Effect of oxygen and hexamethyldisiloxane plasma on morphology, wettability and adhesion properties of polypropylene and lignocellulosics

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Abstract
In this work, the effect of oxygen plasma on the surface characteristics of polypropylene (PP) and birch was investigated. In addition, studies on the effects of hexamethyldisiloxane (HMDSO) plasma on the surface characteristics of lignocellulosics and on the adhesion properties of PP to the HMDSO-treated wood surface were carried out. Atomic force microscopy (AFM) and contact angle measurements were used to study the changes in the topography and surface free energy of the materials due to plasma treatments. AFM revealed distinct changes in the topography of PP due to oxygen plasma. Nodular structure is formed on the PP surface during the treatment and the size of the nodules increases with the treatment time. The extent of the topographical changes was nearly equal in the case of the two power levels studied. A clear increase in the surface free energy of PP and wood due to oxygen plasma was recorded. AFM studies on filter paper, kraft pulp and birch surfaces treated with HMDSO plasma showed that the plasma polymer follows the features of the substrate without forming an actual film on the surface at the treatment levels used. The substrate surfaces became highly hydrophobic when exposed for 5 min or longer to the plasma. No improvement in the adhesion of PP film to wood was achieved by pre-treating the substrate with HMDSO plasma polymer. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: contact angle; atomic force microscopy; polypropylene; lignocellulosics; plasma treatment

1. Introduction
Wood and other lignocellulosic materials in different forms have recently gained increasing popularity in a number of applications as a composite material in combination with thermoplastics. These applications include such products of great potential like automobile parts made of polypropylene reinforced with wood fiber or filled with wood flour. However, the incompatibility of the polar lignocellulosics and non-polar thermoplastics leads to adhesion problems between the components and thereby to low performance like low impact and bending strength of the product [1]. Besides chemical modification [2-4] plasma treatments [5-7], although to less extent, has been applied to improve adhesion between lignocellulosics and thermoplastics.

The aim of the present work was to supplement the previous study [8] on adhesion between wood and polypropylene with more detailed data of the effect of oxygen plasma on the surface properties of the materials. Atomic force microscopy (AFM) and contact angle measurements of water were used to monitor the effect of plasma at two different power levels on the physical and chemical structure of the polypropylene surface. The other type of gas used for modification of wood veneer was hexamethyldisiloxane (HMDSO). HMDSO is expected to form a hydrophobic polymer layer on the wood surface. The effect of hydrophobization of the wood surface on the adhesion properties of polypropylene film and the wood was evaluated using a torque test, in which the bonding strength of the film on the wood surface is evaluated by removing the film by applying a force parallel to the surface.

Contact angle measurement has been shown to be one of the best methods for estimating the nature of chemical
changes occurring on the very outer layer of a substrate due to a surface modification by plasma [9]. The atomic force microscope (AFM) [10] is a technique in which a three-dimensional image of the topography of the surface is created by probing the surface of a sample with a sharp tip. The ability to study local phenomena on different kinds of surfaces with a resolution even down to nanometer scale has made it an essential tool for a wide range of applications. Recently, AFM has successfully been applied for studies of oxygen plasma-modified polymer surfaces, such as, polypropylene [11-13] and poly(tetrafluoroethylene) [14]. Other types of plasma treatments [15-18] and surface coating with plasma polymers [19-21] have also been studied using AFM technique. Consequently, the contact angle measurements and the morphology studies of plasma-modified surfaces by means of AFM complement well each other.

2. Experimental

2.1. Materials

The plastic film used in this study consisted of a polypropylene (PP) and a polyamide (PA) layers and was supplied by Walki Pack Valkeakoski (Finland). The film was specified to have a PP layer of 50 µm and a PA layer of 30 µm in thickness. The films were cut into the shape and size of the plasma electrode and Soxhlet extracted with acetone to remove dirt and additives prior to plasma treatment.

