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Sol-Gel Modification of Wood Substrates to Retard Weathering

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SOL-GEL MODIFICATION OF WOOD SUBSTRATES TO RETARD WEATHERING

1 ABSTRACT

Wood specimens were treated with sol-gel systems based on metalorganic precursors of silicon (Si), iron (Fe), zirconium (Zr), and titanium (Ti). The effect of these sol-gel systems on weathering properties of wood was investigated. These sol-gel systems were found to have a positive effect on surface color stability and water vapor resistance of the specimens. Under accelerated weathering conditions, the sol-gel systems retarded the degradation of the wood fiber. Scanning electron microscopy (SEM) and energy dispersive x-ray analysis (EDXA), after accelerated weathering in a Weather-Ometer™, showed a marked difference between the treated specimens and the controls in the pattern and localization of degradation. Although the controls showed severe micro-fracturing of the cell walls, the treated specimens showed no such micro-fracturing. On the contrary, the sol-gel-treated specimens showed micro-checks that were predominantly confined to weak areas of the cell wall, such as fusiform rays and the tracheid interfaces.

Keywords: Sol-gel, wood, surface, thin film, moisture, weathering

2 INTRODUCTION

Residential construction accounted for 57% of all wood products consumed in the United States in 2003 [1-5]. Growing concerns over sustainable construction mean that wood products will likely continue to outstrip the proportion of non-wood products used in residential construction. Wood is the world's most sustainable resource. It is renewable and environmentally friendly. In a study on environmental performance of renewable building materials in the context of residential construction, Perez-Garcia et al. [6] found that above-grade wood wall subassemblies had superior environmental performance indexes compared with those of steel or concrete wall subassemblies. However, wood is susceptible to degradation caused by moisture and ultraviolet (UV) radiation from the sun, or wood-colonizing microorganisms, including wood-decay fungi and mold, which can severely limit its service life, including its aesthetic value in residential construction. Approaches to prolonging the service life of wood and preserve its aesthetic qualities are being continually refined, and new ones are being developed.

The durability of wood can be improved by surface modification without compromising its intrinsic mechanical properties, including tensile strength. Surface modification of wood can be accomplished by plasma-enhanced chemical vapor deposition (PECVD) methods. Denes et al. [7], Denes and Young [8], and Podgorski et al. [9] modified wood surfaces with polysiloxanes under cold plasma conditions to create water-repellent characteristics and to attenuate damage caused by weathering. Lukowsky and Hora [10] reported use of atmospheric plasma corona treatment and fluorination on wood to improve the wet adhesion of waterborne acrylic dispersions. Rehn et al. [11] reported that plasma pre-treatment of wood surfaces with a dielectric barrier gas discharge at atmospheric pressure under an average process gas temperature of 35°C increased the fracture strength of glued wood. Recently, Bente et al. [12] reported on plasma treatment of wood surfaces with a mixture of silane/nitrogen gases to create water-repellent characteristics using a dielectric barrier gas discharge at atmospheric pressure. The advantages of PECVD methods are that they are intense and efficient. Furthermore, they are dry processes and are confined only to the outermost layers of the wood surface. One disadvantage of PECVD methods is their requirement for expensive vacuum systems. However, dielectric barrier gas discharge at atmospheric pressure may change that situation if simple equipment is developed that can maintain a good homogeneous gas discharge for plasma treatment of wood.

Surface modification of wood can also be accomplished by sol-gel deposition methods. Brebner and Schneider [13] modified wood by sol-gel deposition of alkoxysilanes to decrease its hygroscopicity and improve its anti-swelling efficiency (ASE). Donath et al. [14] compared the properties of wood specimens impregnated with either monomeric or oligomeric silane sols and found that cell wall bulking effect, ASE, moisture resistance, and durability against white-rot fungi were more improved in wood specimens treated with monomeric silanes than in specimens treated with oligomeric silanes. In our laboratories, we have demonstrated that sol-gel deposition of thin barrier films using a mixture of multifunctional alkoxysilanes on wood can be tailored to improve not only its moisture resistance properties but also its color stability under exposure to accelerated weathering conditions [15, 16]. In a recent study, Donath et al. [17] observed that water uptake was considerably diminished in wood treated with sol-gel deposits of multifunctional waterborne silane systems containing both hydrophilic and hydrophobic groups. They concluded that such sol-gel deposits could be applied as a component in complex preservative formulations for wood. In such formulations, the silane, applied at low concentrations, could protect wood against water and prevent leaching of antimicrobial reagents. One major advantage of sol-gel deposition methods is that they allow low-temperature surface modification of wood using non-toxic metal alkoxides of silicon, aluminum, titanium, or zirconium.

Western redcedar belongs to the group of softwood species that have high native resistance to decay but poor resistance to weathering. Thus the primary objective of the present study was to develop sol-gel systems for modifying western redcedar to protect it against weathering under exposure to UV radiation and moisture.

3 MATERIALS AND METHODS

3.1 Materials

Methyltrimethoxysilane (MTMOS) and hexadecyltrimethoxysilane (HDTMOS) were purchased from Fluka (Buchs, Switzerland). Zirconium propoxide (ZrP), titanium isopropoxide (TIP) N-methyl pyrrolidinone (NMP) and 2-methoxyethanol (2-ME) were purchased from Sigma-Aldrich (Milwaukee, Wisconsin). Ferric acetylacetonate (FeAcAc) and trifluoroacetic acid (TFA) were purchased from GFS Chemicals (Powell, Ohio).

Table 1: Composition of treatment sol-gel systems

Sol-gel system	Volume added (mL)			
	MTMOS	Fe-Zr-Ti sol	HDTMOS	TFA
I	30	0	0	2
II	15	15	0	2
III	10	10	10	2

3.2 Sol-gel preparation

The Fe-Zr-Ti sol was prepared from the metalorganic precursors: ZrP, FeAcAc, and TIP according to a modified procedure of the scheme described by Iakovlev et al. [18]. FeAcAc was dissolved in acetic acid in the molar ratio 1:44. This sol (Sol A) was distilled for 5 h at 100°C to remove associated water. ZrP, TIP, and 2-ME were mixed in a separate container in the molar ratio of 1:1:10. This sol (Sol B) was refluxed for 1 h at 80°C. Sol A and Sol B were mixed together and refluxed for 2 h at 135°C to achieve complexation. The resulting Fe-Zr-Ti sol was diluted with 2-ME. Formulations of sol-gel systems, Sol I, Sol II, and Sol III are given in Table 1.

