

Surface Chemistry and Moisture Sorption Properties of Wood Coated with Multifunctional Alkoxysilanes by Sol-Gel Process

Mandla A. Tshabalala,¹ Peter Kingshott,² Mark R. VanLandingham,³ David Plackett⁴

¹U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, One Gifford Pinchot Drive, Madison, Wisconsin 53726-2398

²Danish Polymer Center, Risoe National Laboratory Roskilde, Denmark

³U.S. Department of Commerce, National Institute of Standards and Technology, Building Materials Division, Gaithersburg, Maryland 20899

⁴Danish Polymer Center, Technical University of Denmark, 2800 Lyngby, Denmark

Received 2 May 2002; accepted 10 September 2002

ABSTRACT: Sol-gel surface deposition of a hydrophobic polysiloxane coating on wood was accomplished by using a mixture of a low molecular weight multifunctional alkoxysilane, methyltrimethoxysilane (MTMOS), and a high molecular weight multifunctional alkoxysilane, hexadecyltrimethoxysilane (HDTMOS). Investigation of the surface chemistry and morphology of the wood specimens by means of ATR-FTIR, energy-dispersive X-ray analysis, X-ray photoelectron spectroscopy, SEM, and atomic force microscopy indicated that the sol-gel process results in deposition of polysiloxane networks that are bonded to the wood by polycondensation with surface hydroxyl groups. The surface hydroxyl groups involved in the bonds appear to be located predominantly on the cellulose component of the wood. The sol-gel deposit on the wood substrates lowered the rates of water and water vapor sorption. The low mo-

lecular weight MTMOS apparently penetrated the outer surface layers of the wood and condensed with hydroxyls that may not be readily accessible to the high molecular weight HDTMOS. Once attached to such sites, it is reasonable to assume that some of these surface derivatives of MTMOS condensed with other molecules of MTMOS and HDTMOS with a long hydrocarbon chain to form a polysiloxane network that is hydrophobic. The ultimate effect of the sol-gel deposit can therefore be regarded as not only to decrease the surface concentration of hydrogen-bonding sites, but also to stereochemically hinder the formation of hydrogen bonds between such sites and water molecules. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 2828–2841, 2003

Key words: polysaccharides; surface; coatings; polycondensation; morphology

INTRODUCTION

Chemical groups and their distribution on the surface of fibrous porous materials determine their properties such as water sorption or chemical reactivity. In the case of lignocellulosic polymers such as wood, the surface hydroxyls on the wood polysaccharides or lignin form hydrogen bonds with sorbed water molecules.^{1,2} Water molecules sorbed on the wood surface affect its rate of photochemical degradation during the natural weathering process outdoors.³ However, the presence of a sorbed layer of water molecules on a wood surface can also be used to good advantage to promote bonding of water-repellent multifunctional alkoxysilanes to the wood surface. The objectives of the present study were to investigate the wood surface bonding of hexadecyltrimethoxysilane (HDTMOS) in the presence of methyltrimethoxysilane (MTMOS); to

evaluate the effect of removing polar and nonpolar extractives from the wood prior to reacting it with HDTMOS in the presence of MTMOS; and to evaluate the moisture sorption properties of wood coated with alkoxysilanes by the sol-gel process. Other researchers have reported that reaction of moisture-conditioned wood specimens with low molecular weight alkoxysilanes, such as MTMOS, results in the deposition of SiO₂ gels within the wood cell walls.⁴ It has also been observed that addition of a high molecular weight alkoxysilane to the MTMOS reaction system enhances the water-repellent properties of wood specimens.⁵ In the study reported here, HDTMOS was selected as the high molecular weight alkoxysilane because it is relatively inexpensive and readily available. An aqueous solution of *N*-methyl-2-pyrrolidone (NMP) was used to extract the wood specimens because NMP dissolves many organic wood extractives, including carbohydrates and other polyhydroxy compounds.⁶

Alkoxysilanes are widely used as crosslinking agents in formulations of paint, ink, adhesives, and water repellents.^{7–10} They have also been investigated as possible environmentally acceptable replacements for the exist-

Correspondence to: M. A. Tshabalala (mtshabalala@fs.fed.us).

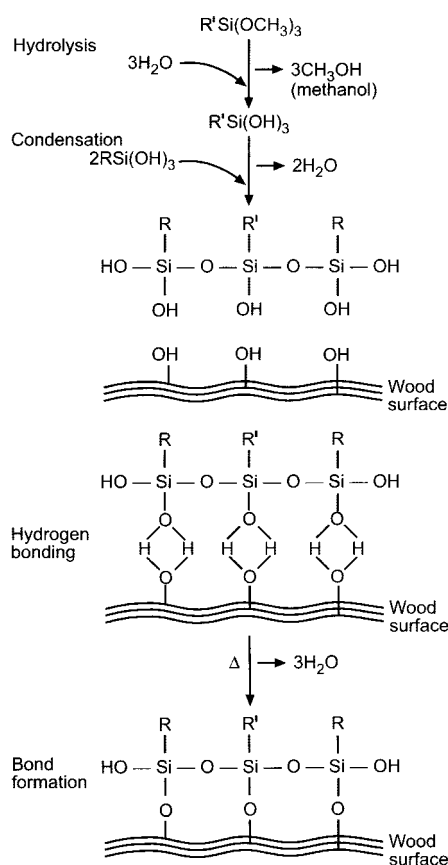


Figure 1 Scheme for sol-gel deposition of alkoxy silane on wood surface.

ing chromatating processes for pretreating sheet metal before painting or as corrosion-inhibiting films on iron.¹¹⁻¹³ Methyltrimethoxysilane, a multifunctional alkoxy silane, has also been shown to be effective for rapid waterproofing of ceramic tiles and blankets used as thermal insulation on aerospace vehicles.¹⁴

The sol-gel process allows the deposition of inorganic-organic polymeric networks on various substrates as a result of controlled hydrolysis and polycondensation of alkoxy silanes.¹⁵⁻¹⁹ Some of these networks have been shown to exhibit high-barrier properties with respect to the permeation rates of oxygen, water vapor, and volatile organic compounds.¹⁵ A recent study showed that sol-gel polycondensation networks of some alkoxy silanes deposited within the wood cell wall enhanced the fire- and water-resistance properties of the wood.⁵ In another recent study, coating of paper or textiles with sol-gel silica layers containing bound dyes improved their leaching stability.²⁰

As illustrated in Figure 1, sol-gel deposition consists of several steps that begin with hydrolysis of alkoxy groups by bound water in the wood cell wall to form free silanols and alcohol. The silanols undergo polycondensation to form polysilanol, which then form hydrogen bonds with the wood surface. Upon heating, these sur-

face hydrogen-bonded polysilanol lose water to form covalent bonds with the wood surface.^{4,7}

EXPERIMENTAL

Certain commercial instruments and materials are identified in this article to adequately describe the experimental procedure. In no case does such identification imply recommendation by the U.S. Department of Agriculture or by the National Institute of Standards and Technology, nor does it imply that the instruments or materials are necessarily the best available for the purpose.

Materials

Wood specimens were prepared from air-dried loblolly pine (*Pinus taeda* L.) boards. NMP and trifluoroacetic acid (TFA) were purchased from Sigma-Aldrich (Milwaukee, WI); HDTMOS and MTMOS were purchased from Fluka (Milwaukee, WI), and methanol was purchased from Fisher (Fair Lawn, NJ).

Procedures

The wood specimens were in the form of thin wafers cut to 0.8 mm thick in the tangential direction, 51.3 mm long in the longitudinal direction, and 15.8 mm wide in the radial direction. Before weighing, dry specimens were always preconditioned to a constant weight in a room with controlled humidity. Previous experiments have shown that constant weight is attained within 1 day.¹

Preconditioning of wood specimens

Specimens were placed in a controlled humidity room to condition at 65% relative humidity (RH), 26.7°C. After conditioning for at least 24 h, each specimen was labeled with a sharp pencil and weighed. After weighing, all specimens were stored in a vacuum desiccator at ambient temperature until required for experimentation.

