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The effect of pH on surface activation of wood polymer composites (WPCs) with hydrogen peroxide for improved adhesion

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Keywords

Wood Plastic Composites, FTIR, surface treatment, adhesion, hydrogen peroxide

Abstract

Wood Polymer Composites (WPCs) have become widely acceptable for use in different products, including furniture. This range of applications could be increased by improvement in effective bonding and jointing techniques. However adhesion between WPC components is problematic because of their low surface energy and the hydrophobic nature of the polyolefin matrices which are commonly used. Surface activation pretreatments using hydrogen peroxide solutions have been investigated, and shown an improvement in lap-joint shear when bonding using epoxy adhesives. The effect on surface energy, roughness and chemical composition was studied. The improvement in adhesion appeared to be governed by the pH of the treatment solution, with clear differences being identified between treatments in acidic and alkaline media.

The best results were achieved with a mild alkaline hydrogen peroxide treatment at a pH of 7.5 (37% improvement); however a mild acidic hydrogen peroxide treatment also showed a suitable level of adhesion improvement (29%, pH 6). In the alkaline medium it was found that the hydroperoxy anion was efficient in altering both the lignin and the hemicellulose component of the wood flour. It was necessary to limit the extent of wood particle degradation by the hydroperoxy anion, explaining the poor adhesion for treatments with pH 9 peroxide solution. This study indicates that mild (pH 7.5) alkaline treatment solution could be employed. In the acidic medium, the free radical based reaction processes dominated, and were likely to have altered the polypropylene matrix of the WPC material.

1 Introduction

As wood plastic composite (WPC) materials gain increased use within the market, the ability to bond the material using conventional adhesives is gaining importance. While some products may use mechanical fasteners and jointing techniques, the use of adhesives within joints will increase the range of potential applications, for example within furniture manufacture, and aesthetic qualities of the finished product. Adhesion will also facilitate the use of small mouldings in domestic goods, where invisible jointing is desired.

Various approaches have been investigated for enhancing adhesion in WPC materials, both for adhesive joint formation, and for adhesion of a surface onto a WPC substrate. In the case of jointing, mechanical abrasion has been shown to be beneficial [1] and has been used throughout this study prior to other surface pre-treatments. Other methods such as chromic acid, flame, plasma, corona and UV irradiation are well suited to both jointing [2, 3, 4] and coating applications [5, 6, 7, 8]. An increase in surface energy and an increase in roughness, leading to increased wettability of the surface are commonly reported as contributing to increased adhesion properties [3].

In a previous study of four potential surface activation techniques, hydrogen peroxide solutions (with the pH controlled by the presence of NaOH) have been successfully used to activate the surface of WPC, with an improvement of up to 37% in the lap-shear adhesion strength depending on pH of the treatment solution [9]. The hydrogen peroxide pre-treatment method showed some interesting aspects, with respect to the pH of the treatment solution, which are explored further in this paper. A previous study used hydrogen peroxide as a surface activator for bamboo [10], but no literature has been found for wood or for wood plastic composites. The mechanism for adhesion improvement in wood plastic composites is more complex than that for solid bamboo as both wood fibre and polymer are present at the product surface after surface abrasion by sanding. It can be hypothesised that any such surface treatments may act on either or both of the materials present at the surface to a greater or lesser extent. The treatment effects seen in the acidic and alkaline solutions appeared significantly different, with both the acidic and the alkaline solutions providing optimal pH values for better adhesion.

Adhesive bonding relates to the mechanical, physical and the chemical properties of the surface. Roughness of the surface morphology allows the adhesive to mechanically lock into the surfaces resulting in good mechanical bonds for adhesion. Also chemical alteration of the surface can enhance the physical aspects by inducing increased polarity of the surface, or increasing the possibility of chemical bonding, e.g. by creation of covalent bonds between substrate and adhesive, although this is not expected in the WPC-adhesive system. To evaluate the mechanical aspects, the properties of the hydrogen peroxide treated WPC surfaces were characterized using a surface roughness determination test and by scanning electron microscopy (SEM). Contact angle measurements were used to evaluate surface energy, and FTIR-ATR spectroscopy was used to further analyse the chemical changes in composition of the treated surfaces.

2 Materials and Methods

The WPC material used in this study was a laboratory produced batch of 35.5% polypropylene, 60.0% Norway spruce flour composite containing 2.0% coupling agent, 1.5% UV-stabiliser and 1% colour pigment, as described in [9]. In the previous work, lap shear tests were performed using a 2-part epoxy resin from Pattex (Saldatutto mix) on 40 x 20mm samples with a 10 mm x 20 mm lap joint area. Samples were tested according to EN 205:2003 with a cross head speed of 1.5 mm min⁻¹. All

samples were sanded prior to treatment (p220 glass paper), and compared with control samples which had also been sanded.

The samples reported here were treated with hydrogen peroxide solutions. The hydrogen peroxide solution (30% w/w) had a low pH, so for use in the experiments, it was adjusted to pH values of 5.0, 6.0, 6.5, 7.0, 7.5, 8.0, 8.5 and 9.0 using 1 M sodium hydroxide solution added dropwise. Both hydrogen peroxide and sodium hydroxide were obtained from Panreac Quimica SAU without further purification. The samples were soaked in the treatment solution for 30 minutes at 20°C and then washed with deionised water and reconditioned (20°C, 65% relative humidity) to constant weight (2 weeks) prior to testing. The samples were prepared at the same time as the samples produced for the mechanical tests, and set aside for contact angle analysis, roughness determination and SEM.

2.1 Surface roughness

The surface roughness was determined by the stylus method using a Mitutoyo SurfTest SJ-210 instrument. The pin radius was 2 µm and the measuring range was from -200 µm below to 160 µm above the horizontal plane. The samples were placed on a horizontal surface which was calibrated as parallel to the direction of travel of the instrument testing pin using a spirit level. Every sample was tested along the two diagonals to cover as much surface as possible. Two samples of every treatment parameter were used for roughness determination. The testing pin speed was 0.5 mm s⁻¹ and the length of the transect measured was 25 mm. Moreover the tested surface was divided into 6 segments for the surface roughness determination. The evaluation of the roughness was made according to ISO 1997 standards.

From each test the roughness average (Ra) was measured, this is the mean of the all measured heights and depths within the transect (Equation 1). It is a typical value to illustrate the general view of the surface roughness of a material.

$$Ra = \frac{1}{n} \sum_{i=1}^n H_j \quad [1]$$

Where n refers to the number of measurement segments, and H_j is the distance from a peak to valley of each segment.

2.2 Contact angle measurements

Contact angle was determined using a Kruss EasyDrop instrument. A high definition camera attached to the instrument was used to observe the liquid drop on the surface. Computer software provided by the manufacturer was also used to calculate the contact angle and the surface energy. The liquid which was used for the contact angle determination was deionised water. The reason for using only water for the surface energy determination was that the main interest for this test was the penetration of the adhesive into the material surface which is more related to the wettability of the material and not to the chemistry which is affecting the surface energy. Five samples of every treatment were tested. Contact angles were recorded every 1 s for the first 4 s from the moment that the drop contacted the material's surface. Untreated samples were also tested to calculate the surface energy and contact angle as control values. The instrument delivers a water droplet to the surface in sessile mode. The camera records the drop on the surface from which the contact angle is measured and the surface energy calculated according the equation of state (EOS). The EOS with known surface tension of the liquid is the most suitable method for determine the surface energy of solids with the use of a single liquid contact angle measurement.

The contact angle (θ) is the angle formed between the tangent of the drop and the surface line (Figure 1). The larger the θ angle is, the more hydrophobic the material is.

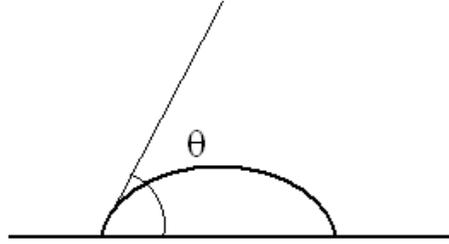


Figure 1: Contact angle measurement of a liquid drop. ϑ is the angle which is measured.

The EOS is derived from Young's equation:

$$\sigma_s = \gamma_{sl} + \sigma_l * \cos \theta \quad [2]$$

σ_s : surface tension of the solid.

σ_l : surface tension of the liquid.

γ_{sl} : interfacial tension between the solid/liquid.

To measure the γ_{sl} a series of contact angle data were taken and experimental resulted to the following equation:

$$\gamma_{sl} = \sigma_l + \sigma_s - 2\sqrt{\sigma_l * \sigma_s} * e^{-\beta(\sigma_l - \sigma_s)^2} \quad [3]$$

The constant β was determined at the value of 0.0001247. Therefore by the combination of the equations [3.2] and [3.3] derives a new equation as follows:

$$\cos \theta = -1 + 2 \sqrt{\frac{\sigma_s}{\sigma_l}} * e^{-\beta(\sigma_l - \sigma_s)^2} \quad [4]$$

Thus if the surface tension of the liquid (σ_l) is known and a single contact angle (θ) is measured it is possible to calculate the surface tension of the solid (σ_s) by the equation [4].

The characteristics of the deionized water which was used for the surface energy determination are presented in Table 1.

Table 1: Characteristic values for deionised water, used for the surface energy determination. Values refer to 25°C temperature. KRUSS GmbH, Hamburg 2004-2011, Software for Drop Shape Analysis DSAI V.1.92 for contact angle measurement systems. User Manual. V. 1

| | |
|--|-------|
| Interfacial Tension (mN m ⁻¹) | 72.8 |
| Dispersive component (mN m ⁻¹) | 21.8 |
| Polar component (mN m ⁻¹) | 51 |
| Density (g cm ⁻³) | 0.998 |
| Viscosity (mPa s) | 1.002 |

2.3 FTIR chemical analysis

A Nicolet 8700 FTIR (Thermo Scientific) with GladiATR vision (Pike Technologies) was used for the surface chemical analysis. The FTIR spectrometry was performed directly on the material surface using the attenuated total reflectance (ATR) mode, so the sample surface was presented intact to the aperture of the ATR. Each spectrum was an average of 32 scans collected, over wavenumbers from 4000 to 600 cm^{-1} . For the FTIR-ATR investigation one sample was used for each treatment, and this sample was scanned five times on different areas on the surface. From the five spectra of the treated sample an average spectrum was produced. To avoid the spectral noise and peaks relating to CO_2 and water vapour relating to environmental changes, background spectra were taken after every two spectra.

