

ESCA Study of Oxidized Wood Surfaces

DAVID N.-S. HON,* *Department of Forest Products, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061*

Synopsis

Results of a preliminary study of the surface of wood exposed to outdoor weathering as well as to UV irradiation showed that ESCA provides valuable information and insight into the manifestation of weathering and photooxidation. From the ESCA spectra, the increase in signal intensities of carbon–oxygen bonds and oxygen–carbon–oxygen bonds (or unsaturated carbon oxygen bond) and oxygen-to-carbon ratio, and the decrease in carbon–carbon and carbon–hydrogen bonds of weathered and UV-irradiated wood surfaces suggested that wood surface was oxidized. Nevertheless, it was a superficial effect. Only a slow oxidation was observed at 100 μm under the exposed wood surfaces. From the oxygen-to-carbon ratio data, it revealed that weathered wood surface was rich in cellulose, poor in lignin. The leached-away degradation products from weathered wood surface accounted for the discrepancy between the ESCA line shapes of UV-irradiated and weathered wood surfaces.

INTRODUCTION

Wood is a major industrial raw material that has a low energy requirement for conversion into manufactured products. Annual timber harvest and use in the United States is comparable in weight to all cement, steel, aluminum, and plastic products combined. Wood is very important in the construction field with about 40% of all manufactured lumber and plywood utilized for this purpose. Over 40% of all exterior siding used in construction is wood and wood based.

Wood is beautiful and durable. It is warm to touch and easy to process. However, since wood is a biological natural product, when used outdoors, it is susceptible to environmental deterioration.^{1,2} This deterioration process is an important consideration in the selection of wood and wood-based materials for outdoor applications. Since wood possesses natural color, it is a good light absorber.³ It interacts with all ranges of electromagnetic energy including fluorescence light and sunlight.⁴ Although weathering and photodegradation of wood are a slow process of surface reaction,⁵ it directs to drastic change in its appearance, i.e., color, loss in brightness, and roughening and checking of surfaces.⁶ At the microscopic level, the cell walls can be deteriorated and pit structures can be destroyed.⁷ Oxygen and singlet oxygen⁸ appear to participate in photooxidation of wood surface, which consists of cellulose, hemicelluloses, and lignin to make the surface chemistry of wood extremely complicated.

Despite its technological importance, little is known about the surface composition of wood, particularly in weathered wood surfaces. Illustration

* Present address: Department of Forestry, Clemson University, Clemson, SC 29631.

of the mechanism has been hampered by a lack of information concerning the actual composition and the chemical nature of the resultant surfaces. The bulk composition of dry extractive-free hardwood is approximately 43% cellulose, 38% hemicelluloses, and 20% lignin.⁹ These components are distributed unevenly across the cell wall, where the secondary wall contains most of the cellulose and lignin; the middle lamella is high in lignin content. However, the surface modification of wood due to weathering is likely to change its surface components from that of the bulk material. Even though knowledge of the chemical composition of wood is important, the understanding of the surface chemistry of weathered wood surface would be of still greater value. The surface structure and the surface composition of weathered wood are of special importance since those properties are vital for wood adhesives and coatings applications. The understanding of the onset of actual weathering and the concomitant changes in the chemistry of the surface of the wood is crucial and is the basis for providing a sound foundation for weathering protection, developing stable finishes and coatings and improving adhesion properties of wood surfaces. One technique especially suited for studying wood surface modification is ESCA (electron spectroscopy for chemical analysis).¹⁰ This technique provides information on the chemical composition, the chemical states (bonding and oxidation), and the location of atoms types with the samples. It has proved very useful in analyzing the surface composition of polymeric materials,¹¹ and, in particular, of polymers with functionally modified surfaces.¹²⁻¹⁴ Its application to the surface analysis of wood and fibers has recently been reported.¹⁵⁻¹⁹

The principal objective of this study is to investigate the changes in surface chemistry of wood associated with outdoor weathering and UV irradiation. It is hoped that the use of this technique will stimulate research in this area to investigate the wood surface characteristic for adhesion and coating application.

