Carbohydrate Polymers 4 (1984) 473–480

Research Note

Photoelectron Spectroscopic Studies of Cellulose, Starch and their Oxidation Products, in Powdered Form*

SUMMARY

The use of X-ray photoelectron spectroscopic techniques (XPS or ESCA) in the characterization of cellulose, starch and their oxidation products is discussed. The ESCA results obtained from these materials in the finely powdered state are presented and compared to the results obtained with celluloses in the fibrous form. A far greater amount of surface impurities were found to be present for the powdered polysaccharides due to their greater surface area. Also, it has been shown that a high full-width at half-maximum (f.w.h.m.) value for the C_{1s} *signal is obtained with 100% periodate oxidized maize starch, while a smaller value was found for 11% periodate oxidized cellulose powder. Finally, cellulosic powders seem to produce the* O_{1s} *signal* $\sim$*0·8 eV downfield (i.e. higher binding energy value) as compared to the starches and this may be related to the rigid, crystalline and linear structure of the cellulose molecule as compared to the more amorphous and branched structure of the starches.*

X-ray photoelectron spectroscopy (XPS or ESCA) has become an important tool in the hands of polymer scientists for the identification of atoms and functional groups of polymers within a depth of about 10 nm of the sample surface, and for the study of morphology and topology (Siegbahn *et al.*, 1967; Clark & Thomas, 1978; Dwight & Thomas, 1981). In recent years the ESCA technique has been found to have such a diversity of uses; textile chemists use it as a tool for studying

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* NCL Communication no. 3078.

Carbohydrate Polymers 0144-8617/84/$03.00 –

treated textiles (Soignet *et al.*, 1976) and wood pulp technologists determine surface composition as a function of the pulping process (Dorris & Gray, 1978; Gray, 1978*a*,*b*; Mjoberg, 1981). Mjoberg (1981) has studied cotton wool, kraft pulp and Asplund fibres; Dorris & Gray (1978) have investigated bleached pulps; Dwight *et al.* (1978) have reported on cellulose acetate; and Clark *et al.* (1981) have described the surface chemistry of nitrated and denitrated cellulosic materials.

However, no group seems to have reported results on cellulose and starch powders, though these are important industrial materials. In our own laboratory we have been involved in developing cellulose and starch powder-based reaction-incorporated fillers for epoxy thermoset polymer systems. We have also prepared periodate oxidized samples of cellulose and starch and obtained very interesting curing characteristics with epoxy resins (Varma *et al.*, 1984). It is well known that the shape of the ESCA curve depends a great deal on the physical form of the sample (powder, solvent cast film, extruded film, etc.) (Clark & Thomas, 1978), on the extent of oxidation (Bishop, 1981) and on surface oxidation and contamination (Clark *et al.*, 1978). In this note we report the qualitative results of our ESCA studies with cellulose, starches and their oxidation products, all in fine powder form, and discuss the differences in their spectral characteristics.

The cellulose powder CP-100 was a commercial product of the Cellulose Products of India Ltd, Ahmedabad. It was a fine white powder, 93% of which could pass through a 240 mesh sieve, with the following specifications: bulk density, 0·3–0·4 g cm^{-3}; moisture at packing, 7% maximum; ash on a dry basis 0·5% maximum; α-cellulose 80–85%, pH 6·0–8·0; and ether extract 0·2% maximum. A pure variety of cellulose powder, cellulose Pulver 123, was procured from Schleicher and Schull, West Germany. This was also a fine white powder, 92% of it passing through a 200 mesh screen, and it contained 86% α-cellulose and ~14% hemicelluloses. Tapioca starch was a commercial product. Cellulose powder CP-100 was subjected to sodium metaperiodate oxidation under conditions which cleaved ~11% of the cellulose monomeric units (Varma *et al.*, 1984), while the 100% oxidized maize starch, also prepared by sodium metaperiodate oxidation, was kindly donated by Miss Khisti of this laboratory.

ESCA spectra were recorded on a VG ESCA 3 MKII instrument at a base pressure of 10^{-7} torr, with AlKα (1486·6 eV) and MgKα (1253·6 eV) as radiation sources. Operating conditions consisted of the X-ray gun at 14 kV and 10 mA. Under the experimental conditions employed, the $Au_{4f7/2}$ level at 84·0 eV, used for calibration of the energy scale, had an f.w.h.m. of 1·6. In obtaining the O/C ratios, peak areas were used rather than peak heights since there are chemical shifts and peak broadening effects on oxidation which make the use of peak heights unreliable (Bishop, 1981).

