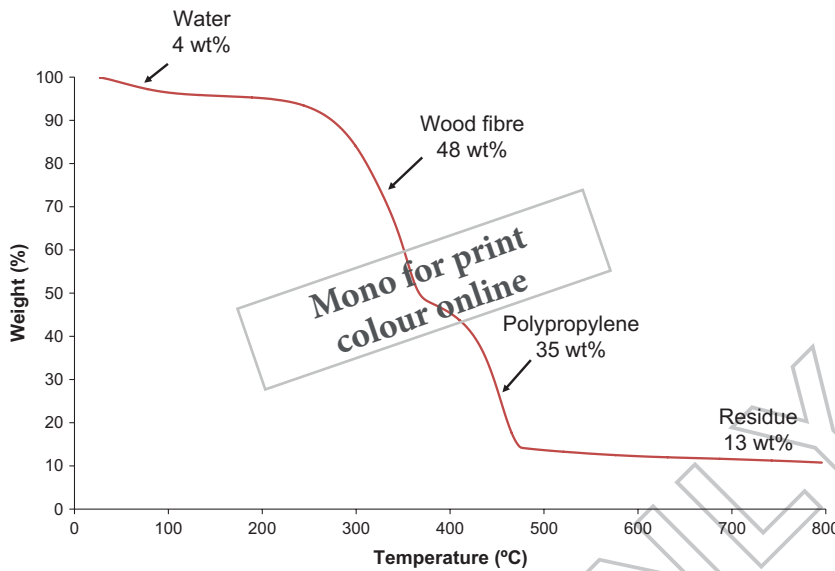


Figure 6. Variation of the weight as a function of the temperature for PP-WPC.
Note: TGA thermogram. Nitrogen atmosphere.

Table 2. Main thermal decompositions of as-received WPC materials.

Compound	PE-WPC		PP-WPC		PVC-WPC	
	T (°C)	Weight loss (%)	T (°C)	Weight loss (%)	T (°C)	Weight loss (%)
Water	70	4	159	4	31	1
Wood fibre	291, 345	43	328	48	258, 279	28
Polymer	449	37	454	35	441	34
CO ₂	-	-	-	-	684	6
Residue at 800 °C (N ₂)	800	16	800	13	800	31
Residue at 800 °C (Air)	800	2	800	0	800	16

Note: TGA experiments [18].

2 were considered more consistent than the results provided by TGA. On the other hand, PVC-WPC composite shows an additional thermal decomposition at 684 °C due to carbon dioxide evolution due to the presence of calcium carbonate filler in its composition [18]. The presence of inorganic compounds in the composition of WPC was addressed by changing nitrogen onto air at 800 °C and monitoring the weight loss during 15 min. According to Table 2, after 800 °C in air, the residual masses of PP-WPC and PE-WPC are 0 and 2 wt% respectively, indicating that the residual masses of 13–16 wt% obtained at the end of TGA experiment in nitrogen corresponds to char formation. However, after 800 °C in air, the residual mass of PVC-WPC is 16 wt%, confirming the existence of inorganic fillers (mainly calcium carbonate) in its composition [18].

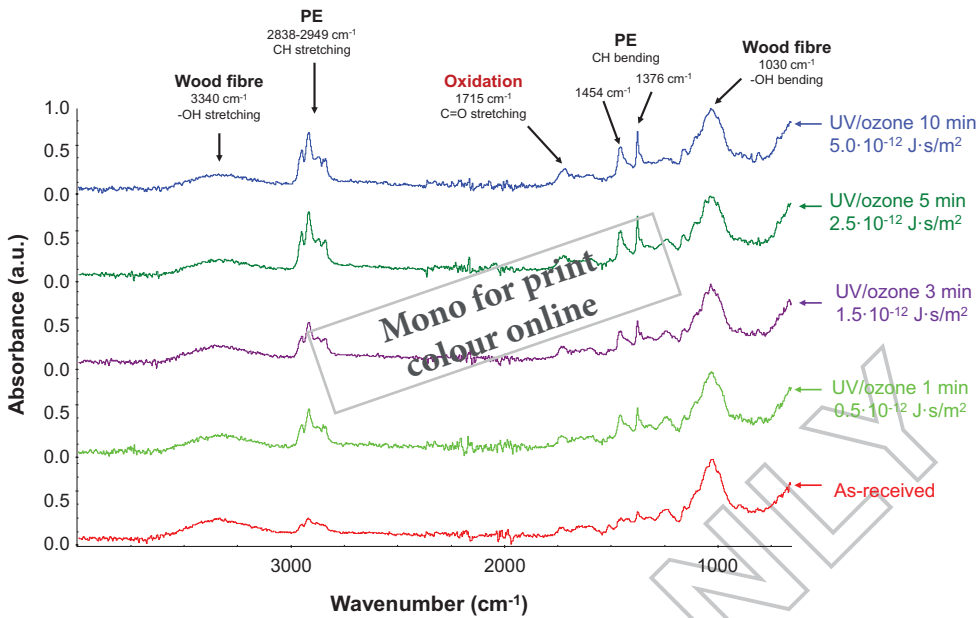


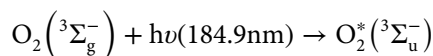
Figure 7. ATR-IR spectra of as-received and UV/ozone treated PE-WPC during different times. Note: UV lamp-WPC surface distance: 10 mm. UV doses are also given.

3.2. Surface treatment of WPC with UV/ozone

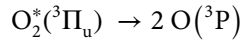
UV/ozone surface treatment of WPC was carried out at different UV lamp-WPC surface distances (10–50 mm) and for different times (1–10 min); under these experimental conditions, UV doses between 2.02×10^{-14} and 5.05×10^{-12} J·s/m² were produced.

5 The chemical modifications produced by UV/ozone treatment of WPC were assessed by ATR-IR spectroscopy. Figure 7 shows, as typical example, the ATR-IR spectra of as-received and UV/ozone treated PE-WPC for different times (the UV lamp-WPC surface distance was set to 10 mm) corresponding to UV doses between 0.5×10^{-13} and 5×10^{-12} J·s/m². The surface treatment of PE-WPC with UV/ozone increases the intensity of the bands at 2838–2949 cm⁻¹ and 1376–1454 cm⁻¹ due to stretching and bending of C–H groups of polyethylene respectively, indicating enrichment in polymer of WPC surface. Furthermore, new band at 1715 cm⁻¹ due to C=O groups is produced by UV/ozone treatment due to oxidation of PE-WPC surface. The longer is the length of the UV/ozone treatment or the higher is UV dose, the more marked are the chemical modifications in PE-WPC surface.