Simple analysis of changes in the absorption at peaks known to relate to wood components or the polypropylene was done using an absorption ratio. This was calculated using the ratio of the absorption at the wavenumber of the component, against the absorption of the polypropylene CH_3 stretch at 2951 cm^{-1} .

To identify the differences between the spectra Principal Component Analysis (PCA) and Partial Least Square regression (PLS) were performed with the Excel add-in Multibase 2015 package by Numerical Dynamics, Japan. Also, to investigate the significant spectra changes and the sequence of the chemical changes in relation to the treatment intensity, 2D synchronous and asynchronous correlation maps were performed with SpectraCorr 1.1 (Thermo Fisher scientific) software. For the PCA and 2D correlation the spectra were baseline corrected and smoothed by 13 cm^{-1} , and analysis was performed using OMNIC 8.3 (Thermo Fisher Scientific). For the PLS modelling 1st derivative corrected spectra were used after scaling by division by the standard deviation.

2.4 SEM observation

The microscopic observation of the surface structure was performed by SEM-EDS. The scanning electron microscope was a JEOL JMS-840A attached to an energy dispersive X-ray (EDS) INCA micro analytical system. The samples were cut to 20 × 20 mm dimensions and carbon coated under vacuum with a JEOL JEE-4X vacuum evaporator. The SEM was carried out with accelerated voltage of 20 kV and probe current 45 nA. The counting time was 60 seconds. To scan the sample surface two types of electron spectrum (primary [backscattered] and secondary electron) were used. The primary electron scanning provides a more clear view of the surface without distinguishing the material components distributions. The surface morphology is more obvious with the primary electron scan than the secondary electron scan.

The secondary electron spectrum shows wood fibres as lighter areas because of the presence of oxygen in the wood cell wall polymers, whereas the darker areas represent the polypropylene matrix. Polypropylene does not contain any oxygen in the polymeric chain in its native state. Therefore, the secondary electron spectrum offers a better view of the condition of the wood fibres after treatment.

3 Results

3.1 Surface energy and surface roughness

The lap joint shear strength was previously determined, as reported in [9]. This data was used with surface roughness and surface energy of these samples treated in the hydrogen peroxide solution at eight different pH values (Table 2).

Table 2: Lap joint shear strength, surface roughness and surface energy results. The values within the brackets are the standard deviation (SD).

| | Control | Treatment solution pH | | | | | | | |
|--|-----------------|-----------------------|-----------------|------------------|------------------|------------------|------------------|-------------------|------------------|
| | | 5 | 6 | 6.5 | 7 | 7.5 | 8 | 8.5 | 9 |
| Shear strength (N) | 554.7 (58.3) | 649.5 (111.9) | 716.5 (71.5) | 669.8 (88.95) | 610.3 (78.99) | 759.5 (97.53) | 714.1 (79.15) | 673.09 (64.82) | 564.4 (77.14) |
| Surface roughness Ra (μm) | 2.3 (0.34) | 4.52 (0.43) | 5.01 (0.25) | 4.91 (0.39) | 3.82 (0.62) | 3.74 (0.74) | 3.73 (0.41) | 3.58 (0.51) | 3.68 (0.11) |
| Surface energy (mN m^{-1}) | 14.7 (1.5) | 15.3 (1.26) | 18.1 (2.39) | 13.9 (2.15) | 16 (2.42) | 15.8 (1.51) | 16.2 (1.9) | 16.9 (1.87) | 21.6 (2.14) |

It is clear that while all hydrogen peroxide treatments led to an increase in surface roughness compared to the untreated control, there were three samples which had greater roughness than the other treatments, these were pH 5, pH 6 and pH 6.5. In Figure 2a and Figure 2b the lap joint shear strength data for WPC samples prepared with the equivalent surface pre-treatment is presented across the surface roughness data. It appeared that the samples treated in acidic solutions have almost a linear relationship, with highest shear strength correlating with greater surface roughness. The linear regression line in this particular fit has an R^2 value of 0.9022 (Figure 2a). The alkaline treated samples did not show this effect, as similar roughness values were observed for all alkaline pH values. Therefore variation in shear strength in alkaline samples appears to relate to another mechanism of adhesion promotion, as the surface roughness does not seem to be affected by the different alkaline treatment solutions (Figure 2b).

The sample means of the surface energy ranged from 13.90 mN m^{-1} (pH 6.5) to 21.62 mN m^{-1} (pH 9), and the control samples had a mean surface energy of 14.76 mN m^{-1} (Table 2). All treatments seemed to have a positive effect on WPC surface energy, with an exception of the pH 6.5 treatment, which was lower than the control. Only the samples treated in pH 6.0 and pH 9 solutions were significantly different from the control (Tukey HSD test), and these had the highest surface energy mean values, while for the other treatments, pH only had a minor effect. The samples treated in pH 6.5 solution seemed to have the lowest surface energy, but this was not significantly lower than the control.

In the same manner as the roughness values and the lap shear test results, the acidic treatment solutions showed a peak value of surface energy at pH 6.0 but without any clear trend (Figure 2c). Interestingly, the majority of alkaline treatments (pH 7.5 to 8.5) showed similar surface energy values, with all being slightly increased compared to the control and with some increase in shear strength. There was no significant trend (Figure 2d), the exception to this observation is the pH 9.0 sample, where surface energy increased markedly but shear strength was lower than the control samples. This may relate to the pH 9 treatment solution exceeding the buffer capacity of the available wood fibre on the sample surface, and the onset of reactions between the hydroxide ions and hemicellulose within the wood particles. Thus degradation may proceed beyond the initial removal of chromophores into a more destructive form of surface chemistry alteration. It appears that treatment solutions with mild alkaline character may induce an increase in surface energy which is useful in adhesion promotion, but that it is possible to exceed the useful treatment window when pH is high, i.e. 9.0.

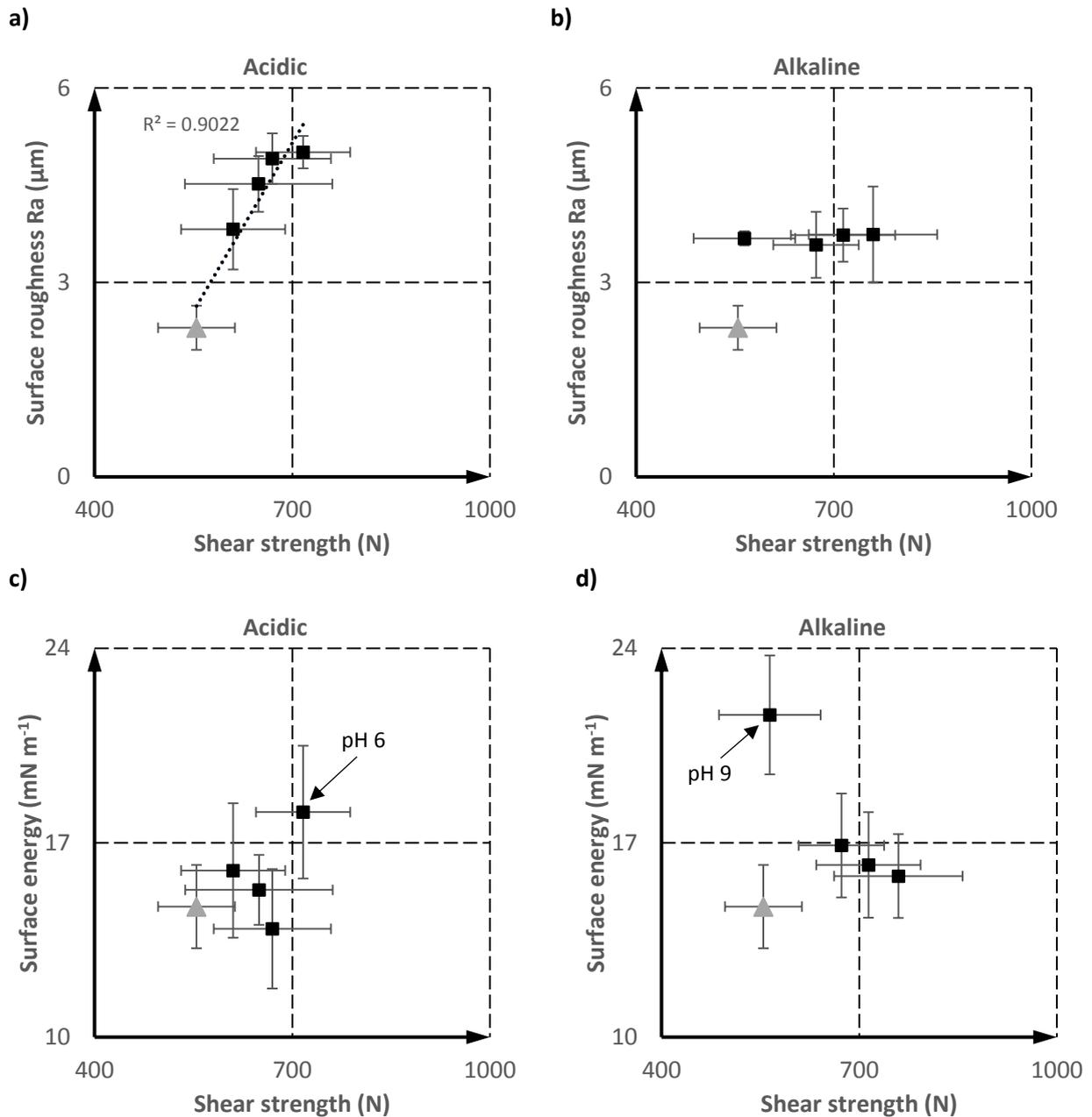


Figure 2: Surface roughness against lap joint shear strength data of samples treated in: a) acidic solutions (pH 5, pH 6, pH 6.5 and pH 7) and b) in alkaline solutions (pH 7.5, pH 8, pH 8.5 and pH 9). Surface energy against lap joint shear strength data of samples treated in: c) acidic solutions (pH 5, pH 6, pH 6.5 and pH 7) and d) in alkaline solutions (pH 7.5, pH 8, pH 8.5 and pH 9). The \blacktriangle marker represent the control samples. Error bars represent the SD (+/-1)

Considering the relationship between surface energy and surface roughness (Figure 3), all treatments caused an increase in surface roughness in comparison to the control. However, in the alkaline treated samples the surface roughness and the surface energy were similar, with the exception of the pH 9 samples, where surface energy was high (due to hydroxide reaction) but roughness remained similar to the other alkaline treatments. The samples treated in acidic solutions did not show a significant change in surface energy, with the exception of the pH 6 treatment, while surface roughness increased for the different acidic pH solutions, and this increase was greater than the change seen for alkaline treatments. It seems that there was no general correlation between surface energy and surface roughness.

