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Hexamethyldisiloxane-Plasma Coating of Wood Surfaces for Creating Water Repellent Characteristics

By Agnes R. Denes, Mandla A. Tshabalala, Roger Rowell, Ferencz Denes, and Raymond A. Young

Department of Forest Ecology and Management and Engineering Research Center for Plasma-Aided Manufacturing, University of Wisconsin-Madison, U.S.A.

Keywords

Cold plasma
Surface modification
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Surface chemistry

Summary

Southern yellow pine wood surfaces were modified under cold plasma conditions in order to create water repellent characteristics. The surface chemistry of the plasma "polymerized" hexamethyldisiloxane (PHMDSO) deposited onto wood surfaces was investigated using Electron Spectroscopy for Chemical Analysis (ESCA) and Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR). The presence of a crosslinked macromolecular structure, based on Si-O-Si and Si-O-C linkages was detected. Pyrolysis Mass Spectroscopy (MS) was carried out to investigate the nature of the building blocks of the plasma generated macromolecular structure. Plasma modified samples exhibited very high water contact angle values (contact angle = 130 degrees) in comparison to the unmodified samples (contact angle ≤ 15 degrees), indicating the presence of a hydrophobic surface. Atomic Force Microscopy (AFM) images, collected both from unmodified and HMDSO-plasma modified samples, indicate the progressive growth of the plasma "polymer", resulting in the deposition of a smooth layer at 10 minutes treatment time. Differential Thermal Analysis (DTA) indicated high thermal stability of the PHMDSO

Introduction

The plasma state, recognized as the fourth state of matter, is broadly defined as a gaseous environment composed of charged and neutral species with a net zero electric charge. This manifestation of matter can be generated by increasing the energy content of atoms and molecules regardless the nature of the energy source. Consequently plasma can be created by involving caloric, radiant, or mechanical energy sources. Plasma states can be divided in two main categories according to their intrinsic energy content: hot plasmas (or near-equilibrium plasmas) and cold plasmas (nonequilibrium plasmas) often called silent discharges or glow discharges. Hot plasmas are characterized by near thermodynamic equilibrium and very high degrees of ionization, and are composed of neutral and charged molecular and atomic species, and electrons having extremely high energies (e.g., electric arcs, rocket jets, plasmas generated by nuclear reactions). Actually, it is estimated that more than 90% of the known Universe exists under the plasma state. All active celestial bodies are hot plasma environments. Cold plasmas are composed of low energy atomic and molecular charged and neutral species and of energetic electrons. However, due to the low caloric capacity of the electrons the energy is not distributed to the reactor walls and consequently, these plasmas operate at reactor temperatures comparable to room temperature. These plasmas are also characterized by very low degrees of ionization. Consequently, these plasmas are suitable for the modification of organic substrates.

Besides natural plasmas like the ionosphere, lightning, the rarefied interplanetary-space-plasma, man-made plasmas can be initiated by increasing the energy content of a gaseous system. Plasmas are loosing energy toward the walls which confine them by collision and radiation, and consequently energy must be supplied in a continuous manner to sustain the plasma state. The easiest way to meet this requirement is by using electrical energy; and this is the reason why the most common plasmas are electrical discharges.

An electrical discharge (e.g. cold plasma) is initiated when omnipresent free electrons (due to cosmic radiation) of a low-pressure gaseous environment are accelerated to kinetic energy levels capable of inducing ionization and fragmentation processes. The newly resulted electrons will also be accelerated leading to further elastic and inelastic collisions and to the generation of the plasma state.

It is noteworthy that the energy levels of the cold plasma species (1-10eV, predominantly 0.5-3eV) are comparable to the chemical bond energies, and consequently this state represents a novel and very significant way for modifying the structure of volatile organic and inorganic matter. The plasma species can also interact with solid-phase substances generating chemical and morphological changes in the very top layers of the plasma-exposed substrates. These features make electrical discharges an excellent tool for generating unconventional reaction mechanisms.

Silicon-based monomers have been widely used (Wrobel and Wertheimer 1990; Cai *et al.* 1992) in low pressure discharge processes for deposition onto various substrate surfaces. These plasma "polymers" impart specific surface characteristics such as hydrophobicity, reduced gas permeability, and hard transparent coatings. It has been shown that

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the chemical composition and surface properties of the plasma "polymer" films strongly depend on the plasma gas composition (e.g. oxygen/monomer ratio). substrate temperature (Favia *et al.* 1994), external plasma parameters like power dissipated to the electrodes, pressure in the reactor chamber, and flow rate of the monomer (Vasile and Smolinsky 1972).

Hexamethyldisiloxane (HMDSO) has been proven to be a very good precursor for the deposition of plasma-generated macromolecular layers (Wrobel and Wertheimer 1990). During plasma processes the monomer molecules undergo selective chemical bond breaking and recombination processes to form macromolecules. The new structures, consisting of Si-C and Si-O-Si functionalities, are found to be chemically inert and crosslinked in nature (Tajima and Yamamoto 1985). Coatings obtained from HMDSO plasmas demonstrated reduced moisture (Sacher *et al.* 1984) and oxygen (Agres *et al.* 1996) permeability, both of which are related to the density and structure of the plasma "polymer" films.

Lignocellulosics are three-dimensional polymeric composites made up primarily of cellulose, hemicelluloses, and lignin. The most abundant functional group on the polymeric components of lignocellulosics is the hydroxyl group, followed by other oxygen containing functionalities that attract water through hydrogen bonding (Rowell 1984). Due to the presence of hydroxyl and other polar groups, lignocellulosic materials have a very high affinity for water. These characteristics can cause several disadvantages like: weathering degradation, biological degradation, or swelling.