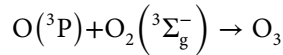
15 The creation of new polar groups on WPC surface can be ascribed to oxidation by UV radiation with wavelengths of 184.9 and 253.7 nm in the presence of air. UV radiation (wavelength = 184.9 nm) removes contaminants from the surface by reacting with atmospheric oxygen to form atomic oxygen and ozone, both strong oxidizing agents. Ozone is produced via a sequence of reactions. In a first step, molecular oxygen absorbs 184.9 nm
20 UV light to form excited-stated molecular oxygen



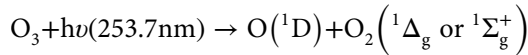
which can dissociate to form two ground-state oxygen atoms.



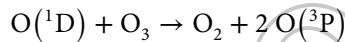
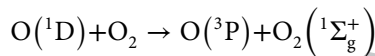
The O(³P) atoms can react with molecular oxygen to form ozone



Photolysis of ozone occurs on exposure to 253.7 nm UV light to form atomic and molecular oxygen



O(¹D) is very reactive form of atomic oxygen and therefore is short-lived, and reacts with molecular oxygen and ozone.

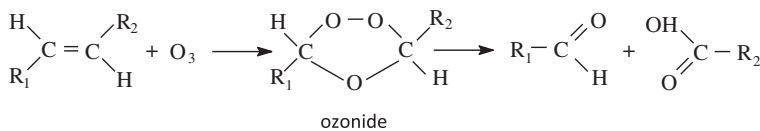


On the other hand, the residual water in WPC may also react with O(¹D) to produce hydroxyl radicals



The O(³P) and O(¹D) forms of atomic oxygen are strong oxidizing agents that may react with polymer surface in different ways. The O(³P) may abstract hydrogen atoms from carbon atoms of the polymer chain, producing radical carbon sites able to form hydroxyl groups [30]. Furthermore, the molecular oxygen also may react with a carbon radical, forming a peroxy group, which can be oxidized to ketone, ester and/or carboxylic acid groups [31]. On the other hand, O(¹D) can react with the polymer chain via an insertion reaction into C–H bonds to form hydroxyl groups or into C–C bonds to form ether groups [32], and further oxidation of hydroxyl and ether groups may occur. Furthermore, it has been demonstrated [33] that the ozone may react with the double C=C bonds of polymers to form ozonides as intermediate moieties that evolve to carbonyl and carboxylic groups (Scheme 1) that are responsible for the increased wettability of treated polymer surfaces.

Figure 8 shows the variation of the surface energy and its polar and dispersive components of as-received and UV/ozone treated PE-WPC as a function of UV dose. According to Figure 2, UV dose increases by increasing the treatment time and by decreasing UV



Scheme 1.

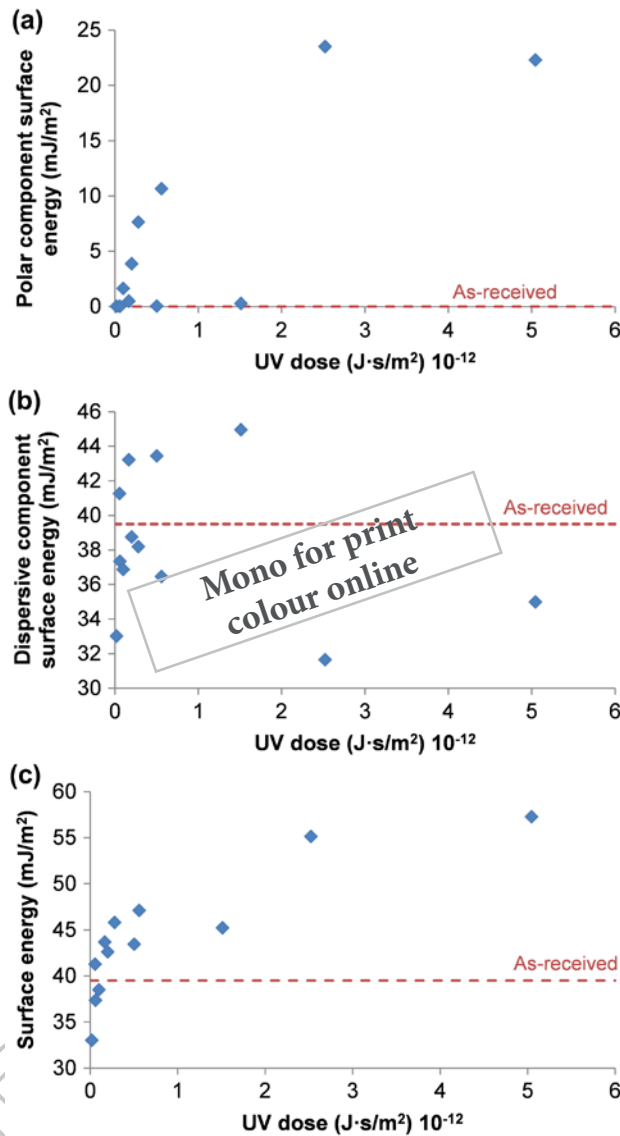


Figure 8. Variation of the (a) polar and (b) dispersive components, and (c) total surface energy of as-received and UV/ozone treated PE-WPC as a function of UV dose.

lamp-WPC surface distance. The surface energy of as-received PE-WPC is low (39 mJ/m²) and corresponds to dispersive component only, indicating that its surface is mostly covered by polymer. The surface treatment with UV/ozone increases the total surface energy of PE-WPC, mainly for UV power higher than 2.5×10^{-12} J·s/m² that correspond to duration of treatment of 5 min or higher and UV lamp-WPC surface distance of 10 mm. The increase in surface energy is mainly due to an important increase of the polar component of PE-WPC likely due to the creation of new polar carbon-oxygen moieties by the UV/ozone treatment, in agreement with previous findings in other polymers [33]. The increase of UV dose enhances more the surface energy of PE-WPC, but less significant change is