3.3 Specimen preparation

Specimens were prepared in the form of small thin wafers, 0.8 x 15.8 x 51.3 mm (radial, tangential, longitudinal, respectively), from western redcedar boards that had been stored in a 30% relative humidity (RH) room at 27°C. The surfaces of the specimens were activated by extraction for 24 h with 10% aqueous solution of NMP in a Soxhlet apparatus. After extraction the specimens were allowed to air-dry at 27°C, 30% RH for at least 24 h before recording their individual weights. Thereafter, the specimens were stored in a 65% RH room until needed for sol-gel treatment.

3.4 Sol-gel treatment

Deposition of a thin sol-gel film on the surface of the specimen was accomplished by dipping the specimens in the sol for 24 h. The treated specimens were allowed to air-dry for 1 h before placing them in an oven at 65°C for 6 h. At the end of this oven-drying period the specimens were conditioned for 24 h in an oven at 105 °C to fix the gel. The treated specimens were allowed to equilibrate in the 30% RH room for 24 h before recording their individual weights or using them in other experiments.

3.5 Weather-Ometer™ exposure

To evaluate the effect of UV radiation only, specimens were exposed round-the-clock to borosilicate-glass-filtered xenon arc radiation in a Weather-Ometer for a total of 960 h. For evaluating weathering characteristics, specimens were exposed, for a total of 960 h, to 102 min of filtered xenon arc radiation and 18 min of combined radiation and water spray per 2-h cycle. During the light-only cycle, the black panel temperature (BPT) was 80 ± 2°C, and the RH was approximately 5%. During the light and spray cycle, the BPT was 40 ± 2°C, and the RH was 70%. The specimens were removed from the Weather-Ometer after every 240 h for measurement of color, weight and water vapor uptake.

Effect of the sol-gel systems on weathering properties of the wood specimens was characterized by weight loss measurements, optical microscopy, scanning electron microscopy (SEM), and energy dispersive x-ray analysis (EDXA).

3.6 Water vapor uptake

Water vapor uptake was determined by measuring weight gain of each specimen at 65% RH relative to its equilibrium weight at 30% RH. Measurements were made before and after exposure to borosilicate-glass-filtered xenon arc radiation in the Weather-Ometer.

4 RESULTS AND DISCUSSION

4.1 Color stability

Color measurements were determined according the CIELab system of three parameters [19]. The L* axis represents lightness and varies from 100 (white) to zero (black). The a* coordinates represent chromaticity, with +a* for red and –a* for green; the b* coordinates represent chromaticity, with +b* for yellow and –b* for blue. The L*, a*, and b* values for each specimen were measured before and after exposure to filtered xenon arc radiation. These values were used to calculate the resulting color differences, ΔE^*, according to the following equations:

$$\Delta L^* = L^*_{(f)} - L^*_{(i)} \quad (1)$$

$$\Delta a^* = a^*_{(f)} - a^*_{(i)} \quad (2)$$

$$\Delta b^* = b^*_{(f)} - b^*_{(i)} \quad (3)$$

$$\Delta E^* = \{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}\}^{1/2} \quad (4)$$

ΔL^*, Δa^*, and Δb^* are the changes between the initial (i) and final (f) values. Higher values of ΔE^* represent greater discoloration.

As shown in Figure 1, after 960 h exposure to borosilicate-glass-filtered xenon arc radiation only, specimens that were treated with sol-gel system I showed the least discoloration (ΔE^* = 2.32), followed by sol-gel systems III (ΔE^* = 5.07) and II (ΔE^* = 7.27). All the sol-gel-treated specimens showed greater color stability compared with that of control specimens (ΔE^* = 10.42).

Figure 2 shows photographic images of specimens before and after 240, 480, 720, and 960 h exposure to filtered Xe arc radiation only in the Weather-Ometer. Although the change in color of control specimens after 240 h exposure is rather obvious, it is less so for the sol-gel-treated specimens. The color change shown by the images correlates reasonably well with the calculated ΔE^* values. Although the non-treated control specimens showed the greatest color change, followed by Sol I-treated specimens, the difference between Sol II- and Sol III-treated specimens is barely distinguishable.

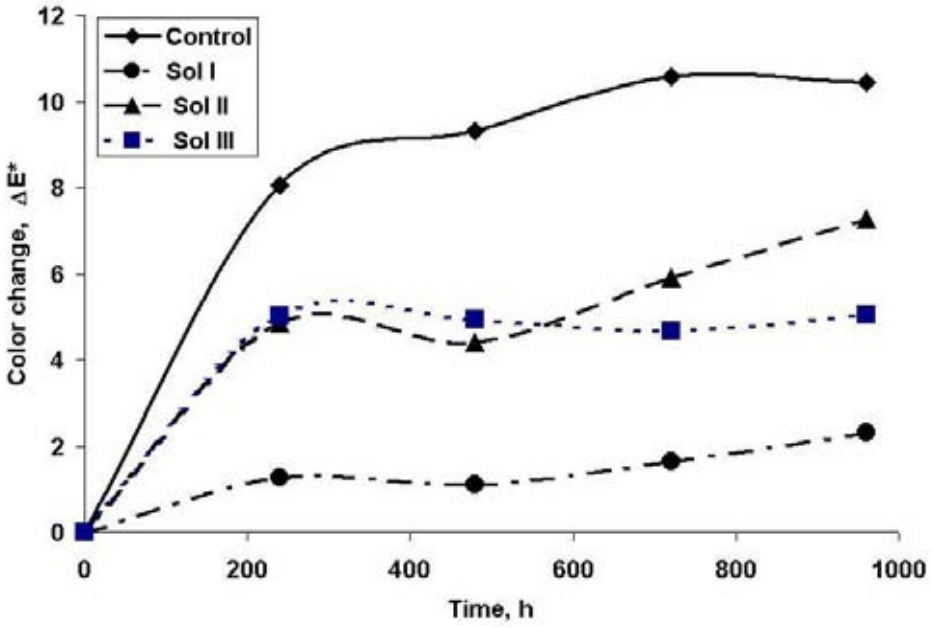

Figure1: Comparison of color change of control and sol-gel-treated specimens after exposure for a total of 960 h to filtered Xe arc radiation only in the Weather-Ometer.

4.2 Water vapor uptake

As shown in Figure 3, the average water vapor uptake at 65% RH was lower (15–20 mg/g) for specimens treated with sol-gel systems I, II, or III compared with that of non-treated control specimens (30–35 mg/g). It is also interesting to note that specimens treated with sol-gel system I showed initial water vapor uptake that was almost equivalent to that of non-treated controls. However, at the 240-h interval, it had dropped closer to that of sol-gel system II, because by this time, the curing process of the sol-gel deposit had quite likely reached equilibrium.