Removal of polar and nonpolar extractives

To remove polar and nonpolar extractives from the outer surfaces, weighed specimens were extracted for 24 h in a Soxhlet apparatus with an aqueous solution of NMP that contained one part by volume of NMP and nine parts by volume of distilled water. Specimens were allowed to air-dry under the hood for 24 h before transferring to a controlled humidity room to condition for 24 h at 65% RH, 26.7°C. After conditioning, the weight of each specimen was recorded, and all specimens were placed in a vacuum desiccator at ambient temperature until required for further experi-

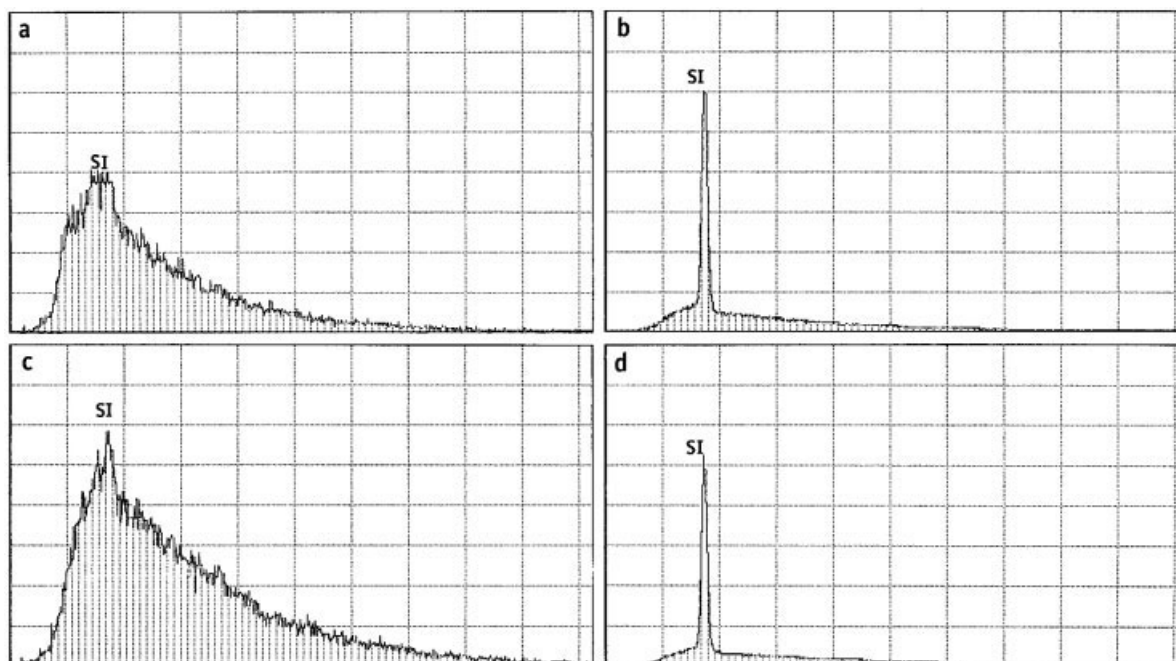


Figure 2 EDXA spectra of wood specimens: (a) nonwashed control, (b) nonwashed coated, (c) washed control, (d) washed coated.

mentation. Specimens subjected to this procedure will be referred to as washed and those not subjected to this procedure will be referred to as nonwashed.

Coating of wood specimens with MTMOS and HDTMOS

Both washed and nonwashed specimens were weighed and then placed in a coating solution at room temperature, under a vacuum of 15 mmHg, for 3 days. Specimens were coated under vacuum to facilitate removal of gases at the solid-liquid interface. The coating solution consisted of methanol, HDTMOS, MTMOS, and TFA mixed in a volume ratio of 40 : 20 : 5 : 1. After coating, specimens were dried in an oven at 65°C for 24 h. At the end of the drying period, specimens were allowed to cure for 24 h in an oven at 105°C. After curing, specimens were placed in a vacuum desiccator to cool to room temperature overnight. Thereafter, specimens were placed in a controlled humidity room and allowed to condition for 24 h at 65% RH, 26.7°C. After conditioning, the weight of each specimen was recorded; all specimens were placed in a vacuum desiccator at ambient temperature until required for further evaluation.

Characterization of surface properties of sol-gel-coated wood

Surface morphology

Surface images of specimens were obtained by atomic force microscopy (AFM) and scanning electron mi-

croscopy (SEM). AFM images were acquired on a Dimension 3100 scanning probe microscope (Digital Instruments, Santa Barbara, CA). Topographic and phase images were recorded simultaneously at ambient conditions. Commercial silicon cantilever probes, each with a nominal tip radius of 5 to 10 nm and spring constant in the range of 20 to 100 N/m (values provided by manufacturer) were oscillated at their fundamental resonance frequencies, which ranged between 250 and 300 kHz. Because the frequency response of the cantilever can shift due to tip-sample interactions, the oscillation frequency was readjusted after engaging the tip on the surface such that the operating frequency was near resonance but just on the low-frequency side of resonance during imaging. Oscillation amplitudes were approximately 30 nm (1 V as output by the optical lever system) and set-point amplitudes were 25 nm. Scan rates were between 0.5 and 1 Hz.

SEM images were obtained on a Jeol JSM-840 scanning electron microscope (Jeol USA, Inc., Peabody, MA). Images were obtained at 15 kV and recorded on Polaroid film.

Surface chemistry

Surface chemistry of specimens was characterized by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), energy dispersive X-ray analysis (EDXA), and X-ray photoelectron spectroscopy (XPS).

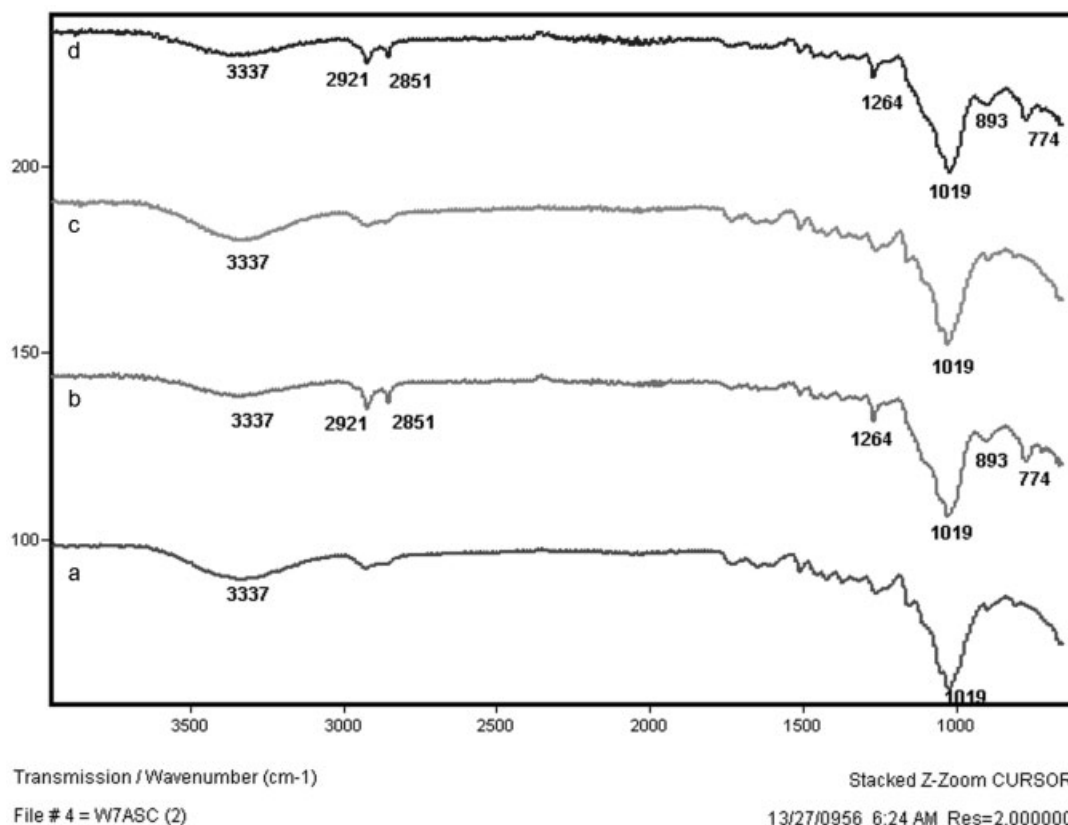


Figure 3 ATR-FTIR spectra of wood specimens: (a) nonwashed control, (b) nonwashed coated, (c) washed control, (d) washed coated.

ATR-FTIR was carried out on a Perkin-Elmer Spectrum One FTIR spectrometer, operated in the ATR mode. The spectrometer was set to collect 32 scans at 2-cm^{-1} resolution in the range of 4000 to 650 cm^{-1} .