The results shown in Table 1 are qualitative since it is well known that there is strong adsorption of hydrocarbon-like impurities on cellulosic surfaces (Gray, 1978*a*,*b*; Mjoberg, 1981), and this feature can only be expected to be greatly enhanced for finely powdered samples. Also, no attempt was made to purify the samples (by solvent washing) just prior to the ESCA experiment, since these samples are used as received from the suppliers in our epoxy resin systems and also in

TABLE 1

Atomic Ratio of Oxygen to Carbon Obtained by ESCA (O_{1s} and C_{1s} Peak Area Ratios; Photoelectron Cross-sectional Value for O_{1s} is 2·93 for AlKα; X-ray source), and by Elemental Analysis; and the O_{1s} Binding Energy Peak Position (Relative to the C_{1s} Binding Energy Peak at 285 eV) along with the f.w.h.m. Values for O_{1s} and C_{1s}

Sample	*Surface O/C (ESCA)*	*Bulk O/C (elemental analysis)*	*O_{1s} peak position/ f.w.h.m. (eV)*	*f.w.h.m. for C_{1s} peak (eV)*
Cellulose CP-100 (as received from manufacturer)	0·25	–	532·9/2·8	2·8
Cellulose CP-100 (washed and stored)	0·32	0·91	533·0/2·8	3·2
Cellulose, Pulver 123	0·31	0·94	–	–
Cotton wool	0·58[a]	–	–	–
11% Periodate oxidized cellulose CP-100	0·27	0·93	533·0/2·8	3·5
Tapioca starch	0·39	0·96	532·3/2·5	3·1
100% Oxidized maize starch	0·45	0·84	531·1/3·0	4·6

[a] From Mjoberg (1981).

industrial processes. However, it was ascertained that when a particular cellulose sample received from a supplier was washed thoroughly with water and acetone, dried in a vacuum oven and then stored in a tightly closed polythene container for about a week, the O/C value obtained was only slightly better than the unwashed sample, but well below the theoretical value of ~0·8 (cellulose has the formula $(C_6H_{10}O_5)_n$ which gives an O/C of 0·83, while hemicelluloses such as xylans combined with uronic acids have an O/C of ~0·8 (Schuerch, 1963)). This is seen from the O/C values for cellulose and washed cellulose in Table 1. Also, the pure cellulose Pulver 123 of West German origin gave the same results as the washed and stored cellulose CP-100 from India.

This confirms that the adsorption of hydrocarbon-like impurities on cellulosic powders is very strong and quite rapid and the O/C value of 0·25 may be a lower limiting value for a sample such as our cellulose CP-100, as seen from Table 1. Similar trends have been noted with cellulose fibres (Mjoberg, 1981); however, in the case of fibres, due to their smaller surface areas as compared to the powders, the O/C values are somewhat closer to the expected value of ~0·8. It is seen from Table 1 that even cotton wool, considered a very pure form of cellulose, has an O/C value of only 0·58 (Mjoberg, 1981). Since elemental analysis of our cellulosic samples shows them to be essentially pure polysaccharides (the O/C values being slightly higher than the expected ones due to the moisture present) it is apparent that the low surface energy hydrocarbon-like impurities are present only in minute quantities and dominate the uppermost surface, as reflected by the ESCA results. It is estimated that the contribution of the ESCA signal from the outermost surface layer is ~30% of the total intensity and ~80% of the photoelectron signal is generated from a depth of 2λ below the surface, λ being the electron escape depth (Carley *et al.*, 1980). Also, with the help of two photon sources MgKα ($h\nu = 1253{\cdot}7$ eV) and TiKα ($h\nu = 4510$ eV) it has been shown that once account has been taken of the extraneous C_{1s} hydrocarbon component at 285 eV in the C_{1s} core level spectra of cotton linters which show two main components at 288·0 eV and 286·5 eV, the analysis of the core levels to obtain stoichiometries is straightforward (Clark *et al.*, 1981). Holm and Storp (1980) also recommend that only the contamination independent part of the C_{1s} peaks should be considered (e.g. the carbonyl group line) for obtaining stoichiometric information. However, the chemical shift range for the C_{1s} levels for polymers such as cellulose, starches and their oxidation products is sufficiently large and line shape analysis was not considered necessary for identifying structural features.

Table 1 shows that all the cellulose powders have surface O/C values in the range 0·25–0·32. This was true also for the ~11% periodate oxidized cellulose powder, where one would have expected a somewhat higher O/C value than the 0·27 obtained, since after the oxidation reaction the product is washed several times with water, acetone and methanol to remove any adhering oxidizing agent, and this process should have purified the product relative to the starting cellulose sample. Perhaps the greater amorphous nature of this oxidized cellulose, as shown by X-ray diffraction studies makes available a greater surface area for the hydrocarbon-like impurities to get adsorbed. However, the C_{1s} peak for this product has a greater f.w.h.m. than the cellulose CP-100 due to the new functional groups created (aldehyde and hemiacetal) (Nevell, 1963; Zhbankov, 1966; Varma *et al.*, 1984). This is seen from Table 1 and in Fig. 1. No change, however, was seen in the f.w.h.m. of the O_{1s} peak.

Similar trends are seen for the starches and, even though they are largely amorphous, the somewhat improved O/C values obtained may be due to the fact that the presence of lignins are not a problem here.