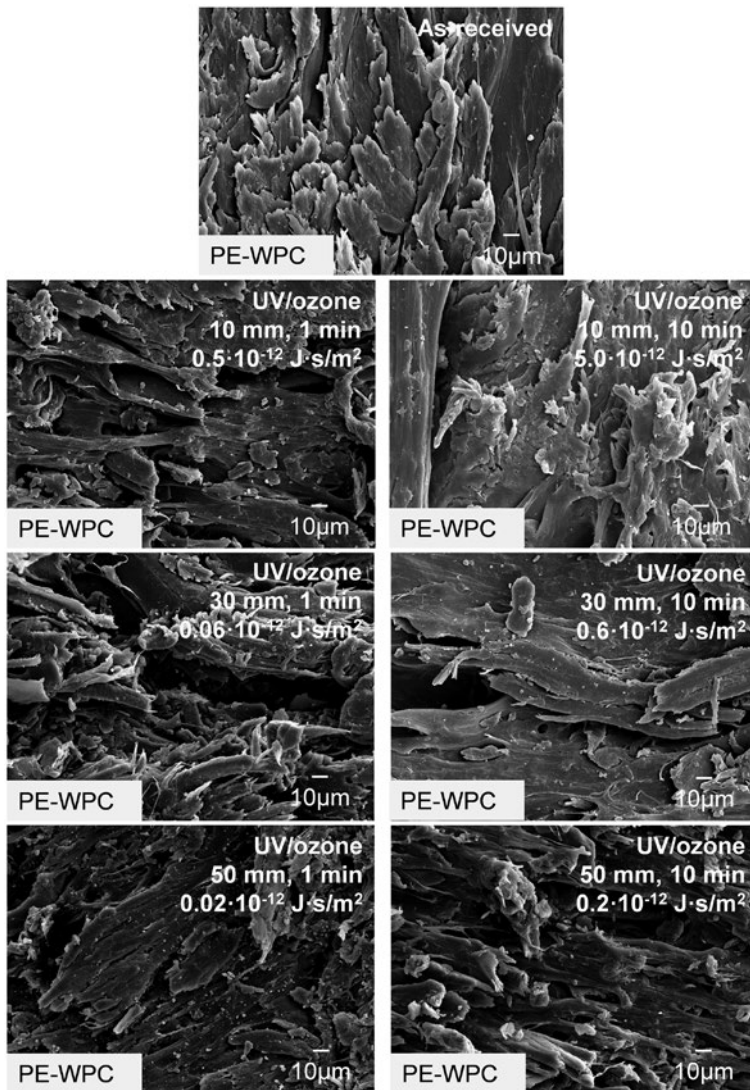


Figure 9. SEM micrographs of as-received and UV/ozone treated PE-WPC.

produced for UV dose higher than $2.5 \times 10^{-12} \text{ J}\cdot\text{s}/\text{m}^2$. This could be an indication of the dominant influence of the ablation over the chemical modification during UV/ozone surface treatment of WPC that is confirmed by the decrease in the dispersive component of the surface energy. On the other hand, the surface energy of UV/ozone treated PE-WPC with UV dose of $0.1 \times 10^{-14} \text{ J}\cdot\text{s}/\text{m}^2$ or lower (i.e., during 5 min or less at UV lamp-WPC surface distance of 50 mm) is lower than the one of as-received PE-WPC; because of the surface energy of UV/ozone treated PE-WPC is mainly due to polar component, that decrease in surface energy can be likely due to insufficient extent of the chemical modification during UV/ozone treatment at low UV dose. Similar findings were obtained elsewhere for different polymers treated with UV/ozone [34,35] and the decrease in the dispersive component of the surface energy was ascribed to the creation of new roughness.

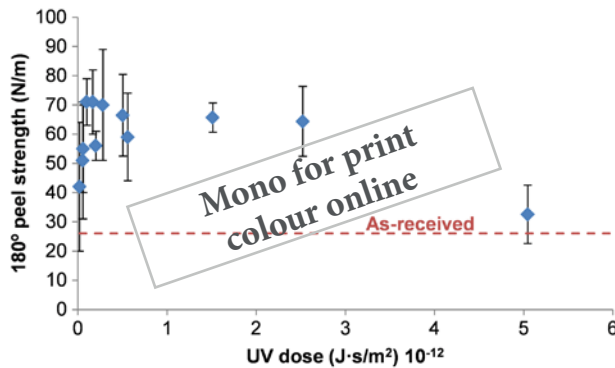


Figure 10. Variation of 180° peel adhesive strength of as-received and UV/ozone treated PE-WPC – acrylic tape joints as a function of UV dose.

Note: An adhesion failure was always obtained.

The surface topography of as-received PE-WPC was analyzed by SEM. Figure 9 shows that the surface of as-received PE-WPC is heterogeneous and rough, showing some wood fibers and some filaments of polymer between the wood fibers. The surface topography of PE-WPC is modified by treatment with UV/ozone. Figure 9 shows that the surface treatment reduces the heterogeneity and roughness of PE-WPC surface in greater extent by increasing the UV dose and the most noticeable modification of the surface topography is produced by treatment at 10 mm distance during 10 min (UV dose: 5.0×10^{-12} J·s/m²). By increasing the duration or UV dose of UV/ozone treatment, surface ablation can be expected and wood material can be exposed to the surface too, and for duration of UV/ozone treatment higher than 5 min, the ablation becomes dominant and new roughness is created, in agreement with previous findings [34,35]. On the other hand, UV lamp-WPC surface distance seems to modify more the surface topography of PE-WPC than the duration of UV/ozone treatment does.

Because of the surface modifications produced on PE-WPC surface by treatment with UV/ozone, an increase in adhesion can be expected. In order to quantify the ‘intrinsic’ adhesion, 180° peel tests of as-received and UV/ozone treated-adhesive tape joints were carried out (Figure 10). The treatment with UV/ozone increases the 180° peel strength values, the highest 180° peel strength values are obtained by using UV doses between 0.5×10^{-14} and 2.5×10^{-12} J·s/m², i.e., during 5 min or less at UV lamp-WPC surface distances of 10–30 mm. The adhesive strength is noticeably increased by decreasing the UV lamp-WPC surface distance during the treatment of PE-WPC with UV/ozone treatment for 1 min only (UV dose $<1.10^{-12}$ J·s/m²) but it is less marked by increasing the duration of the treatment and by using UV dose higher than 3.10^{-12} J·s/m². The increased 180° peel strength of PE-WPC can be ascribed to the combination of new oxidized polar groups, increase in surface energy, surface ablation and creation of new roughness. On the other hand, the lower value of peel strength in the joint made with PE-WPC treated with the highest UV dose (5.05×10^{-12} J·s/m²), i.e., at 10 mm distance during 10 min, can be ascribed to higher smoothness and noticeable ablation which should inhibit the mechanical interlocking with the acrylic adhesive of the tape.