Considerable work has been done in the past years to create water repellent lignocellulosic substrates (Kiguchi 1996). However, the introduction of specific groups onto lignocellulosics substrate surfaces (e.g. fibers, powder, wood wafers) has been generally achieved using liquid phase reagents. Due to the porous character and to the swelling of the cell wall, usually excess reagent is required. In addition, the use of corrosive or toxic chemicals and the requirements for the post-treatment removal of the un-reacted compounds add extra time and cost to the procedures.

Some detrimental effects that accompany wet chemical reactions can be eliminated by using cold plasma techniques. Plasma induced surface modifications are dry processes, and are confined only to the outermost layer of the surface. Plasma reactions are fairly intense, and it was demonstrated (Sarmadi *et al.* 1996) that even short treatment times (30-60sec exposure to plasma) are enough for achieving efficient surface modification.

Strong interaction of wood with water can result in undesired dimensional instability and accelerated biodegradation processes. Reduced water penetration into wood surfaces by deposition, for instance, of PHMDSO has already been reported (Cho and Sjoblom 1990), and organosilicon films deposited on paper surfaces were also examined (Sapieha *et al.* 1989).

The following work extends the knowledge in the area of the modification of wood surfaces under hexamethyldisiloxane cold plasma conditions for creating water repellent characteristics. A detailed investigation of the plasma-induced surface chemistry and the newly developed properties of HMDSO-plasma coated yellow pine is presented.

Experimental

Materials and Methods

Southern yellow pine wood wafers (5cm x 1.5cm x 0.1 cm) were obtained from the USDA-Forest Products Laboratory in Madison, WI. High purity (ACS grade) toluene, ethanol, and hexamethyldisiloxane were purchased from Aldrich Chemical Co.

Subjected to an electrical discharge, the extractives present in wood might migrate to the surface of the samples, leading to undesired surface chemical composition. Consequently, toluene/ethanol solvents were used to remove extractives from the surfaces of lignocellulosics. Samples were Soxhlet extracted in toluene/ethanol (2/1 v/v) solvent for 8 hours. The solvent mixture was selected to remove both polar and non-polar constituents. Soxhlet extracted samples were stored under vacuum oven conditions until reactions were initiated.

Plasma reactions were carried out in a stainless steel, parallel plate, cold plasma reactor described in detail elsewhere (Sarmadi *et al.* 1996). The schematic diagram of the reactor is presented in Figure 1. In order to remove contaminants from previous experiments, the reactor was cleaned using an oxygen discharge (300 W, 200 mTorr, and 20 minutes). Wood samples were subjected to HMDSO-plasma modification under the external plasma parameters presented in Table 1. Aluminum foil was also used as substrates for PHMDSO depositions.

Electron Spectroscopy for Chemical Analysis (ESCA) was performed on a Perkin Elmer Physical Electronics 5400 Small Area Spectrometer (Experimental conditions: source: Mg, 15 keV, take-off angle: 45 degrees; acquisition cycles: 3). Survey and High Resolution ESCA was used to evaluate the relative surface composition of unmodified and plasma modified samples and to estimate the presence of non-equivalent carbon functionalities.

Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectroscopy measurements from unmodified and HMDSO-plasma coated wood surfaces were carried out using an ATI-Mattson Research Series instrument, provided with a GRASEBY SPECIAL Benchmark Series ATR in-compartment P/N 11160 unit. All the IR evaluations were performed under nitrogen atmosphere. Data were collected from $400cm^{-1}$ – $4000cm^{-1}$ wavelength range with 256 scans for each sample.

Water contact angle measurements were performed using a Rame Hart, Inc. contact angle goniometer Model 100-00 (Experimental conditions: deionized water; 0.1 µl water drop).

Differential thermal analysis (DTA; TG) was employed to evaluate the thermal properties of PHMDSO. "Polymer" samples were carefully removed from the reactor wall and investigated by DTA-TG technique under nitrogen atmosphere. A TG-DTA Seiko apparatus was used for the measurements (Experimental conditions: gas environment of the sample: nitrogen; sample amount: 1.723mg fine powder; reference: 16mg Al pan; temperature range: 25–600°C; heating rate: 5°C/minute; flow rate nitrogen: 100ml/minute).

The Pyrolysis Mass Spectroscopy of PHMDSO was carried out using an HR-MS, Kratos MSX80 double focusing mass spectrometer provided with electrostatic analyzer and magnet (Experimental conditions: solid probe introduction system; electron energy: 50eV; pyrolysis temperatures: 100, 200, 300, and 400°C).

Atomic Force Microscopy studies were used to analyze surface topographies employing a Digital Instrument Nanoscopy III AFM (Experimental conditions: scan size = 1 μm^2; sampling number = 512; scan rate = 1.969 Hz).

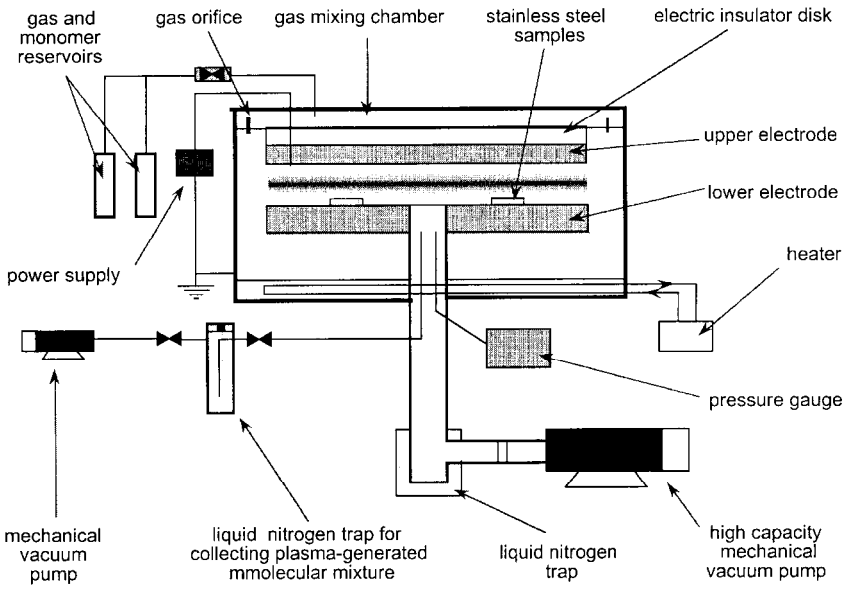


Fig. 1. Schematic of capacitively-coupled cold plasma reactor

Results and Discussions

Plasma treatment of wood

As shown in Table 1, the pine wafers were treated with HMDSO plasma at two power levels (150 and 250W) and three treatment times (1, 5, and 10 minutes). The surfaces of the samples were than characterized as described below.