4.3 Weight loss

To determine the extent of degradation, the weight of each specimen at 65% RH was recorded at 240-h intervals over the course of the accelerated weathering experiments. Figure 4 shows weight loss of the specimens as a function of irradiance during 960 h exposure to filtered Xe arc radiation and water spray in the Weather-Ometer. All three sol-gel systems, I, II, and III, were equally effective in decreasing weight loss of the specimens compared with non-treated control.

Note that the break in the trendlines early in the weathering experiments (between 200 and 300 kJ m^{-2} points) was a result of instrument failure.

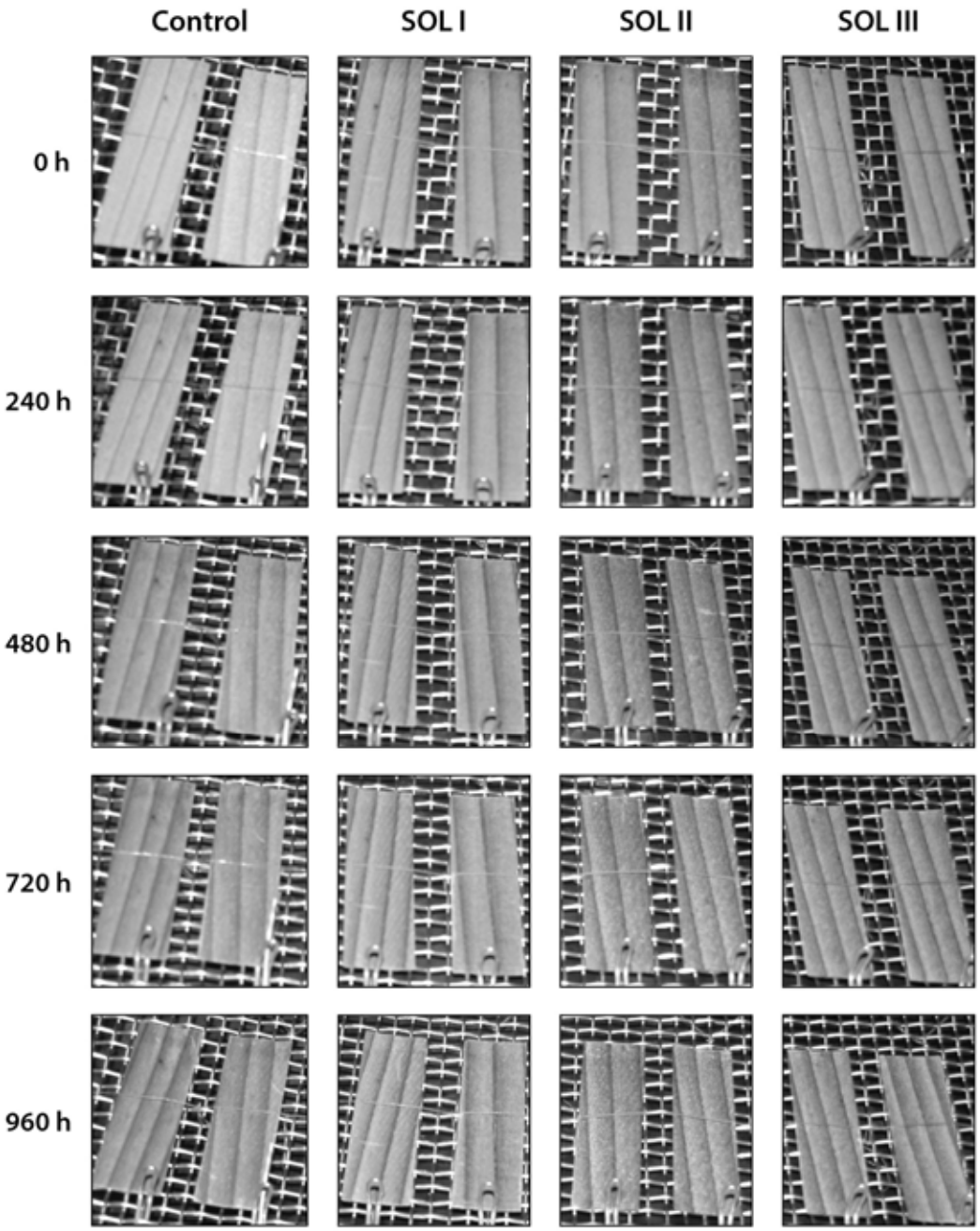

Figure 2: Photographic images of control and sol-treated specimens before and after 240, 480, 720, and 960 h exposure to filtered Xe arc radiation only in the Weather-Ometer.

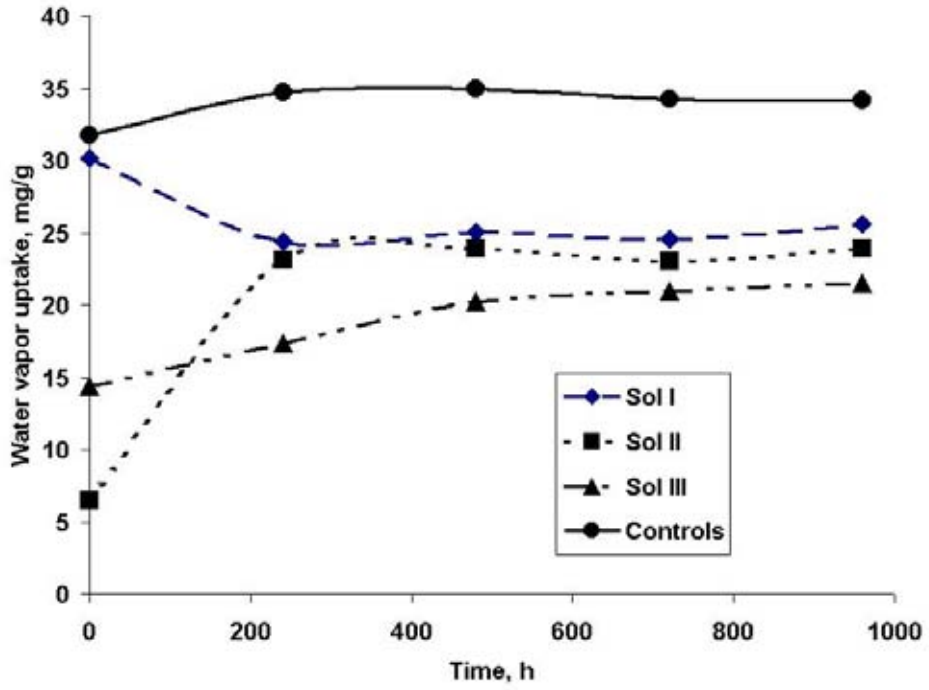

Figure 3: Water vapor uptake of control and sol-treated specimens after exposure to filtered Xe arc radiation only for a total of 960 h in Weather-Ometer.