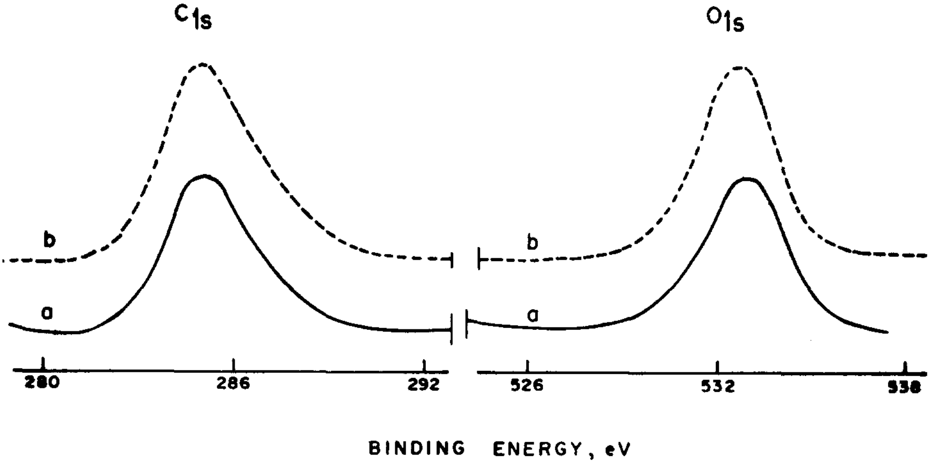

Fig. 1. C_{1s} and O_{1s} spectrum of (a) cellulose powder CP-100 (——) and (b) 11% periodate oxidized cellulose powder CP-100 (- - -).

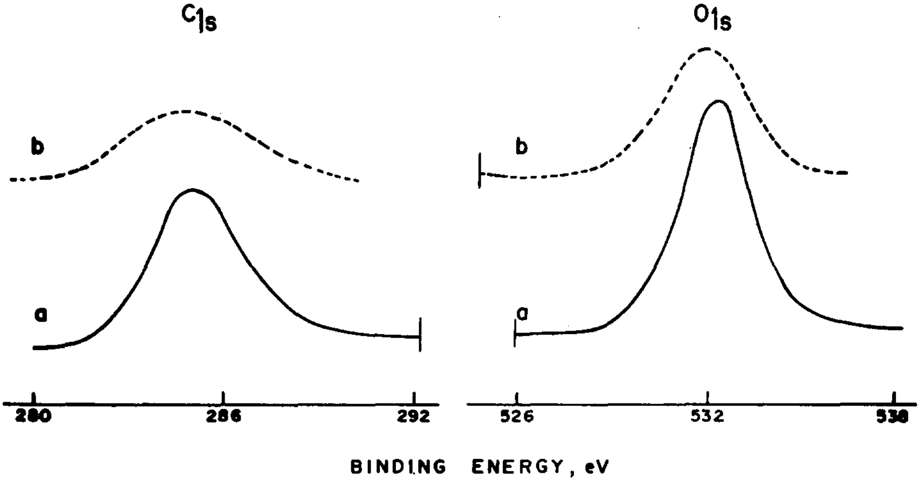

Fig. 2. C_{1s} and O_{1s} spectrum of (a) tapioca starch powder (——) and (b) 100% periodate oxidized maize starch (- - -).

Mjoberg (1981) has shown kraft pulp, made so that it was just under the point of fibre liberation, had an O/C ratio of 0·49, which indicated a surface rich in lignin. The f.w.h.m. for the C_{1s} peak of the 100% oxidized maize starch shows a high degree of line broadening (Fig. 2) due to the presence of C—C, C—OH, C—$(OH)_2$ and C=O bonds (Mehltretter, 1964). The O_{1s} peak is also quite broad. The f.w.h.m. broadening effects for the C_{1s} and O_{1s} peaks for the 11% oxidized cellulose powder were less compared to the respective peaks of the 100% oxidized starch, most likely due to the lower degree of oxidation. Finally, it is of interest to note that the O_{1s} peak maxima of the celluloses are ~0·8 eV more downfield (showing a higher binding energy value) as compared to the starches. Since both are polymers of D(+)-glucose, cellulose containing linear β-1,4-linked glucose units exclusively and starch consisting of both linear α-1,4-linked glucose chains (i.e. amylose) and chains containing about 20–25 α-1,4-linked glucose units which are in turn connected to each other by α-1,6-linkages (i.e. amylopectin), the chemical shift of ~0·8 eV downfield for cellulose compared to starches may be due to the rigid, crystalline and linear β-1,4-linked structure of cellulose. Thus, it is seen that ESCA is a useful technique for the characterization of polysaccharides. By noting the position of the O_{1s} signal (relative to the C_{1s} signal at 285 eV), starches can be distinguished from cellulose, and by studying the f.w.h.m. of the peaks one can get an idea of the extent of oxidation.

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(Received: 21 December 1983)