Table 1. External plasma parameters

Pressure in the reactor chamber	50 mTorr
Power dissipated to the electrodes	150 and 250W
Pressure in the reaction chamber in the absence of plasma	300mTorr
Flow rate of monomer	5.5 sccm (oxygen units)
Plasma treatment time	1, 5, and 10 minutes

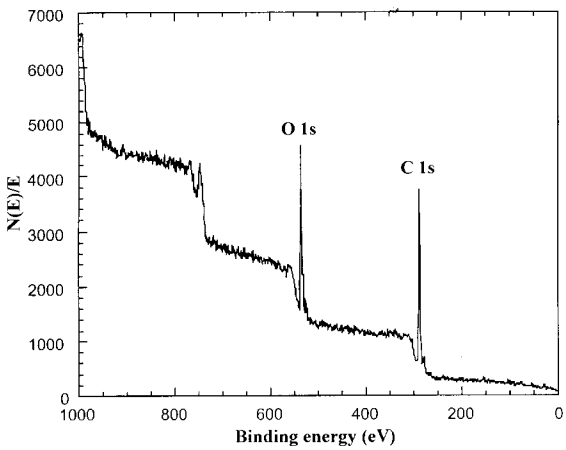


Fig. 2. Survey ESCA spectrum of unextracted wood

Electron spectroscopy for chemical analysis

The ESCA survey spectrum of the un-extracted southern yellow pine wood is presented in Figure 2. Toluene/ethanol solvent extracted wood surfaces exhibit identical binding energy peaks, however, owing to the extraction, the relative surface atomic composition had a lower carbon content in this case (Table 2). This can be attributed to the removal of

Table 2. Relative surface atomic composition of unextracted and toluene/ethanol extracted wood wafers

Sample	C 1s (%)	O 1s (%)
Unextracted wood	71.8	28.8
Extracted wood	63.7	36.2

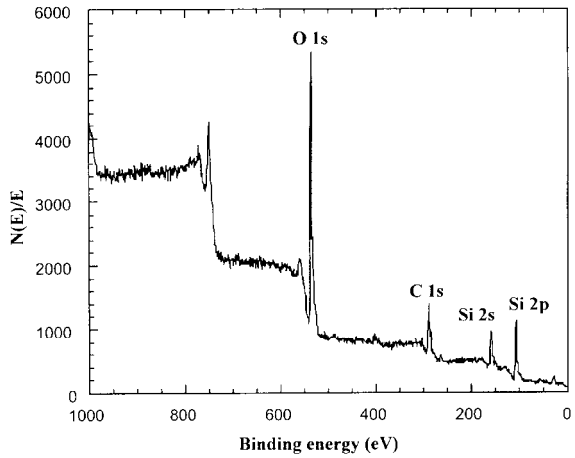


Fig. 3. Survey ESCA spectrum of HMDSO-plasma modified wood.

Table 3. Binding energy assignements for the C1s peak

C1	C2	C3	C4	C5	C6
C-C; C-H 285.0eV	C-O; C-O-C 286.2–286.6eV	HO-C = O 289.2eV	O-CO-O 290.6eV	C-Si;C=C 284.7eV	$MgK_{3,4}$ 282.4

extractives (e.g. fatty acids, resins) incorporated into the wood structure. The apparent higher oxygen content of extracted samples can also be explained by the diminished carbon concentration.

The survey ESCA spectrum of extracted wood surfaces coated with PHMDSO is presented in Figure 3. The presence of Si2s and Si2p peaks – in addition to the C1s and O1s peaks – indicate the presence of silicon atom-based functionalities on the wood surfaces. The relative dependence of surface atomic composition on the plasma treatment time is presented in Figure 4. It can be seen that HMDSO-plasma exposures as short as 1 minute are adequate to reach elevated silicon atom concentrations. Longer treatment periods did not significantly influence the relative atomic composition values due to the gradual deposition of fairly thick PHMDSO layers within the first minute of plasma treatment.

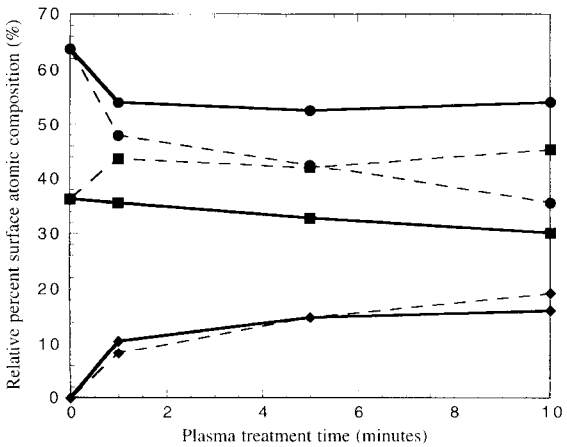


Fig. 4. Influence of plasma treatment time on the relative surface atomic composition of southern yellow pine wood surfaces (solid lines – 150 W, dashed lines – 250 W, circles – C 1s, squares – O 1s, diamonds – Si 2p).