EXPERIMENTAL

Materials

Yellow poplar (*Liriodendron tulipifera*, sapwood) was used for this study. Four sets of tangential sections of wood with 100 μm thickness were prepared. A set of samples were stored in dark for 3 months before the ESCA study; a set of samples was prepared immediately prior to the ESCA study by cutting 100 μm below the surface. Two other sets of samples were weathered outdoors at Blacksburg, Virginia for 90 days (July to October) and subjected to UV irradiation for 100 h, respectively. Milled wood lignin (MWL) was isolated from red mulberry (*Morus rubra*) using a modified Bjorkman procedure.²⁰ Fresh filter paper obtained from Fisher Scientific was used as the cellulose sample.

Procedures

All ESCA spectra were measured with a DuPont Model 650 Electron Spectrometer with a $\text{MgK}\alpha$ X-ray source and equipped with a multichannel analyzer and data reduction system. The samples were analyzed for the

carbon 1s (C_{1s}) and oxygen 1s (O_{1s}) peaks. Where binding energy assignments for particular functionalities were made, the C_{1s} peak for hydrocarbon species was used as the reference and assigned the value of 285.0 eV to compensate for charging effect. The C_{1s} peaks were analyzed by digitizing them and then using a curve fitting procedure. The relative stoichiometric ratio of oxygen to carbon was calculated using the formula listed below:

$$I = FkSbN$$

where I represents peak in intensity, F and K represent instrument constants, S , cross section, N , numbers of atoms per unit area, and d , mean free path (which is a function of the electron kinetics energy).

Rearrangement of this equation for oxygen and carbon, the ratios of oxygen-to-carbon can then be obtained as shown below:

$$\begin{aligned} \frac{N_o}{N_c} &= \frac{FkS_c d_c I_o}{FkS_o d_o I_c} \\ &= \frac{S_c d_c I_o}{S_o d_o I_c} \end{aligned}$$

Relative values of $S \times d$ for an atom's specific atomic orbital is essentially a constant for each X-ray source. These values have been published for aluminum and magnesium alpha X-ray sources.²¹ The values for C_{1s} and O_{1s} are 1.00 and 2.85, respectively. The peak intensities were calculated based on the peak areas.

RESULTS AND DISCUSSION

ESCA Spectra of Surfaces of Wood, Cellulose, and Lignin

The ESCA spectra of all wood specimens consist of a single O_{1s} peak and a C_{1s} peak made up of three components. A typical ESCA spectra of the C_{1s} for wood surface is shown in Figure 1. It is apparent that two high binding energy shoulders are visually discernible, indicating the occurrence of chemical shift due to the different environments of the carbon atoms in cellulose and lignin at the wood surface. This C_{1s} spectrum is essentially superimposed with three components which can be resolved by a DuPont 310 curve: The

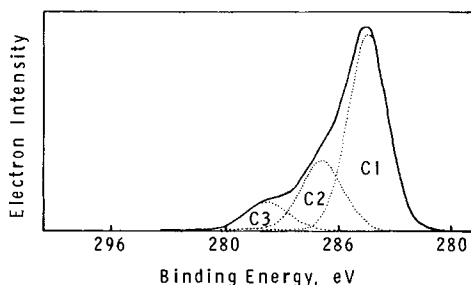


Fig. 1. A typical ESCA spectrum of wood surface.

principal peak (C_2) arising at 287.0 eV is assigned to —C—O— bonds, the higher-energy shoulder (C_3) at 289.5 eV to —C=O or —O—C—O— bonds, and the lower-energy shoulder (C_1) at 285.0 eV to carbon bonded only to carbon and hydrogen.^{6,15} The C_3 peak possibly contributed to the cyclic hemiacetal linkage of the cellulose. A small amount of carbonyl or carboxylic groups or acetyl groups at the wood surfaces may also contribute to this signal. From the relative size of the oxygen and carbon ESCA peaks, the ratio of oxygen atoms to carbon atoms in the surface of wood, N_o/N_c , can be obtained as discussed earlier. This ratio gives a direct measurement of the surface associated with oxygen, with a high oxygen content normally signifying a surface that has been oxidized. The oxygen-to-carbon ratio of a fresh surface (i.e., 100 μm below surface) was 0.27. The ESCA spectrum of cellulose (a fresh filter paper), as shown in Figure 2, was also a composite of three components at the C_{1s} peak resembled the wood surface. Because of cellulose chemical structure, namely, carbons bonded to carbon and to oxygen, it can account for C_1 and C_2 peaks. C_3 peak is due to hemiacetal linkage. In principle, cellulose has the gross formula $(\text{C}_6\text{H}_{10}\text{O}_5)$ and thus the oxygen-to-carbon ratio should be 0.83. However, the ESCA experimental data showed an unsatisfactory low oxygen-to-carbon ratio value, i.e., 0.62. This implies that impurities with hydrocarbon nature are possibly deposited at the cellulose surface. The ESCA spectrum of MWL (Fig. 3) should give an indication of its contribution to the C_{1s} peak. Due to its aromatic nature, lignin also exhibits a shakeup satellite peak. The oxygen-to-carbon ratio of lignin surface was 0.34. In comparison the ESCA spectra and oxygen-to-carbon ratios of wood surface to cellulose and to lignin, it is apparent that wood surface was relatively high in carbon-to-carbon and carbon-to-hydrogen bondings, i.e., hydrocarbon characteristic (hydrophobic in nature). The same surface characteristics was for lignin. But cellulose was high in oxygen-to-carbon bondings, i.e., more hydrophilic in nature.