Sliced birch (Betula pendula) veneer with a nominal thickness of 0.8 mm (radial direction) was used. For the plasma treatments, the veneer sheets were cut into dimensions of 60 mm × 170 mm (tangential × longitudinal). In order to eliminate the effect of surface roughness on contact angles, the veneer surfaces were sanded with a sand paper of 150 grid prior to the plasma treatments.

Kraft pulp (from loblolly pine and with a kappa number of 123) pressed into sheets and filter paper (Schleicher and Schuell) were used as substrates in plasma treatments with hexamethyldisiloxane in order to facilitate the monitoring of the film formation of the plasma polymer.

2.2. Contact angle measurements

Wettability of the material surfaces with different liquids were measured as contact angles of advancing droplets by means of a videotape technique [22]. The contact angles of the veneer surfaces were measured in longitudinal direction to the grain. The values of the left and right angles of six droplets were averaged. Microsyringes were used to place droplets on the surfaces. The droplet sizes varied from 7 to 10 µl depending on the liquid. The liquids used for the measurements were as follows: deionized water, analytical grades of formamide, ethylene glycol and methylene iodide. The contact angle measurements for all the samples were carried out within 48 to 72 h of the plasma treatments. After the treatments to the point of the contact angle measurements, the samples were stored in tightly sealed freezer bags in a desiccator.

According to Young’s Eq. (1) the contact angle of a liquid on a material can be used to determine the surface tension of the substrate:

\[ \gamma_{LV} \cos \theta = \gamma_{SV} - \gamma_{SL} \]  

(1)

where \( \gamma_{SL} \) and \( \gamma_{SV} \) are the surface free energies of the interface between the solid and the liquid and of the solid and saturated vapor, respectively, \( \gamma_{LV} \) is the interfacial surface tension between the liquid and vapor and \( \theta \) is the contact angle.

On the other hand, the thermodynamic energy of interactions, the work of adhesion \( W_a \) has been defined as a sum of the following terms:

\[ W_a = \gamma_{LV} (1 + \cos \theta) \]  

(2)

The combination of Eqs. (1) and (2) gives

\[ W_a = \gamma_{SV} - \gamma_{SL} \]  

(3)

In addition, it has been proposed that two different interactions of the work of adhesion \( W_a \) can be obtained: \( W_a^d \) derived from the London dispersion forces and \( W_a^{ab} \) derived from the non-dispersive i.e. acid-base interactions:

\[ W_a = W_a^d + W_a^{ab} \]  

(4)

When there are only dispersion forces involved, the work of adhesion deriving from the dispersion forces can be expressed by the geometric mean of the dispersion component:

\[ W_a^d = 2(\gamma_{LV} \gamma_{SV})^{1/2} \]  

(5)

Similarly, the non-dispersion contribution (deriving from electrostatic, metallic, hydrogen bonding and dipole-dipole interactions) to the equation of the work of adhesion can be defined as the geometric mean of polar components. This results in the following equation [23]:

\[ \gamma_{LV} (1 + \cos \theta)/2(\gamma_{d}^{1/2} + \gamma_{p}^{1/2})^{1/2} = (\gamma_{SL}^{1/2} + \gamma_{SV}^{1/2})^{1/2} \]  

(6)

Eq. (6) can be rearranged to form equation:

\[ \gamma_{LV} (1 + \cos \theta)/2(\gamma_{d}^{1/2} + \gamma_{p}^{1/2})^{1/2} = (\gamma_{SL}^{1/2} + \gamma_{SV}^{1/2})^{1/2} \]  

(7)

Thus, the dispersive \( \gamma_{d}^{1/2} \) and the polar \( \gamma_{p}^{1/2} \) components of surface free energy of the substrate can be calculated from the intercept and the slope of the linear graph when the left-hand side of Eq. (7) is plotted against \( (\gamma_{SL}^{1/2} + \gamma_{SV}^{1/2})^{1/2} \) (Fowkes plot) [24].