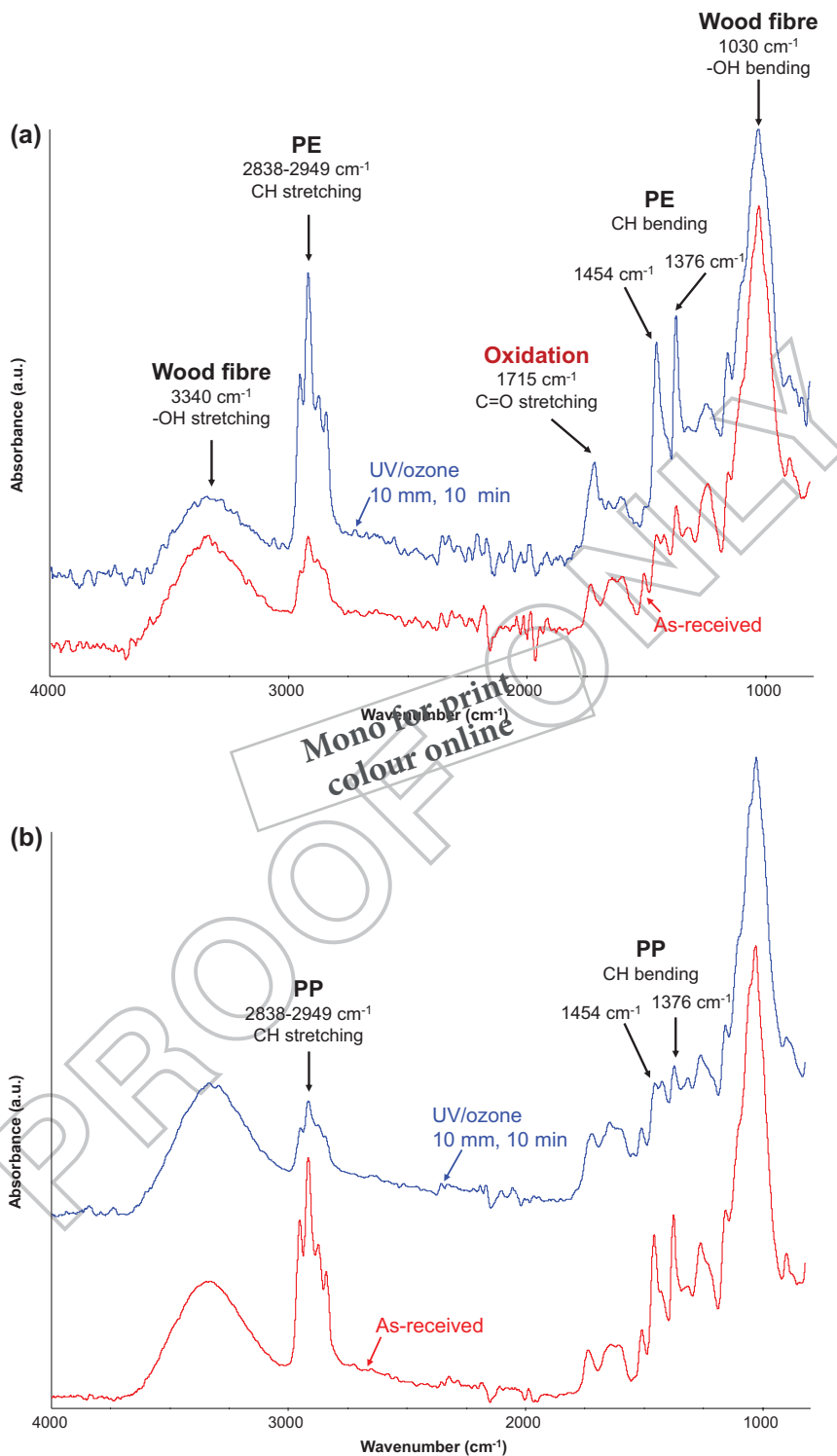


Figure 11. (a) ATR-IR spectra of as-received and UV/ozone treated (10 mm, 10 min) PE-WPC. (b) ATR-IR spectra of as-received and UV/ozone treated (10 mm, 10 min) PP-WPC. (c) ATR-IR spectra of as-received and UV/ozone treated (10 mm, 10 min) PVC-WPC.

Note: UV dose: 5.05×10^{-12} J/s/m².

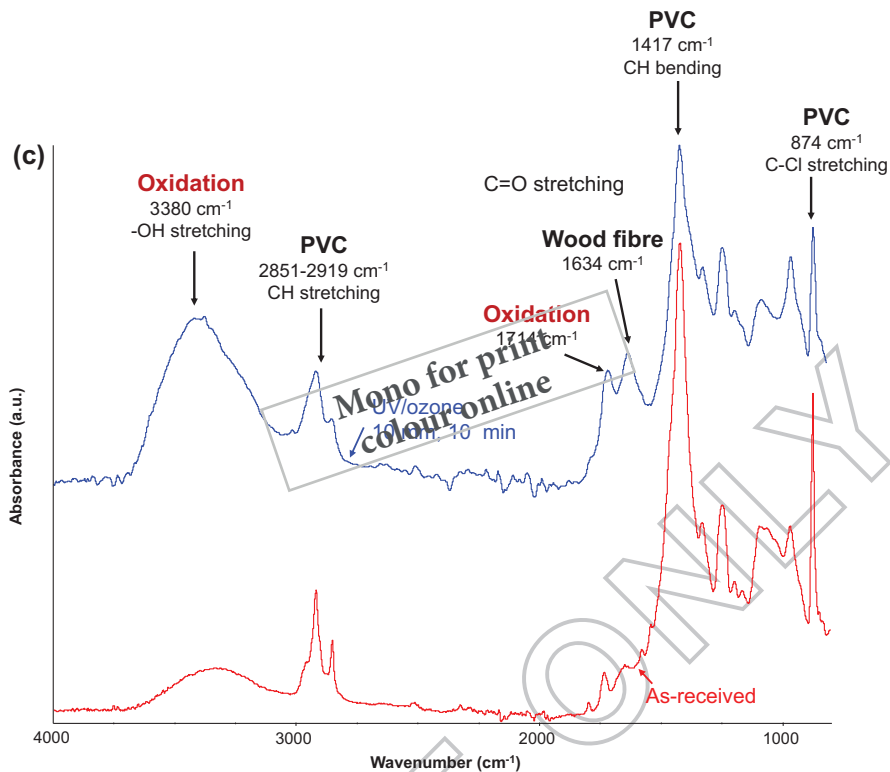


Figure 11. (Continued).