EDXA was carried out on a Tracor Noran TN-5500 energy dispersive X-ray analyzer (ThermoNoran, Middleton, WI). Analysis was carried out at 15 kV with a detector take-off angle of 40° and a collection time of 60 s .

Survey and high-resolution XPS of specimens was carried out on a Specs Sage 100 instrument by using a nonmonochromatic $\text{Al}_{K\alpha}$ X-ray source operating at 300 W (15 kV , 20 mA). Charge neutralization was performed with a flood gun that utilizes low-energy electrons generated from a tungsten filament. The pressure in the analysis chamber was typically $<5 \times 10^7\text{ mbar}$. Chemical elements on the wood surface were identified and quantified from survey scans ($0\text{--}1100\text{ eV}$; detector pass energy, 100 eV). High-resolution C1s spectra were acquired at a pass energy of 22.50 eV . Spectral deconvolution was performed by using Spectra Data Processor Version 2.3 curve-fitting software. Peak shifts were referenced to aliphatic hydrocarbon binding energy ($\text{BE} = 285.0\text{ eV}$).

Evaluation of moisture sorption properties of sol-gel-coated wood

Rate of water vapor uptake

Each specimen was removed from the vacuum desiccator and placed on a balance. The initial weight was recorded. Thereafter, specimen weight was recorded every 15 min for approximately 24 h in a controlled humidity atmosphere.

Rate of liquid water uptake

Each specimen was removed from the vacuum desiccator, weighed, and placed in distilled water at 25°C in a 120-mL Qorpak[®] bottle equipped with a cap. After equilibrating for 24 h , each specimen was removed from the distilled water and blotted dry with a sheet of absorbent paper. The wet specimen was weighed quickly and then returned to the distilled water to equilibrate for another day. This procedure was repeated each day for all specimens for the following 8 days. To saturate the specimens with water, on the eighth day a vacuum was applied to the specimens in the water and then released. Each specimen was then blotted dry and weighed quickly as before.

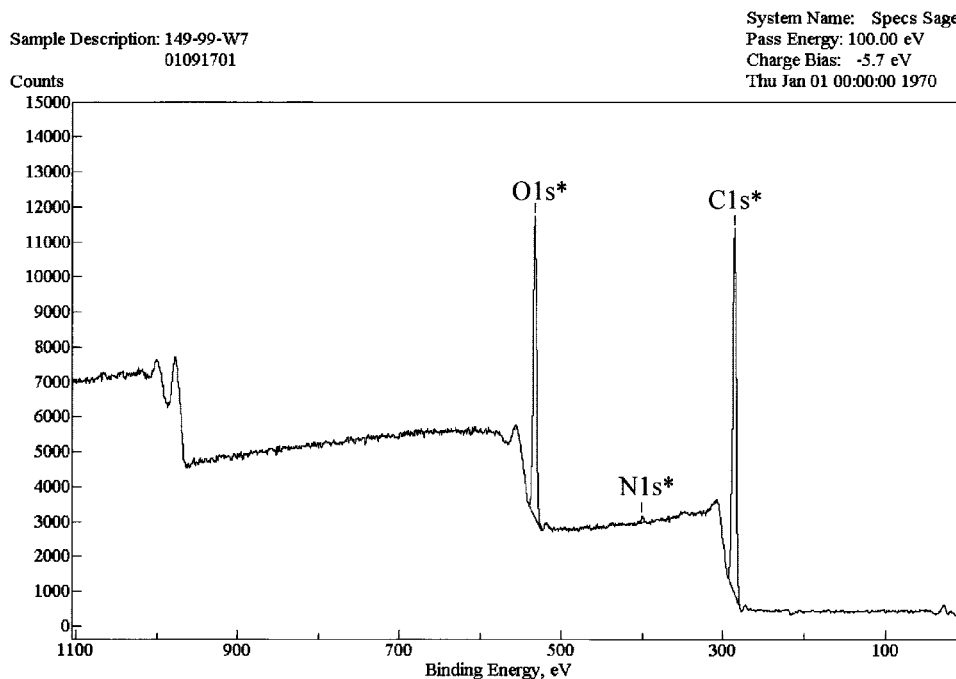


Figure 4 Survey spectrum of nonwashed control specimen.

RESULTS AND DISCUSSION

Surface chemistry of sol-gel-coated wood

Figure 2 shows EDXA spectra of coated and uncoated wood specimens. The presence of a significant Si peak in the spectra of the coated specimens suggests that the SiO_2 gel was successfully deposited within the wood cell wall by the sol-gel process.

Figure 3 compares the ATR-FTIR spectra of non-washed and washed control specimens before and after sol-gel coating. The spectra of coated specimens [Fig. 3(b, d)] show peaks resulting from Si- CH_3 bonds (1264 cm^{-1}) and Si-O, Si-C, or Si-O-C bonds (774 cm^{-1}).²¹ Note that the broad peak at 3337 cm^{-1} due to the O-H stretch of the wood components is somewhat reduced in intensity in the spectra

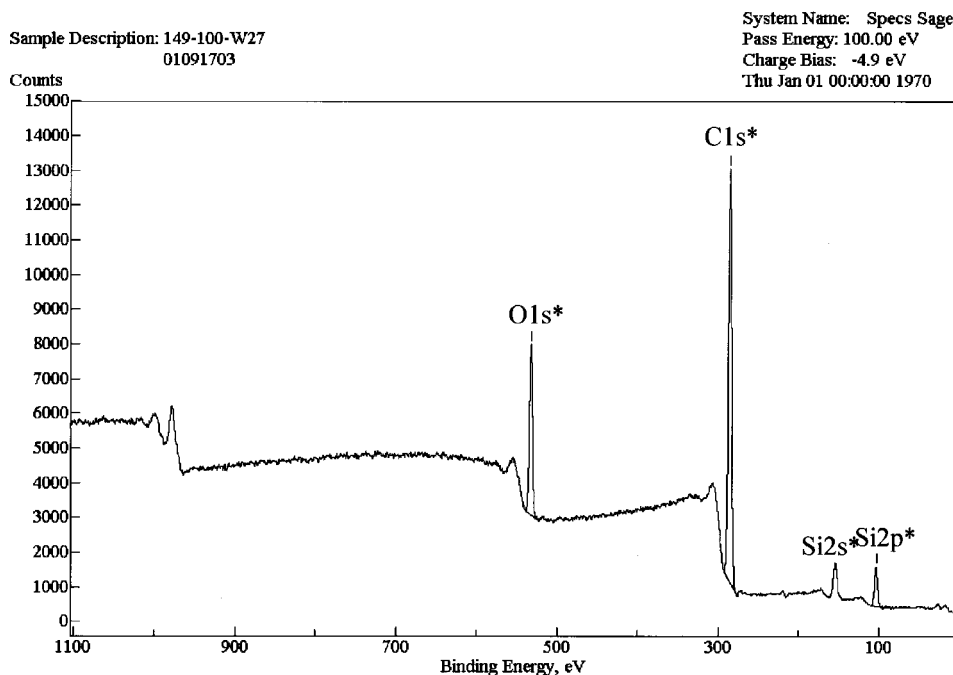


Figure 5 Survey spectrum of nonwashed coated specimen.

TABLE I
XPS Elemental Composition of Wood Specimens

Sample	% C	% O	% Si	% N
Nonwashed control	75.4	23.8	0	0.8
Washed control	76.2	22.6	1.2	0
Nonwashed coated	79.5	14.0	6.5	0
Washed coated	78.7	13.7	7.3	0.2

of coated specimens. In addition, the weak peaks at 2921 and 2851 cm^{-1} caused by the C—H stretch of the wood components have been replaced by sharper and much stronger peaks resulting from the C—H stretch of the long hydrocarbon chain of HDTMOS bound to the wood by the sol-gel process.

Figures 4 and 5 show representative XPS survey spectra of nonwashed control and nonwashed coated specimens, respectively. In addition to O1s* and C1s* peaks, the spectra of the coated specimens showed Si2s* and Si2p* peaks resulting from the deposition of the polysiloxane film on the wood surface. The XPS elemental composition of the specimens is summarized in Table I.