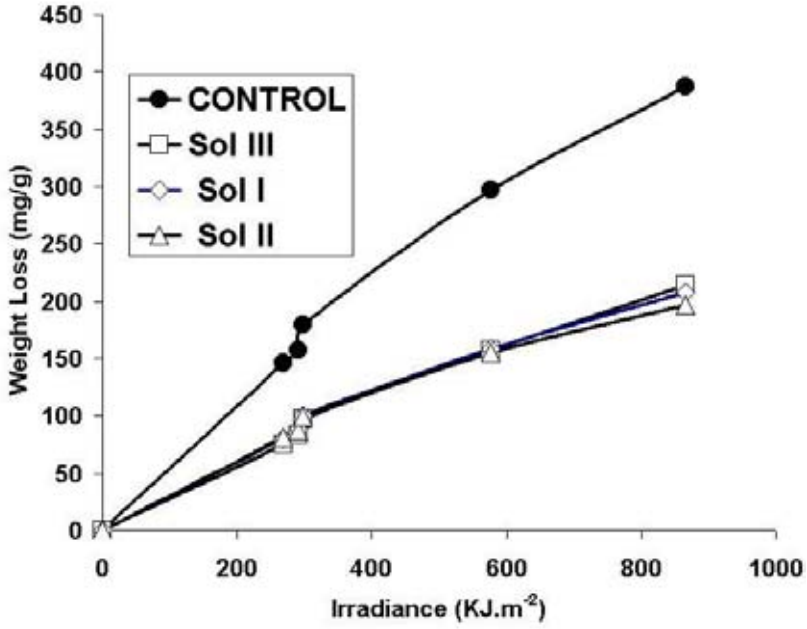

Figure 4: Weight loss of control and sol-treated specimens as a function of irradiance during 960 h exposure to filtered Xe arc radiation and water spray in the Weather-Ometer.

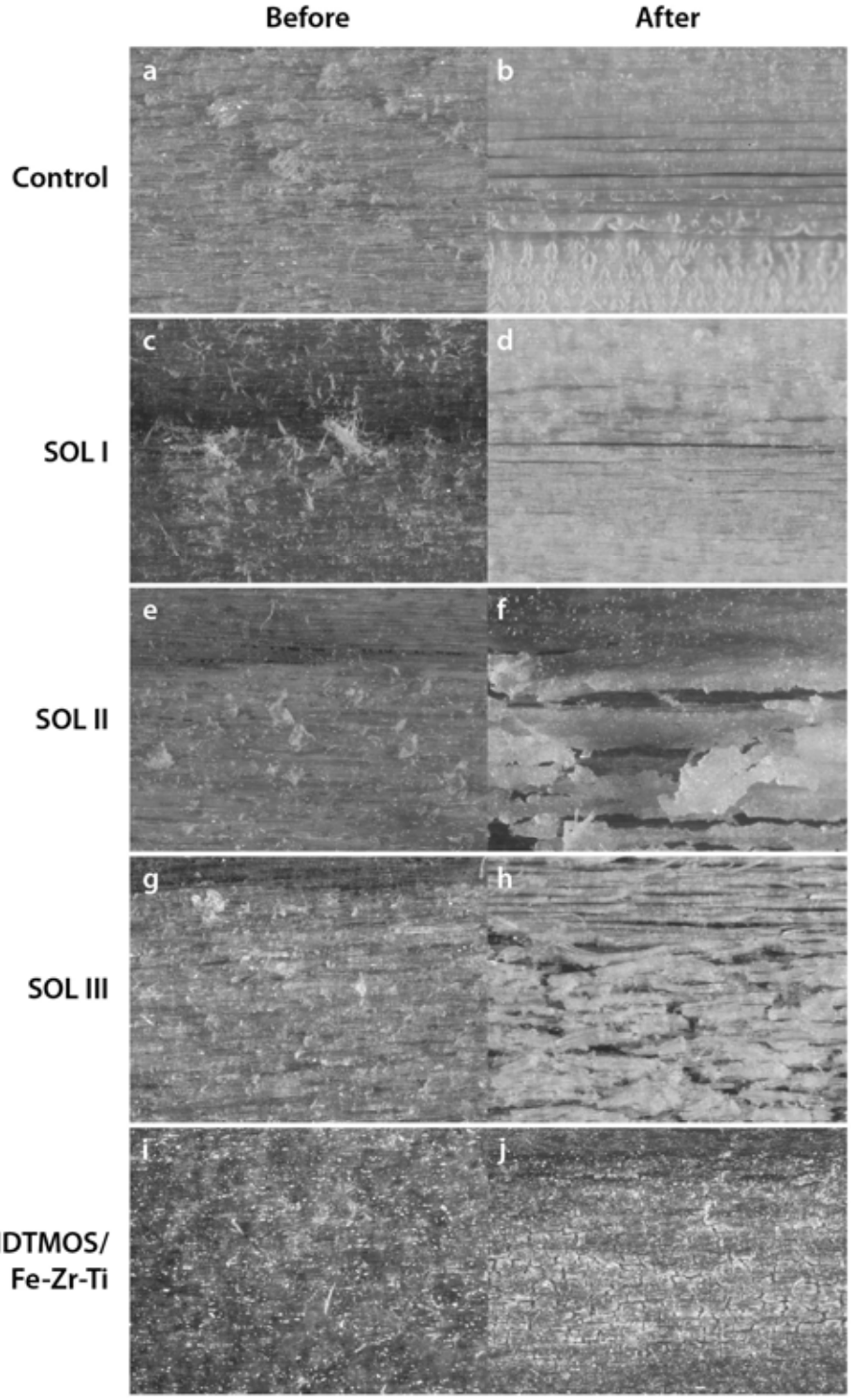

Figure 5: Optical microscopy images of control and sol-treated specimens before and after 960 h exposure to filtered Xe arc radiation and water spray in the Weather-Ometer.

4.4 Optical microscopy

Representative optical microscopy images of non-treated controls and specimens treated with sol-gel systems I, II, and III are shown in Figures 5. Non-treated control specimens showed slight micro-checking and bleaching after 960 h exposure to filtered Xe arc radiation and water spray in the Weather-Ometer (Figure 5b). The Sol I-treated specimens also showed somewhat similar micro-checking and bleaching after weathering (Figure 5d). The Sol II-treated specimens showed a much different erosion pattern (Figure 5f). A smooth layer of Sol II with occasional flaking was visible after 960 h of accelerated weathering. In addition,

Sol II-treated specimens suffered the least bleaching. Sol II clearly had a strongly positive effect on surface color stability. By comparison with Sol I and Sol II, the Sol III-treated specimens showed rather severe erosion and bleaching that was marked by purple areas (Figure 5h). However, when the specimens were treated with a sol formulated from a mixture of HDTMOS and Fe-Zr-Ti, they showed relatively better color stability after 960 h exposure to filtered Xe arc radiation and water spray in the Weather-Ometer (Figure 5j).