Because of the less favorable conditions of UV/ozone treatment correspond to 10 mm distance and 10 min of duration or UV dose of 5.05×10^{-12} J·s/m², the influence of the polymer used in the manufacture of different WPC materials on the effectiveness of UV/ozone treatment was determined by using these less favorable treatment conditions. ATR-IR spectra of as-received and UV/ozone treated (UV dose: 5.05×10^{-12} J·s/m²) PE-WPC, PP-WPC and PVC-WPC are shown in Figures 11(a)–(c) respectively. The extent of the chemical modifications of the different WPC materials treated with UV/ozone depends on the nature of the polymer. Thus, the treatment of PE-WPC with UV/ozone increases the intensity of the bands at 2838 and 2949 cm⁻¹ (C–H groups) and at 1376 and 1454 cm⁻¹ (CH₂ groups) of polyethylene, indicating the surface enrichment in polymer; additional, new polar C=O groups (band at 1715 cm⁻¹) are produced (Figure 11(a)). On the other hand, a decrease of the intensity of the bands at 2838, 2949, 1454 and 1376 cm⁻¹ due to C–H and methylene groups of the polypropylene respectively is evidenced in ATR-IR spectrum of UV/ozone treated PP-WPC composite (Figure 11(b)), indicating the partial removal of polymer from the surface; moreover, the intensity of the IR bands due to wood component is not changed by the surface treatment and new polar groups are not produced (Figure 11(b)), pointing to dominant ablation with respect to chemical functionalization. In contrast, UV/ozone treatment produces the oxidation of PVC-WPC because of the creation of new OH groups evidenced by the stretching band at 3380 cm⁻¹ (the OH groups of the wood component appear at 3340 cm⁻¹ in as-received PVC-WPC) and the creation of new C=O groups evidenced by the stretching band at 1714 cm⁻¹ (Figure 11(c)).

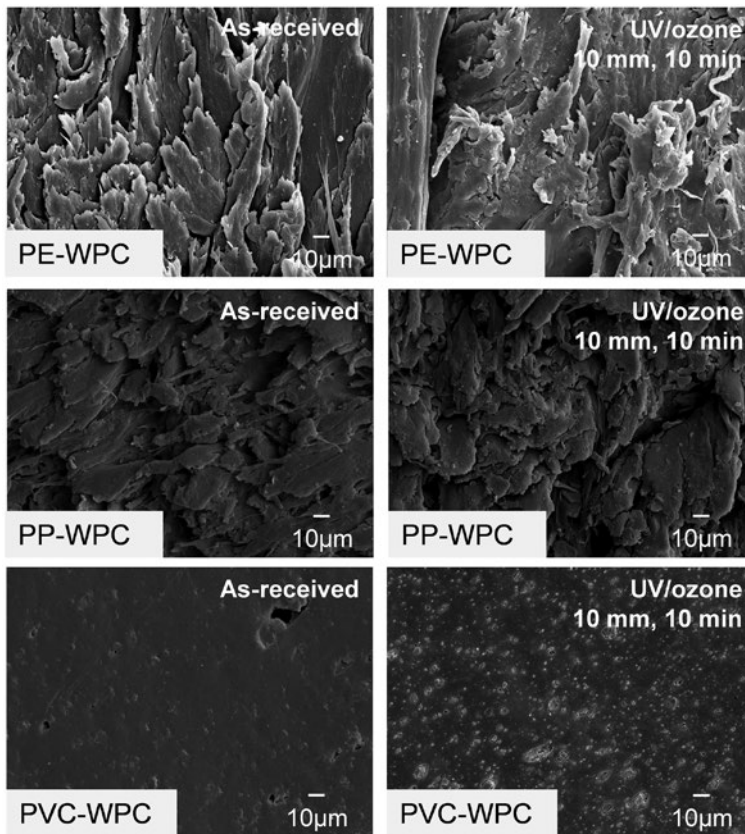


Figure 12. SEM micrographs of as-received and UV/ozone treated (10 mm, 10 min) WPC materials.
Note: UV dose: 5.05×10^{-12} J-s/m².

Table 3. Total (γ_s), polar (γ_s^p) and dispersive (γ_s^d) components of the surface energy of as-received and UV/ozone (10 mm, 10 min) treated WPC materials.

WPC	As-received WPC			UV/ozone treated WPC		
	γ_s^p (mJ/m ²)	γ_s^d (mJ/m ²)	γ_s (mJ/m ²)	γ_s^p (mJ/m ²)	γ_s^d (mJ/m ²)	γ_s (mJ/m ²)
PE-WPC	0	39	39	22	35	57
PP-WPC	0	26	26	8	25	33
PVC-WPC	7	21	28	37	25	62

Note: UV dose: 5.05×10^{-12} J-s/m²

5 The surface energies of as-received WPC materials are low (26–39 mJ/m²) and the lower values correspond to as-received PP-WPC and PVC-WPC (Table 3). The dispersive components are dominant in the surface energies of as-received WPC materials except for small polar component in PVC-WPC (due to the chlorine atoms). Therefore, the outermost surfaces of the WPC materials are mainly composed of polymer because of their wood components are highly polar. The treatment with UV/ozone changes the polarity and surface energy of WPC in different manner depending on the polymer. Because of the creation of new carbon-oxygen groups by treatment with UV/ozone, the surface energies of PE-WPC and PVC-WPC increase noticeably (57–62 mJ/m²), this increase is mainly due

