# Hydroxyl accessibility in celluloses

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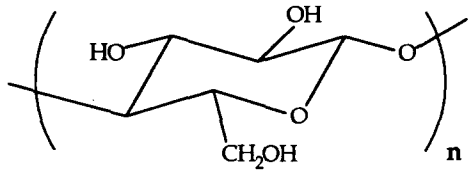
The crystalline content of a range of celluloses has been evaluated by X-ray diffraction and infrared spectroscopy. Chemical derivatization of these materials with trifluoroacetic anhydride in conjunction with X-ray photoelectron spectroscopy has been used to measure hydroxyl accessibility. A linear relationship is found between cellulose crystallinity and the rate of hydroxyl labelling.

**(Keywords: cellulose; hydroxyl accessibility; crystallinity)**

## INTRODUCTION

Cellulose is traditionally renowned for being the major molecular constituent of wood and cotton related products[1]. It can be employed as a naturally occurring substitute for synthetic polymers, and applications for its use include hemodialysis, electrophoresis and protein separation[2–5].




Cellulose belongs to the class of materials which are commonly referred to as polysaccharides; it is built up of anhydro β-D-glucopyranose units. Chemical reaction with its hydroxyl groups is a useful way of introducing new functionalities into the polymer[6]. Hydrogen bonding is the primary source of cohesion between the polymer chains, giving rise to crystalline (ordered) and amorphous (disordered) regions. A number of attempts have been made in the past to establish whether any correlation exists between hydroxyl group reactivity and the microstructural nature of cellulose. For instance, this accessibility has been reported to be a function of the degree of cellulose crystallinity[7]. Derivatization reactions are believed to occur preferentially at the surfaces of cellulose fibrils, whereas the interior of such fibrils tend to be inaccessible to ordinary chemical attack due to the close packed (strongly hydrogen bonded) nature of the polymer matrix[8]. A variety of chemical methods have been previously utilized to rationalize this behaviour: Hessler and Power[9] used iodine sorption to measure cellulose crystallinity, whereas Verlac *et al.*[10] and Rowland and Howley[11] attempted to probe the absolute and relative reactivities of the primary and secondary hydroxyls within the monomer unit by chemical microstructural analysis (CMA).

The major limitation of chemical methods devised in the past for hydroxyl determination has been their wet nature, which in turn can perturb the polymer structure via swelling. In this article, a gas phase labelling reagent is used: trifluoroacetic anhydride (TFAA) vapour (*Scheme 1*). This molecule reacts exclusively with hydroxyl groups and generates a volatile by-product[12]. Direct quantification of this reaction can be easily achieved by using X-ray photoelectron spectroscopy (X.p.s.)[13–15], since the $-CF_3$ group exhibits a large C(1s) core level shift towards higher binding energy[16]. A range of cellulosic materials (with varing degrees of crystallinity) have been evaluated by this method for hydroxyl accessibility.

## EXPERIMENTAL

Four types of cellulose with differing crystallinities were used in these studies: Avicell (Fluka Chemie AG), Sigmacell (Sigma Chemical Company Ltd), regenerated sponge cellulose (BPS Separations Ltd), and bacterial cellulose (BPS Separations Ltd). Poly(vinyl alcohol) $(-CH_2CH(OH)-)_n$ (PVA, Aldrich Chemicals, 98% purity, 100% hydrolysed) served as a model polymer substrate for the surface derivatization experiments. Each material was washed in a Soxhlet solvent extraction apparatus for 12 h with isopropanol (Analar grade), and then for a further 12 h with dry hexane (Analar grade). Any remaining solvent was subsequently driven off under vacuum at 60°C over several days. The cleaned

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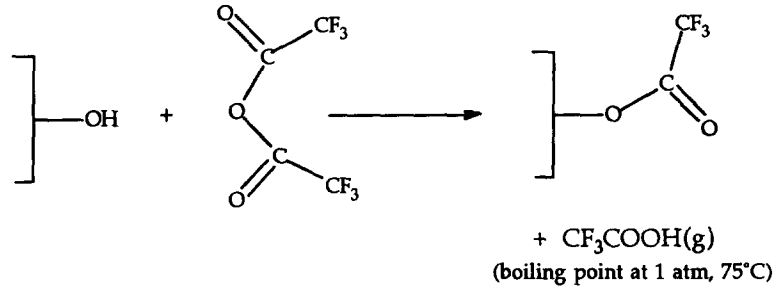


