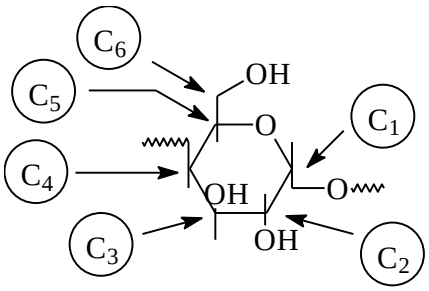
Appendix

The calculation of degree of substitution of the surface (DSS)

This parameter was deduced from the deconvoluted carbon (C1s) signal of XPS spectra. In this context, cellulose substrate displays, mainly three associated with carbon signal and centred at 285.0, 286.7, 288.3 and 289.0 eV. These moieties were attributed to C1 (C-H), C2 (C-O) and C3 (O-C-O and/or C=O), respectively (Belgacem et al. 1995). C1 peak at 285 eV is, not present in the cellulose structure. It was associated with the presence of some aliphatic and/or aromatic impurities could be partly removed by solvent extraction or by corona treatment (Belgacem et al. 1995).

C2 and C3 are the two peaks present in cellulose structure (see Scheme 1), C2 appears at 286.7 eV and it is associated to alcohols and ethers groups (C-O). This peak corresponds to 5 carbon atoms (C_2-C_6 in Scheme 2), and C3 is detected at 288.3 and attributed to acetal moieties (O-C-O). This signal corresponds to one carbon atom (C_1 in Scheme 1).



Scheme 1

C4 are present can also be detected although is a very slight intensity. This peak was assigned to carboxylic functions originating from glucoronic acids borne by hemicelluloses and present at the surface of lignocellulosic fibres and pulps destined to papermaking (Belgacem el al., 1995). In our case C4 was practically not detected in the original material. It, therefore, could be used as relevant peak to calculate the degree of substitution of the substrate surface. Thus:

$$\%C4 = \frac{Ncarbon_{C4}}{Ntot}$$

Where $Ncarbon_{C4}$ is the content of C4 carbon in one grafted glucose unit. As mensioned early, cellulose substrate did not display this carbon type but after grafting this signal has appeared. Ntot is the total number of carbon of one grafted glucose unit. From these considerations, the following equation can be established:

$$\%C4 = \frac{DSS \times Mc}{M_{AGU} + DSS \times M_{grafts}}$$

Where:

- DSS is the degree of substitution of the surface;
- M_C is the mass of carbon atom (12g/mol);
- M_{AGU} is the mass of anhydro-glucose unit (162 g/mol);
- M_{grafts} is the mass of the grafted moiety (depending on the grafting agent);

Then, following equations can be deduced:

$$(M_{AGU} \times \%C4) + (DSS \times M_{grafts} \times \%C4) = DSS \times Mc$$

$$(DSS \times \%C4 \times M_{grafts}) - (DSS \times Mc) = -\%C4 \times M_{AGU}$$

The combination of these equations, gives a final expression, as follows:

$$DSS = \frac{-\%C4 \times M_{AGU}}{\%C4 \times M_{grafts} - Mc}$$

M.N. Belgacem, G. Czeremuszkin, S. Sapieha, A. Gandini, *Cellulose* 1995, 2, 145-157.