These data confirmed that the sol-gel deposition of MTMOS and HDTMOS on the wood specimens led to significant changes in their surface chemistry. The surface carbon content of coated specimens increased approximately 4% (from 75.4 to 79.5%) for nonwashed specimens and approximately 3% (76.2 to 78.7%) for washed specimens. In addition, the surface silicon content of coated specimens increased approximately 6%—from 0 to 6.5% for nonwashed specimens and

from 1.2 to 7.3% for washed specimens. On the other hand, the oxygen content decreased approximately 10% (23.8 to 14%) for nonwashed specimens and approximately 9% (22.6 to 13.7%) for washed specimens.

The increase in the surface carbon content of the coated specimens correlates well with the appearance of relatively intense C—H stretch bands (2921 and 2851 cm^{-1}) observed in the ATR-FTIR spectra. It is also reasonable to assume that the decrease in the surface oxygen content of the coated specimens is related to the apparent decrease of approximately 3 to 6% in the intensity of the O—H stretch band (3337 cm^{-1}) observed in the ATR-FTIR spectra [Fig. 3(b, d)].

Figures 6 and 7 show representative XPS high-resolution C1s* and O1s* spectra of nonwashed control specimens, respectively. The binding energy of the C1s* peak consists of contributions from components C1, C2, C3, and C4. C1 corresponds to carbon linked to hydrogen or carbon (—C—H or —C—C), C2 to carbon linked to one oxygen (—C—O), C3 to carbon linked to two noncarbonyl oxygens (—O—C—O—), or one carbonyl oxygen (—C=O), and C4 to carbon linked to carbonyl and noncarbonyl oxygen (O=C—O—).²² The binding energy of the O1s* peak consists of contributions from components O1 and O2. The O1 component, which has lower binding energy, is tentatively assigned to oxygen in lignin; O2 is assigned to oxygen in carbohydrates.²³

Figures 8, 9, and 10 show representative high-resolution C1s*, O1s*, and Si2p* spectra of nonwashed coated specimens. The binding energy components of

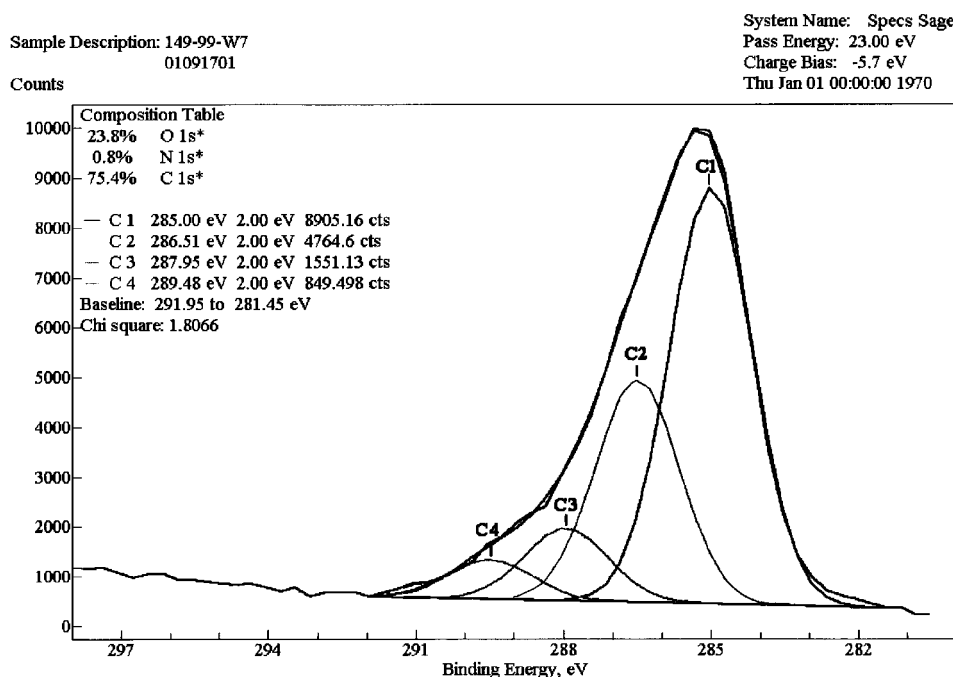


Figure 6 C1s* high-resolution spectrum of nonwashed control specimen.

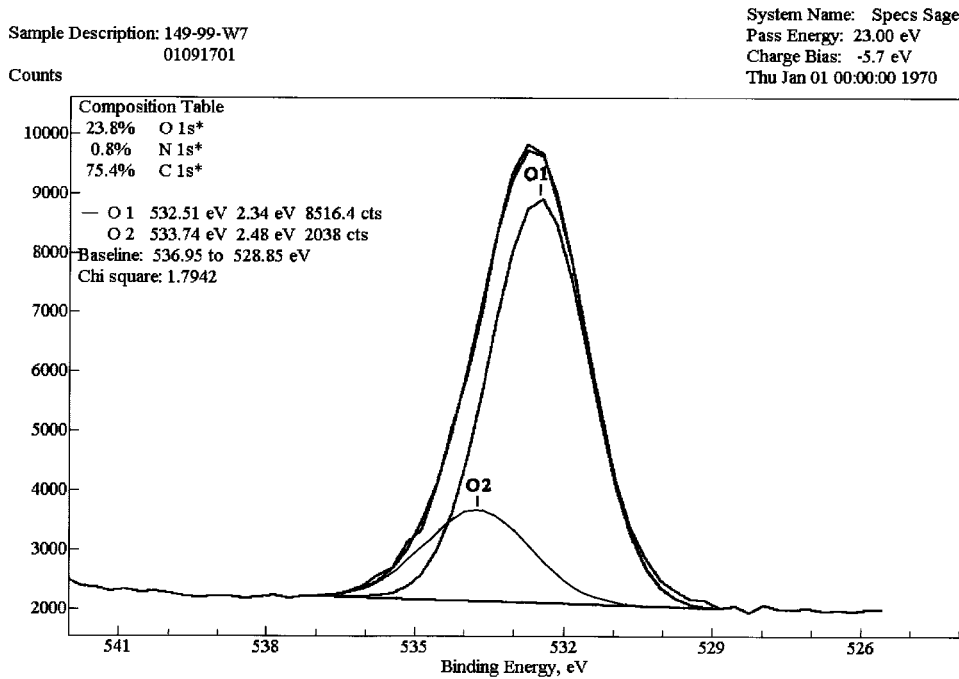


Figure 7 O1s* high-resolution spectrum of nonwashed control specimen.

the C1s*, O1s*, and Si2p* peaks and their respective surface concentrations are summarized in Table II.

The high-resolution XPS spectra show that sol-gel surface deposition of MTMOS and HDTMOS led to the disappearance of the C3, C4, and O2 components of the C1s* peaks (Fig. 8) and O1s* peaks (Fig. 9). In addition to a decrease in the intensity of the C2 component of the C1s* peak (Fig. 8), there was also a shift,

from 286.4 to 287.3 eV, in the binding energy of the C2 component. This shift in binding energy is consistent with the presence of a carbon atom linked to an oxygen atom and a silicon atom as in C—O—Si or O—C—Si. However, the value of the binding energy (103.2 eV) of the Si1 component of the Si2p* peak (Fig. 10) is consistent with the presence of a silicon atom linked to an oxygen atom as in Si—O—C. The increase in the

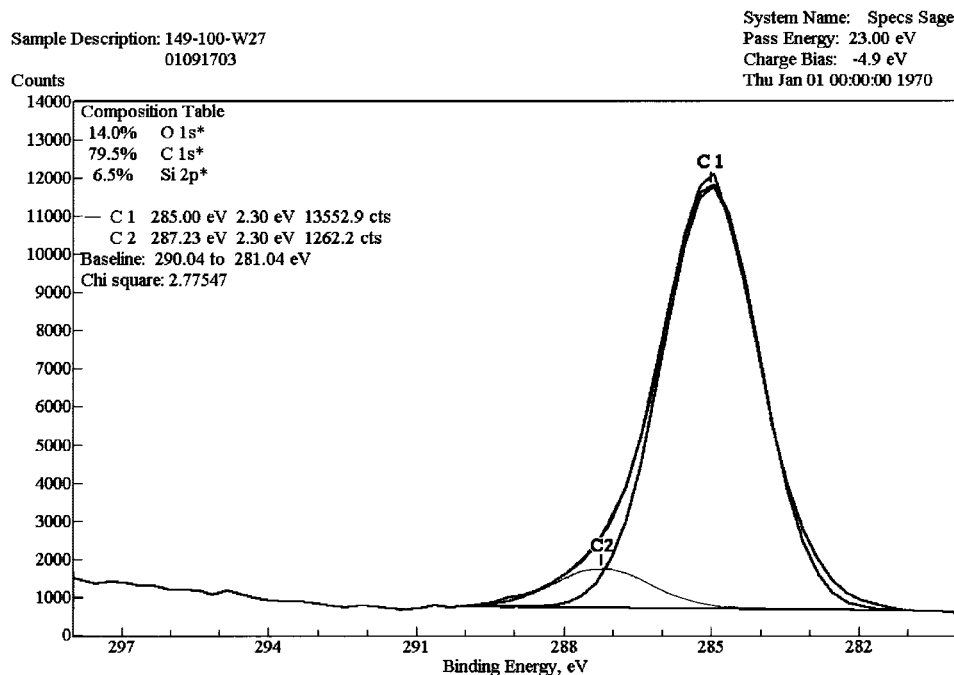


Figure 8 C1s* high-resolution spectrum of nonwashed coated specimen.