Literature values (Table 1) were used in the calculations for the surface energies of the probe liquids.
2.3. Plasma installations and treatments

Plasma treatments were carried out in the plasma reactor of the Engineering Research Center for Plasma-Aided Manufacturing of the University of Wisconsin. The reactor is composed of a cylindrical, capacitively coupled, parallel plate 50 kHz-RF reactor chamber made of stainless steel. Prior to the plasma treatments, decontamination procedure of the reactor was performed in order to avoid possible contamination of the material surfaces from reactor wall depositions derived from previous treatments. In the decontamination procedure, the lower electrode was heated to 200°C and oxygen plasma (250 mTorr, 200 W, 10 min) was introduced to the chamber. The oxygen plasma phase was followed by argon plasma under similar conditions, cooling down the electrode and promoting the reactor to low pressure level.

For the oxygen plasma treatments, polypropylene samples were placed in the reactor, which was then evacuated in order to reach a ground pressure of around 30 mTorr. The evacuation state was followed by introducing oxygen into the chamber with the flow rate of 6.5 sccm (pressure 200 mTorr). The pressure while oxygen plasma present varied from 250 to 300 mTorr. The combinations of the RF power levels and treatment times used are shown in Table 2.

The plasma polymerization procedures were carried out by placing the veneer samples in the plasma reactor followed by evacuation of the chamber. When base pressure of 40 to 43 mTorr was reached, hexamethyldisiloxane monomer (NMR grade) was introduced into the plasma chamber with the flow rate of 6.3 sccm (in oxygen units). The monomer pressure was 200 mTorr and the RF power used to create the plasma was 200 W. The duration of the hexamethyldisiloxane treatments was 2, 5 and 8 min.

2.4. Experimental details of atomic force microscopy

The AFM imaging was performed with a commercial NanoScope III multimode AFM [28] for surface morphology characterizing of kraft pulp, filter paper and wood. All measurements were conducted in normal air pressure and room temperature. Only tapping mode™ operating in height mode was applied. The samples were attached with adhesive tape to a metal plate. Commercial silicon tips [28] were used. Each tip was tested before measurements with a calibration sample [29]. Tips were often estimated after measurements too. Each sample treated for different time was measured with a new unused and checked tip in order to avoid any contamination of the tip. The 200 µm scanner and scan rates of 0.4 to 1.0 Hz were employed. No filtering was needed, however, flattening was used in order to remove the tilt. In few cases, contrast enhancement has been utilized to improve the printing quality.

2.5. SEM and EDS analyses

For excess topography studies and for estimation of the relative quantity of the plasma polymer on different veneer samples, scanning electron microscopy (SEM) imaging together with energy dispersive spectroscopy (EDS) (detection of Si) were carried out. Specimens with the dimensions of about 7 mm × 7 mm (longitudinal × tangential) were cut from the veneer samples treated with HMDSO plasma. These specimens were mounted on specimen stubs and vacuum coated with a thin layer of carbon. The specimens were examined in a Jeol JSM-820 scanning electron microscope and the Si analyses were carried out by using an energy dispersive PGT IMIX spectroscopy hooked up with the SEM.

2.6. Adhesion measurements

For the adhesion studies, PP/PA film was pressed on the HMDSO-treated birch veneer (6 mm × 12 mm) using a laboratory size (150 mm × 150 mm) hot press and the following pressing parameters: temperature 150°C, pressing time 5 min, pressure 5.1 MPa. Conditioning of the coated specimens at 65% relative humidity took place prior to adhesion tests. A torque method similar to the method developed by Holloway and Walker [30] was used for determination of the adhesion between the polypropylene film and the HMDSO-treated veneer [31]. In this method, steel studs are glued on the coating (using in this case a cyanoacrylate adhesive) and a slot is drilled around the stud through the film until the substrate is reached. The bonding strength of the coating to the
substrate is determined by removing the studs with a torque wrench. The failure type is evaluated visually and the shear stress is calculated using the following equation:

\[ T = \frac{16I}{\pi d^3} \]  

(8)

where \( I \) is the torque measured and \( d \) is the diameter of the stud (12.5 mm). For the adhesion measurements, three replicate veneer specimens for each treatment (0, 2, 5 and 8 min in HMDSO plasma) were used, each veneer specimen tested with five studs. A two way variance analysis was used to evaluate the differences between the means of the adhesion values and to determine the significance level of the results.