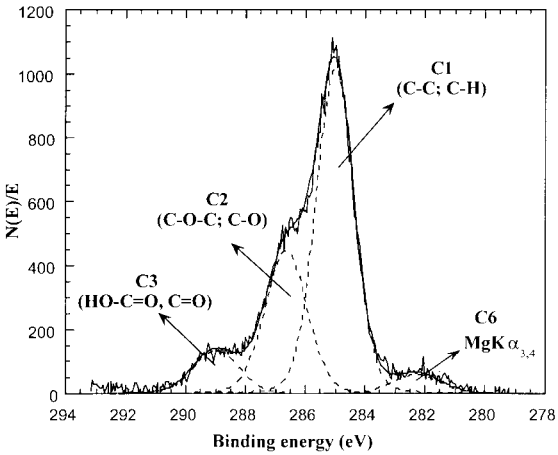


Fig. 5. High resolution C1s ESCA spectrum of unextracted wood.

High Resolution ESCA permits the identification of non-equivalent carbon functionalities located in the surface layers. All binding energy assignments for the C1s peaks were made using the SCIENTA 300 ESCA database (Bramson and Briggs 1992), and are presented in Table 3. The high resolution C1s spectrum of un-extracted and toluene/ethanol-extracted wood are shown in Figures 5 and 6. It can be observed that the ESCA diagram of virgin wood is characterized by a tetramodal pattern. Besides the dominant 285eV binding energy value C1 (C-C, C-H) peak related to the presence of resins- and lignin-based components, the existence of C2 (C-O-C, C-O) and C3 (HO-C = O) peaks can also be observed. It should be mentioned that these linkages are present in the major components of

Table 4. Relative percent peak areas of non-equivalent carbon functionalities of unmodified and plasma coated samples

Sample	C1(%) C-C C-H	C2(5) C-O C-O-C	C3(%) O-C=O C=O	C4(%) OCOO	C5(%) C-Si
Unextracted	58.2	28.1	9.2	0	0
Extracted	33.4	44.3	11.3	0	0
PHMDSO on Al foil 250W, 10 minutes	0	21.1	16.2	6.2	54.0
PHMDSO on wood 150W, 10 minutes	0	11.0	2.6	0	83.48
PHMDSO on wood 250W, 10 minutes	0	47.8	16.0	5.87	10.60

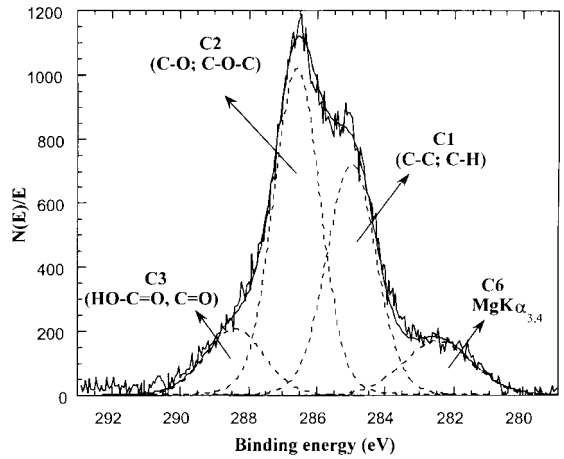


Fig. 6. High resolution C1s ESCA spectrum of toluene/ethanol extracted wood.

wood (cellulose, hemicelluloses, lignin, and extractives). One also can notice the existence of a C6 binding energy peak, a source contribution from Mg K α3,4 radiation. The high resolution peak areas (Table 4) of specific binding energy values reflect the relative surface concentrations of specific chemical linkages. The extraction of wood samples had a significant influence on the relative ratios of corresponding peak areas. The C1 peak (Fig. 6) does not have the largest area any more, and the C2 contribution dominates the pattern. This indicates that hydrocarbon-type derivatives have been partially removed from the surfaces of the substrates as a result of the extraction procedure.

The non-equivalent C1s linkages of HMDSO-plasma generated macromolecular structure, deposited on an aluminum substrate, are shown in Figure 7. The successful deposition of macromolecular layers is evidentiated by the presence of a dominant C5 (C-Si) peak. The presence of C2 (C-O, C-O-C), C3 (C = O and COOH), and even carbonate C4 (O-CO-O) groups can be identified in the structure of PHMDSO. These data allow us to suggest the presence of a plasma induced fragmentation and that the macromolecular structures exposed to open environment conditions probably undergo further oxidation reactions. The absence of a Cl peak (C-C and C-H) can also be explained by post plasma oxidation reactions with the involvement of carbon-based and plasma created free radical sites.

The structure of PHMDSO deposited on extracted wood surfaces at relatively low RF-power value is fairly similar to that deposited on an aluminum substrate (Fig. 8). However, a more intense 283.5–285.5eV broad binding energy peak is present in the high resolution ESCA diagram of the wood substrate-based deposition. This might be explained by the fact that the extracted wood surfaces still contain hydrocarbon-type structures (C-C, 285eV) and due to the low thickness of plasma-deposited layers the ESCA diagram can also include functionalities of the wood surface in addition those of PHMDSO structures.

Higher RF-power values result in a dramatic change of the relative C1s peak areas of the spectrum of PHMDSO-coated wood surface (Fig. 9). The existence of a substantially reduced C-C and Si-C binding energy area (284.7–285eV) can be observed relative to the C-O-C (C2, 286.6eV) contribution, It can be suggested that a higher RF-power values a more intense and probably more complex fragmentation/etching mechanism control the formation of PHMDSO. These networks will certainly have a higher affinity for post-plasma oxidation mechanisms. The significantly diminished Si-C and C-C areas should also be explained by the formation of Si-O and C-O linkages.

It is noteworthy that acetone-extracted and PHMDSO coated wood substrates present identical ESCA patterns in comparison to the un-extracted and PHMDSO coated samples. This allow us to suggest the presence of a cross-linked-macromolecular network and the fact that the macromolecular structures might be chemically linked to the wood surface. Literature data (d'Agostino 1990) clearly indicate that the plasma induced free-radical sites from various substrate surfaces can mediate grafting mechanisms by involving gas phase plasma species.