**Scheme 1** Labelling of surface hydroxyls with trifluoroacetic anhydride (TFAA)

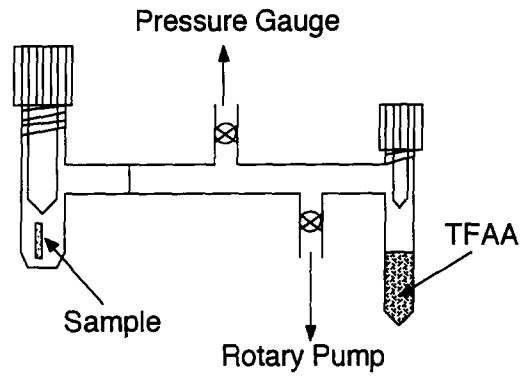


**Figure 1** TFAA labelling apparatus

samples were then cryomilled to ensure a similar particle size distribution (50 $\mu$m) prior to derivatization and characterization. TFAA (99% purity, Aldrich Chemicals) vapour was used as the labelling reagent.

A specially designed labelling apparatus was assembled[17] (*Figure 1*). All joints were grease-free. The whole system routinely achieved a base pressure of better than 6.7 Pa and a leak rate[18] of less than 1.3 Pa min$^{-1}$ by using an Edwards single stage rotary pump fitted with a liquid nitrogen cold trap. Following evacuation of the sample cell, it was isolated from the vacuum pump, and then TFAA vapour was allowed to equilibrate into the empty volume at ambient temperature (~25°C). At this point, timing of the labelling reaction commenced. Upon termination of exposure, the TFAA reservoir was isolated, and the apparatus/sample pumped back down to its initial base pressure. For each material, a reaction profile was compiled by varying the length of contact time with TFAA followed by X.p.s. quantification of the level of hydroxyl functionalization.

X.p.s. analysis was carried out on a Kratos ES200 X-ray photoelectron spectrometer operating in the fixed analyser transmission (FAT) mode, at a pass energy of 65 eV, and an electron take-off angle of 30° from the substrate normal. Mg $K\alpha_{1,2}$ (1253.6 eV) ionizing radiation was used as the photoexcitation source. C(1s) photoelectron spectra were fitted with Gaussian components having equal full widths at half maximum intensity (*FWHM*). All spectra are referenced to the C(1s) core level shift for adventitious hydrocarbon at 285.0 eV[19].

Attenuated total reflection infrared (a.t.r.-i.r.) measurements were taken on a Mattson Polaris *FT*i.r. instrument, equipped with a Specac optical table and a KRS-5 a.t.r. crystal. Cryomilled samples were pressed into discs and then mounted into the cell. I.r. spectra were accumulated at 4 cm$^{-1}$ resolution in the range 400 cm$^{-1}$ to 4000 cm$^{-1}$ over 100 scans.

X-ray diffraction measurements were taken at room temperature on a Siemens D5000 diffractometer, using a Cu $K\alpha_{1,2}$ source operating at 40 kV and 40 mA, over a $2\theta$ = 5–60° angular range.

## RESULTS

### *X.p.s. and TFAA labelling*

C(1s) X.p.s. spectra of unlabelled and labelled PVA are shown in *Figure 2*. Chemical information about each modified polymer surface was obtained by fitting the C(1s) X.p.s. spectrum to a range of carbon functionalities: hydrocarbon ($\underline{C}H_x$ ~285.0 eV), carbon singly bonded to one oxygen atom ($\underline{C}$–O ~286.6 eV), carbon singly bonded to two oxygen atoms (O–$\underline{C}$–O ~288.1 eV), carboxylate groups (O–$\underline{C}$=O ~289.1 eV), central carbon in a trifluoroacetate group (O=$\underline{C}OCF_3$ ~289.7 eV), and trifluoromethyl carbon ($\underline{C}F_3$ ~292.8 eV)[16]. Any contribution from Mg $K\alpha_{3,4}$ radiation was also taken into consideration, e.g. the $CF_3$ group introduces a satellite feature around 283.5 eV in the C(1s) spectra. The percentage of labelled hydroxyl groups was calculated from the $C(1s)_{CF_3}/C(1s)_{tot}$ peak area* ratios normalized with respect to the maximum hydroxyl functionalization theoretically possible.