4.5 Scanning electron microscopy and energy dispersive x-ray analysis

SEM micrographs and corresponding EDXA spectra of the specimens before and after 960 h exposure to filtered Xe arc radiation and water spray in the Weather-Ometer are shown in Figures 6–10. A marked difference is apparent in the pattern and localization of micro-checks between the treated specimens and the controls. Although the non-treated controls showed severe micro-fracturing of the cell walls after exposure in the Weather-Ometer (Figure 6b), the treated specimens showed no such micro-fracturing. On the contrary, the micro-checks were predominantly confined to weak areas of the cell wall, such as fusiform rays and the tracheid interfaces.

Further, it can be seen that after exposure in the Weather-Ometer, the sol-treated specimens still showed good retention of the surface barrier thin films as evidenced by the respective EDXA spectra, which showed presence of Si peaks with high net counts, before and after exposure in the Weather-Ometer. These elements, together with carbon and oxygen, constitute the chemistry of the sol-gel systems used in this study. In addition to Si peaks, the EDXA spectra of the Sol III-treated specimens also showed presence of Fe, Zr, and Ti, as expected (Figure 9).

The EDXA spectra of Sol III-treated specimens before and after exposure in the Weather-Ometer (Figure 9) showed Fe, Zr, or Ti with relatively low net peak counts. To find an explanation for this unexpected result, a separate set of experiments was conducted where one set of specimens was treated with HDTMOS/Fe-Zr-Ti sol and another set was treated with MTMOS/Fe-Zr-Ti sol. Both sets of experiments showed identical EDXA spectra with equally low net peak counts for Fe, Zr, and Ti (Figure 10). This suggests that for Sol III-treated specimens, which contained both MTMOS and HDTMOS, the high net peak counts for Si dwarfed the relatively low net counts for Fe, Zr, or Ti. The positive effect of HDTMOS/Fe-Zr-Ti sol on color stability was confirmed by optical microscopy (Figure 5j).

5 CONCLUSIONS

These results indicated that the sol-gel systems developed in this study have the potential to stabilize the surface color of western redcedar. In addition to improving the surface color stability of western redcedar, all three sol-gel systems decreased water vapor uptake of the specimens to varying degrees. Effect of the sol-gel systems on color stability of the treated specimens increased in the order Sol I > Sol III > Sol II.

Weight loss of specimens treated with these sol-gel systems was considerably lower compared with that of non-treated control specimens after 960 h exposure to borosilicate-glass-filtered Xe arc radiation and water spray in the Weather-Ometer.

Compared with non-treated controls, sol-gel-treated specimens showed a marked difference in the pattern and localization of degradation after 960 h exposure to borosilicate-glass-filtered Xe arc radiation and water spray in the Weather-Ometer.

6 ACKNOWLEDGMENTS

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7 REFERENCES

1. C. Adair, Regional Production and Market Outlook for Structural Panels and Engineered Wood Products, 2004–2009. APA Economics Report E170. APA–The Engineered Wood Association, Tacoma, WA (2004).
2. J.L. Howard, U.S. Timber Production, Trade, Consumption, and Price Statistics 1965 to 2002, Research Paper. FPL-RP-615. U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, Madison, WI (2003).
3. J.L. Howard, U.S. Timber Production, Trade, Consumption, and Price Statistics 1965 to 2005. Preliminary draft, U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, Madison, WI (2006).
4. Wood Products Council, Wood Products Used in New Residential Construction in the U.S. and Canada—2003. APA–The Engineered Wood Association, Tacoma, WA (2005).
5. Wood Products Council, Wood Products Used in Residential Repair & Remodeling in the U.S. and Canada—2003. APA–The Engineered Wood Association, Tacoma, WA (2005).
6. J. Perez-Garcia, B. Lippke, D. Briggs, J.B. Wilson, J. Bowyer, and J. Meil, Wood Fiber Sci., Vol. 37; 3-17 (2005).
7. A.R. Denes, M.A. Tshabalala, R. Rowell, F. Denes, and R.A. Young, Holzforschung, Vol. 53; 318-326 (1999).
8. A.R. Denes and R.A. Young, Holzforschung, Vol. 53; 632-640 (1999).
9. L. Podgorski, C. Bousta, F. Schambourg, J. Maguin, and B. Chevet, Pigment Resin Technol., Vol. 31; 33-40 (2001).
10. D. Lukowsky, G. Hora, Macromolecular Symposia, Vol. 187; 77-85 (2002)
11. P. Rehn, A. Wolkenhauer, M. Bente, S. Förster, W. Viöl, Surface and Coatings Technology, Vol.174-175; 515-518 (2003).
12. M. Bente, G. Avramidis, S. Föster, E.G. Rohwer, and W. Viöl, Holz als Roh- und Werkstoff, Vol. 62; 157-163 (2004).
13. K.I. Brebner and M.H. Schneider, Wood Sci. Technol., Vol. 19; 75-81 (1985).
14. S. Donath, H. Militz, and C. Mai, Wood Sci. Technol., Vol. 38; 555-566 (2004).
15. M.A. Tshabalala, P. Kingshott, M.R. VanLandingham, and D. Plackett, J. Appl. Polym. Sci., Vol. 88; 2828-2841 (2003).
16. M.A. Tshabalala and J.E. Gangstad, J. Coatings Technol. Vol. 75(943); 37-43 (2003).
17. S. Donath, H. Militz, and C. Mai, Holzforschung, Vol. 60; 40-46 (2006)
18. S. Iakovlev, C. –H. Solterbeck, A. Piorra, M. Es-Souni, Thin Solid Films Vol. 414; 216-223 (2002)
19. Osman Goktas, M. Emin Duru, Mehmet Yeniocak, Ertan Ozen, Forest Products Journal, Vol. 58(1/2); 77-80 (2008)