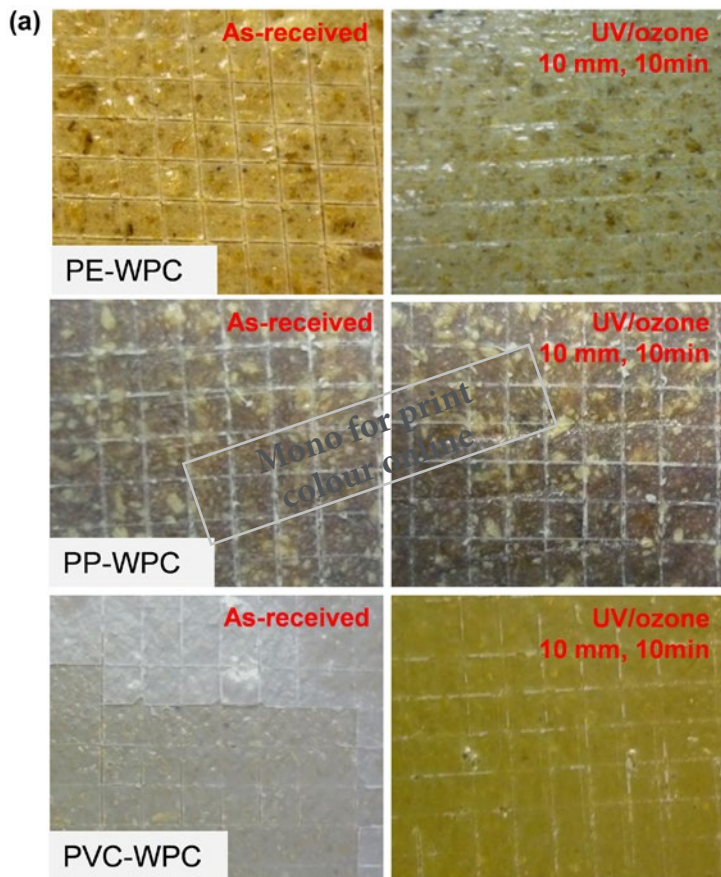


Figure 13a. Photos of the polyvinyl acetate coated as-received and UV/ozone treated (10 mm, 10 min) WPC materials, after cross-hatch adhesion test.

Note: UV dose: 5.05×10^{-12} J·s/m².

to the increase in the polar component of the surface energy which is more noticeable for PVC-WPC (Table 3). However, the treatment of PP-WPC with UV/ozone does not produce an important increase in surface energy because of the absence of polar groups evidenced by ATR-IR spectroscopy.

5 Figure 12 shows the SEM micrographs of as-received WPC materials. PVC-WPC shows smooth outermost surface in which some holes and pores appear, confirming that almost all surface is covered by PVC polymer; furthermore, PVC-WPC composite has the lowest wood content with respect to the other WPC materials. On the other hand, as-received PE-WPC and PP-WPC surfaces are heterogeneous and rough showing some wood fibers and some filaments of polymer between the wood fibers (Figure 12). UV/ozone treatment of WPC changes its surface roughness and topography in different manner depending of the polymer. Figure 12 shows that UV/ozone surface treatment produces ablation of PE-WPC surface and new roughness and porosity are created. However, UV/ozone treatment of PP-WPC produces ablation mainly, and UV/ozone treatment of PVC-WPC creates some roughness and increases the number of pores/small holes, although the surface is still smoother than
10
15 for the other UV/ozone treated WPC materials.

Table 4. 180° peel strength values of as-received and UV/ozone treated WPC/acrylic adhesive tape joints.

WPC	180° peel strength (N/m)	
	As-received	UV/ozone (10 mm, 10 min)
PE-WPC	26 ± 7	33 ± 10
PP-WPC	90 ± 5	114 ± 4
PVC-WPC	59 ± 16	2 ± 1

Note: UV dose: 5.05×10^{-12} J-s/m².

Table 4 shows the 180° peel strength values of joints made with adhesive tape and as-received and UV/ozone treated WPC. Adhesive strength of the joint made with as-received PE-WPC is the lowest and the one made with as-received PP-WPC is the highest, but all values are small. A moderate increase in adhesive strength is obtained in the joints made with UV/ozone treated PE-WPC or PP-WPC because of dominant ablation caused by the treatment. However, the 180° peel strength of the joint made with PVC-WPC is smaller than the one of as-received PVC-WPC (Table 4), because of the poor mechanical interaction between the acrylic adhesive on the tape and the surface heterogeneities created by UV/ozone treatment. In fact, it should be kept in mind the poor wettability of the solid acrylic adhesive tape and its pressure sensitive adhesive character, i.e., the adhesion expected cannot be high because of this type of adhesive never cures. Therefore, the intrinsic adhesion of WPC is not increased by treatment with UV/ozone by using UV dose of 5.05×10^{-12} J-s/m², but it is improved by treatment with UV dose lower than 2×10^{-12} J-s/m².

3.3. Adhesion of UV/ozone treated WPC to coatings

The 'experimental' adhesion in joints is affected by the surface modification of the substrate and by the chemical characteristics of the adhesive or the coating, among other factors. The modifications produced by UV/ozone treatment anticipate an increase in adhesion of WPC that was unexpectedly moderate in 180° peel strength values ('intrinsic' adhesion) of the joints made with acrylic adhesive tape (see Section 3.2). Therefore, the experimental adhesion of as-received and UV/ozone treated WPC was also measured in joints made with different coatings. For assuring adequate wettability, polyvinyl acetate (PVA) and silane modified polyurethane (PU) coatings were applied as liquids on the WPC surface. After being cured, the cross-hatch adhesion of the coatings on as-received and UV/ozone treated WPC with UV dose of 5.05×10^{-12} J-s/m² was measured.

Figure 13a shows the aspect of the polyvinyl acetate (PVA) coated WPC surfaces after cross-hatch adhesion tests, and the values of cross-hatch adhesion according to ASTM D3359 standard are shown in Table 5. The cross-hatch adhesion values of the PVA coated as-received PE-WPC and PP-WPC are good as values of 4B are obtained, i.e., there is no detachment of the squares of the coating from the WPC surface, but deep scratches due to the penetration of the multiblade cut device can be distinguished. However, the cross-hatch adhesion of the PVA coated PVC-WPC is quite poor (a value of 0B is obtained) and most of the squares of the coating are detached from the surface. After treating with UV/ozone, the cross-hatch adhesion of WPC materials increase to 5B in PVA coated PE-WPC and PP-PVC, and to 4B in PVA coated PVC-WPC; none of the coatings are detached from the UV/ozone treated surfaces, confirming the effectiveness of the UV/ozone treatment in