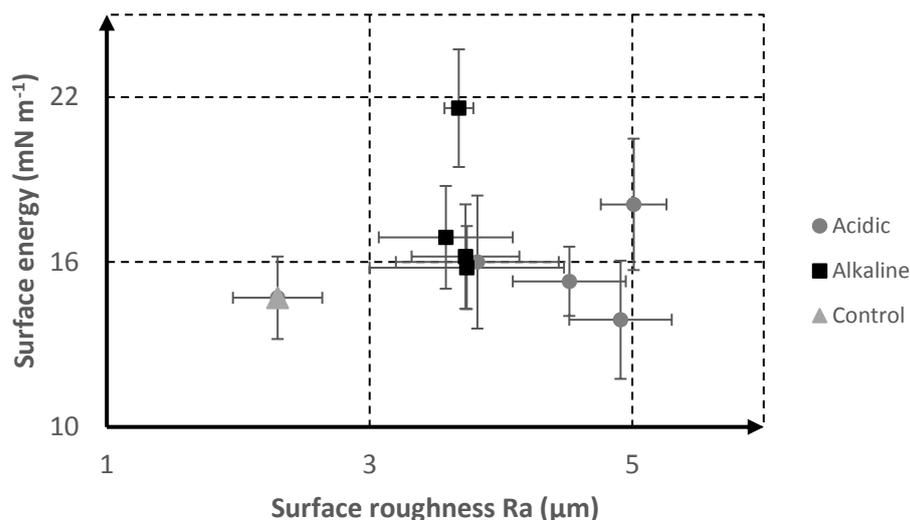


Figure 3: Surface energy and surface roughness plotted for acid and alkaline treatments.

3.2 FTIR-ATR spectroscopy

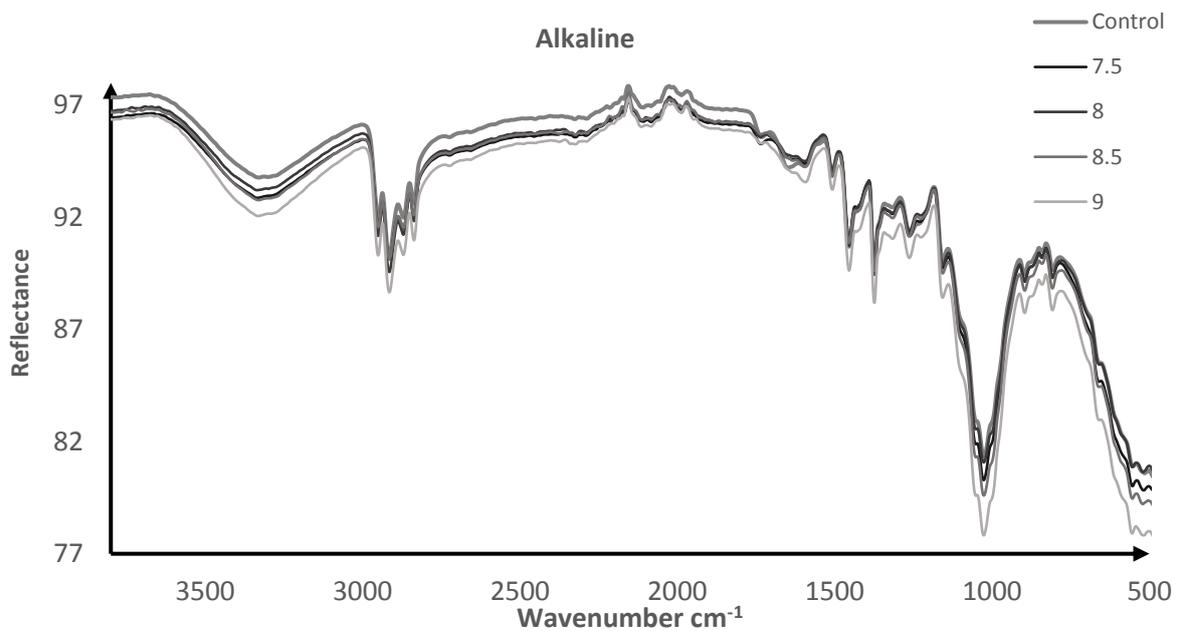
The FTIR spectra of each WPC sample (Figure 4) showed characteristic absorptions for polypropylene 2947, 2917, 2867 and 2833 cm^{-1} relating to CH_2 and CH_3 symmetric and asymmetric stretches, as well as 1454, 1435 and 1358 cm^{-1} relating to CH_2 and CH_3 bending vibrations (Table 3). The wood flour (WF) component of the WPC also gave rise to characteristic absorptions. To minimise the effect of variability in the WF to PP ratio at the area of the surface which was presented for ATR, five sample locations were used for each sample of WPC, and an average spectrum was calculated. The resulting spectrum shows the pervasive differences in chemical composition due to the peroxide treatment, rather than localised effects.

Table 3: Wavenumbers and attributions for typical absorptions for a polypropylene matrix WPC material

| Wavenumber (cm^{-1}) | Functional group | Component | Description |
|---------------------------------|------------------|---------------|---|
| 3338 | C-OH | Wood flour | Cellulose |
| 3284 | C-OH | Wood flour | Cellulose |
| 2947 | CH_3 | Polypropylene | CH_3 asymmetric stretch |
| 2917 | CH_2 | Polypropylene | CH_2 asymmetric stretch |
| 2903 | CH | Wood fibre | CH stretch in cellulose and hemicelluloses |
| 2867 | CH_3 | Polypropylene | CH_3 symmetric stretch |
| 2833 | CH_2 | Polypropylene | CH_2 symmetric stretch |
| 1732 | Ester | Wood flour | Ester carbonyl in cellulose and hemicellulose |
| 1708 | Carbonyl | Wood flour | Unconjugated carbonyl in lignin |
| 1656 | Carbonyl | Wood flour | Conjugated carbonyl in lignin |
| 1640 | CH | Polypropylene | Monosubstituted alkene |
| 1595 | Aromatic ring | Wood flour | Lignin aromatic ring vibration and C=O stretch |
| 1510 | Aromatic ring | Wood flour | Lignin aromatic ring vibration |
| 1454 | CH_2 | Polypropylene | CH_2 symmetric bend |
| 1435 | CH_3 | Polypropylene | CH_3 asymmetric bend |
| 1422 | CH-OH | Wood flour | C-O stretch and CH or OH bending in hemicellulose and cellulose |

| | | | |
|------|-----------------|---------------|---|
| 1420 | Aromatic ring | Wood flour | Lignin aromatic ring vibration |
| 1375 | CH | Wood flour | CH bend in cellulose |
| 1358 | CH ₃ | Polypropylene | CH ₃ symmetric bend |
| 1263 | Aromatic ring | Wood flour | Lignin aromatic ring breathing and C=O stretch |
| 1230 | | Wood flour | C-O and C=O stretch |
| 1223 | | Wood flour | Lignin |
| 1208 | C-OH | Wood flour | In plane bend at C6 |
| 1168 | C-O-C | Wood flour | Cellulose and hemicellulose C-O-C glycosidic link |
| 1100 | Ester | Wood flour | Cellulose ester OCC stretch |
| 1096 | C-OH | Wood flour | C-OH bending in hemicellulose |
| 1064 | | Wood flour | Cellulose C-O stretch at C3 |
| 1049 | C-O-C | Wood flour | Glycosidic link in xylan (hemicellulose) |
| 1022 | | Wood flour | Cellulose C-C and C-O stretch |
| 903 | C-O-C | Wood flour | β -glycosidic linkages |
| 897 | C-O-C | Wood flour | C-O-C stretching of β -glycosidic link in cellulose and hemicellulose |
| 782 | C-O-C | Wood flour | hemicellulose α -linkage in α -pyranose |

a)



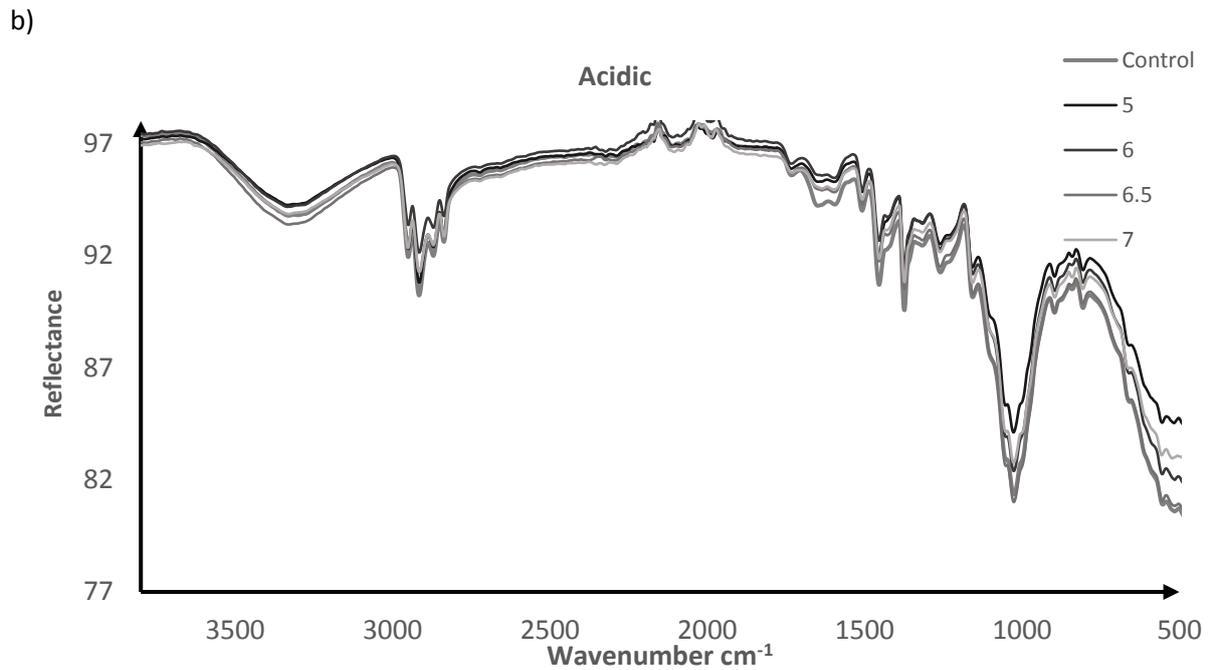


Figure 4: FTIR spectra for sample surfaces prepared using (a) alkaline and (b) acidic treatment solutions.

