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Research Note

X-Ray Photoelectron Spectroscopic Study of Wood Lignins

In the course of investigating the possibility of using various renewable raw materials such as lignins as reaction-incorporated fillers for highly-filled thermoset polymer systems, we found it necessary to determine the concentration of the functional groups on the surface of these materials, since these are the only groups that can react with the polymer resin. Information can be obtained by u.v.-visible and i.r. spectroscopy combined with elemental analysis, but the x-ray photoelectron spectroscopic (XPS or ESCA) method has advantages in terms of speed and the large amount of previously published data. The availability of the latter makes it possible to compare quantitative data on the *exposed surfaces* of such complex materials as wood fibres, lignins, wool fibres, etc. (Mjoberg, 1981; Tillen *et al.*, 1980).

The samples of hardwood hydrolysis lignin and softwood sodium lignosulphonate were kindly donated by Mr Bendale of this laboratory. The hydrolysis lignin had been prepared by soaking hardwood chips in concentrated sulphuric acid, heating and then extracting the hydrolysed polysaccharides into water. The process was repeated several times, the temperature being raised each time, until at the final stage the temperature was about 160°C. The hydrolysis lignin thus obtained was a dry dark brown powder insoluble in pure water and partially soluble in aqueous alkaline solution. A Molisch test (Mackenzie, 1967) carried out on the latter solution was positive indicating the presence of some carbohydrate materials. Elemental analysis gave an ash content of 2·5%.

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The sodium lignosulphonate was of industrial origin in the form of a moist hard cake, dark brown in colour, and easily soluble in water. This material gave a negative Molisch test showing that no soluble carbohydrates were present. This was confirmed when a 1 g litre^{-1} solution in water gave no optical rotation. The u.v. spectrum gave a maximum at 282 mμ, which is consistent with previously reported spectra for lignosulphonates (Aulin-Erdtman, 1958).

ESCA measurements were recorded for the above materials on a VG ESCA 3 Mk II instrument at a base pressure of 10^{-8} Torr, with Alk$_\alpha$ (1486·6 eV) as the radiation source. Typical operating conditions for the x-ray tube were 14 kV and 10 mA. The Au$_{4f\,7/2}$ level at 84·0 eV was used for calibration of the energy scale with a full-width at half maximum of 1·6 eV. The hydrolysis lignin was loaded onto double-sided scotch tape attached directly to the spectrometer probe. For sodium lignosulphonate a paste had to be made in isopropyl alcohol and then smeared onto the tape with a clean spatula. The O/C ratios obtained are presented in Table 1, along with the values for another lignin sample reported by Mjoberg (1981). In the case of hydrolysis lignin the ESCA O/C value is 0·37, considerably lower than the bulk O/C value of 0·72 obtained by elemental analysis. A contributing factor to the higher latter value is the presence of small

TABLE 1
Atomic Ratios of Oxygen to Carbon Obtained by Comparison of O$_{1s}$ and C$_{1s}$ Peaks in the ESCA Experiment. (The Photoelectron Cross-section Value for the O$_{1s}$ Signal was Taken as 2·93.)

Sample	*O/C*
Hydrolysis lignin[a]	0·37
Sodium lignosulphonate[b]	0·38
Milled wood lignin[c]	0·39

[a] C, 47·93%; H, 5·71%; O, by difference.
[b] C, 33·40%; H, 5·48%; S, 5·05%; O, by difference.
[c] From Mjoberg (1981).

amounts of carbohydrate materials (as proved by a positive Molisch test) with O/C ratios in the region of 0·8 (for example cellulose has the formula $(C_6H_{10}O_5)_n$ with O/C = 0·83 and the hemicellulose xylan is $(C_5H_8O_4)_n$ with O/C = 0·80). On the other hand, it has been widely reported that impurities of the hydrocarbon type dominate the uppermost layers (Holm & Storp, 1980), and these can contribute significantly to the C_{1s} signal. Thus, it seems that the true O/C value lies somewhere in-between the ESCA and elemental analysis values. A similar general result was obtained for the sodium lignosulphonate case, except that here the elemental analysis O/C value was even higher (~ 1·2). Since no carbohydrate material was shown to be present (negative Molisch test, no optical rotation), this anomalously high value must be attributed to the high moisture content of this polymer. This ionic polymer rapidly absorbed atmospheric moisture after drying. In the ESCA experiment, the high vacuum environment precludes the possibility of moisture contamination; thus in this case the ESCA result is much more reliable.

In conclusion it can be said that the routinely used bulk O/C values obtained by elemental analysis do not always give a true picture of the functional groups available in lignin materials, since the possibility of a tenaciously held hydrocarbon-like impurity on the uppermost surface of the lignin is not taken into account. These surface impurities can only be revealed by ESCA. In considering the use of lignins as reaction-incorporated fillers with thermoset resins, allowance should be made for the fact that not all the functional groups will be available for reaction, since the highly aromatic nature of the lignins makes it easy for inert hydrocarbon-like materials to adhere to the top surface. At least for the non-hygroscopic lignins such as the hydrolysis lignin in a preparation such as ours, the true O/C value may be somewhere in-between the ESCA and the elemental analysis value. For very pure milled wood lignin the O/C value is reported to be 0·35, close to the ESCA value (Bjorkman & Person, 1957). Since in our case the ESCA values are close to 0·35, but the bulk values are much higher, it seems probable that a tenaciously held hydrocarbon-like layer dominates the top surface of lignin systems, and a combination of bulk elemental analysis and ESCA may give a more exact picture of the actual O/C ratio in such a system. However, this composite value is likely to be much closer to the ESCA value than the bulk value.

REFERENCES

Aulin-Erdtman, G. (1958). *Svensk Kem. Tidskr.* **70**, 145.

Bjorkman, A. & Person, B. (1957). *Svensk Papperstid.* **60**, 158.

Holm, R. & Storp, S. (1980). *Surface and Interf. Anal.* **2**, 96.

Mackenzie, C. A. (1967). *Experimental Organic Chemistry*, Prentice-Hall Inc., New Jersey.

Mjoberg, P. J. (1981). *Cellulose Chem. Technol.* **15**, 481.

Tillen, S. J., Pavlath, A. E., Zeronian, S. H. & Pittman, A. G. (1980). *Text. Res. J.* **50** (12), 724.

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