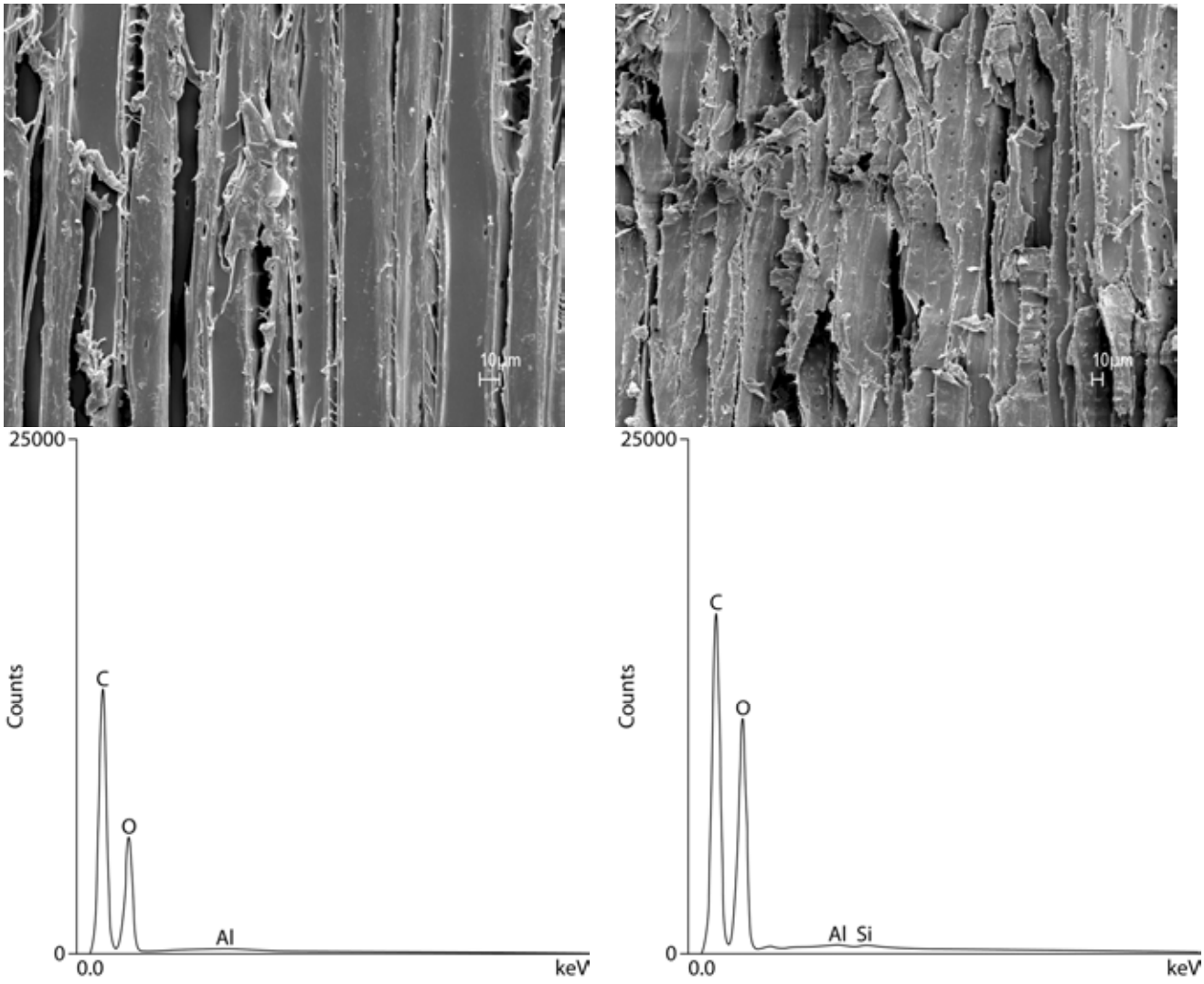


Figure 6: SEM micrographs and corresponding EDXA spectra of control specimen (a) before and (b) after 960 h exposure to filtered Xe arc radiation and water spray in the Weather-Ometer.