3. Results

3.1. Contact angle measurements

3.1.1. Effect of oxygen plasma on contact angle of water on PP

The effect of oxygen plasma treatment time and power on the contact angles for deionized water is presented in Fig. 1. The graph shows the contact angles for the low (60 W) and the high (100 W) power level with the treatment time from 15 to 45 s and from 15 to 90 s, respectively. The contact angle of water on PP treated with the power of 60 W did not differ from the values of PP treated with the power of 100 W. The change in contact angles of water was significant already after a very short treatment time (15 s). The plasma treatment for 15 s (60 W) decreased the contact angle from approx. 90° for untreated PP to approx. 65°. The contact angle decreased gradually with the treatment time and reached the lowest value (approx. 55°) at the treatment duration of 60 s. A slight increase in contact angle values was observed when the treatment time was prolonged to 90 s.

Fig. 2 represents the effect of oxygen plasma on the contact angle of water on sanded birch surface. A declining trend in the contact angles of water with the treatment time could be seen for the birch surfaces. Plasma treatment for 30 s decreased the contact angle values from 60° down to 45°. Prolonging the treatment by 30 more seconds did not change the contact angles much further.

In order to better understand the nature of the changes in the surface properties of PP and wood due to plasma treatment, the dispersion and polar interaction contributions to the surface energy of the materials were calculated using the Fowkes plot presented above. Fig. 3 shows the Fowkes plot presentation for untreated PP and PP treated with oxygen plasma for 30 and 60 s. The dispersion and polar components of the surface energies calculated from the intercept and the slope values of the Fowkes plots for PP and wood surfaces are listed in Table 3.

The results derived from the graphic presentation show that the polar component of the surface free energy of PP is considerable increased by the plasma treatments studied (30 and 60 s). The PP surface became hydrophilic already due to oxygen plasma treatment of 30 s and stayed at that level still after 60 s of plasma treatment. No significant difference was observed between the dispersion components of the untreated and treated PP, which indicates that the polar component is responsible for the increase of the total surface energy due to plasma treatment. Plasma treatments significantly increase the polar component of the birch surfaces, as well. The increase of the total surface energy of wood due to the
treatments is solely related to the increase of the polar component, since reduction in the dispersion interactions takes place when birch is exposed to plasma.

3.1.2. Plasma polymerization of HMDSO on lignocellulosics

As an indication of the hydrophobization of the lignocellulosic surfaces by HMDSO plasma, water droplets on the treated surfaces appear as beads in which no spreading or penetration into the material takes place (Fig. 4). When a water droplet on an untreated filter paper or kraft pulp penetrates the substrate in less than 1 s ($q = 0$), water forms on a treated material a stable droplet with a contact angle of about 130°.

The contact angles of water on birch surface treated with HMDSO plasma for different times are given in Fig. 5. The results show that the HMDSO plasma treatment of 2 min was not sufficient enough to make the wood surface hydrophobic and water repellent. However, the treatment for 5 min significantly increased the contact angle values from around 60° (for controls) up to 95°–135°. The water repellency of birch can be further improved by exposing the wood to the plasma 3 more minutes, i.e. 8 min altogether.