TABLE II
Summary of XPS Curve-Fitting Results for Wood Specimens

Sample	C1	C2	C3	C4	O1	O2	Si
Nonwashed control							
Binding energy	285.0	286.5	288.0	289.5	532.5	533.8	—
Surface concentration (%)	55.4	29.6	9.7	5.3	83.9	16.1	—
Washed control							
Binding energy	285.0	286.4	287.8	289.4	532.5	533.8	—
Surface concentration (%)	59.0	25.7	10.6	4.6	84.6	15.4	—
Nonwashed coated							
Binding energy	285.0	287.3	—	—	532.3	—	103.2
Surface concentration (%)	91.6	8.4	—	—	100.0	—	100.0
Washed coated							
Binding energy	285.0	287.2	—	—	532.1	—	103.2
Surface concentration (%)	94.4	5.6	—	—	100.0	—	100.0

surface concentration of the C1 component, from 55.4 to 91.6% for nonwashed coated specimens and from 59 to 94% for washed coated specimens, is evidence of the presence C—C and C—H structures contributed by the long hydrocarbon chain of HDTMOS on the surface. The decrease in the surface concentration of the C2 component, from 29.6 to 8.4% for nonwashed coated specimens and from 25.7 to 8.6% for washed coated specimens, coupled with the shift of the binding energy of the C2 component, from 286.5 to 287.3 eV for nonwashed coated specimens and from 286.4 to 287.2 eV for washed coated specimens, is compelling evidence of the presence of C—O—Si structures. These structures may be contributed by bonding of the polysilanol network via polycondensation with surface hydroxyl groups located on the cellulose component of the wood surface, as illustrated in Figure 1.

The disappearance of the C3 and C4 components in the coated specimens can be attributed to their very low surface concentration, which makes them undetectable after coating with HDTMOS with its long hydrocarbon chain. The increase in the surface concentration of the O1 component, from 84.6 to 100% for washed coated specimens and from 83.9 to 100% for nonwashed coated specimens, can be attributed to an increase in the surface concentration of —O—CH₃ structures, associated with the polysiloxane coating. If one takes into account that the surface concentration of the O2 component is lower in the washed control specimen compared to that in the nonwashed control (possibly due to removal of hemicellulose by the extraction solution), then its disappearance in the coated specimens can be attributed to the hiding effect of the polysiloxane coating, the presence of which renders

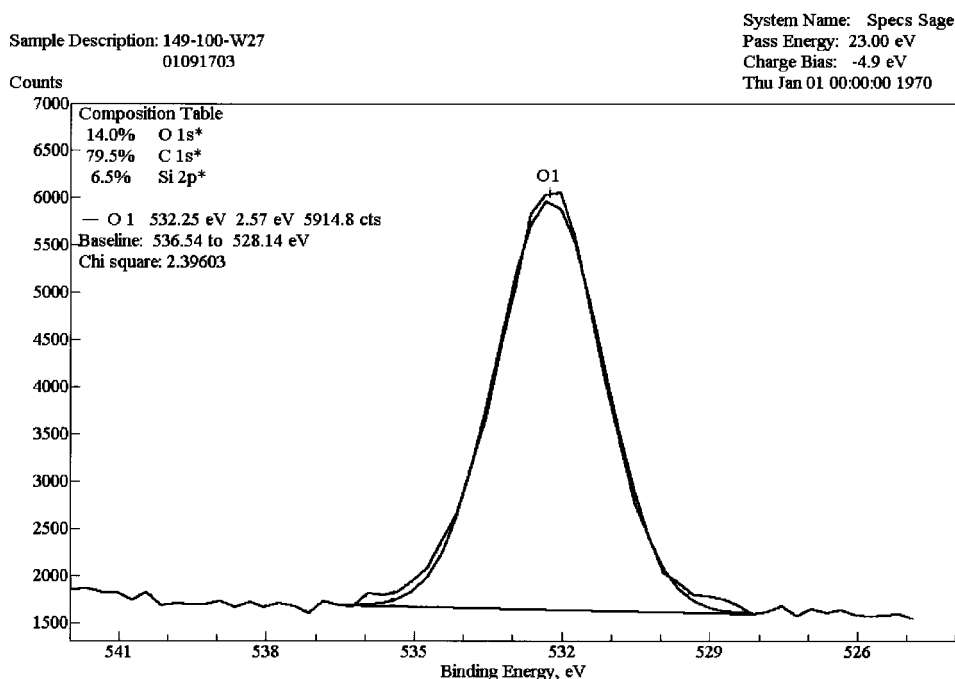


Figure 9 O1s* high-resolution spectrum of nonwashed coated specimen.

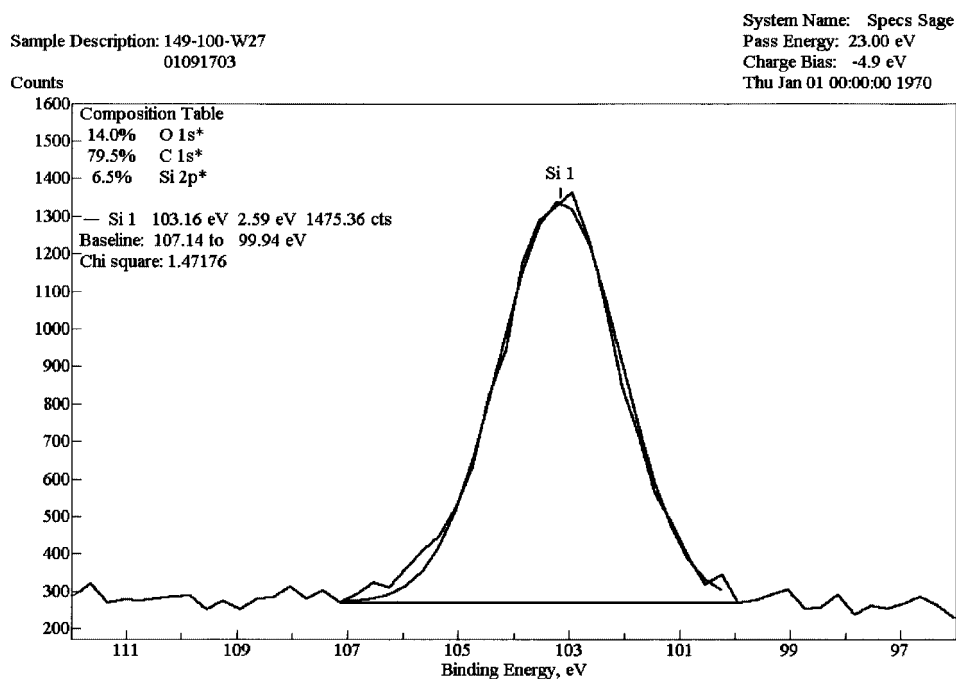


Figure 10 Si2p* high-resolution spectrum of nonwashed coated specimen.