Principal component analysis (PCA) was performed in order to investigate the differences among the spectra of treated samples. According to the PCA score graph (Figure 5a) it is clear that the surface chemistry of the treated samples differs from the control samples. Moreover the samples treated in acidic solutions show a different surface chemistry profile to the alkaline treated samples. This confirms the differences in treatment mechanism between the two groups, as indicated in the initial review of surface roughness and surface energy data. The samples treated in pH 7 solutions seemed to undergo chemical changes similar to the acidic group. The samples treated in alkaline solutions formed a close cluster, but the pH 9 treated samples were clearly different from the lower pH alkaline samples. This means that the pH 9 could be considered as an extreme value, or an example of over treatment, which also agrees with the surface energy results.

The PCA loadings graph (Figure 5b) showed that the most important variables for the separation of the spectra of the different sample treatments into clusters is the FTIR wavenumbers between 500-1200 cm^{-1} for PC1 and 1200-1600 cm^{-1} and 2700-3000 cm^{-1} for PC2. Notably the absorptions within the 500-1200 cm^{-1} range contributing to PC1 relate to the wood component of the WPC (Figure 5d), while the absorptions at 1200 to 1600 cm^{-1} and 2700-3000 cm^{-1} for PC2 are clearly related to the methylene and methyl absorptions of polypropylene.

a)

b)

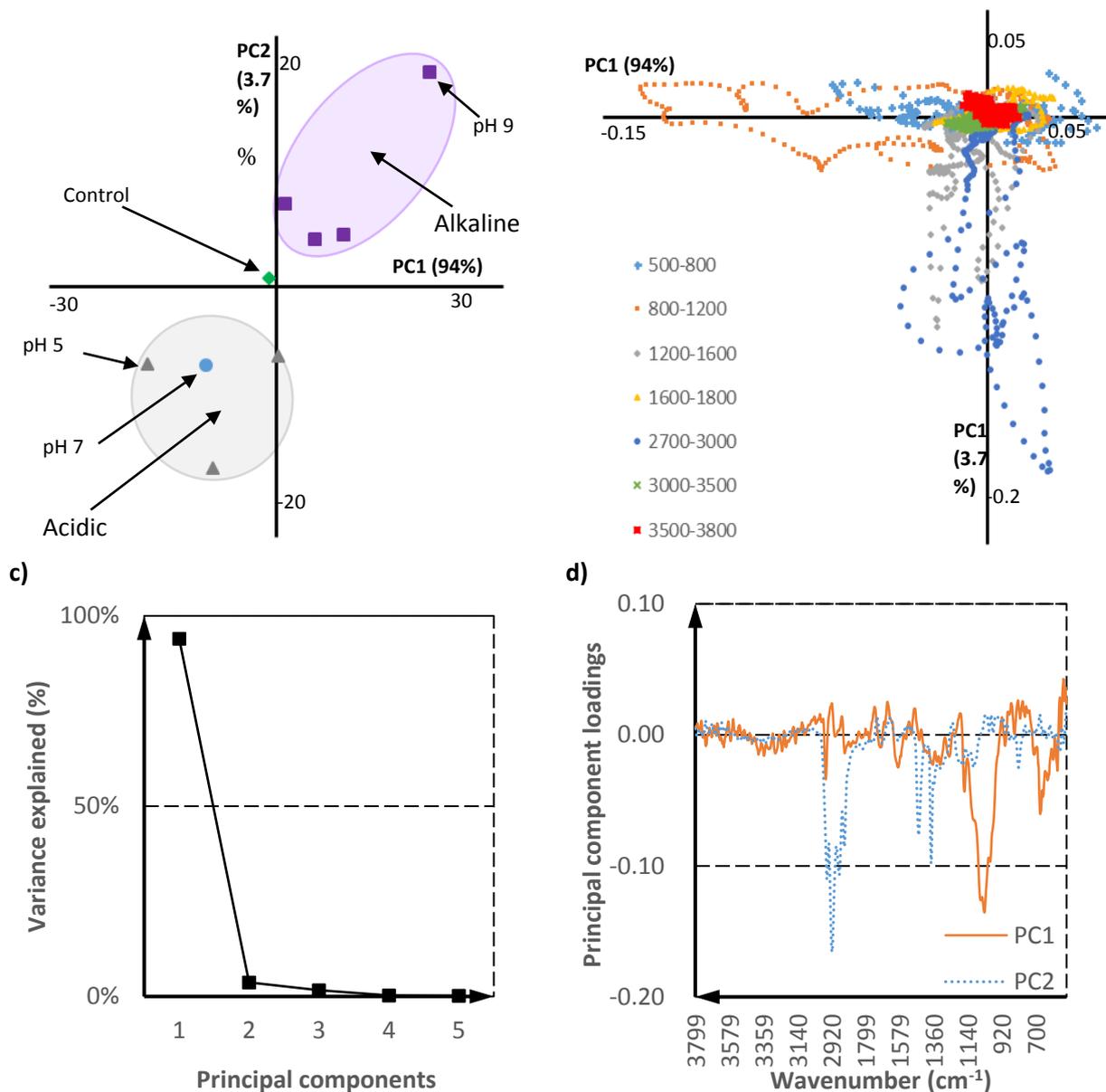


Figure 5: Principal Component Analysis (PCA) of the FTIR-ATR spectra of treated and untreated samples. a) PCA score plot, b) variables load plot. c) Scree plot of the variance explained by principle components d) Wavenumber loads of PC1 and PC2 plot

To further investigate the chemical changes that occur during the treatment, and the differences between the acidic and the alkaline chemical mechanisms, a 2D FTIR-ATR spectra correlation was performed. The synchronous and asynchronous correlation maps are presented in (Figure 6). Using 2D correlation it is possible to identify the correlations between the spectral bands, and also to identify the changes sequence as the treatment intensity increases [11]. By the investigation of the 2D correlation map it is observed that the main spectral regions that are altered by the treatment are in agreement with the PCA score plot. Moreover it is apparent that the acidic solution results in different chemical changes than the alkaline treatment solutions. 2D synchronous autocorrelation (Figures 6 a and c) showed that the most significant chemical changes can be grouped into those affecting both acidic and alkaline treated surfaces (510, 1026 (cellulose), 1372 (cellulose), 1455 (CH and C-OH), and the olefinic CH_2 and CH_3 stretches: 2838, 2871, 2917, 2950); and those affecting only

the alkaline treated surfaces (1313, 1589 (lignin), 1784 (carboxylic acid salt), 2091, 3330 (OH stretch)).

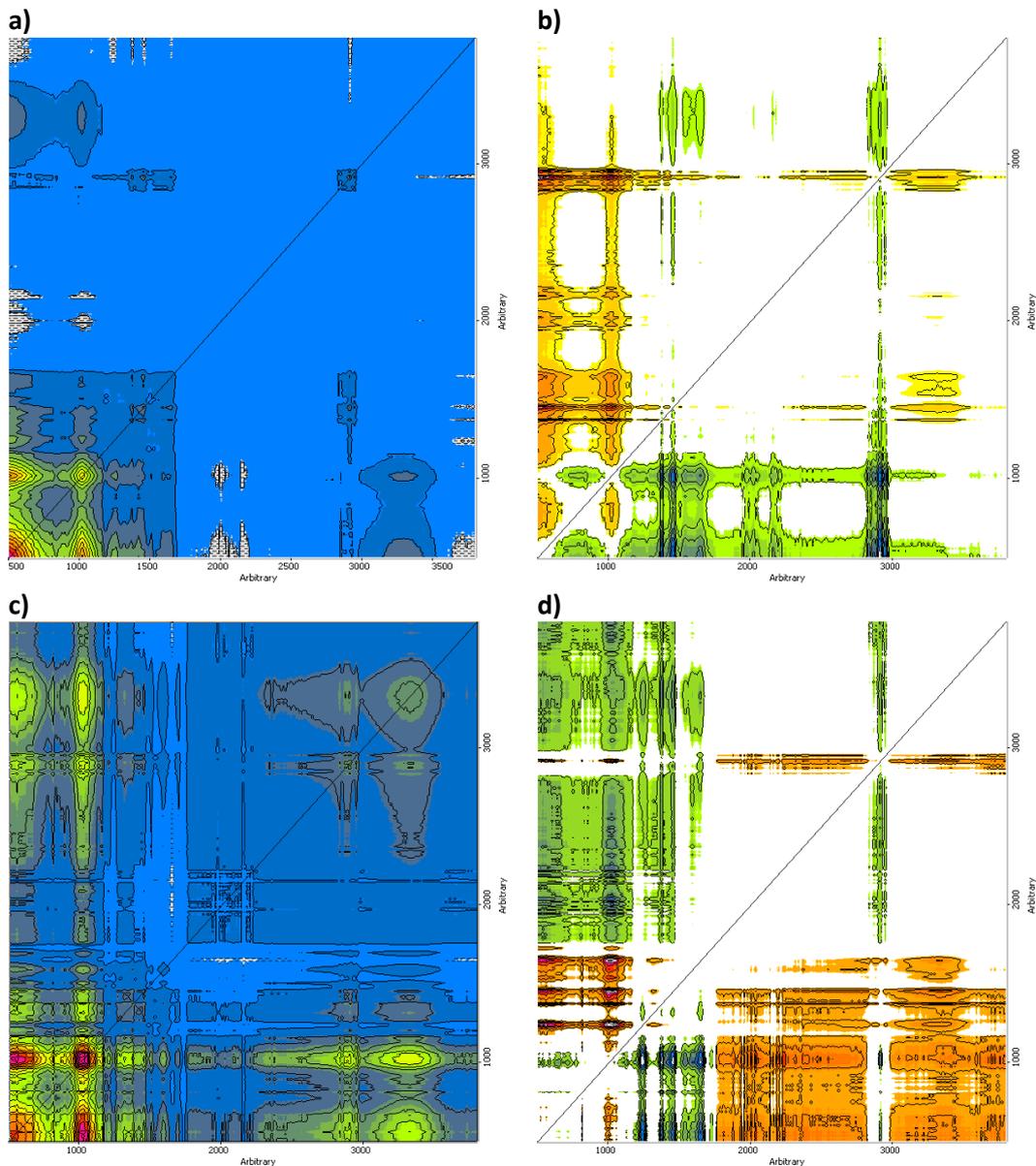


Figure 6: FTIR-ATR 2D correlation map. a) and b) are the acidic treatment synchronous and asynchronous correlation map; c) and d) are the alkaline treatment synchronous and asynchronous correlation map. On the synchronous correlation map the dashed white region represents negative area. On the asynchronous correlation map the green region represents the negative area.