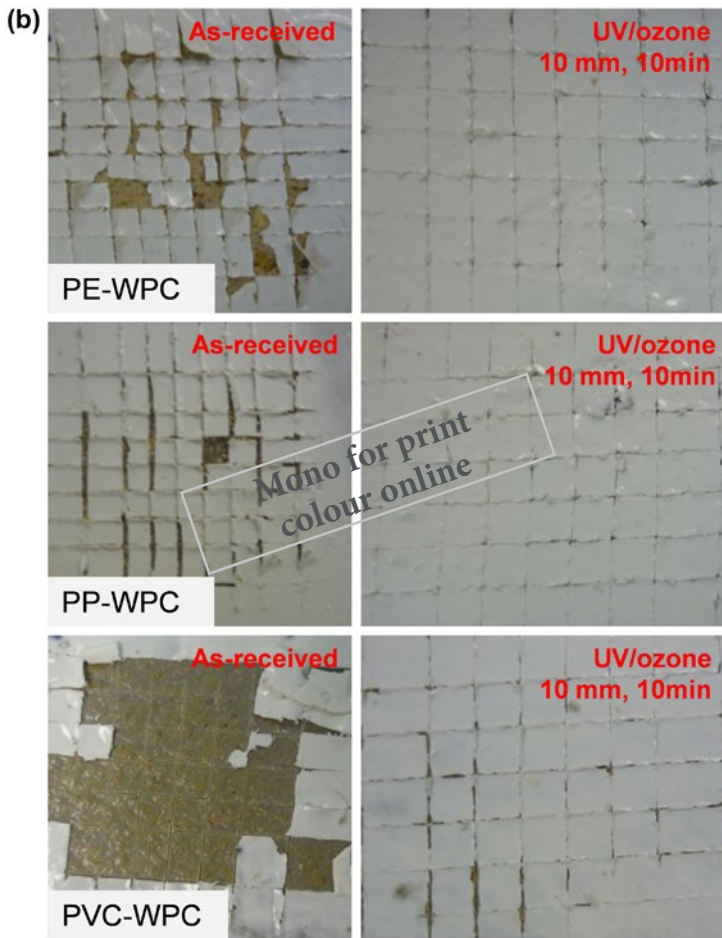


Figure 13b. Photos of the polyurethane coated as-received and UV/ozone treated (10 mm, 10 min) WPC materials, after cross-hatch adhesion test.

Note: UV dose: 5.05×10^{-12} J/s/m².

AQ6

improving the adhesion of WPC materials made with polymers of different nature, irrespective of their wood content.

Figure 13b shows the aspect of the polyurethane (PU) coated WPC surfaces after cross-hatch adhesion tests, and the values of cross-hatch adhesion according to ASTM D3359 standard are shown in Table 5. The cross-hatch adhesion values of PU coated as-received WPC materials are 3B or lower – 3B (PU coated as-received PP-WPC), 2B (PU coated as-received PE-WPC), 0B (PU coated as-received PVC-WPC) –, and the detachment of several squares of the coating from WPC surface is noticed (Figure 13b). After surface treatment with UV/ozone, all WPC materials show much improved cross-hatch adhesion and values of 5B for PU coated UV/ozone treated PE-WPC and PP-WPC and value of 4B for PU coated UV/ozone treated PVC-WPC composite are obtained (Table 5), and none of the squares of the coatings are removed from the UV/ozone treated WPC surface.

The improved cross-hatch adhesion of UV/ozone treated WPC can be ascribed to the combination of creation of polarity and roughness, increase in surface energy, and ablation

Table 5. Cross-hatch adhesion values of polyvinyl acetate (PVA) and polyurethane (PU) coated WPC.

WPC	Cross-hatch adhesion (a.u.) – ASTM D3359			
	As-received		UV/ozone (10 mm, 10 min)	
	PVA	PU	PVA	PU
PE-WPC	4B	2B	5B	5B
PP-WPC	4B	3B	5B	5B
PVC-WPC	0B	0B	4B	4B

Note: UV dose: 5.05×10^{-12} J·s/m².

caused by the treatment. Therefore, the adhesion of WPC is not strongly affected by its structure but it is severely modified by the polymer nature, the surface composition and modifications caused by surface UV/ozone treatment. The effectiveness of the UV/ozone treatment, even under the less favorable treatment conditions, in improving the adhesion of WPC materials made with polymers of different nature to different coatings is confirmed. The surface modifications and adhesion of UV/ozone treated WPC are more marked when its wood content is higher and by using UV dose between 0.10×10^{-12} and 2.53×10^{-12} J·s/m².

4. Conclusions

UV/ozone surface treatment of WPC materials made with different polymers increased their surface energy, mainly their polar component, caused ablation and the creation of new roughness, and increased the adhesion to different coatings. UV lamp-WPC surface distance and the duration of the treatment determined the effectiveness of UV/ozone treatment of WPC. UV/ozone treatment at short distance (10–30 mm) and for less than 5 min or UV dose lower 2.5×10^{-12} J·s/m² was sufficient to increase the polarity, surface energy and adhesion of PP-WPC composite. The use of more aggressive conditions (10 mm distance and 10 min – UV dose lower 5.05×10^{-12} J·s/m²) reduced the intrinsic adhesion of the WPC to acrylic adhesive tape because of the dominance of ablation over the creation of new chemical groups. However, even under these unfavorable conditions, improved cross-hatch adhesion to different coatings was obtained. The surface modifications and adhesion of UV/ozone treated WPC are more marked when its wood content is higher and by using UV dose between 0.10×10^{-12} and 2.53×10^{-12} J·s/m². The treatment with UV/ozone is promising for improving the adhesion of WPC materials made with different polymers and it is environmentally friendly.

Disclosure statement

No potential conflict of interest was reported by the authors.

[AQ3](#)

Funding

This work was supported by Spanish Ministry of Economy and Competitiveness – INNPACTO [grant number IPT-2011-1454-020000].

[AQ2](#)