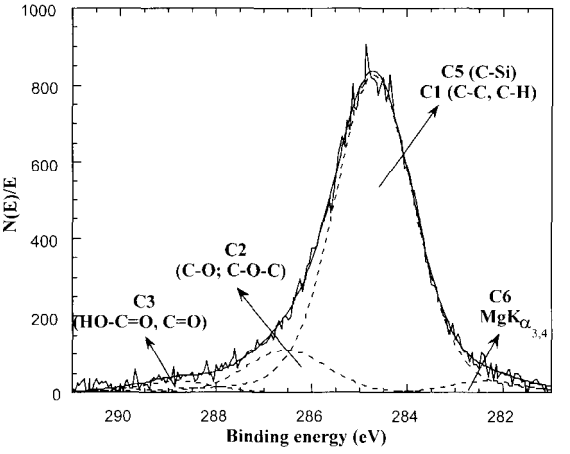


Fig. 8. High Resolution C1s ESCA spectrum of PHMDSO coated wood (150W, 10 minutes).

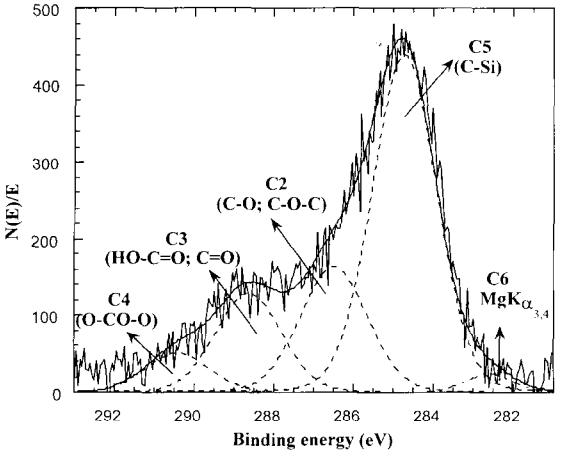


Fig. 7. High Resolution C1s ESCA spectrum of PHMDSO coated Al foil (250W, 10 minutes).

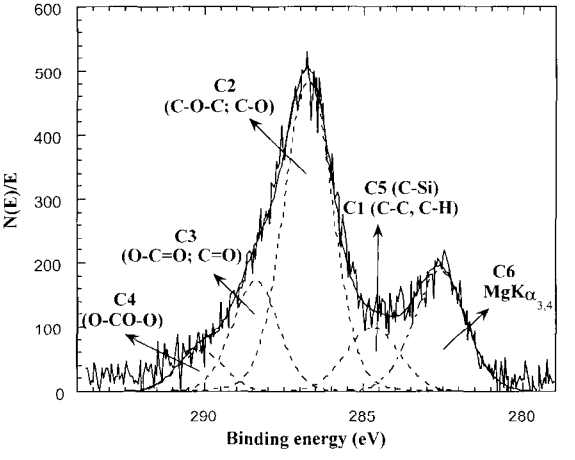


Fig. 9. High Resolution C1s ESCA spectrum of PHMDSO coated wood (250W, 10 minutes).

Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy analysis

Variable-angle multiple reflectance ATR-FTIR sampling depth is usually in the 10-20 µm micrometer range depending on the IR beam-angle, number of reflections and wavenumber (Urban 1996). Due to the thickness of plasma deposited films it is difficult to obtain information with conventional ATR-FTIR techniques. The ATR-FTIR data will reveal more about the layers located below the newly created surface than on the top surface structure. However. substracting the ATR-FTIR spectrum of the unmodified substrate from the spectra of the plasma-coated surfaces exposes details of the chemical structure of the discharge created layers.

Figure 10 shows the high resolution ATR-FTIR spectrum of extracted yellow pine and that of the PHMDSO coated yellow pine in the 600–1400cm^{-1} wavenumber region. Both diagrams indicate only the characteristic adsorptions related to the bonds in the cellulose and lignin: 1023 and 1058 cm^{-1} C-O stretching from the pyranosidic ring, C-OH antisymetric bending; 995cm^{-1} C-O and C-C, C-H bending or CH_2 (amorphous band) stretching; 727cm^{-2} OH out of plane bending; 1125 cm^{-1} C-O-C stretching. Even a close examination of the two diagrams do not reveal significant differences in the patterns of the spectra. Obviously, the data show structural information of the substrate due to the very thin nature of the deposition.

The difference spectrum, obtained from the substraction technique, clearly indicates the presence of a Si-O and Si-C based structures (Fig. 11). One can observe three major and very strong vibration regions identified as: 720-780cm^{-1} characteristic of $Si(CH_3)$- end groups; 800–850cm^{-1} peculiar for Si-CH3 and Si-$(CH_3)_2$- stretching vibration of the Si-C linkage, and 1100-1180cm^{-1} related to Si-O stretching vibrations (Bellamy 1966). The relatively high intensity of the 800–850cm^{-1} band zone indicates the presence of a cross-linked structure and that $Si(CH_3)_x$ ($_x$< 2) plasma-generated molecular fragments played a significant role in the formation of the surface deposited macromolecular structures.

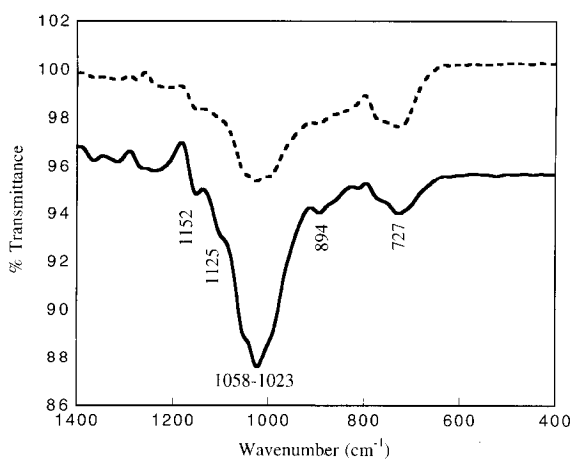


Fig. 10. ATR-FTIR spectra of toluene/ethanol extracted and 10 minutes HMDSO-plasma coated wood (400–1400cm^{-1}, solid line – extracted wood, dashed line – 10min HMDSO).