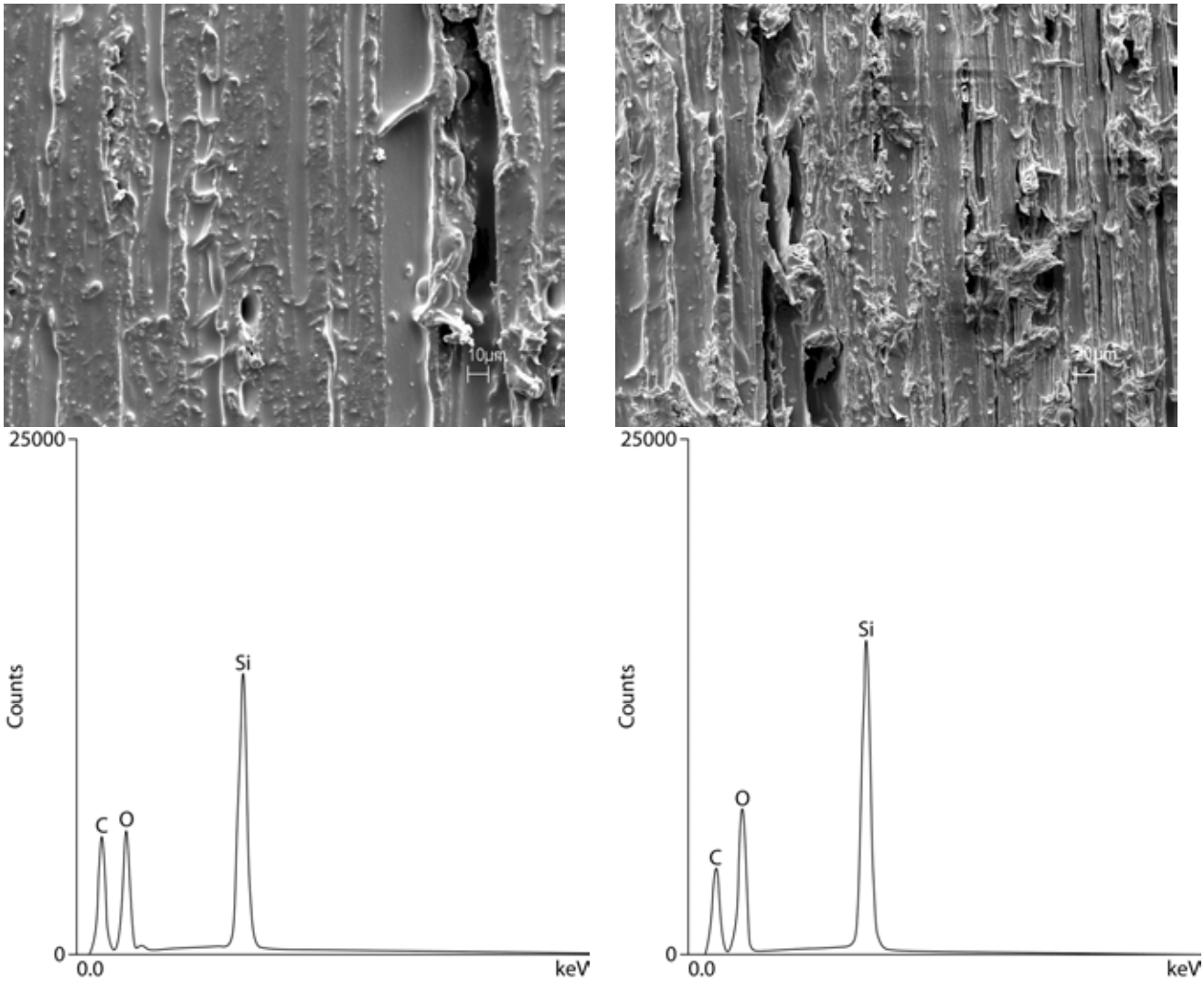


Figure 7: SEM micrographs and corresponding EDXA spectra of Sol I-treated specimen (a) before and (b) after 960 h exposure to filtered Xe arc radiation and water spray in the Weather-Ometer.

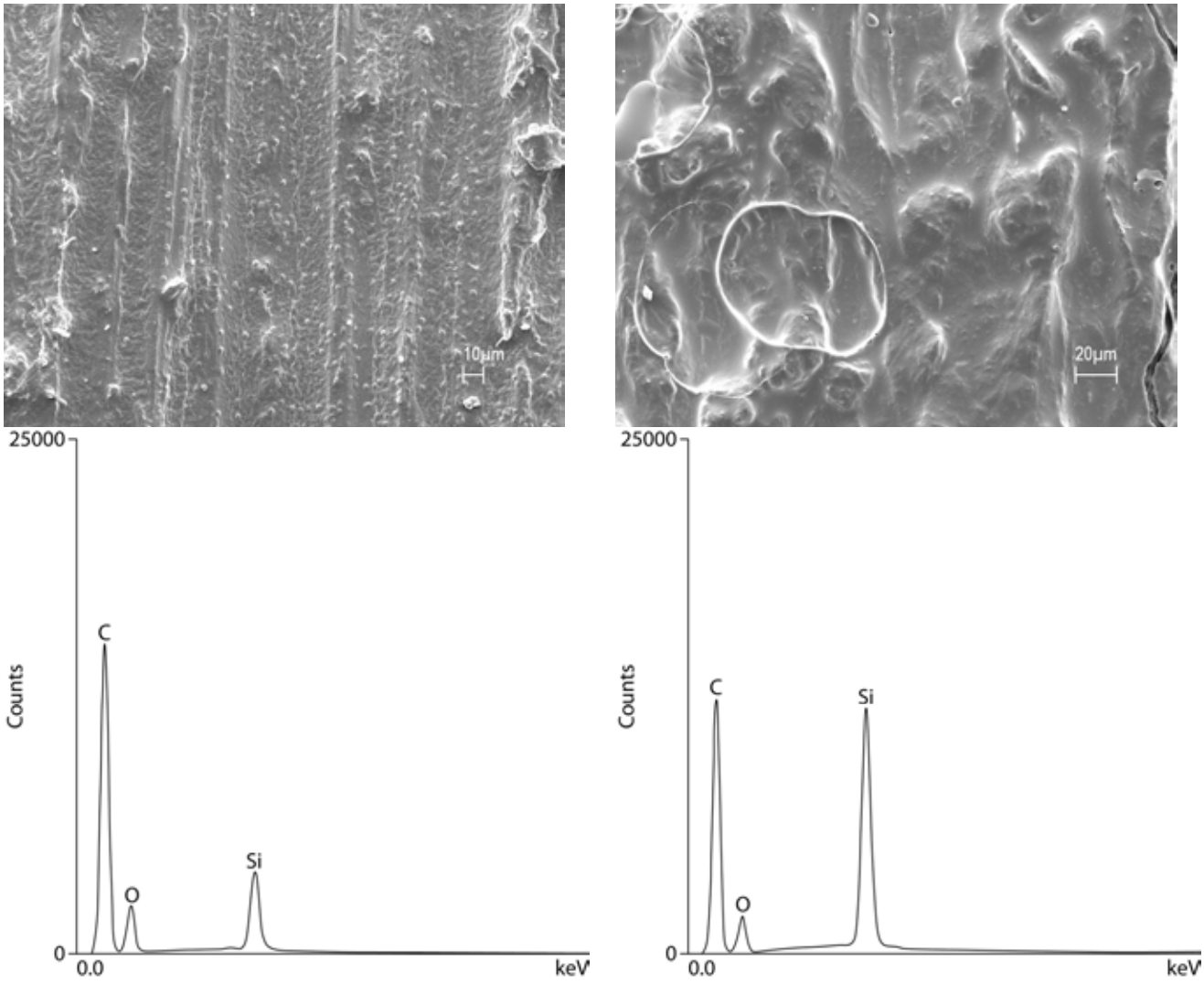
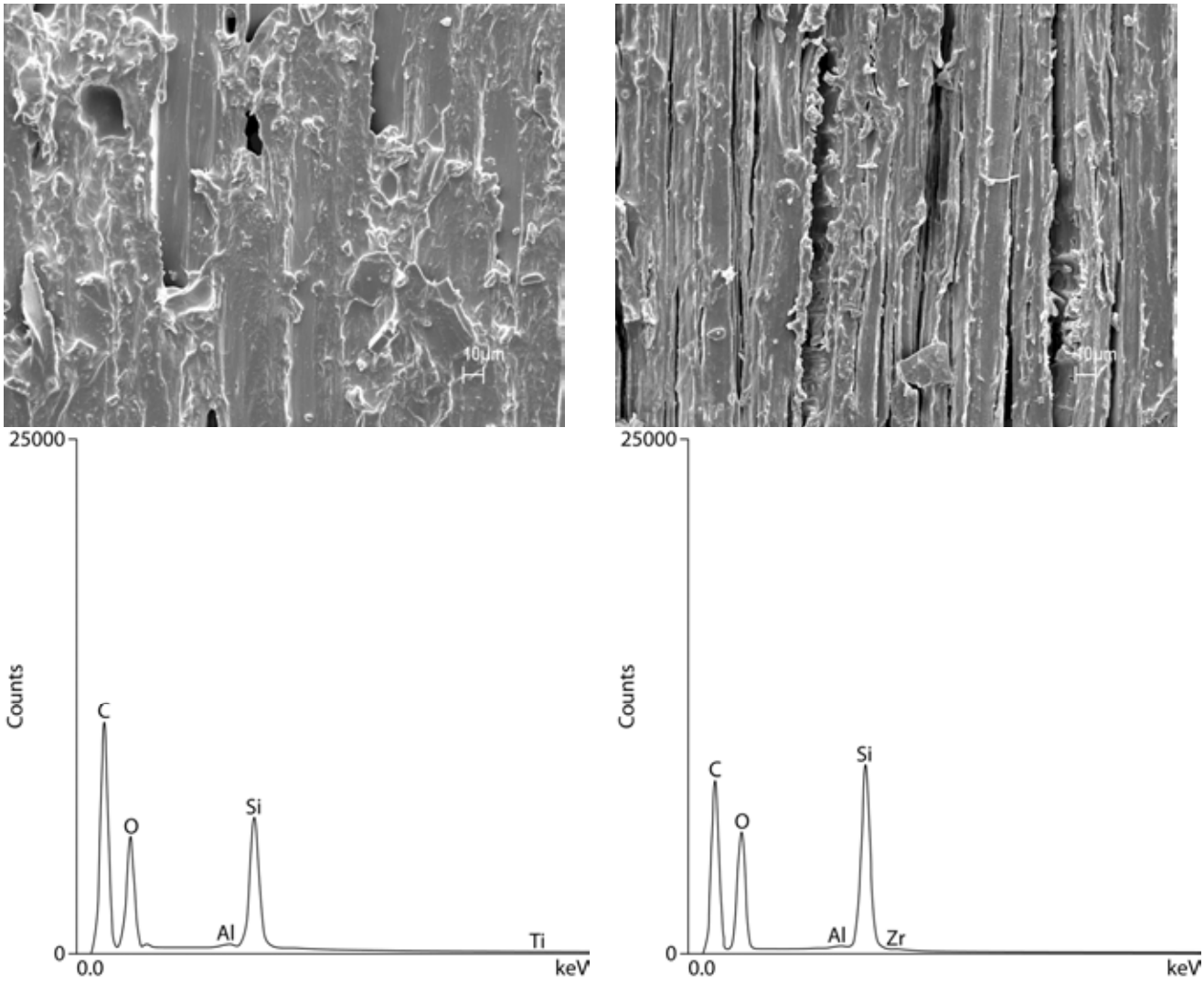