<table>
<thead>
<tr>
<th>Surface</th>
<th>$\gamma_s$ (mJ m$^{-2}$)</th>
<th>$\gamma_d$ (mJ m$^{-2}$)</th>
<th>$\gamma_a$ (mJ m$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated PP</td>
<td>1.2</td>
<td>27.6</td>
<td>28.8</td>
</tr>
<tr>
<td>PP treated for 30 s</td>
<td>19.4</td>
<td>32.3</td>
<td>51.7</td>
</tr>
<tr>
<td>PP treated for 60 s</td>
<td>25.4</td>
<td>26.3</td>
<td>51.7</td>
</tr>
<tr>
<td>Untreated birch</td>
<td>12.2</td>
<td>39.8</td>
<td>52.0</td>
</tr>
<tr>
<td>Birch treated for 30 s</td>
<td>39.9</td>
<td>24.9</td>
<td>64.8</td>
</tr>
<tr>
<td>Birch treated for 60 s</td>
<td>36.9</td>
<td>28.2</td>
<td>65.1</td>
</tr>
</tbody>
</table>

Fig. 3. Presentation of the calculations for dispersion and polar components of the surface free energy for PP (Fowkes plot). Symbols: untreated ( ), treatment time of 30 s (— — ) and treatment time of 60 s ( - - ).
3.2. Adhesion of PP film to birch treated with HMDSO

Table 4 contains the data for the bonding strength between PP film and the birch veneer pre-treated with HMDSO plasma. The results show a slight decrease in the bonding strength for PP film when the film is pressed on the veneer surface treated for 2 and 8 min in HMDSO plasma, whereas treatment for 5 min increases the bonding strength to some extent. However, the statistical analyses showed that the differences in the adhesion values between the treated and untreated specimens were not significant. A slight increase in the wood failure values seems to be related to the drop in the bonding strength. The changes in the failure types due to the pre-treatment are not statistically significant.

3.3. SEM and EDS analyses of HMDSO-treated wood

Comparison of the untreated and HMDSO-treated wood surfaces with SEM (magnification up to × 5000) did not reveal any differences between the surface structure of the treated and untreated wood. No signs of the plasma polymer covering the surfaces were detected. On the other hand, fragments of wood cells resulting from the sanding procedure were seen all over on the wood surfaces making the detection of the coating difficult. However, with some effort it was possible to find and image larger undamaged areas (like cell wall surfaces of vessels) on the surfaces. These SEM images indicated that either the coverage of the treated wood by the plasma polymer is incomplete or the features of the coating were not detected with this magnification.

Contrary to the SEM imaging, the EDS analyses of the same treated and untreated wood specimens showed a clear evidence of the plasma polymer present on the treated surfaces. The EDS spectra for the Si-analyses are presented in Fig. 6. The concentration of Si on the wood surfaces increases with the treatment time.

3.4. Results of AFM microscopy

3.4.1. Oxygen plasma treatment of polypropylene

Fig. 7a presents a 3-D AFM image of the control sample of polypropylene. The surface is filled with small details and the structure is spherulitic. No such structure
Table 4
Adhesion of PP film to birch veneer treated in HMDSO plasma for different treatment times

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Bonding strength (MN m⁻²) Mean</th>
<th>Std. deviation</th>
<th>Wood failure (%) Mean</th>
<th>Std. deviation</th>
<th>Failure between PP and wood (%) Mean</th>
<th>Std. deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated wood surface + PP film</td>
<td>9.7</td>
<td>1.5</td>
<td>53</td>
<td>20</td>
<td>47</td>
<td>20</td>
</tr>
<tr>
<td>Wood treated for 2 min with HMDSO + PP</td>
<td>9.1</td>
<td>1.9</td>
<td>74</td>
<td>9</td>
<td>26</td>
<td>9</td>
</tr>
<tr>
<td>Wood treated for 5 min with HMDSO + PP</td>
<td>11.8</td>
<td>2.3</td>
<td>58</td>
<td>20</td>
<td>42</td>
<td>20</td>
</tr>
<tr>
<td>Wood treated for 8 min with HMDSO + PP</td>
<td>7.9</td>
<td>1.7</td>
<td>70</td>
<td>12</td>
<td>30</td>
<td>12</td>
</tr>
</tbody>
</table>

Fig. 6. Comparison of EDS spectra of birch treated with HMDSO plasma for different times.

is visible in the oxygen plasma modified sample that has been treated applying a RF power of 60 W for 15 s shown in Fig. 7b. The surface of the treated polypropylene is, instead, slightly dented but otherwise nearly smooth and completely covered with small spherical nodules. After oxygen plasma treatment of 45 s with the same power, a small increase in the size of the nodules is noticed as can be seen in Fig. 7c. The amount of dents has decreased. The 2-D images of the polypropylene surfaces treated for 30 s presented in Fig. 8a and for 45 s in Fig. 8b using the RF power of 60 W show only minor differences.