C(1s) X.p.s. spectra of clean and labelled cellulose are shown in *Figure 3*. C(1s) binding energies for clean cellulose are in close agreement with those reported by Brown *et al*[20]. A minor carboxylate impurity at 289.1 eV, was also detected for all of the cleaned celluloses[20]; however, this was assumed to be negligible (less than 3% of the total C(1s) area). The extent of hydroxyl derivatization has been plotted against time for each of the cellulose samples studied (*Figure 4*). It can be concluded that the relative rates of labelling decrease in the following order: bacterial > regenerated > Sigmacell > Avicell. The limiting level of hydroxyl functionalization in each case was around 80% of the maximum theoretical value. The times taken to reach this plateau value are summarized in *Table 1*. The cryomilling process itself was not found to influence the TFAA labelling behaviour.

### *A.t.r.–FTi.r. of cellulose materials*

*Figure 5* shows an a.t.r.–*FT*i.r. spectrum of Avicell, which can be assigned as follows: 670 cm$^{-1}$ (OH wagging)[21], 893 cm$^{-1}$ ($C_1$ group vibration)[22],

* $C(1s)_{tot}$ was calculated as total C(1s) area less any contribution due to adventitious hydrocarbon contamination present on the surface

**Table 1** Summary of labelling and crystallinity results

| Sample | Plateau time (min) | Crystallinity ratio (X.r.d.) | Crystallinity indices (a.t.r.–*FT*i.r.) | |
|---|---|---|---|---|
| | | | $C_\alpha$ (1370/670) | $C_\beta$ (1429/2900) |
| PVA | 3 | – | – | – |
| Bacterial | 20 | 0.69 | 2.31 | 0.043 |
| BPS | 200 | 0.49 | 2.45 | 0.068 |
| Sigmacell | 600 | 0.85 | 2.61 | 0.088 |
| Avicell | 1500 | 0.85 | 3.26 | 0.161 |