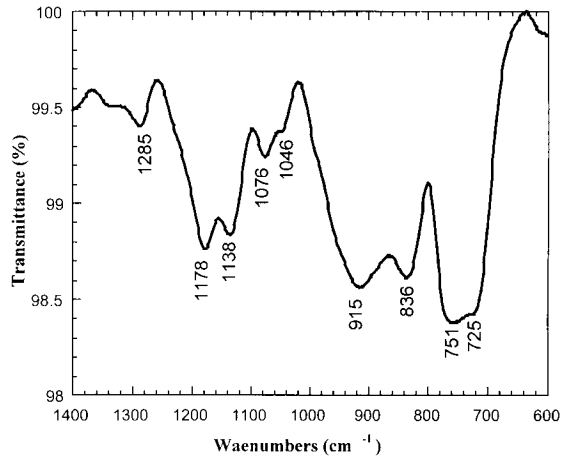


Fig. 11. Difference ATR-FTIR spectrum obtained by substracting the spectrum of the unmodified substrate from the spectrum of the plasma-coated surfaces.

Water contact angle estimations

Water contact angle estimations were performed both on the untreated and plasma modified samples. Extracted wood surfaces are highly hydrophilic in nature. Contact angle values of extracted wood surfaces are extremely low; water droplets instantly spread on the surface and are absorbed in the structure of the substrate, making it difficult to obtain an accurate reading of contact angle values. A value of 5 degrees was assigned for the toluene/ethanol extracted samples.

Wood samples treated under relatively low RF-power settings exhibit very high water contact angle values (Fig. 12), revealing the hydrophobic character of the HMDSO-plasma coating. Samples exposed to higher power settings (250W) exhibit relatively lower values for the contact angle. These observations are in good agreement with the results from ESCA and ATR-FTIR, leading to the conclusion that lower power settings lead to the formation of a

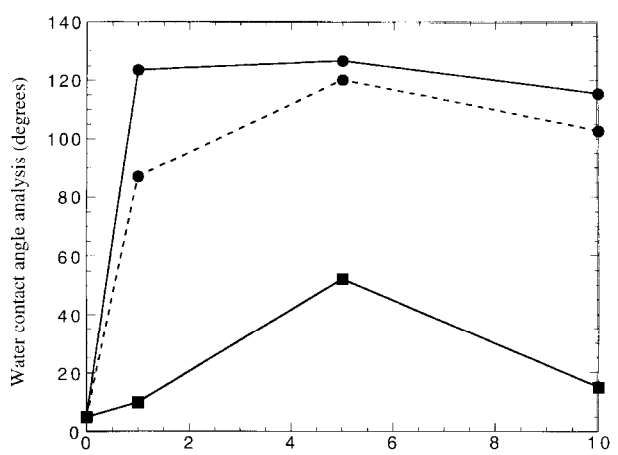


Fig. 12. Water contact angle of the extracted and PHMDSO coated wood surfaces (solid line – immediate measurement following plasma treatment, dashed line – measurement repeated after four months, circles – 150W, squares – 250W). Note: contact angle value of unextracted wood = 31.1 degrees.

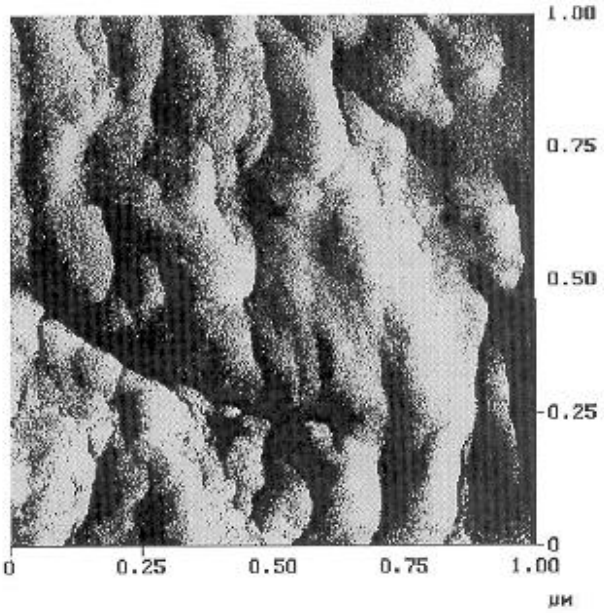


Fig. 13. AFM image of unmodified wood surface

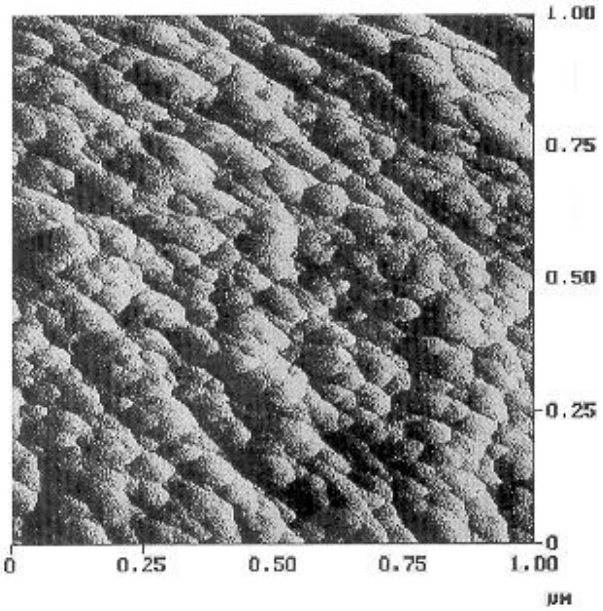


Fig. 1.5. AFM image of 5 minute plasma modified wood surface

hydrophobic film on the surface of the wood wafers; higher power result in more extensive oxidation processes, leading to the higher concentration in oxygen-based functionalities (e.g. Si-O based structures) on the surface.