ORCID

José Miguel Martín-Martínez  <http://orcid.org/0000-0002-7230-6581>

References

- 5 [1] Gramlich WM, Gardner DJ, Neivandt DJ. Surface treatments of wood-plastic composites (WPCs) to improve adhesion. *J Adhes Sci Technol*. 2006;20:1873–1887. AQ4
- [2] Kraus E, Baudrit B, Heidemeyer P, et al. Problems in adhesion bonding of WPC. *Polym Res J*. 2015;9:327–335.
- [3] Oporto GS, Gardner DJ, Bernhardt G, et al. Characterizing the mechanism of improved adhesion of modified wood plastic composite (WPC) surfaces. *J Adhes Sci Technol*. 2007;21:1097–1116.
- 10 [4] Gupta BS, Laborie M-PG. Surface activation and adhesion properties of wood-fiber reinforced thermoplastic composites. *J Adhes*. 2007;83:939–955.
- [5] Dimitriou A, Hale MD, Spear MJ. The effect of four methods of surface activation for improved adhesion of wood polymer composites (WPCs). *Int J Adhes Adhes*. 2016;68:816–194.
- [6] Moghadamzadeh H, Rahimi H, Asadollahzadeh M, et al. Surface treatment of wood polymer composites for adhesive bonding. *Int J Adhes Adhes*. 2011;31:816–821.
- 15 [7] Akhtarkhavari A, Kortschot MT, Spelt JK. Adhesion and durability of latex paint on wood fiber reinforced polyethylene. *Prog Org Coat*. 2004;49:33–41.
- [8] Di M, Liu Y. Stability and ageing of plasma treated Wood/Polyethylenecomposites surfaces. *Adv Mat Res*. 2011;150–151:829–833.
- 20 [9] Tao Y, Di M. Study on plasma treatment and adhesion of wood/polyethylenecomposites. *Appl Mech Mater*. 2011;66–68:911–915.
- [10] Tao Y, Wang H, Di M. Evolution of surface properties for plasma treated wood/polyethylene composites under water soaking. *Mat Eng*. 2012;2:94–98.
- [11] Gupta BS, Laborie M-PG. Surface activation and adhesion properties of wood-fiber reinforced thermoplastic composites. *J Adhes*. 2007;83:939–955.
- 25 [12] Constantinescu G, Totolin M, Cojocariu A, et al. Study of the surface properties of some polyolefin/lignocellulosic composites treated by plasma. *Cell Chem Technol*. 2007;41:463–472.
- [13] Wolkenhauer A, Avramidis G, Hauswald E, et al. Plasma treatment of wood-plastic composites to enhance their adhesion properties. *J Adhes Sci Technol*. 2008;22:2025–2037.
- 30 [14] Liu Y, Tao Y, Lv X, et al. Study on the surface properties of wood/polyethylene composites treated under plasma. *Appl Surf Sci*. 2010;257:1112–1118.
- [15] Hünnekens B, Peters F, Avramidis G, et al. Plasma treatment of wood-polymer composites: a comparison of three different discharge types and their effect on surface properties. *J App Polym Sci*. 2016;133:43376. (1-9).
- 35 [16] Oporto GS, Gardner DJ, Bernhardt G, et al. Forced air plasma treatment (FAPT) of hybrid wood plastic composite (WPC)-fiber reinforced plastic (FRP) surfaces. *Compos. Interfaces*. 2009;16:847–867.
- [17] Hämäläinen K, Kärki T. Effects of atmospheric plasma treatment on the surface properties of wood-plastic composites. *Adv Mat Res*. 2013;718–720:176–185.
- 40 [18] Yañez-Pacios AJ, Martín-Martínez JM. Surface modification and improved adhesion of wood-plastic composites (WPCs) made with different polymers by treatment with atmospheric pressure rotating plasma jet. *Int J Adhesion Adhes*. (in press). AQ5
- [19] Walzak MJ, Flynn S, Foerch R, et al. UV and ozone treatment of polypropylene and poly (ethylene terephthalate). *J Adhes Sci Technol*. 1995;9:1229–1248.
- 45 [20] Mathieson I, Bradley RH. Improved adhesion to polymers by UV/ozone surface activation. *Int J Adhes Adhes*. 1996;16:29–31.
- [21] Romero-Sánchez MD, Pastor-Blas MM, Martín-Martínez JM, et al. UV treatment of synthetic styrene-butadiene-styrene rubber. *J Adhes Sci Technol*. 2003;17:25–45.
- 50 [22] Bhurke AS, Askeland PA, Drzal LT. Ultraviolet radiation surface treatment of polymers. Proceedings of the 23rd Annual Meeting of the Adhesion Society; 2000 Feb 20–23; South Carolina, SC. p. 285–287.

- [23] Gongjian B, Yunxnan W, Xingzhou H. Surface modification of polyolefin by UV light/ozone treatment. *J Appl Polym Sci.* **1996**;60:2397–2402.
- [24] Kaczmarek H, Zielińska A, Sionkowski G, et al. The resistance of wood fibers-poly(vinyl chloride) composites to UV-irradiation. *Polimery-W.* **2008**;53:60–63.
- 5 [25] Lee Ch-H, Hung K-C, Chen Y-L, et al. Effects of polymeric matrix on accelerated UV weathering properties of wood-plastic composites. *Holzforschung.* **2012**;66:981–987.
- [26] Peng Y, Liu R, Cao J, et al. Effects of UV weathering on surface properties of polypropylene composites reinforced with wood flour, lignin, and cellulose. *Appl Surf Sci.* **2014**;317:385–392.
- 10 [27] Gulmine JV, Janissek PR, Heise HM, et al. Polyethylene characterization by FTIR. *Polym Testing.* **2002**;21:557–563.
- [28] Stark NM, Matuana LM. Surface chemistry changes of weathered HDPE/wood-flour composites studied by XPS and FTIR spectroscopy. *Polym Degrad Stab.* **2004**;86:1–9.
- [29] Stark NM, Matuana LM, Clemons CM. Effect of processing method on surface and weathering characteristics of wood-flour/HDPE composites. *J Appl Polym Sci.* **2004**;93:1021–1030.
- 15 [30] MacManus LF, Walzak MJ, McIntyre NS. Study of ultraviolet light and ozone surface modification of polypropylene. *J Polym Sci Part A Polym Chem.* **1999**;37:2489–2501.
- [31] Cheng F, Hong SG, Ho CA. The adhesion properties of an ozone modified thermoplastic olefin elastomer. *J Adhes.* **1998**;67:123–137.
- 20 [32] Kill G, Hunter DH, McIntyre NS. Reactions of polyethylene surfaces with the downstream products of an air plasma: gas phase and surface spectroscopic studies. *J Polym Sci Part A Polym Chem.* **1996**;34:2299–2310.
- [33] Rodríguez FHA, Santos EF, Feitosa JPA, et al. Ozonation of unstretched natural rubber: part I. Effect of film thickness. *Rubber Chem Technol.* **2001**;74:57–68.
- 25 [34] Borcia C, Borcia G, Dumitrascu N. Surface treatment of polymers by plasma and UV radiation. *Rom J Phys.* **2011**;56(1–2):224–232.
- [35] Jofre-Reche JA, Martín-Martínez JM. Selective surface modification of ethylene-vinyl acetate and ethylene polymer blend by UV-ozone treatment. *Int J Adhes Adhes.* **2013**;43:42–53.