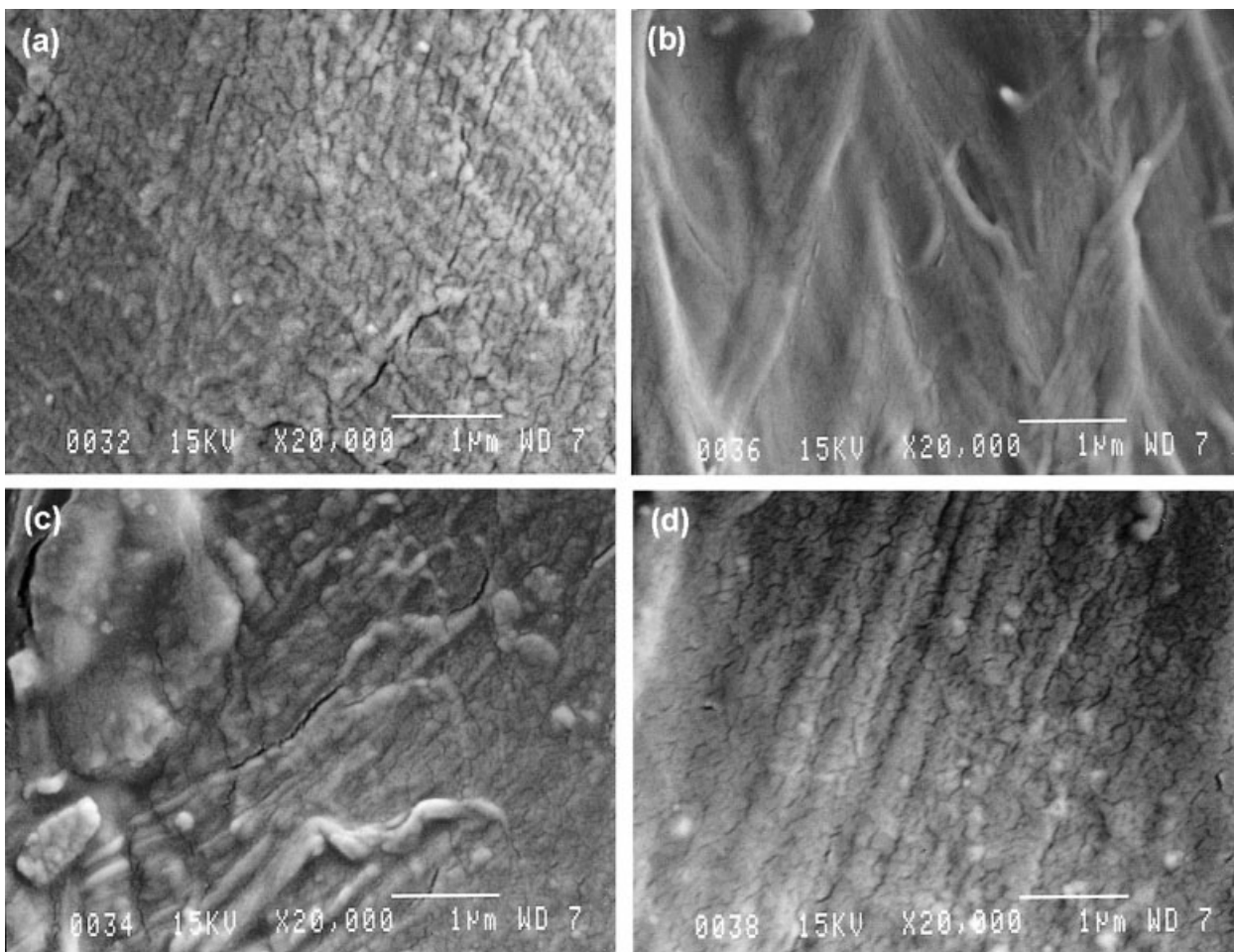


Figure 11 SEM images of selected regions on the surfaces of specimens: (a) nonwashed control, (b) nonwashed coated, (c) washed control, (d) washed coated.

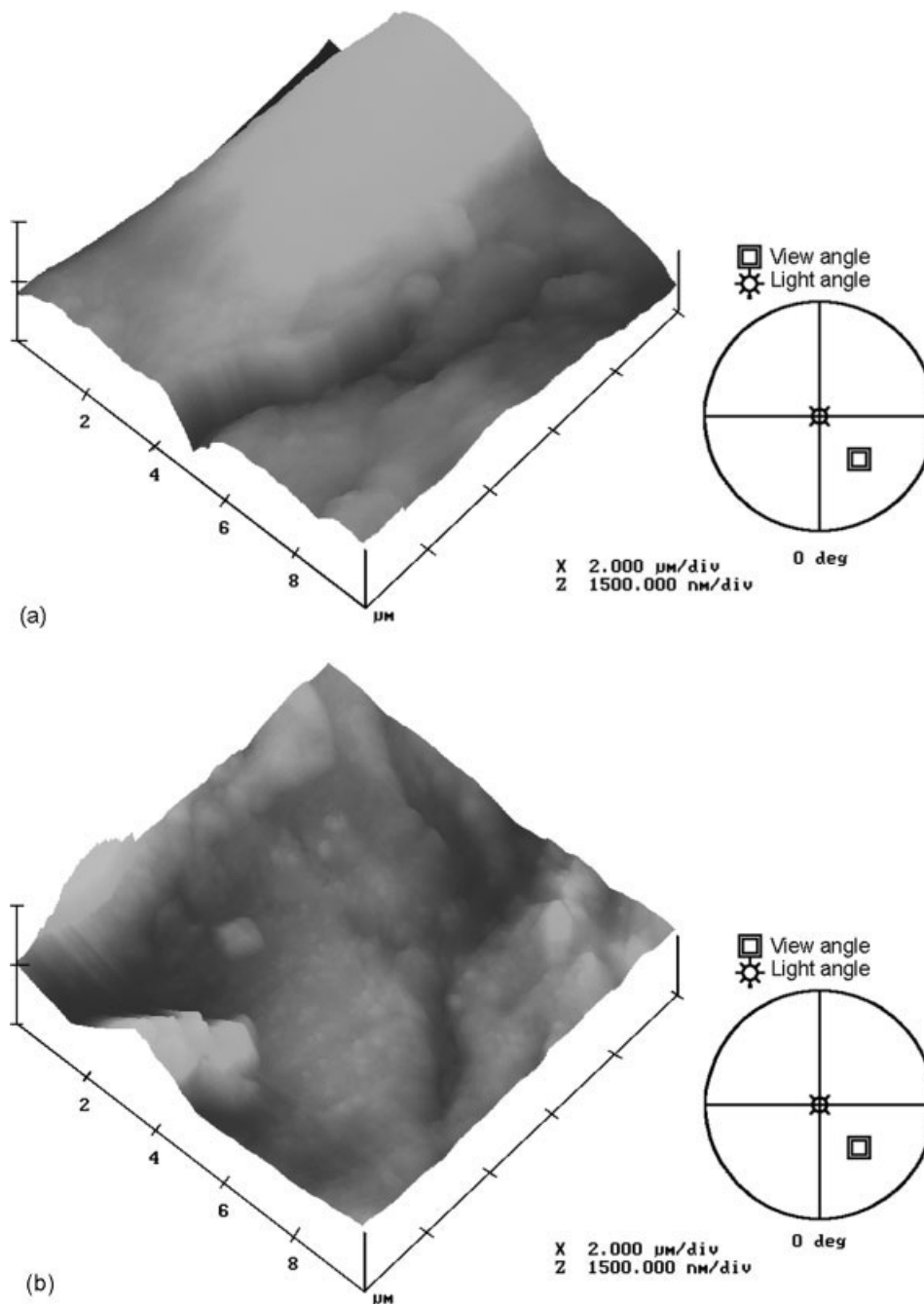


Figure 12 AFM images of selected regions on the surfaces of (a) nonwashed control and (b) nonwashed coated specimens.

the hemicellulose undetectable because of its low-surface concentration (Table II).

Surface morphology of sol-gel-coated wood

Figure 11 shows SEM images of selected regions on the surface of the specimens. The nonwashed control specimens appeared to have a uniform surface of coarse-textured intact microfibrils [Fig. 11(a)]. The surface of the nonwashed coated specimens showed a fine-textured film, possibly due to the deposition of the polysiloxane network on the surface of the micro-

fibrils [Fig. 11(b)]. The washed control specimens appeared to have a nonuniform surface of severely damaged microfibrils due to extraction with the aqueous solution of NMP [Fig. 11(c)]. The washed coated specimens showed a coarse-textured film on the damaged microfibrils, which was almost the same as the texture of the nonwashed control specimens [Fig. 11(d)].

Figure 12 shows AFM height images of selected regions of nonwashed specimens before and after coating. Any changes that may have occurred as a result of coating the nonwashed specimens with the polysiloxane network were not detectable by AFM.