Polypropylene surfaces that have been treated with oxygen plasma using different exposure times and applying a RF power of 100 W are shown in Fig. 9. The surface treated for 30 is slightly dented but otherwise smooth as can be seen in Fig. 9a. After a treatment of 45 s there are less of these shallow dents and the nodule size has increased as shown in Fig. 9b. The polypropylene surface is completely smoothened, the dents have vanished and the size of the nodules has increased when the surface has been treated for 75 as can be seen in Fig. 9c. The polypropylene surface treated with oxygen plasma for 90 s shown in Fig. 9d looks much the same as the previous sample treated for 75 s. It must be recognized, that the smoothening taking place as the treatment time increases is valid only beneath 2 µm × 2 µm areas. On larger scale images (not shown here) unevenness is still visible. There is no notable difference between the surfaces treated with RF power of 60 W compared to that of 100 W as can be observed from the comparison of
Fig. 7. AFM image of (a) untreated PP showing spherulitic structure, (b) PP surface treated in oxygen plasma for 15 s using RF power of 60 W presenting nodular nanostructure and slightly dented microstructure and (c) PP treated in oxygen plasma for 45 s showing smoothening of the surface compared to the untreated PP.

Fig. 8. Effect of treatment time (a) 30 s and (b) 45 s on the surface morphology of PP when RF power of 60 W has been used (2 µm × 2 µm)
The growth of the nodule size as the treatment time increases can clearly be noticed from the 3-D images of the 30 s (100 W) sample in Fig. 10a and of the 75 s (100 W) sample in Fig. 10b. The polypropylene surface treated with plasma for 75 s is covered with nodules which are about twice in size compared to the other one treated for 30 s.

3.5. Plasma polymerization of HMDSO on lignocellulosics

3.5.1. Kraft pulp

A typical large scale image (20 µm × 20 µm) of untreated kraft pulp is presented in Fig. 11a. The surface is folded and smooth areas situate between these folds. The surface of corresponding kraft pulp coated by plasma polymerization shows no distinctive difference from the control one on this scale as can be seen from Fig. 11b.
When the comparison is done on 5 micrometer level or less, it can be noticed that no special features are visible on the folded untreated surface shown in Fig. 12a, instead, a thin layer seems to cover the kraft pulp surface that has been coated by plasma polymerization as can be seen in Fig. 12b. It seems as if the layers would be running over the edges of the folds. A closer look at the nanometer scale reveals a distinct difference between the two surfaces. The untreated surface consisting of small irregular fine structure is shown in Fig. 12c and the roundish particles forming a layer on the treated surface are presented in Fig. 12d. The preceding image has been taken from the area 1 shown in Fig. 12b. A thinner layer formed on the nanofibrillar structure is shown in Fig. 13. This image has been taken from area 2 shown in Fig. 12b. The fibrillar structure is partly visible at the lower right corner of the figure and the roundish particles covering the surface at the upper left.
Fig. 11. AFM image of (a) kraft pulp without treatment and (b) treated in HMDSO plasma for 8 min showing no clear differences in morphology at micrometer level.

Fig. 12. At 5 micrometer level differences between (a) untreated and (b) HMDSO treated (8 min) kraft pulp can be observed. A closer look at the surfaces reveals (c) irregular structure on the untreated and (d) nodules on the treated surface.
corner. In larger images these layers often seem as obscure layers on the surface.