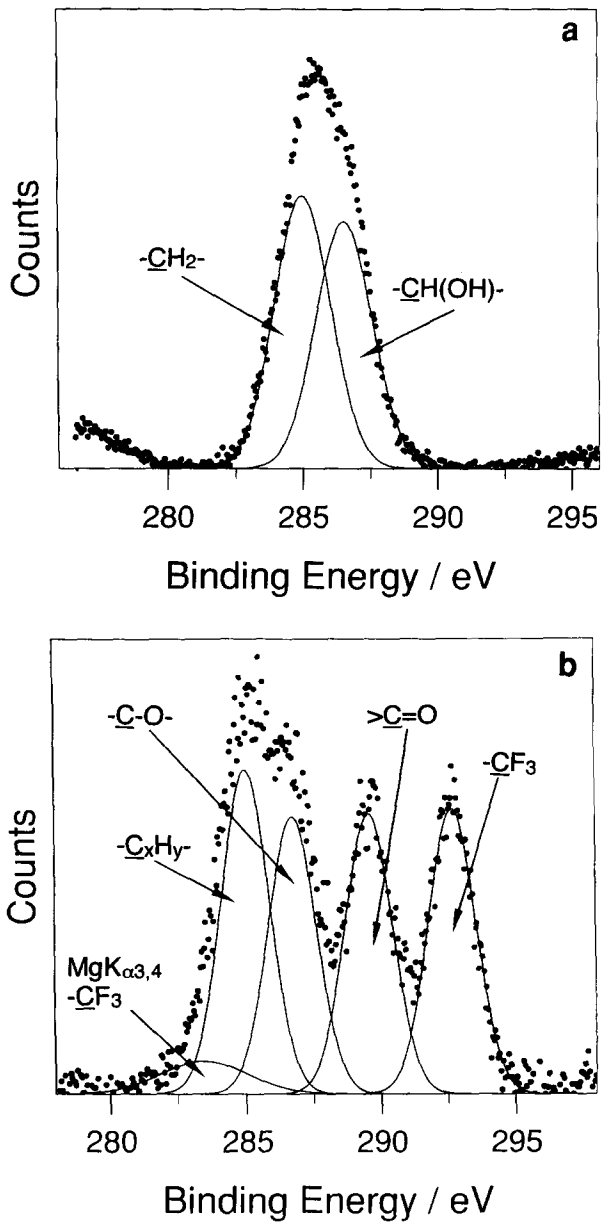


**Figure 2** C(1s) X.p.s. spectra of (a) clean PVA and (b) TFAA labelled PVA

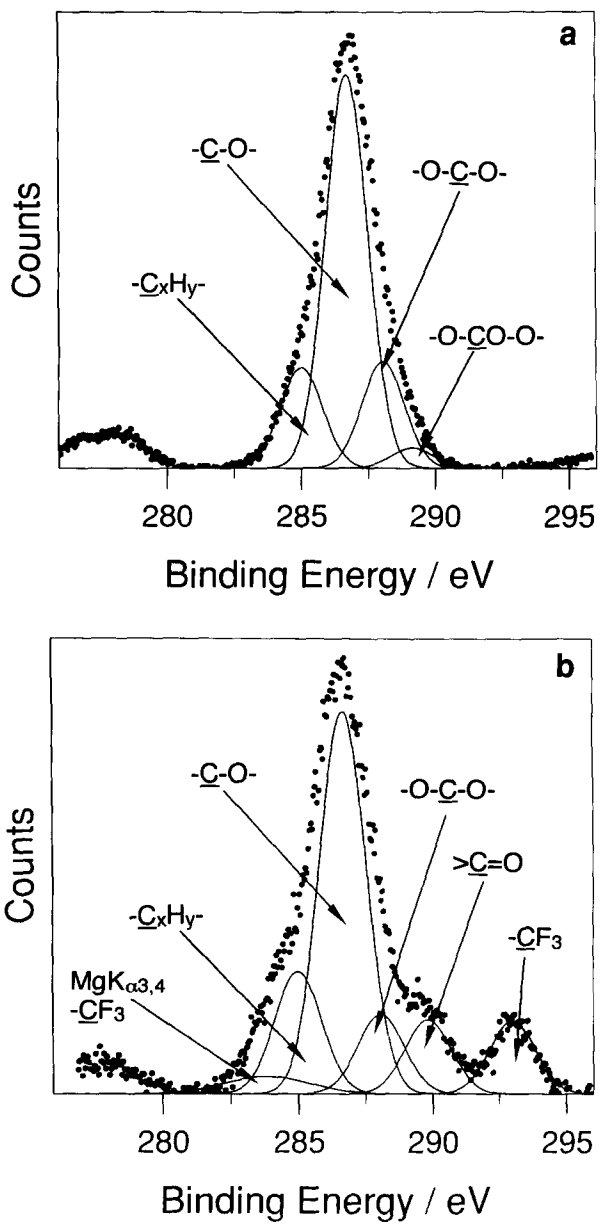


**Figure 3** C(1s) X.p.s. spectra of (a) clean Avicell cellulose and (b) TFAA labelled Avicell cellulose

1000 $cm^{-1}$ (C–C stretching modes)[23], 1060 $cm^{-1}$ (C–C–O stretching mode)[23], 1120 $cm^{-1}$ (C–O–C asymmetric stretch)[23], 1370 $cm^{-1}$ ($CH_2$ bending mode)[21], 1429 $cm^{-1}$ (in-plane OH bend)[23], 2893 $cm^{-1}$ (C–H stretching mode)[23], 3300 $cm^{-1}$ (intermolecularly bonded OH stretching mode)[23]. I.r. crystallinity indices ($C$) were calculated from the absorbance peak area ratios[21,22]:

$$C_\alpha = \frac{A_{1370}}{A_{670}}$$

$$C_\beta = \frac{A_{1429}}{A_{2900}}$$

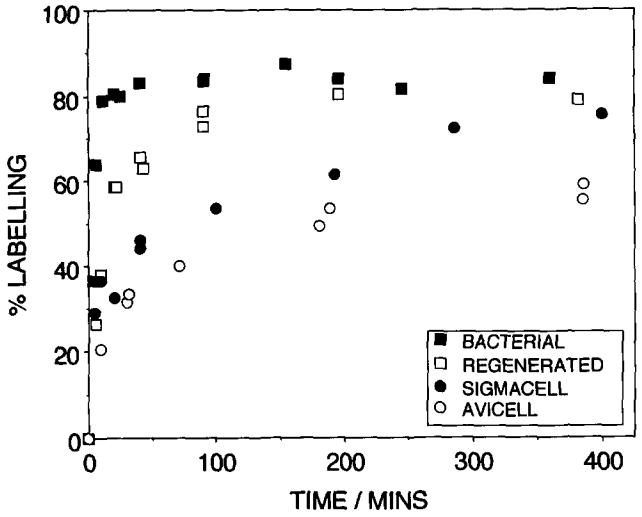


**Figure 4** Relative rates of hydroxyl functionalization by TFAA as measured by X.p.s.

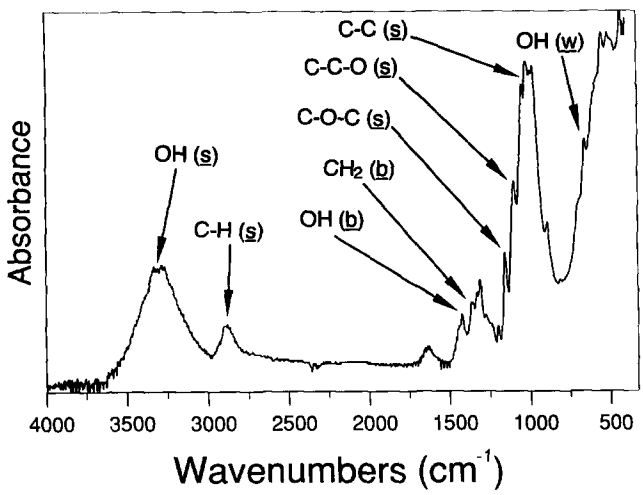


**Figure 5** A.t.r.–*FT*i.r. spectrum of Avicell cellulose: stretching (s), bending (b), and wagging (w)

*Table 1* lists the crystallinity indices $C_\alpha$ and $C_\beta$ as determined by a.t.r.–*FT*i.r. measurements. A linear correlation is found between the crystallinity indices and the limiting X.p.s. labelling times, as illustrated in *Figure 6*. Laszkiewicz and Wcislo[24] have previously suggested that the 1429/893 $cm^{-1}$ peak area ratio is representative of cellulose crystallinity; however, no such linear relationship was found in this study.

*X-ray diffraction*

The observed X-ray diffraction (X.r.d.) peaks for powdered cellulose can be attributed to crystalline scattering, and the diffuse background to disordered regions (*Figure 7*). Marked difierences are evident between the four types of cellulose used in this study. Spectra corresponding to Sigmacell, Avicell and bacterial cellulose exhibit diffraction features at the following $2\theta$ angles[22]: 23° (002), 21° (021), 17° ($10\bar{1}$) and 15° (101), which can be assigned to a type I polymorphic phase of cellulose. The regenerated cellulose is a type II material; the 23° (002) and 20° ($10\bar{1}$) lattice planes have similar intensity, therefore we would expect to see another diffraction feature around $2\theta = 15°$ due to the (101) lattice plane[22], but this seems to be obscured by the amorphous background scatter. Crystallinity ratio values have been calculated by using the method described by Buschle-Diller and Zeronian[25] (*Table 1*). From these measurements it can be concluded that Sigmacell and Avicell have comparable crystallinities, the bacterial sample is more disordered, and the regenerated cellulose has the largest amorphous content. No obvious correlation is evident between the X.r.d. crystallinity ratio and the limiting TFAA labelling time (*Table 1*). For a polycrystalline specimen, the profile of each diffraction line is determined by crystallite size distribution, the