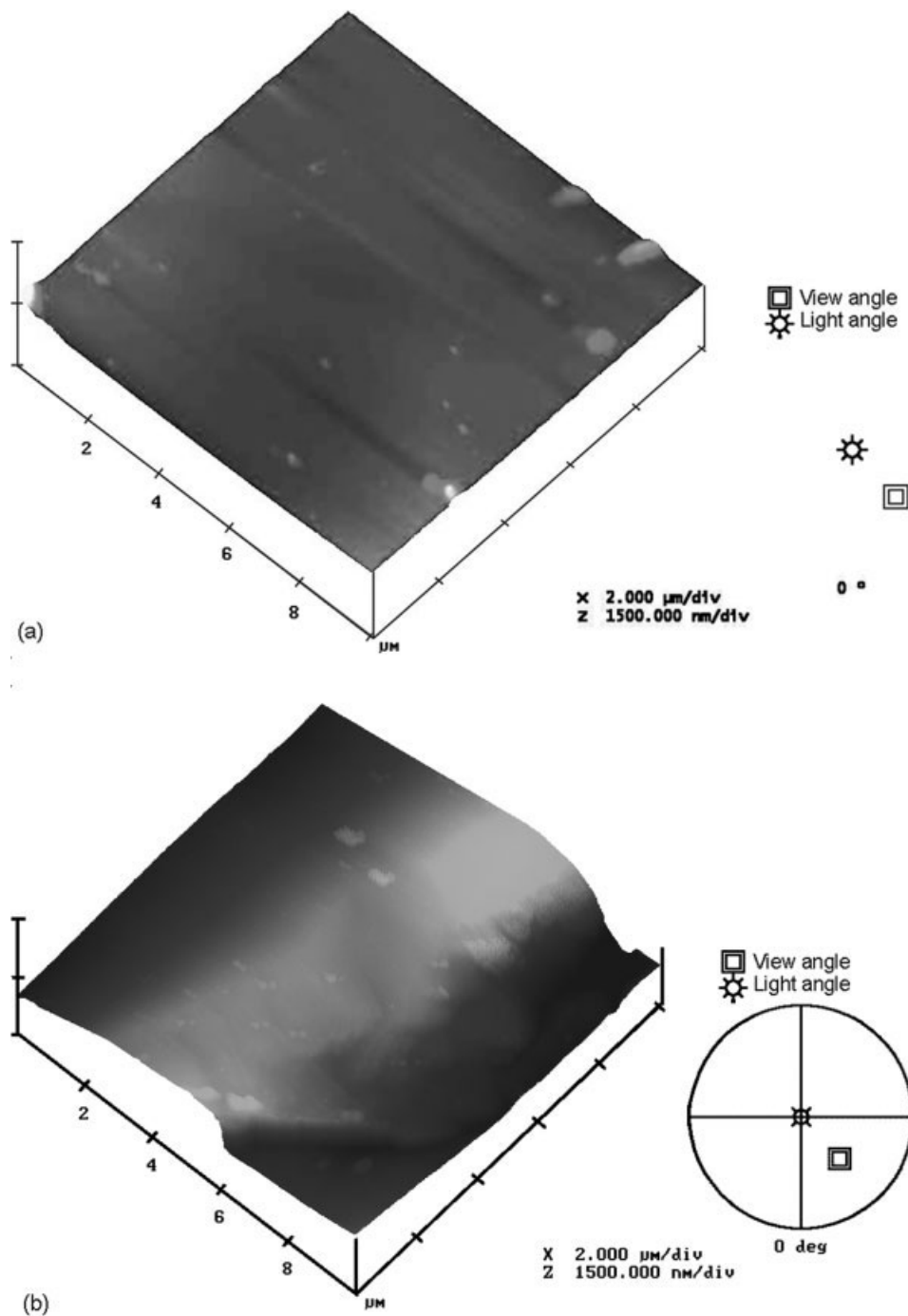


Figure 13 AFM images of selected regions on the surfaces of (a) washed control and (b) washed coated specimens.

The surfaces were so rough at the micrometer scale level that stable AFM imaging was almost impossible. Figure 13 shows AFM height images of selected regions of washed specimens before and after coating. Contours of strand tracheids, longitudinal thin- and thick-walled parenchyma, and stubbles protruding from the surface are barely visible on the surface of the washed control specimen [Fig. 13(a)]. The location of these stubbles, as shown in the phase image of the surface in Figure 14, is consistent with torn mem-

branes of bordered pits²⁴ caused by washing with the aqueous solution of NMP. By comparison, the AFM image of the surface of the washed coated specimens [Fig. 13(b)] did not show any of the surface detail observed in the washed uncoated specimen. This suggests that the polysiloxane deposit obscured some surface features that were barely distinguishable in the washed uncoated specimen.

Comparison of the SEM and AFM images of the specimens suggests that sol-gel deposition of alkox-

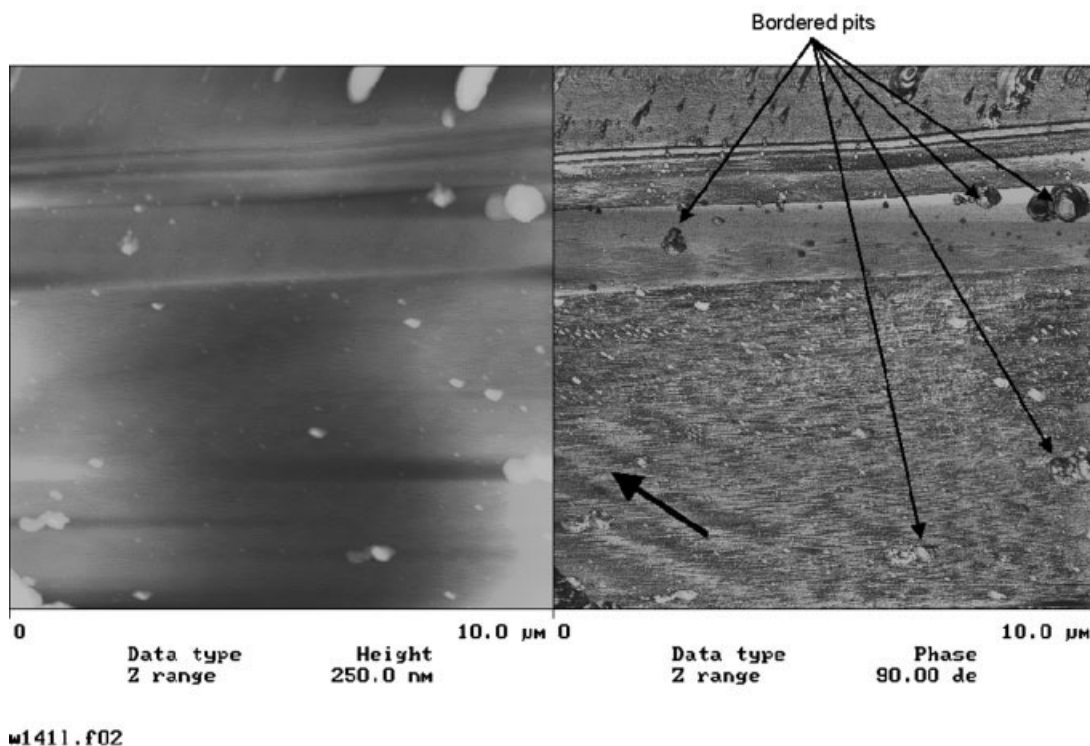


Figure 14 AFM phase image of washed control specimen showing location of bordered pits and orientation of microfibrils in direction of large arrow.

ysilanes resulted in a surface deposit that was sufficiently thick to result in changes in the surface morphology of the specimens at the micrometer scale level. It is particularly remarkable that in the case of those microfibrils that were severely damaged as a result of extraction with the aqueous solution of NMP, the sol-gel coating had a hiding effect. It should also be observed that the SEM and AFM results did not show conclusively whether or not the sol-gel coating was evenly distributed on the surface of microfibrils.

Moisture sorption properties of sol-gel-coated wood

Water vapor uptake

As shown in Figure 15, both washed and nonwashed coated specimens showed a slight decrease in the rate of water vapor uptake compared to that of washed or nonwashed controls. For example, after 1485 min in a humid atmosphere of 80 to 82% RH, the weight percentage gain of coated specimens was approximately 4%; weight percentage gain of uncoated controls was approximately 5 and 6% for nonwashed and washed specimens, respectively.