3.5.2. Filter paper

An AFM image of untreated filter paper surface is shown in Fig. 14a and filter paper coated by plasma polymerization in Fig. 14b presenting the same kind of areas. The fibrillar structure with incidentally crossing nanofibrils is visible in both images, only the width of the fibrils vary naturally. It is hard to find any distinct differences on this scale. Not until a closer look at the fibril surfaces is done, a distinction can be made between these two surfaces. The fibril surfaces of the untreated filter paper seem bare, smooth and structureless as can be seen in Fig. 15a. The surfaces of the fibrils in the filter paper coated by plasma polymerization shown in Fig. 15b are not smooth, instead they are covered with something forming a nodular structure on the surface.

3.5.3. Wood

AFM imaging of a wood surface was more difficult than imaging of the kraft pulp and filter paper surfaces. As the surface of the birch slice had been polished, the fundamental structure of the wood surface had been “destroyed” in a way. The surface of the control sample was uneven with no special structure. On some regions, slight difference were observed between the wood surface covered by plasma polymerization, shown in Fig. 16a, compared to the control sample. The HMDSO-treated wood surface is covered with some amorphous layer having small pinholes. One of these pinholes is shown with an arrow. The enlargement of the same area in Fig. 16b shows these holes more clearly. This kind of structures are not typical unmodified wood and were not found on the control samples. On flat areas nodular coverage similar to kraft pulp and filter paper was found as can be seen in Fig. 17.

4. Discussion

The results of AFM microscopy showed that a slight change in the morphology of polypropylene surface takes place when oxygen plasma treatment even as short as 15 s is applied. The morphological changes of polypropylene surface appear as a nodular structure which is an indication of a deposition of some substance on the film while exposed to plasma. The two power levels studied (60 and 100 W) did not show any difference in terms of
Fig. 15. At the fibrillar level differences between (a) untreated and (b) HMDSO-treated (8 min) filter paper can be observed. The lumpy structure covering the treated fibril surface is not seen on the untreated surface.

Fig. 16. AFM image of wood surface coated by plasma polymerization with HMDSO. (a) On larger scale an amorphous layer on top of the wood surface can be clearly seen. (b) An enlargement of this area shows pinhole-like features.

morphological changes, i.e. the size of the nodules for the same treatment lengths were of the same order of magnitude regardless of the power used. The results of the water contact angle measurements were in good agreement with the AFM measurement in that sense that the first signs of the effect of plasma are seen already after 15 s of treatment. The authors [8] among other researchers [14] have shown that the nodules are formed by deposition of low molecular weight compounds on the surface. The contact angle measurements show that the substance covering the treated PP is hydrophilic, different from the hydrophobic bulk of polypropylene. The change in wettability of PP due to oxygen plasma is expected, since polar groups are introduced to the surface during the treatment [11, 13, 16]. The increase in the polar nature of the polypropylene surfaces due to plasma is clearly proved by the Fowkes plot calculations which show that the polar component of the surface free energy for PP increases in the treatments from almost negligible to the level of contributing 2/5 of the total surface energy. The findings of our adhesion studies [8] show that the highest adhesion values for the interaction between polypropylene and wood are observed when short treatment times are used. Therefore, it can be assumed that at the treatment level of around 15 s (100 W or 60 W, 200 mTorr) the chemical changes due to plasma are already favorable and sufficient enough to increase the compatibility of PP with lignocellulosics.
Indirect additional indication of the changes in the composition of the surface layer with treatment time was
given by the AFM microscopy. The morphology studies showed that the texture of the surface layer on PP was
first (short treatment) soft based on the fact that the silicon tip got easily contaminated by the substance on
the surface leading to modification of the surface layer. In addition, it was observed that the PP surfaces
of the longer treatment times were easier to approach with the silicon tip causing no damages to the surface,
which makes us believe that the surface of PP became more rigid with a prolonged treatment. It is not excluded
that the stiffening of the surface layer with the treatment time is due to cross-linking reactions on the surface.
The results of the higher adhesion values between PP and wood in the case of the short exposures rather than of the
longer ones, could be explained to partly derived from better interdiffusion properties of a soft matter with an
other leading to enhanced adhesion. In this connection, thickness of the interface may also play an important
role; in other words, when the thickness of an interface increases, the internal stresses within the interface be-
come more prominent giving a major contribution to the failure of adhesion. Similar results in terms of decreased
mobility of the fluorinated ethylene propylene (FEP) surface when treated with oxygen plasma was observed
by Gengenbach [16] and explained to be due to cross-linking.