Atomic force microscopy

Comparative surface morphology evaluation of untreated and HMDSO-plasma-coated wood samples were performed using Atomic Force Microscopy. It can be seen that the large structures in the topography of extracted wood samples (Fig. 13) are replaced by finer grain-type morphology even at plasma exposures as short as I minute (Fig. 14). It was also observed that short treatment times did not lead to the coverage of the entire surface. Five minutes exposure (Fig. 15) of the wood samples to the HMDSO-plasma environments also result in a grain-type very uniform coating, while longer plasma irradiation generates smooth substrate surfaces (Fig. 16). This surface deposition pattern with treatment time can be explained by simultaneous nucleation and progressive generation of PHMDSO on wood substrate surfaces at different location on the surface of the sample. The crosslinked nature of the deposited macromolecular structures and the presence of totally coated surfaces explain the hydrophobic nature of the plasma modified substrates.

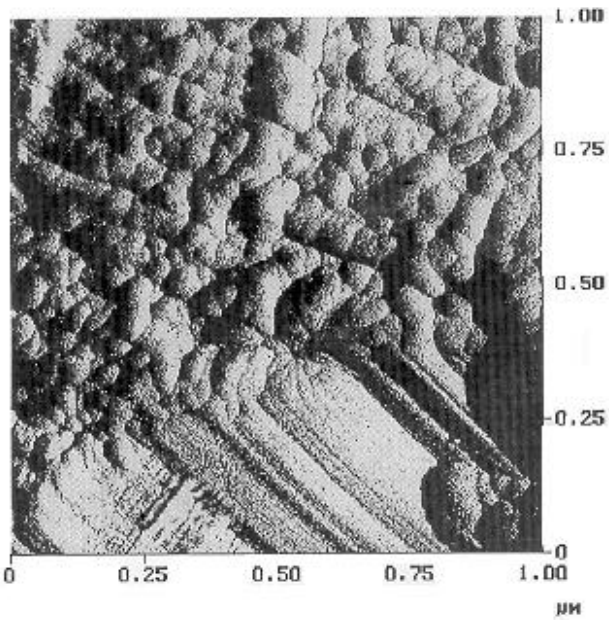


Fig. 14. AFM image of 1 minute plasma modified wood surface.

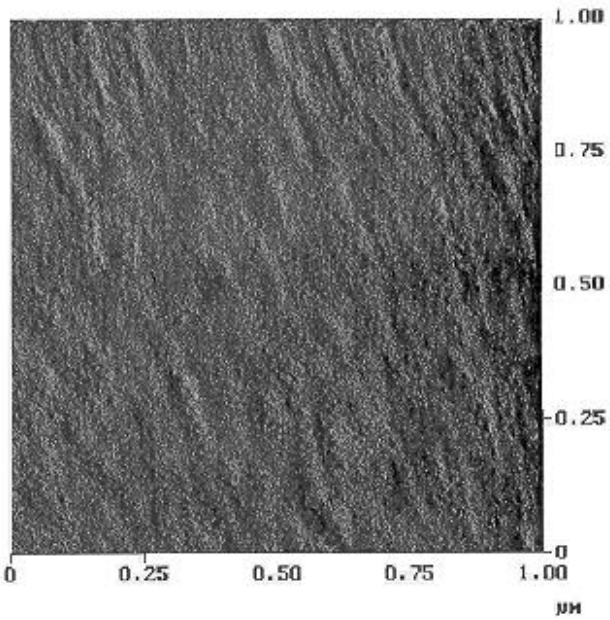


Fig. 16. AFM image of 10 minute plasma modified wood surface.

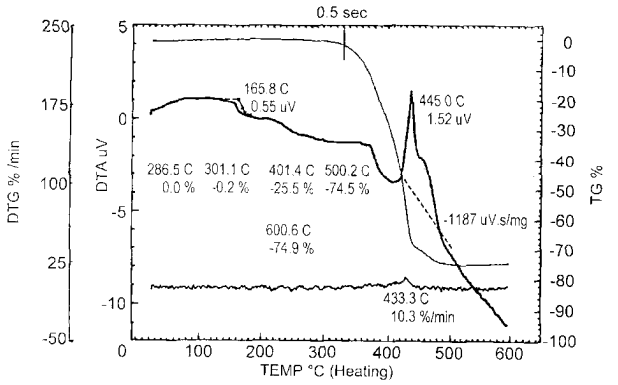


Fig. 17. DTA spectrum showing the thermal behavior of PHMDSO.

Differential thermal analysis

The thermal behavior of plasma-synthesized PHMDSO layers has been evaluated by DTA-TG investigations. It can be observed (Fig. 17) that the PHMDSO sample has a fairly high thermal stability; negligible weight loss can be noticed at temperatures as high as 300°C, and at 400°C 7.5 % of the sample is still retained. The DTA profile allows us to observe that a moderate exothermic effect characterized the first part of the process and this might be related to structural reorganization phenomena. The strong exothermic behavior in the 350-500°C region is generated by molecular fragmentation processes. This high thermal stability of the PHMDSO indicates the presence of a crosslinked structure.