ESCA Spectra of Weathered and UV-Irradiated Wood Surfaces

The ESCA patterns of outdoor weathered and UV irradiated wood surfaces were detected and shown in Figures 4 and 5, respectively. The C_2 and C_3 peaks of C_{1s} (for both exposed specimens) were intensified, especially for the C_3 peak, indicating that the exposed wood surfaces increased in higher oxidation states over the control. The oxygen-to-carbon ratios for weathered (0.57) and UV-irradiated wood (0.61) were much higher than that of the

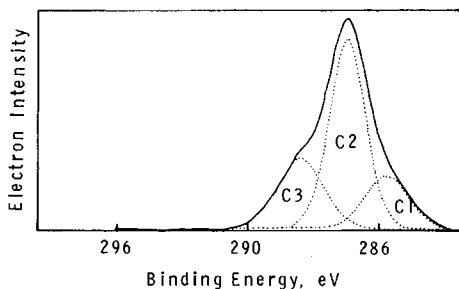


Fig. 2. ESCA spectrum of cellulose surface.

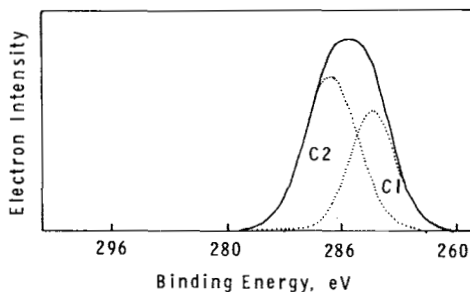


Fig. 3. ESCA spectrum of milled wood lignin.

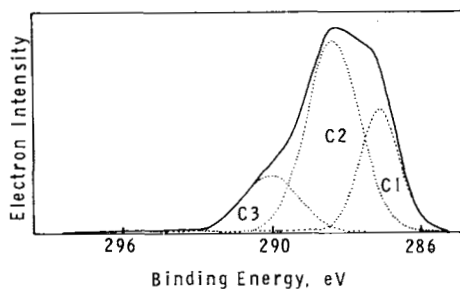


Fig. 4. ESCA spectrum of outdoor weathered wood surface.

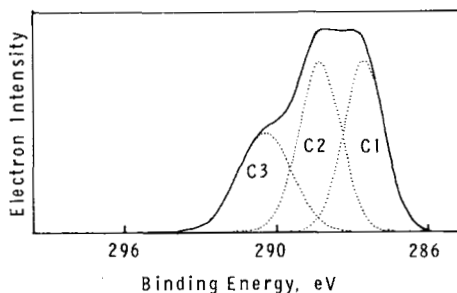


Fig. 5. ESCA spectrum of ultraviolet light irradiated wood surface.

control (0.27). Careful analysis of the line shapes and intensities of each component at exposed surface, it is of interest to notice that the outdoor weathered wood surface exhibited similar ESCA patterns to that of cellulose filter paper. This implies that weathered wood surface was rich in cellulose, poor in lignin. Although the UV irradiated wood surface was oxidized, its surface exhibited the characteristic ESCA line shape of lignin. Since UV light used in this study emitted shorter wavelength below 289 nm (a shortest wavelength emitted from solar energy), it is believed that UV irradiated wood, due to stronger energy from the light source, suffered severe oxidation than weathered wood, as evident from the stronger intensities of C_3 peak from UV irradiated wood. Furthermore, in addition to solar irradiation, water (due to moisture, rain, or dew) is also participated in outdoor weathering. In a previous study of surface degradations of wood by UV light using IR and UV spectrophotometers,^{1,2,5} it was found that low molecular weight degradation products derived from lignin were water-soluble. During the