Figure 8: SEM micrographs and corresponding EDXA spectra of Sol II-treated specimen (a) before and (b) after 960 h exposure to filtered Xe arc radiation and water spray in the Weather-Ometer.



(a) (b)

Figure 9: SEM micrographs and corresponding EDXA spectra of Sol III-treated specimen (a) before and (b) after 960 h exposure to filtered Xe arc radiation and water spray in the Weather-Ometer.

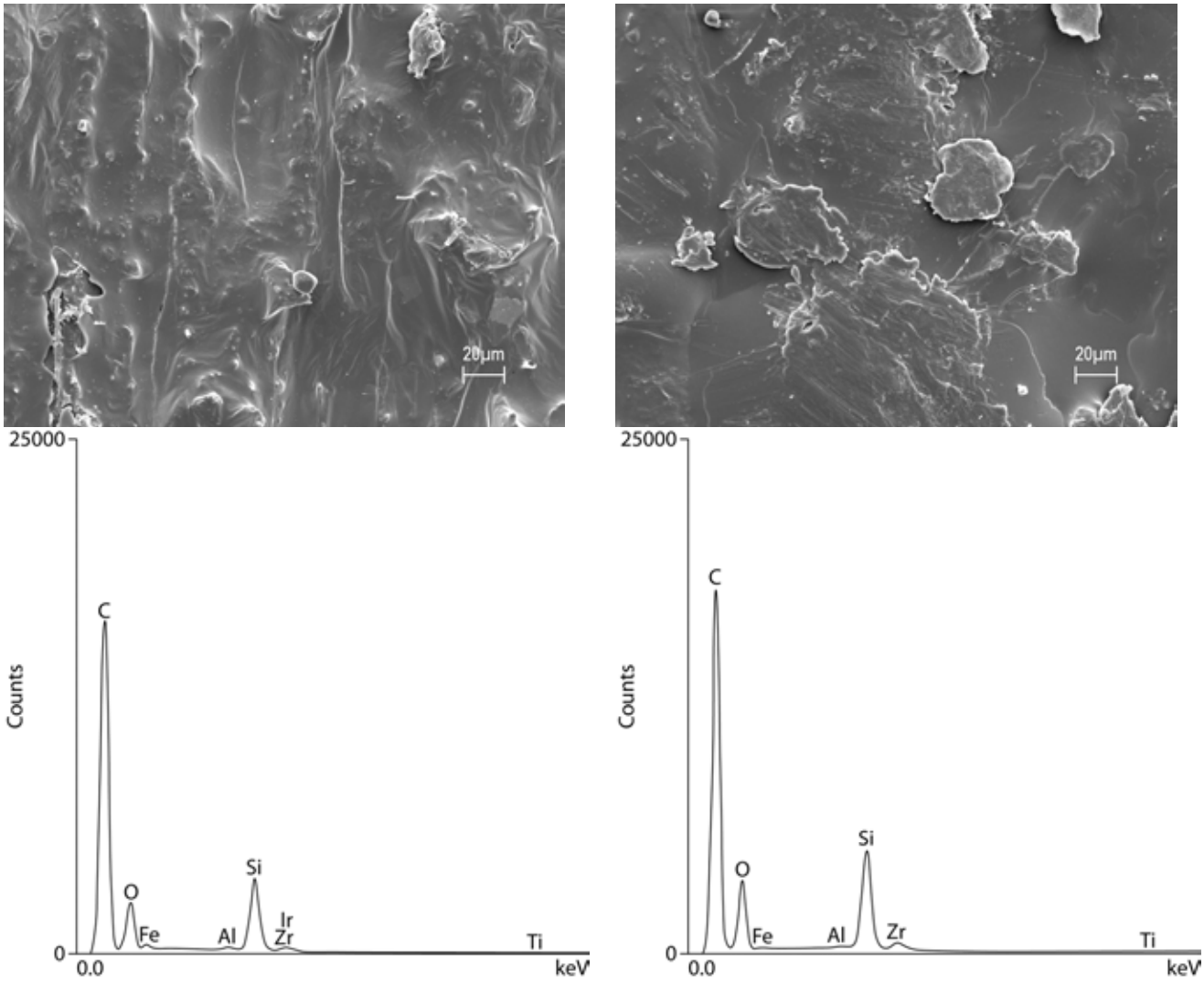


Figure 10: SEM micrographs and corresponding EDXA spectra of HDTMOS/Fe-Zr-Ti-treated specimen (a) before and (b) after 960 h exposure to filtered Xe arc radiation and water spray in the Weather-Ometer.

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