The 2D correlation map shows the differences that occur during the hydrogen peroxide treatment. However those chemical changes are not directly related to the adhesion improvement. In order to further investigate the relationship of the FTIR spectra and the adhesion properties of the WPC a PLS regression was performed. The PLS regression is presented in Figure 7 and the variable importance in Figure 8.

The aim of including PLS regression is to aid identification of possible correlations within the current data. It should be noted that the PLS regression was not validated using a second set of data, so the regression model could not be used as a treatment prediction method. Similarly, the PLS variable

importance has been extracted in an attempt to identify the importance of the different properties and mechanisms relating to adhesion performance of the sample surfaces. By comparing Figures 7a and b it is clear that the samples treated in pH 9 do not follow the same chemical principles as the rest of the samples which is the reason the PLS score increases ($R^2=0.9917$ when pH 9 is excluded, $R^2=0.661$ when the samples treated in pH 9 were included). This indicates that the samples treated with pH 9 are an extreme case, and that this treatment solution over treats the samples, which is in agreement with the PCA observation, as well as poor performance in lap shear tests. From Figure 8 it is clear that the acidic and the alkaline treatments result in different chemical changes that are related to the adhesion properties of the treated WPC surfaces. As a first observation it is clear that the regions of the spectra which are related to the polypropylene characteristic peaks were more important for the adhesion properties in the acidic treatment than in the alkaline treatment.

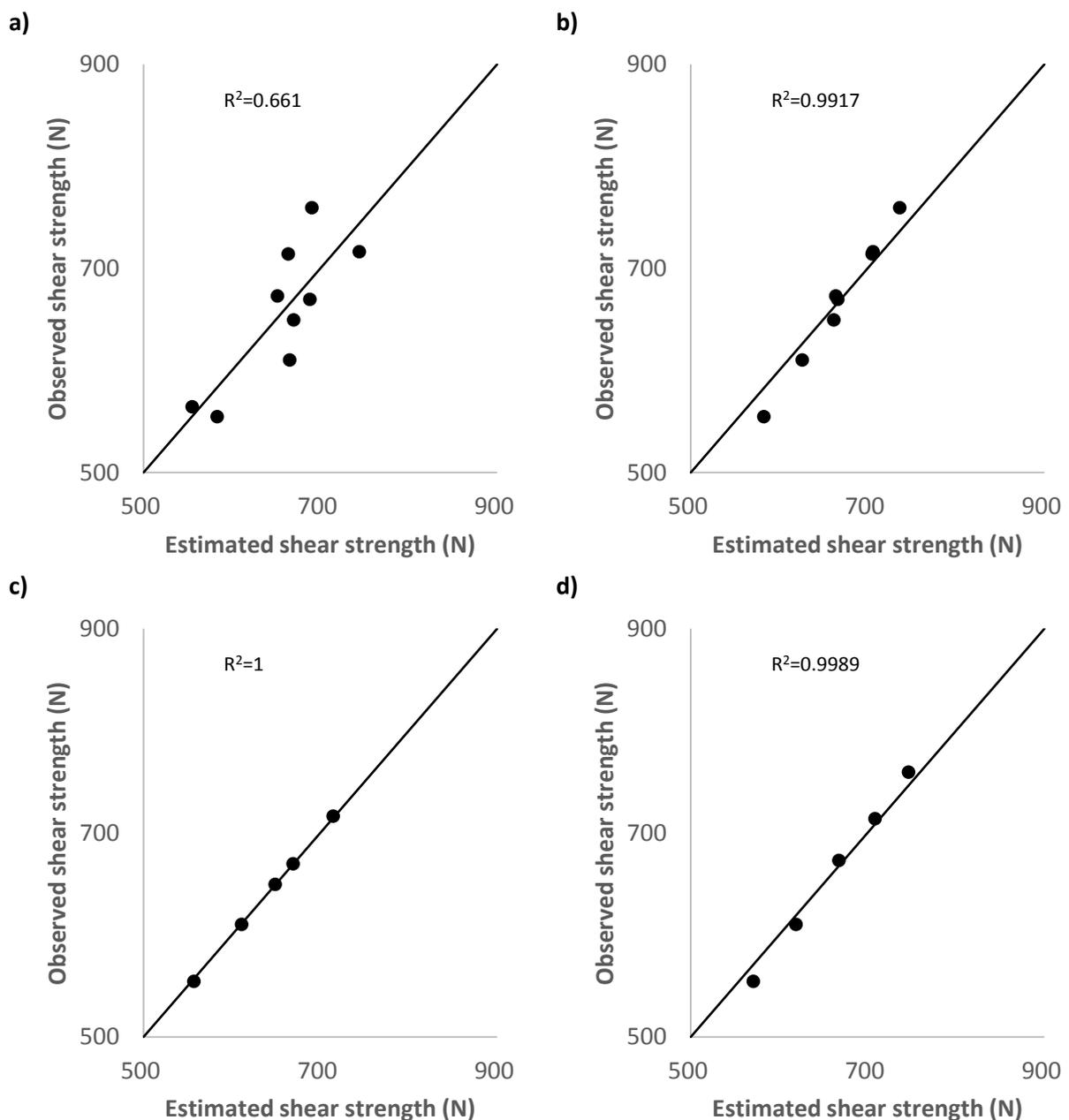


Figure 7: PLS regression model of FTIR-ATR spectra in correlation to adhesion shear strength. a) All treated and untreated samples. b) All samples excluding pH 9 treated samples. c) Untreated and treated in acidic solution samples. d) Untreated and treated in alkaline solution samples excluding pH 9.

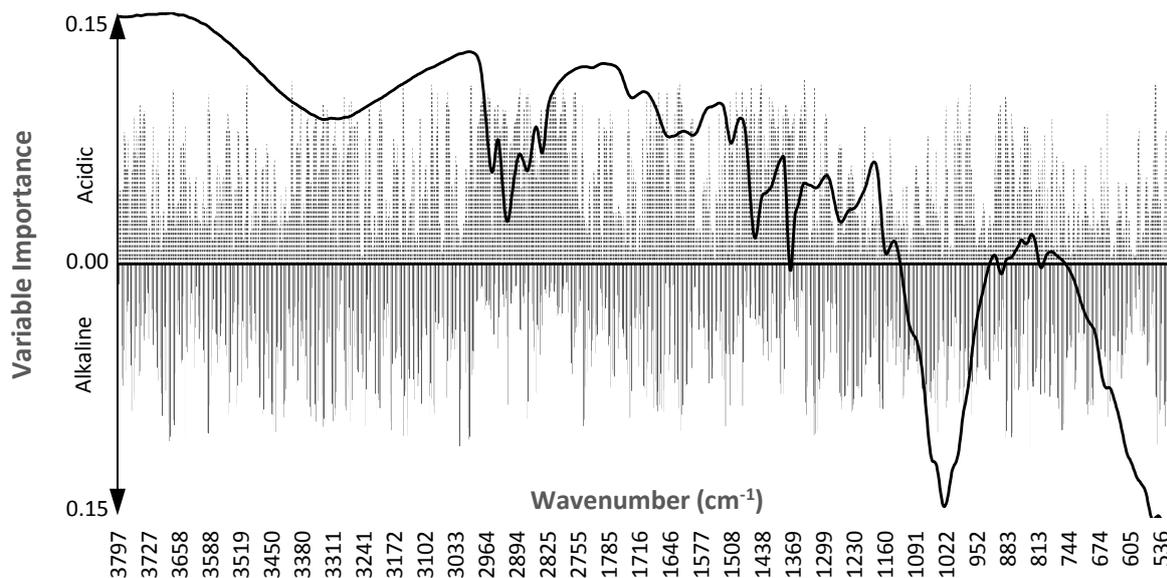


Figure 8: Variable importance of PLS regression in relation to adhesion strength. Samples treated in pH 9 solution were excluded.

In the same manner, PLS model was also performed to identify the important regions of the spectra that related to the surface energy. The PLS model is presented in Figure 9 and the variable importance in Figure 10. The variable importance clearly shows the different chemical changes that result in the surface energy difference. Moreover it is clear that the spectral regions which are related to the surface energy were different from the spectral regions that are affecting the adhesion strength. This observation explains the lack of visible trend between surface energy and adhesion strength.