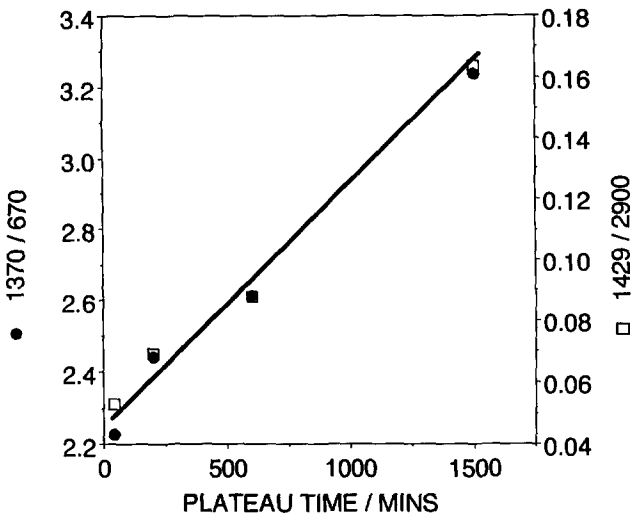


**Figure 6** Crystallinity indices (as determined by a.t.r.–*FT*i.r.) *versus* limiting TFAA labelling times

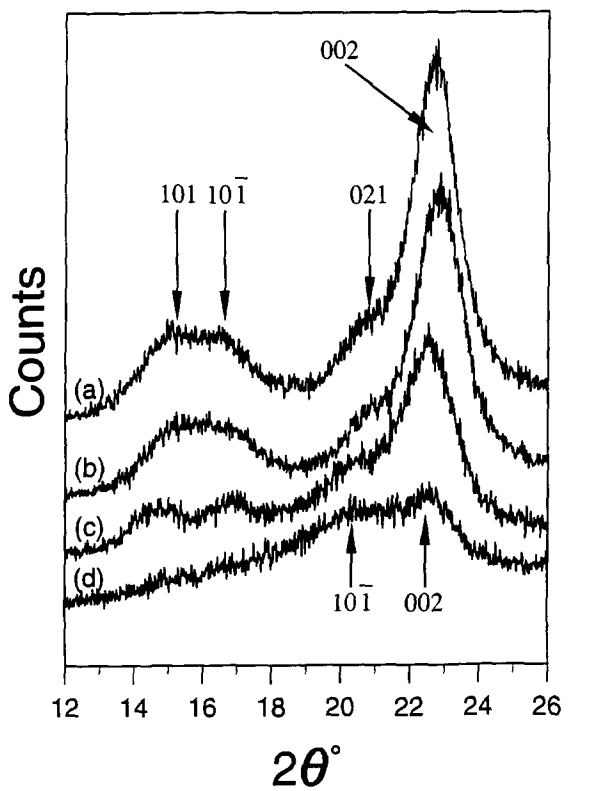


**Figure 7** Powder X-ray difiraction patterns for (a) Sigmacell, (b) Avicell, (c) bacterial cellulose and (d) regenerated cellulose

nature and magnitude of lattice distortions, and the spectral distribution of energy in the incident radiation[26]. The cellulosic materials under investigation potentially have varying crystallite size distributions and therefore would be expected to exhibit different broadening effects.

## DISCUSSION

PVA labelling occurs very rapidly, and to total completion[13–15,26], whereas TFAA derivatization of the cellulosic materials was very sluggish and never reached the predicted theoretical value. In contrast to previous techniques used for determining surface hydroxyl accessibility in celluloses, this method is non-solvent based and is therefore far less likely to suffer from swelling effects. Clearly the rate of labelling by TFAA is influenced by the degree of cellulose crystallinity. Hydroxyl accessibility is dependent upon the packing efficiency of the cellulose polymer chains. Well packed cellulose chains experience strong hydrogen bonding, whereas an amorphous structure will be more open. Hence the efficiency of hydroxyl derivatization is dependent upon the degree of cellulose crystallinity under consideration. Reaction with TFAA could lead to disruption of hydrogen bonding, which in turn may influence accessibility to hydroxyl centres. This was evident during the TFAA labelling experiments of PVA, where over long exposure times, a visible swelling of the polymer was discernible. No comparable swelling was found for the cellulosic materials. This may be attributed to one or more of the following factors: (i) cellulose possesses a greater porosity[27,28], and this pore structure may accommodate any swelling; (ii) hydrogen bonding may be more extensive within cellulose; or (iii) since surface hydroxyl density is much lower in cellulose, this should result in a smaller number of trifluoroacetyl groups being incorporated into the material. The only limitation of the TFAA labelling technique appears to be that it is unable to discriminate between the three different types of hydroxyl groups present within an individual cellulose monomer unit.

Xp.s. samples the topmost 20–50 Å, whereas a.t.r.–*FT*i.r. probes deeper down into the 100–1000 Å range, and X.r.d. is a bulk characterization technique. Since there is a linear correlation between the X.p.s. and i.r. data, it can be concluded that the crystallinity measured at the surface resembles that present within the subsurface region. The non-linear dependence of the X.p.s. data upon crystallinity determined by X.r.d. can be explained in terms of X.r.d. being sensitive only to well-ordered regions above a minimum crystallite size[29,30], whereas i.r. spectroscopy measures crystallinity at the molecular level (i.e. interchain packing has a direct influence on the vibrational behaviour of the cellulose polymer)[22].

## CONCLUSIONS

Hydroxyl reactivity can be quantified by exposure to TFAA vapour followed by X.p.s. analysis. The ease with which a hydroxyl centre can be derivatized in a cellulosic material is found to be directly dependent upon its crystallinity. Amorphous celluloses can be functionalized much more readily than their crystalline counterparts.

## ACKNOWLEDGEMENTS

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