In the second approach to use plasma modification to improve compatibility and adhesion properties between
polypropylene and lignocellulosics, attention was focused on treating the lignocellulosic materials with
hexamethyldisiloxane (HMDSO) plasma and using the hydrophobically modified surface as substrate for poly-
propylene film. The HMDSO monomer introduced on the substrates under plasma conditions is known to re-
sult in plasma polymerization. The contact angle measurements on HMDSO-treated filter paper, kraft
pulp and wood clearly showed that a highly hydrophobic layer was formed on the surfaces during the treatments.
However, the treatment time should exceed 2 min (using the relevant plasma conditions) in order to achieve a sur-
face with increased hydrophobicity. No visible difference in the appearance of the untreated and treated surfaces
was observed, since HMDSO plasma treatments of 2, 5 and 8 min did not form a film (visible with the naked
eye) in its strict sense on the lignocellulosics. However, a slight discoloration of the treated materials (assumingly
due to the effect of UV-light during the treatment) was observed after the treatment of 5 and 8 min. Clear signs
(pinholes in the substance covering the surface) of deposition of HMDSO polymer were seen by means of AFM
analyses, when the surfaces were treated for 8 min. In general, the HMDSO layer on the lignocellulosics are
extremely thin and it seems to follow so closely the features of the substrate surface that no real film forma-
tion on a micrometer scale using either AFM or SEM is detected. However, a closer look (on nanometer scale) at
the kraft pulp and filter paper surfaces reveals that the fibrils are covered by a material of lumpy structure. This
observation is supported by some other studies on different plasma polymers [19, 21, 32] in which it has been
reported that formation of the polymers occur in a manner corresponding our findings.

The results of the EDS analyses agree well with the contact angle measurement and AFM studies, showing
that the concentration of Si and herefore the quantity of the plasma polymer was considerable higher at the treat-
ment levels of 5 and 8 min than after 2 min of exposure to HMDSO. Based on these results, it can be assumed that
the improvement in adhesion, if at all, takes place with a pre-treatment of 5 min or longer. The pressing condi-
tions were such that even the adhesion and wood failure values for PP on untreated wood were relatively high,
9.7 MN m$^{-2}$ and 53%, respectively. However, a slight increase, although not statistically significant, in these
values (11.8 MN m$^{-2}$ and 58%) was seen, when the wood was treated for 5 min in HMDSO plasma. Consequently,
it can be concluded that HMDSO treatment is not bene-
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treatment time, the easier it was to image the PP surfaces without contamination of AFM tips. This phenomenon might be related to changes in the chemical composition making the surface layer more rigid in the course of time and hence easier to monitor with AFM. Considerable increase in the surface free energy of PP and birch is observed due to the oxygen plasma. This change takes place at very short treatment times. Thus, the preconditions for improvement of adhesion should already exist at the low treatment time levels.

Treatment of lignocellulosics for 5 min or more with HMDSO plasma changes the surface of the material highly hydrophobic. The polymer layer formed is extremely thin and follows closely the features of the substrate. The hydrophobic pre-treatment of wood surface with HMDSO plasma polymer was not beneficial for adhesion between wood and polypropylene film. Although the HMDSO plasma treatment can not be used as a pre-treatment and as an adhesion promoter between PP and lignocellulosics, it may have some prospects as a water barrier in applications in which the material is not exposed to abrasion.

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References

[28] Digital Instruments, Inc.