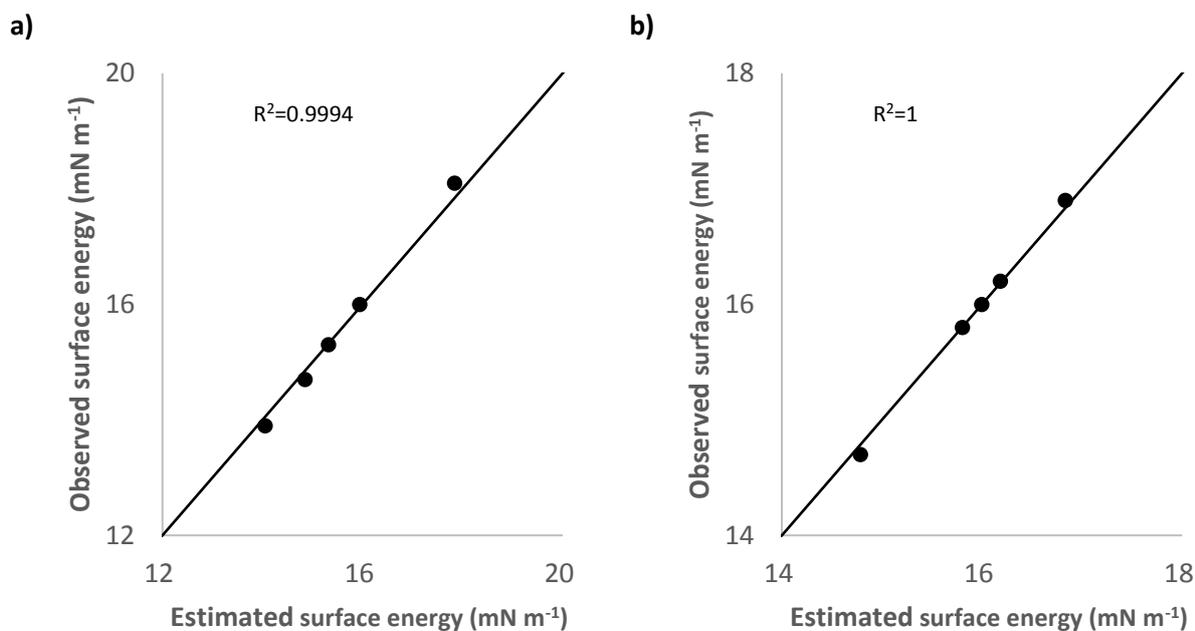


Figure 9: PLS regression model of FTIR-ATR spectra in correlation to surface energy. a) Untreated and treated in acidic solution samples. b) Untreated and treated in alkaline solution samples. Samples treated in pH 9 solution were excluded.

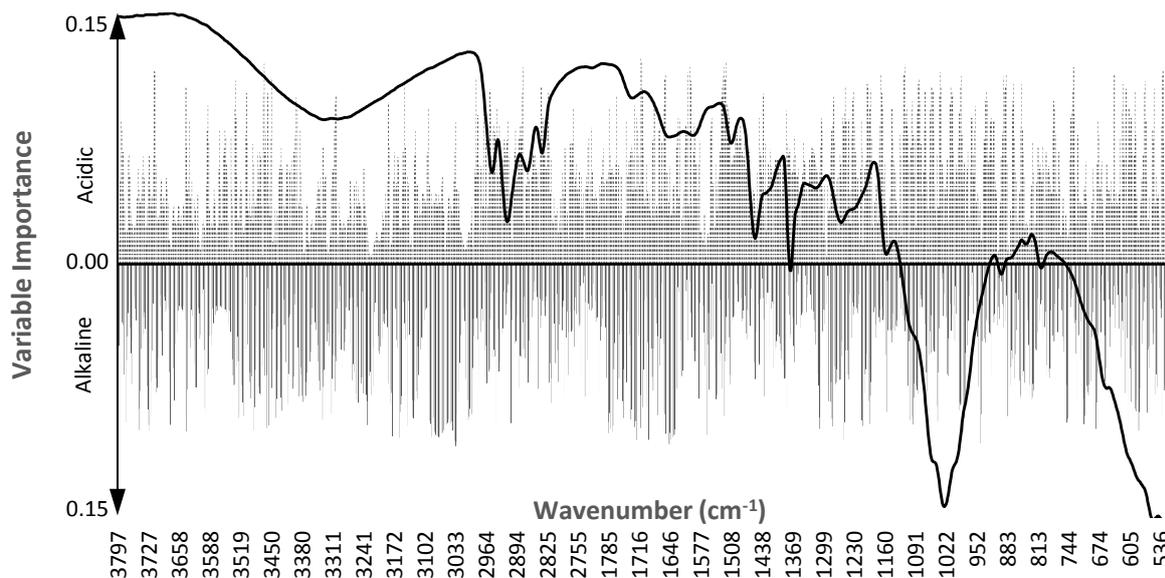


Figure 10: Variable importance of PLS regression in relation to surface energy. Samples treated in pH 9 solution were excluded.

4 Discussion

It is likely that there are several factors contributing to the pH dependence of the changes in surface chemistry, and resulting altered suitability for adhesive bonding, seen in this experiment. The main issue is the chemistry of hydrogen peroxide at acidic and alkaline conditions. Hydrogen peroxide can act as an electron donor or acceptor, depending on pH (Equations 5, 6). In the light of the different behaviours reported in this study, it appears relevant to segregate the treatments into those conducted in acidic peroxide solutions, and those using alkaline treatment solution.



Under alkaline conditions one mole of hydrogen peroxide may react with one mole of hydroxide to form the hydroperoxide anion (HOO^-) and water, Equation 7, this is widely attributed as the dominant reagent in peroxide bleaching reactions [12]. The use of an activator, such as sodium hydroxide, or sodium carbonate is therefore common [13, 10]. However, transition metals must be controlled or removed to avoid homolytic decomposition of the alkaline peroxide system to water and oxygen, Equation 8. The hydroxy radicals thus formed have also been linked to lignin degradation, however the reactions are less controlled.



Peroxide reactions with lignocellulosic materials in alkaline solution are well investigated for bleaching paper pulps, these include hydroperoxide anion reactions affecting the lignin component, such as side chain cleavage at α -carbonyls in ring conjugated structures, and ring degradation by hydroxylation followed by oxidation to maleic derivatives [13, 14, 15]. In addition, hydroperoxy radicals ($\text{HOO}\cdot$) and hydroxy radicals ($\text{HO}\cdot$) have been reported to contribute to degradation of hemicellulose in pre-treatments for biomass conversion [16, 17].

By contrast, there is relatively little work addressing the reactions of hydrogen peroxide in the acidic medium. Hydrogen peroxide is relatively stable under acidic conditions, so transition metal activators, such as Cu (II) ions, can be used [18]. However this may induce hydroxy (OH·) radicals if pH is later elevated, for example in two stage bleaching. These are reported to exhibit poor selectivity between cellulose and lignin, potentially reducing the degree of polymerisation of the cellulose component, especially when two-stage bleaching processes are used, so stabilisers such as sodium silicate or magnesium sulphate are required for the alkaline step.

The chemistry of room temperature reactions between hydrogen peroxide and wood is rarely discussed, however in pulp bleaching, alkaline hydrogen peroxide may be used with wood pulp at higher temperatures (circa 90°C) resulting in delignification reactions [13, 18]. In the surface activation for adhesion the hydroperoxy anion initiated reactions, and the free radical initiated processes, are likely to occur but at a considerably slower rate than utilised in bleaching. Reaction with the lignin (by hydroperoxy anion) and dissolution of hemicellulose oligomer (by free radical processes) are both possible for the treatment solutions of pH 7.5 and above. This may explain the relatively strong reduction in both ester and lignin functional groups which was seen in FTIR spectra for alkaline treatments. The 2D correlation map of the alkaline samples (Figure 4 c and d) showed positive cross peaks in the area between the esters (1726 cm⁻¹) and the cellulose C-O and C-C stretch (at 1022 cm⁻¹) in both the synchronous and asynchronous correlation maps. This indicates that the mild reduction in hemicellulose C-O and C-C stretches predominates, occurring at smaller pH changes than the reduction in ester moieties, however the decrease in esters as the pH of the treatment pH increases from 7.5 to 9 was very strong, with a reduction of -28% at pH 7.5 which strengthened to -57% at pH 9.

Using the 2D synchronous and asynchronous correlation maps, similar observations were made for the lignin bands around 1230 cm⁻¹ and 1600 cm⁻¹ and the cellulose C-O and C-C stretches. The cross peaks at those coordinates in the 2D correlation maps revealed that the lignin absorption is reduced as pH increases, after the initial changes in cellulose C-O and C-C stretch which are seen at pH 7.5.

The lower reactivity of the hydrogen peroxide at low pH (in this experiment no transition metal activators were used) explains the less severe loss of lignin functionalities in the acidic treatments. There is also a lack of ester functionality cross peak correlation for the same samples (Figures 6 **Error! Reference source not found.**a and b). The cross peaks at the coordinates of C-O and C-C stretch with the lignin bands in the correlation maps of acidic treated samples showed that the increase of the C-O and C-C stretch predominates the increase of the lignin bands. Both components indicate a difference between the acidic and the alkaline state reactions.

In contrast to the synchronous correlation map of the acidic treated samples (Figure 6a), the asynchronous cross correlation map (Figure 6b) does not have the cross peak at the coordinates of 1026 cm⁻¹ and 3330 cm⁻¹. This indicates that the reactions with OH formation (3330 cm⁻¹) and altered cellulosic C-C and C-O stretches (1026 cm⁻¹) are happening simultaneously with the treatment conditions.

By comparing the cross peak correlation graphs for the acidic and the alkaline treatments it is clear that reactions in the two systems differ. The selection of acidic or alkaline conditions will alter the production of peroxy radicals (HOO·) and hydroxy radicals (HO·). The reaction with the polypropylene component is dependent on the free radical generation by the hydrogen peroxide, this is likely also to be the case for the acidic medium reactions with the wood of the WPC material. Stronger reactions seen in the alkaline medium treatments relate to the hydroperoxy anion which was generated by reaction with OH⁻ from the sodium hydroxide. The hydroperoxy anion permits

reaction with the lignin and the hemicellulose of the wood flour. In the acidic medium, which is free-radical mediated, a series of stochastic processes will result, including the generation of polypropylene macroradicals, which will form aldehyde and ketone functional groups on the polypropylene chain [19]. However, due to the dominance of carbonyl groups within the wood spectra, it was not possible to isolate the expected increase in absorption at 1700, 1710, 1715 and 1718 cm^{-1} , which would relate to this new aldehyde carbonyl. The cross peak correlation graphs also did not show significant trends at the 940 or the 765 cm^{-1} absorptions due to proximity to strong absorptions from the wood component of the WPC material.