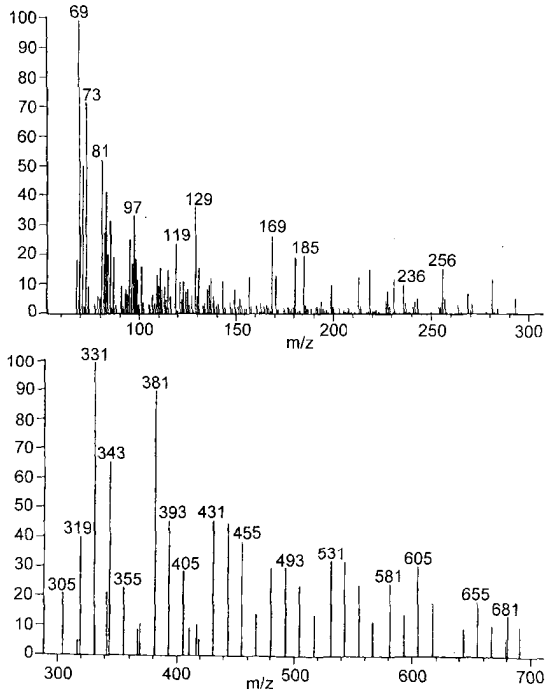


Fig. 18. High resolution MS-pyrolysis molecular fragment ion-pattern of PHMDSO films (100°C)

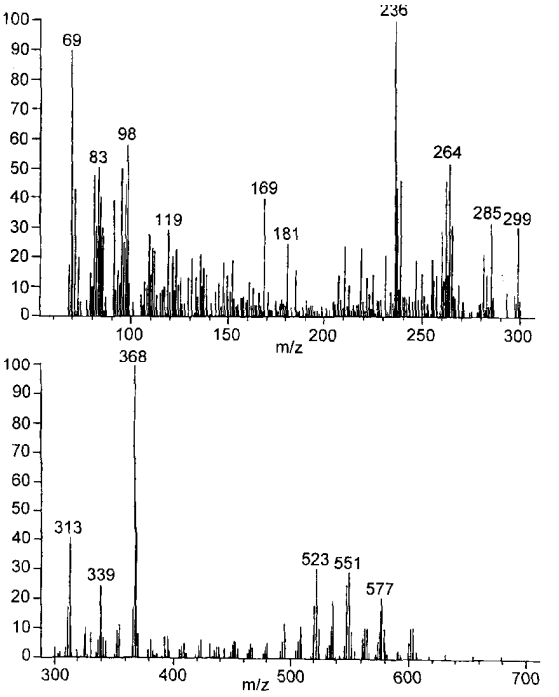
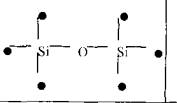
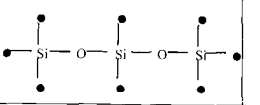
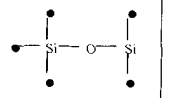
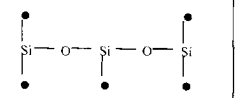
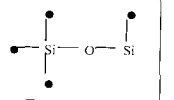
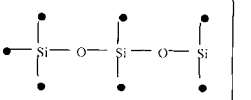
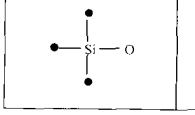
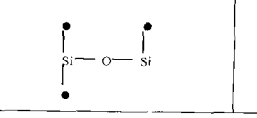
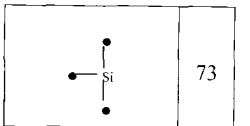
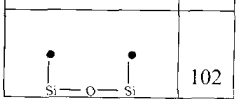


Fig. 19. High resolution MS-pyrolysis molecular fragment ion-pattern of PHMDSO films (400°C).

Mass spectroscopy

In order to obtain more information on the nature of the building blocks of the plasma generated macromolecular structure, MS pyrolysis analysis was performed on

Table 5. Molecular fragments resulting from pyrolysis MS of PHMDSO (the bullet stands for CH,)

Fragment	m/z	Fragment	m/z
	162		236
	147		185
	132		221
	89		117
	73		
	102		

PHMDSO deposited on Al substrates. Figures 18 and 19 exhibit some typical MS spectra of PHMDSO collected at 100 and 400°C. It can be noticed that. regardless of the pyrolysis temperature, almost identical low molecular weight ion-molecular structures can be identified (m/z = 83, 98, 111, 119, 185) which correspond to Si-, O-, and CH_x-based fragments (Table 5). It can also be observed that at higher temperatures higher molecular weight cationic species are released (m/z = 236, 264, 368 and also fragments of m/z = 523, 551, and 603). These findings and the cluster nature of the fragments (related to the corresponding multitude of dehydrogenated species) suggest the presence of a crosslinked macromolecular structure, which substantiates the earlier conclusion that the PHMDSO is a thermally stable, hydrophobic structure.

Conclusions

Hexamethyldisiloxane cold plasma treatment of southern yellow pine wood resulted in the deposition of a hydrophobic film (high contact angle values) on the surface. ESCA and ATR-FTIR analysis revealed the presence of a macromolecular structure, based on Si-C and Si-O-Si bonds. The fragmentation pattern of PHMDSO, obtained from pyrolysis MS analysis, indicate the highly crosslinked nature of the deposited film. It was demonstrated that short treatment times are enough for efficient surface modification. However, it was found that the power dissipated to the electrodes influences the plasma induced surface chemistry and the characteristics of the resulted layers. Higher power settings lead to more intense fragmentation processes of the monomer, resulting in the loss of Si-C bonds and hydrocarbon type structures and in the formation of polar functionalities.

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Agnes R. Denes
Raymond Young
University of Wisconsin-Madison
Department of Forest Ecology and Management
and Engineering Research
Center for Plasma-Aided Manufacturing
1630 Linden Drive
Madison. WI 53706
USA

Mandla A. Tshabalala
USDA, Forest Service
Forest Products Laboratory
One Gifford Pinchot Drive
Madison, WI 53705
USA

Roger Rowell
University of Wisconsin-Madison
Department of Forest Ecology and Management
Biological Systems Engineering
Engineering Research Center for Plasma-Aided Manufacturing
USDA Forest Service
Forest Products Laboratory
One Gifford Pinchot Drive
Madison, Wl 53705
USA

Ferencz Denes
University of Wisconsin-Madison
Engineering Research Center for Plasma-Aided Manufacturing
1410 Engineering Drive
Madison, WI 53706
USA