Liquid water uptake

Coated specimens showed a significant decrease in liquid water uptake compared to the water uptake

of noncoated specimens (Fig. 16). For example, after saturation with liquid water on day 8, the final weight percentage gain of washed coated specimens was only 61% compared to a final weight percentage gain of 150% for washed control specimens. Similarly, the weight percentage gain of nonwashed coated specimens was only 64% compared to 164% for the nonwashed control specimens. It is also important to note that nonwashed controls tended to sorb slightly more liquid water compared to washed controls. This suggests that the extraction solution used to wash the specimens in this experiment also

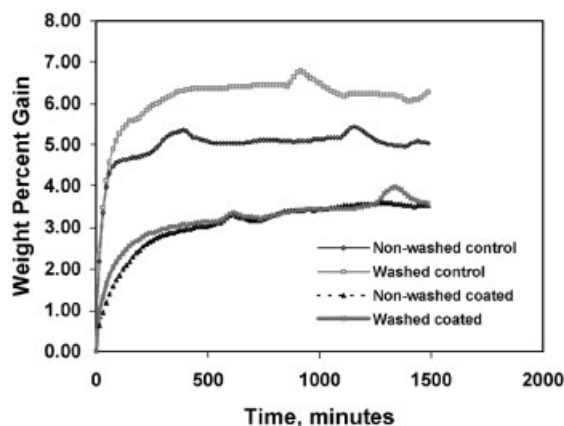


Figure 15 Weight percentage gain of specimens in humid atmosphere at 80–82% RH and 28–32°C.

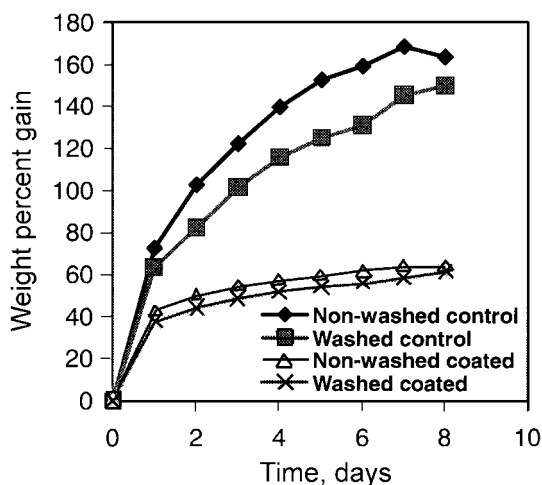


Figure 16 Weight percentage gain of specimens soaked in distilled water at 25°C.

had the effect of removing hydrophilic components, such as hemicellulose, from the specimen surface, thereby rendering the washed specimens less prone to take up liquid water. This decreased affinity for liquid water was further amplified by subsequent surface deposition, by the sol-gel process, of an alkoxy silane with a long hydrocarbon chain that is hydrophobic.

CONCLUSION

The surface chemistry and morphology of wood coated by the sol-gel process with a mixture of multifunctional alkoxy silanes (MTMOS and HDTMOS) were investigated by means of ATR-FTIR, EDXA, XPS, SEM, and AFM. The surface chemistry data suggest that the sol-gel process results in deposition of a polysiloxane network that is bonded to the wood by polycondensation with surface hydroxyl groups. These data further suggest that surface hydroxyls, located predominantly on the cellulose component of the wood, are involved in these polysiloxane-wood bonds. The SEM and AFM images of the coated specimens suggest that the sol-gel deposit on the surface was of such thickness as to cause detectable changes in the surface morphology of specimens at the micrometer scale level.

The sol-gel deposit on the wood substrates resulted in lowered rates of moisture sorption. The low molecular weight MTMOS apparently penetrated the outer surface layers of the wood and condensed with hydroxyls that may not be readily accessible to the high molecular weight HDTMOS. Once attached to such sites, it is reasonable to assume that some of these surface derivatives of MTMOS condensed with other MTMOS molecules and the high molecular weight

HDTMOS with a long hydrocarbon chain to form a polysiloxane network that is hydrophobic. The net effect of the sol-gel deposit can therefore be regarded as not only to decrease the surface concentration of hydrogen-bonding sites, but also to stereochemically hinder the formation of hydrogen bonds between such sites and water molecules.

The presence of a low molecular weight multifunctional alkoxy silane in the sol-gel reaction mixture facilitated the attachment of the high molecular weight multifunctional alkoxy silane to the wood substrate by penetrating the outer layer of the wood surface and providing additional highly reactive polycondensation sites.

Specimens washed with an aqueous solution of NMP prior to reaction with HDTMOS and MTMOS showed a higher weight percentage gain of 35.36 ± 5.21 ($n = 10$) compared to those that were not washed prior to this reaction, which showed a weight percentage gain of 28.82 ± 5.47 ($n = 10$). Evidently, washing the specimens before reaction with HDTMOS and MTMOS activated the surface for more efficient bonding to the hydrophobic polysiloxane network.

The Forest Products Laboratory is maintained in cooperation with the University of Wisconsin. This article was written and prepared by U.S. Government employees on official time and is therefore in the public domain and not subject to copyright. The use of trade or firm names in this publication is for reader information only and does not imply endorsement by the U.S. Department of Agriculture of any product or service.

References

1. Tshabalala, M. A.; Denes, A. R.; Williams, R. S. *J Appl Polym Sci* 1999, 73, 399.
2. Yasuda, R.; Minato, K.; Norimoto, M. *Holzforchung* 1995, 49(6), 548.
3. Feist, W. C.; Hon, D.-S. *Advanced Chemistry Series 207*; American Chemical Society: Washington, DC, 1984.
4. Saka, S. in *Wood and Cellulosic Chemistry*; Hon, D. A.-S.; Shiraishi, S., Eds., Marcel Dekker: New York, 2001, Chapter 20, pp 781-794.
5. Saka, S.; Ueno, T. *Wood Sci Technol* 1997, 31, 457.
6. M-Pyrol®, *N-methyl-2-pyrrolidone Handbook*; GAF Corp., Chemical Division: New York, 1972.
7. Witucki, G. L. *J Coatings Technol* 1993, 65(822), 57.
8. Chen, M. J.; Osterholtz, F. D.; Chaves, A.; Ramdatt, P. E.; Waldman, B. A. *J Coatings Technol* 1997, 69(875), 49.
9. Chen, M. J.; Osterholtz, F. D.; Chaves, A.; Ramdatt, P. E.; Waldman, B. A. *Modern Paints Coatings* 1998, 43.
10. Mayer, H. *JOCCA-Surface Coatings Int* 1998, 81(2), 89.
11. Puomi, P.; Fagernholm, H. M. *Anti-Corrosion Methods Mat* 2001, 48(1), 7.
12. Subramanian, V.; van Ooij, W. J. *Corrosion* 1998, 54(3), 204.
13. Izumi, K.; Minami, N.; Uchida, Y. *Key Eng Mater* 1998, 150, 77.
14. Cagliostro, D. E.; Pallix, J.; Ridge, J.; Chao, S.; Hsu, M. T. *J Adv Mater* 1999, 31(1), 27.

15. Amberg-Schwab, A.; Hoffman, M. *J Sol-Gel Sci Technol* 1998, 2, 141.
16. Mansur, H. S.; Vasconcelos, W. L.; Lenza, R. F. S.; Orefice, R. L.; Reis, E. F.; Lobato, Z. P. *J Non-Crystalline Solids* 2000, 273, 109.
17. Oikawa, N. *J Sol-Gel Sci Technol* 2000, 19, 729.
18. Vorotilov, K. A.; Vasiljev, V. A.; Sobolevsky, M. V.; Sigov, A. S. *J Sol-Gel Sci Technol* 1998, 13, 467.
19. Abel, M.-L.; Watts, J. F.; Digby, R. P. *Int J Adhesion Adhesives* 1998, 18, 179.
20. Trepte, J.; Böttcher, H. *J Sol-Gel Sci Technol* 2000, 19, 691.
21. Bogart, K. H. A.; Ramirez, S. K.; Gonzales, L. A.; Bogart, G. R.; Fisher, E. R. *J Vac Sci Technol, A* 1998, 16(6), 3175.
22. Hua, X.; Kaliaguine, S.; Kokta, B. V.; Adnot, A. *Wood Sci Technol* 1993, 27, 449.
23. Hua, X.; Kaliaguine, S.; Kokta, B. V.; Adnot, A. *Wood Sci Technol* 1993, 28, 1.
24. Siau, J. F. *Wood: Influence of Moisture on Physical Properties*. Department of Wood Science and Forest Products, Virginia Polytechnic Institute and State University: Blacksburg, VA, 1995, Chapter 2.