In the WPC samples treated with alkaline hydrogen peroxide solutions (Figures 6 c and d) the lignin content at the sample surface appeared to decrease, as evidenced by a general reduction of the ring vibration (1595 cm^{-1}) and the carbonyl stretch (1656 cm^{-1}). Absorption ratios were reduced by 34% and 46% at pH 8 respectively. This reduction also appeared to follow after the reduction of C-O and C-C stretch as seen by the 2D correlation maps. For treatments in the alkaline state, this reduction was seen strongly, whereas it seems that when the pH is below 7 this reduction was smaller. This is likely to relate to the presence of hydroperoxy anions in the alkaline medium, which are efficient in removing chromophores (which are carbonyl structures) from the lignin. Wójciak et al. [18] reported a decrease in the absorption at 1510 cm^{-1} which also relates to lignin aromatic functionalities, for wood fibre bleached using acidic and alkaline hydrogen peroxide solutions (albeit at higher temperatures than those employed in this surface activation experiment). A similar decrease in this absorption was seen for the alkaline treated samples in this study (26% reduction in absorption ratio at pH 8). Some degradation of the lignin may have contributed to the wood degradation and fibres decomposition observed by SEM.

It was reported for relatively high pH reactions with wheat straw by Sun et al. [12] that in addition to the peroxide mediated reactions, some alkali-labile linkages within the lignin could also have been cleaved by the presence of alkali. This included the cleavage of ester linkages with cinnamic acids such as ferulic acid and p-coumaric acid. It is possible that similar side reactions could occur to a small extent in the high pH treatments of WPC surfaces conducted for the adhesion study. If so, this could have further contributed to the delignification of fibres within the wood flour particles visible in Figures 12 and 13. It is also known that the hemicellulose component of wood can undergo hydrolysis reactions in the presence of alkalis such as sodium hydroxide, with removal of acetyl groups, cleavage of glycosidic bonds and peeling reactions (from the reducing end of both the cellulose and hemicellulose polymers) being possible at ambient temperature [20]. In addition nucleophilic attack on the lignin via the α -carbon of the phenyl propane structure is possible in alkaline medium without the presence of hydrogen peroxide [20].

Amongst the alkaline treatments, the pH 7.5 samples showed the lowest reduction in ester carbonyl absorption at 1732 cm^{-1} (approx. -25%), whereas higher pH values led to reductions in ester absorption ratio of 47 to 57%. These higher pH treatments showed lower improvements in lap shear strength. This indicates that aggressive degradation of the wood component at higher pH values may reduce the benefit of surface treatment. In the study on adhesion of bamboo, Lu [10] showed a relative increase in ester carbonyl for treatments at pH 8 and pH 9, reporting that the increase in carbonyl content of the surface had led to an increase in contact angle at these pH values. This was the opposite of the trend seen here, where surface energy increased despite a decrease in carbonyl content of the surface. One difference in method between this study (ATR-FTIR) and that of [10], FTIR, is that ATR measures only the surface region of the sample, whereas preparation of KBr disks for transmission FTIR requires pulverised samples, and represents the whole sample not just the

surface region. The available surface for bonding on the WPC material can therefore be considered to have fewer ester carbonyl functional groups.

A second reason for the difference in results compared to [10] may be that the CH absorption band used in that study (2900 cm^{-1}) relates to C-H stretches within cellulose, whereas the CH_2 stretch used in this study is in the polypropylene component of the composite. Due to the strength of CH_2 and CH_3 absorptions in this region the cellulosic and lignin C-H stretches were difficult to resolve within the spectra gathered. It should be noted therefore that while the results of [10] indicate an increase in ester relative to the natural level seen in bamboo, the results of this study show only a decrease in ester content relative to the matrix material surrounding the wood particles.

Control samples and two peroxide pre-treatments (pH 7.5 and 9) were selected for SEM observation. These were selected for having the highest lap shear strength (pH 7.5, 759.59 N) and the lowest lap shear strength (pH 9, 564.40 N). The main difference which was visible between the control (Figures 11 a and b) and the peroxide treated samples (Figures 12 and 13) was the fissures which were visible near the wood particles in the peroxide treated sample surfaces. It is interesting that both of these alkaline treatment solutions had created these fissures, despite the relatively high and low shear strength of the two different treatments. Other than this, there were no visible differences between pH 9 and pH 7.5 treated samples that could explain the different adhesion behaviour. The mean shear strength of the pH 9 samples was similar to that of the control (554.7 N).

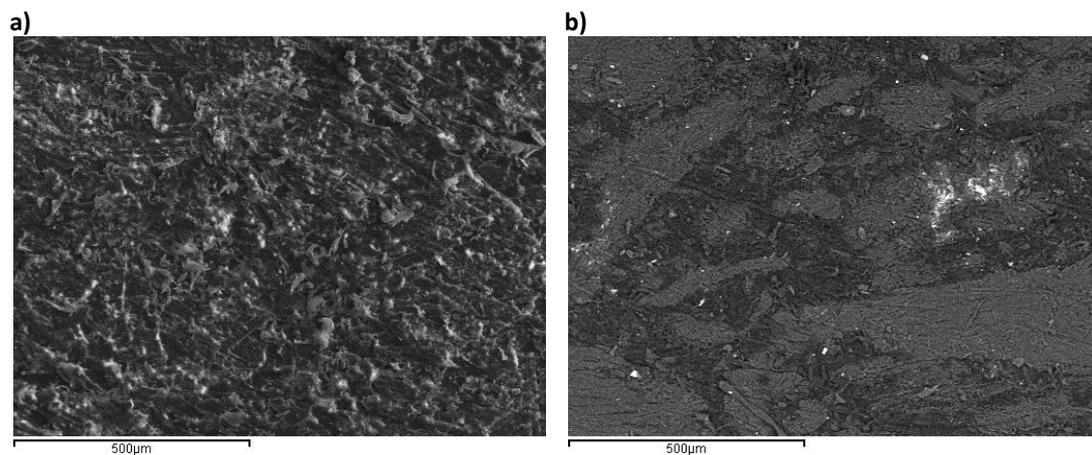


Figure 11: Control sample a) Surface under SEM primary electron scanning. b) Control sample under secondary electron scanning. The photos are from the same region.

a)

b)

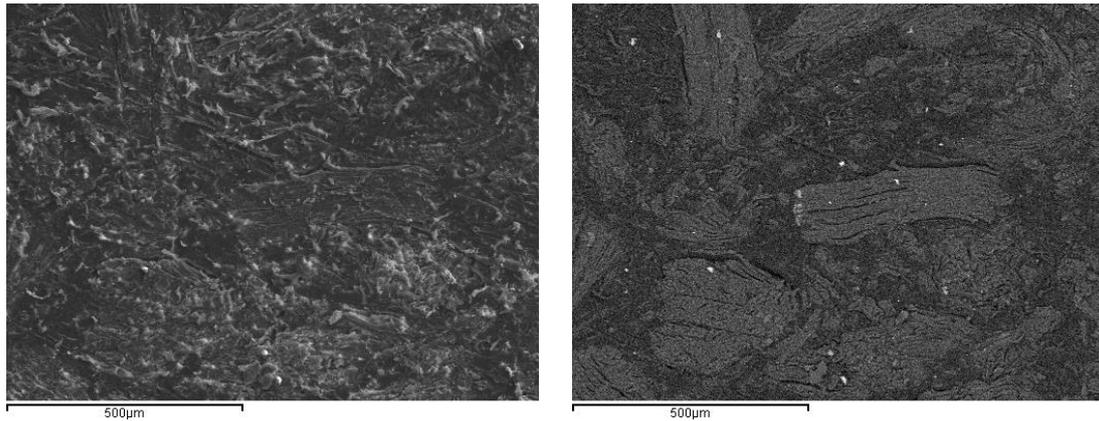


Figure 12: pH 7.5 solution treated sample. a) Backscattered image of the surface. b) The same region seen as a secondary electron image.

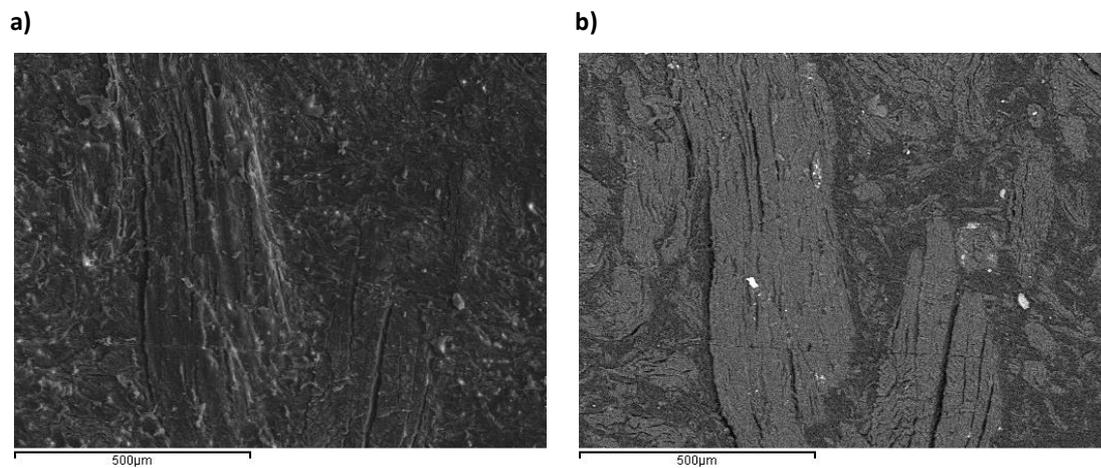


Figure 13: pH 9 solution treated sample. a) Surface under SEM backscattered electron image. b) Secondary electron image of the same region

The internal cracking of the wood particles in both alkaline peroxide treated surfaces, and the regions of separation from the polypropylene are likely to be formed by a swelling effect caused by the sodium hydroxide content of the solution, and subsequent shrinkage after reconditioning to ambient moisture content. Aqueous hydrogen peroxide is a relatively strong swelling solvent for wood. Figures 12 and 13 clearly show that the wood particles are degraded, which may also relate to removal of soluble fragments of hemicellulose from the surface. It could also relate to altered wood particle dimensions due to the action of the hydroxide ions on the hemicellulose component. The formation of these fissures might also be the reason ~~that~~ for the higher surface roughness values for alkaline treated samples.

