

Surface Chemical Analysis of Thermally Degraded Cotton

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Introduction

- Development of flame retardant textiles relies on understanding the thermal decomposition of the polymer and interaction with flame retardant.
- Historically, cotton has been the dominant textile - hence flame retardant systems developed for cellulosic materials.
- **Levoglucosan (1,6-anhydro-β-D-glucopyranose)** is major cellulose pyrolysis product.
- Most studies have focussed on **BULK CHARACTERISATION**, ignoring the vital **SURFACE** region where the heat source “contacts” the fibre.
- ToFSIMS and XPS have been used to characterise the **SURFACE** of thermally degraded cotton.

Experimental

Materials - 100% cotton interlock fabric supplied by Phoenix Calico Ltd. Prepared by boil bleaching, scour/rinse/dry. Pure levoglucosan powder supplied by Sigma Aldrich Ltd.

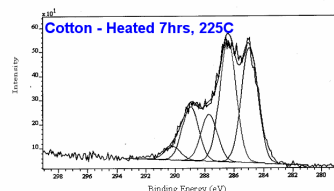
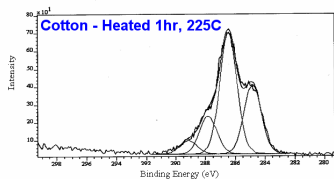
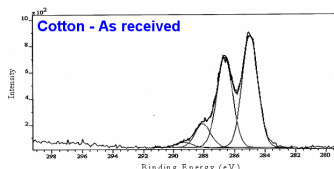
Thermal Treatments – Cotton fabrics, 10cm x 10cm, heated in an oven @ 225C – removed at 0, 1, 3, 7, 15 and 23 hour intervals

XPS – Al Kα X-rays (1486.6eV), elliptical spot size 1mm x 0.4mm, 180W, ~7eV electron flood

ToFSIMS – Phi 7000 instrument, 8keV Cs⁺ primary ion beam, pulse length 1.25ns, ~60eV pulsed electron flood

Results

XPS spectra



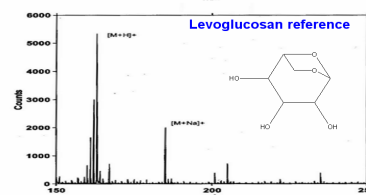
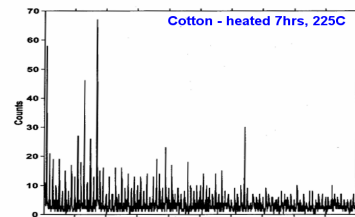
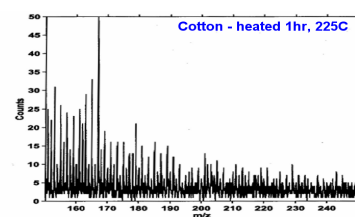
From XPS :-

- **Initial heating** - reduction in C-C and C-H bonding (285eV) – increase in C-O-C, O-C-O, -C=O bonding (286.6-288.0eV) – see table 1.
- **Beyond 7hrs at 225C** – increased formation of -C=O, O-C=O and CO₃ functionality (289.0 –290.2eV).
- Elemental composition, oxidation state and simple functionality only – from XPS.

XPS	% Contribution to C (1s) Peak Intensity					
	Unheated	1 hr*	3 hrs*	7 hrs*	15 hrs*	23 hrs*
C-C/C-H	33.4	18.3	15.5	14.6	15.8	19.8
C-OH	27.2	32.4	33.8	30.3	28.4	20.9
O-C-O	7.0	10.1	9.2	10.1	9.4	8.0
O=C-O	1.5	3.6	5.7	6.6	6.6	9.3
CO ₃	-	-	-	1.1	1.1	2.3
Total Carbon %	69.1	64.4	64.2	62.7	61.3	60.3

Table 1. Spectral Component Contributions to the XPS C (1s) Spectra of Cotton Fabrics heated at 225C

ToFSIMS spectra



From ToFSIMS :-

- Levoglucosan identified on surface of unheated cotton – m/z 163⁺ (M+H⁺) –see ref. spectrum
- Relative increase in surface levoglucosan concentration with heating, up to ~7hrs at 225C – monitored by peak area ratios – see table 2.
- Extended heating decreases cellulosic character of surface as monitored by negative ion fragments e.g. ⁷¹CH₂=CHCOO⁻, ⁸⁷HOCH=CHCOO⁻
- General increase in inorganic material, including magnesium-containing species, noted in XPS and ToFSIMS

Peak Area Ratio for m/z 163⁺ (Protonated Levoglucosan)

Unheated	1 hr	3 hrs	7 hrs	15 hrs	23 hrs
-	0.46	0.63	1.23	0.84	0.79

Table 2. Peak area ratio calculations for Levoglucosan at extended heating times derived from ToFSIMS Spectra.

Conclusions

- The formation of Levoglucosan at the surface of heated cotton fabric has been demonstrated by ToFSIMS
- Extended heating at 225C produces initial increase in levoglucosan concentration, followed by a decrease as other thermal degradation products form to a constant level at 23hrs
- XPS shows loss of C-C, C-H character in early stages of heating. In the later stages, oxidised carbon functionality, inc. carbonyl and carbonate are identified.