process of outdoor weathering, the water-soluble degradation products of lignin being generated at wood surface were likely washed or leached away from the wood surface; accordingly the weathered wood surface was rich in cellulose, poor in lignin. This is accounted for the low intensities of C_1 peak for the weathered wood surface. These ESCA findings were further supported by earlier conclusions based on IR studies that carbonyl or carboxylic groups were generated at wood surface, and lignin were degraded preferentially by UV light.⁵ The washed-away lignin degradation products were contributed to the disappearance of lignin infrared absorbant peak at 1510 cm^{-1} .

The examination of ESCA spectra of wood $100\text{ }\mu\text{m}$ below the weathered surface, as shown in Figure 6, revealed that ESCA spectra of the wood surface slightly changed its line shape, with an oxygen-to-carbon ratio of 0.36, which was slightly higher than the controlled sample (0.27). This suggested that the degree of oxidation of the wood surface below $100\text{ }\mu\text{m}$ of weathered surface was very small. In addition, the ESCA spectrum of wood surface $200\text{ }\mu\text{m}$ below the weathered wood surface showed identical signal with the control (Fig. 1) suggested that no oxidation took place at this depth under the exposed surface. It is obvious that weathering of wood surface was a superficial phenomenon, in accordance with earlier findings obtained from IR and ESR studies.^{1,3,5}

In summary, the area of each peak of the C_{1s} peak within the binding energy and their width at half-maximum and oxygen-to-carbon ratio for all wood species, cellulose and lignin samples, are tabulated in Table I.

CONCLUSIONS

The deleterious effect on wood surface induced by outdoor weathering and UV irradiation was straightforwardly monitored by ESCA. The use of ESCA technique has thus proved to be a useful method for wood surface studies. It shows great potential for future studies on weathering and oxidation of wood surfaces, and wood surface preparation for adhesives and coatings application. The ESCA spectra obtained from weathered and UV-irradiated wood surfaces showed further evidence for the proposed degradation mechanisms for wood during weathering and UV irradiation. In essence, ESCA spectrum exhibited an increase in the oxygen-to-carbon ratio, and an increase in higher oxidation states. In outdoor exposures, ESCA

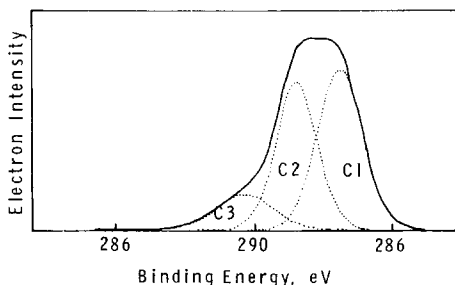


Fig. 6. ESCA spectrum of wood surface $100\text{ }\mu\text{m}$ underneath outdoor weathered wood surface.

TABLE I
Analysis of ESCA Carbon 1s Peaks

Sample	Oxygen-to-carbon ratio	Area (%)			Position (eV)			Full width at half- maximum (eV)		
		C ₁	C ₂	C ₃	C ₁	C ₂	C ₃	C ₁	C ₂	C ₃
Wood surface	0.27	64	26	10	285.0	287.0	289.5	2.1	2.3	2.2
Cellulose surface	0.62	18	56	26	285.0	286.5	288.3	1.9	1.7	2.1
Milled wood lignin	0.34	40	60	0	285.0	286.8	—	2.3	2.8	—
Weathered wood surface	0.57	27	56	17	285.0	286.6	288.7	1.6	2.1	2.2
UV-irradiated wood surface	0.61	36	37	27	285.0	286.5	288.3	1.6	1.7	2.1
Wood surface 100 μm un- derneath weathered wood surface	0.36	47	40	13	285.0	286.6	288.4	1.9	1.8	2.3

spectra also implied that wood surfaces was severely oxidized and degraded. The low molecular weight oxidation products, by and large, from lignin was leached away from surface by water or moisture. Nevertheless, the oxygen-to-carbon ratios of the outdoor exposed sample remained high, suggesting that oxidized wood surface was rich in cellulose and poor in lignin, after the oxidation products have been leached.

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