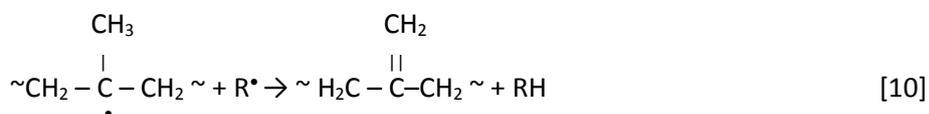
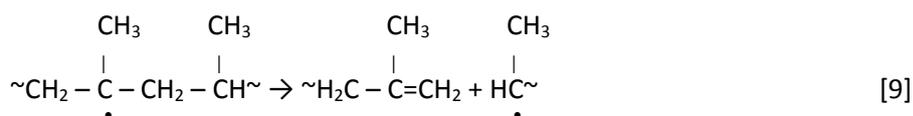
The surface energy and surface roughness measurements did not show good correlation with the trends seen in lap shear tests. For example, the highest surface energy was recorded for treatment at pH 9, yet this performed least well in lap shear, recording values of 564.4 N, which showed no statistical difference compared to the untreated control samples (554.7 N). The pH 7.5 samples however, which had the greatest increase in lap shear strength (759.59 N), showed relatively minor improvement in surface roughness and surface energy (Figure 2 c and d). However the PLS model showed a good correlation between the FTIR spectra and the surface energy (Figure 9). According to the importance of variables (Figure 10), it seems that in the acidic solutions the most important

factors ~~that~~ affecting the surface energy were related to the CH₂ and CH₃ symmetric and asymmetric stretches of the polypropylene, the lignin and the cellulose. In contrast the changes in surface energy seen in alkaline treatments is related more to alteration in the hydroxyl group content, i.e. changes in the lignin and the polysaccharide components of the wood. It seems that in the acidic solutions the surface energy changes relate more to the polypropylene polymer than the wood fibres. However in the alkaline solutions there is a peak in the importance of variables graph in the region around 1650 cm⁻¹ (Figure 10) which is related to the C=C bonds which is possible to be related to the polymer chain scission.

A similar relationship can be seen between the chemistry and adhesion strength using the importance of variables from the PLS regression in Figure 7. It seems that for the samples treated in acidic solutions the most important functions which affect the adhesion strength are more related to the polypropylene and the lignin degradation. In contrast the alkaline treated samples showed that the main functions that attribute to the PLS model were not significantly related to the polypropylene but to the lignin and the cellulose.

It might also be hypothesised that free radical reactions with the polypropylene would induce carbonyl or other polar functional groups on the polymer component of the WPC material, however this does not seem to have been observed. Gaudhil and Halek [21] also report that they were not able to confirm any increase of carbonyls by FTIR after polypropylene surface exposure to hydrogen peroxide. Figure 10 a presents the average spectra of treated in alkali solution (pH 8.5) and untreated spruce samples. It is obvious that the esters are significantly reduced, which is also supporting the hypothesis that the esters are dramatically cleaved from the structure of the wood fibres.

The chemical changes that ~~which~~ took place on the polypropylene surface after the treatment were not known. However, a polymer scission process could be possible during the oxidation. Lazar et al [22] reported that double bonds were formed on polypropylene after peroxide decomposition, and indicated that this occurred by fragmentation reactions (Equation 9) and by disproportionation of polypropylene macroradicals with the transfer of protons from the β-carbon to the carbon of the radical centre of the second radical R· (Equation 10).



Accordingly a small supplementary study was conducted on pure polypropylene to investigate this chemical reaction. A sample of pure polypropylene was also subjected to hydrogen peroxide treatment in alkali solution (pH 8.5 at 20°C). The average spectra before and after the peroxide treatment are presented in Figure 12b. An increase in the peak at 1650 cm⁻¹ was noticed which refers to C=C bonds [23]. This observation agrees with the polypropylene scission and formation of an alkene chemical reaction which was reported by [22]. In the polypropylene, the esters and carbonyls did not seem to change when treated with hydrogen peroxide, which also agrees with the observations of [21].

Furthermore, there was a slight difference in the peak at 1558 cm^{-1} which refers to sodium carboxylate salts (R-COONa) [24]. It is possible that some carboxylic acid moieties reacted with the NaOH and produced the sodium salts. Any sodium salts thus formed could contribute to an increase in the surface energy of the samples treated in alkaline solution, possibly increasing the hydrophilic properties of the surface.

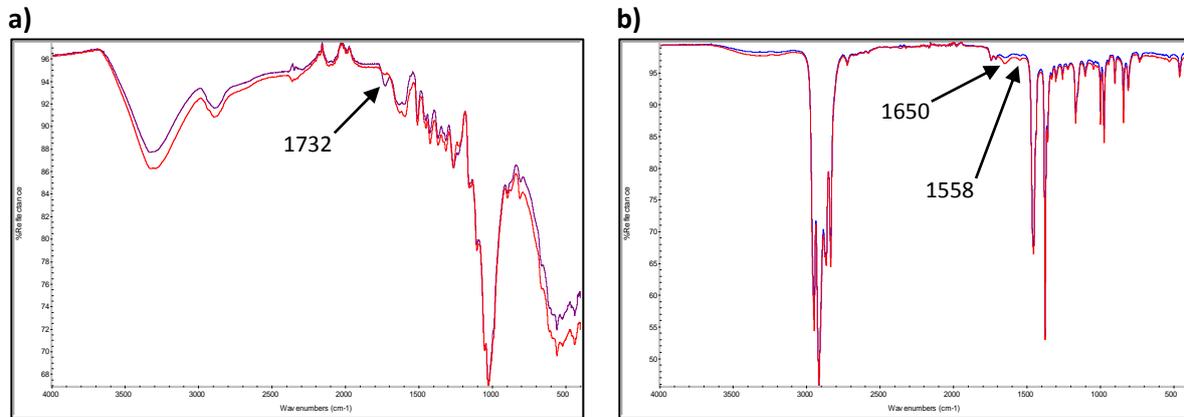


Figure 14: Treated (red line) and untreated (blue line) spruce a) and polypropylene b) in pH 8.5 solution of hydrogen peroxide.

In some of the acidic solutions, the ester ratio showed an increase which corresponded with an increase in surface energy, e.g. at pH 5, 6 and 6.5. The C=O and esters region have been indicated to be correlated to surface energy by the importance of variables, with this relationship having greater importance in the alkaline solutions. However, at higher pH (8 to 9) an increase in surface energy corresponded with a decrease in the ester ratio, which can be largely attributed to the effect of alkali on the wood component. It therefore could be considered that two different mechanisms occur, one in the acid medium and the other in the alkaline medium. This supports the hypothesis that the action of the alkaline treatment solution is on the esters in hemicellulose, thereby increasing surface energy.

5 Conclusions

This study has investigated the surface properties of polypropylene matrix WPC treated using hydrogen peroxide solutions in the presence of sodium hydroxide to achieve a range of pH values. This was primarily an investigation of the surface chemistry in order to understand the chemical mechanisms underpinning the observed improvement of adhesion. Clear differences were seen between treatments undertaken in acidic and alkaline peroxide solutions. While both acidic and alkaline treatment solutions resulted in an increase in lap shear strength, it is proposed that this is achieved by different chemical mechanisms for the two groups of pH treatments. PCA of FTIR-ATR spectra taken on the treated surfaces clearly showed differences between the acidic and the alkaline treated material. This related both to the wood ($500\text{-}1200\text{ cm}^{-1}$, PC1) and the polypropylene ($2700\text{-}3000\text{ cm}^{-1}$, PC2) elements of the composite surface. We propose that treatment solution pH results in different reaction mechanisms that provide different optima for the acidic and alkaline solutions, but in both cases increase the adhesion strength.

In the acidic case, the improvements in lap shear correlated with increased surface roughness and surface energy. Both may contribute to improved adhesion. According to the PLS model, the polypropylene absorption bands of the FTIR spectrum were more influential in explaining the change in adhesion behaviour. This indicates that a peroxide initiated free radical reaction with the polypropylene component occurs in acidic treatment solution, resulting in increased surface energy.

This is the classical mechanism employed in functionalisation of polymer surfaces to improve adhesion by increasing surface energy.

The alkaline peroxide solutions showed two trends, depending on solution pH. For the mild alkaline peroxide solutions (pH 7.5 to 8.5) lap shear increased relative to the control, relating to surface activation. However as pH increased, a decline in lap shear strength was seen, and at pH 9 the lap shear strength decreased below the values of untreated controls. It is proposed that the hydroperoxy anion generated in higher pH solutions dominated the reaction mechanism, leading to a degradation reaction with the wood component of the WPC surface. FTIR of pure PP and spruce sample material confirmed this, and revealed changes in the wood surface relating to a decrease in ester absorption at 1732 cm^{-1} , in the same manner as that seen on WPC samples treated with solutions of pH 8 to 9. At pH 9 the degradation of the wood particles within WPC surfaces seen in SEM confirmed an increased roughness in this treatment. We propose this degradation may in fact relate to lower surface integrity, acting to decrease rather than increase adhesion.

As pH increased from 7.5 to 8.5 the reaction of wood and hydroperoxy anions has a mildly beneficial effect, and the corresponding increase in surface energy was sufficient to induce additional adhesion. However at pH 9 the treatment had a degradative effect on the surface, reducing bond strength. All surface analyses indicated that the pH 9 treatment was an outlier, and had different surface energy and surface chemistry compared to the mild alkaline treatments, resulting from a stronger reaction with the esters of the wood, as confirmed by PCA of FTIR data. This has been interpreted to mean that degradation occurred to this sample, possibly relating to the high hydroperoxy anion content, and at the highest pH values, the onset of hydroxide anion reactions (cleavage of alkali labile linkages in lignin and induction of peeling reactions in the hemicellulose polysaccharides). It is therefore recommended that good control of solution pH is important if using peroxide as a surface treatment agent for WPC materials. When using alkaline peroxide to enhance adhesion of WPC materials it appears that a treatment solution of pH 7.5 to 8 gives optimum benefit.

6 References

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