X-RAY PHOTOELECTRON SPECTROSCOPY ANALYSIS OF REGENERATE CELLULOSIC FIBRES

Liberato Venant Haule

University of Dar es Salaam, College of Engineering and Technology, Department of Mechanical and Industrial Engineering, P. O. BOX 35131, Dar es salaam , Tanzania. E-mail: liberatohaule@yahoo.co.uk ; liberato.haule@udsm.ac.tz

Abstract

X-ray Photoelectron Spectroscopy (XPS) technique was used to study four different types of regenerated cellulosic fibres; fibres regenerated form 100% plain woven waste cotton garment, fibres reclaimed from 100% indigo dyed waste denim, fibres regenerated from blend of wood pulp and waste garment pulp and fibres regenerated from high purity wood pulp. The fibres were regenerated from N-methyl N- morpholine oxide (NMMO) solution and then analysed using XPS. The high resolution spectra of the analysed fibres indicated that the fibres regenerated from cotton waste garments were affected by oxidative degradation either during its first life cycle or during the purification and regeneration processes. The fibres reclaimed from indigo dyed waste denim revealed presence of traces of dyes on the surface.

Key words: XPS, Cellulose, Waste garments, Regenerate fibres, Cotton

1 Introduction

X-ray Photoelectron Spectroscopy (XPS) technique is an analytical technique which is used to study the surface chemical composition of solids. With XPS, the sample is bombarded by X-ray beam under highly evacuated chamber. The x-ray beam interacts with the substrate's atoms, causes excitation and escape of electron from the surface of the specimen; the electrons are collected depending on the atomic binding energies. The electrons are escaping from those atoms which are within 50A on the surface of the specimen. In order for the electrons to escape from the surface of the specimen the electrons' kinetic energy must exceed its binding energy. An exhaustive reading about the surface chemical analysis of polymers is presentment in the literature (Ratner. and Castner., 1997)

The binding energies provide the type of atoms and their chemical environment while spectral intensity provides atomic composition of the solids. With XPS, the chemical composition, atomic states and location of atom types can be established on a specimen. XPS is commonly used in surface chemical analysis of textile substrates.

For instance XPS was used to determine the location of the flame retardants, soil repellence and easy care finishes following application of the finishes on the cotton fabrics. Results indicated that in order to understand the effectiveness of the application of the finishes, it is necessary to determine both surface and bulk analysis of the treated fabrics. This is due to the fact that some of the finishes reacts in both the surface and bulk of the substrates (Soignet et al., 1976). XPS was used to probe surface changes of the cotton substrates which were plasma treated and chemically modified with flame retardants (Benerito et al., 1981). XPS was also used to investigate the wash durability of an easy care finished cotton fabrics whereby the stability of the methylol-based easy care finishes on different wash programmes was determined. By the use of XPS it was possible to determine the type of crosslinking between the easy care finish and the cotton fabrics in relation to the crease recovery angle performance (Haule et al., 2012b). Other applications of the XPS in textiles include assessment of the stripping of the easy care finishes from cotton fabrics in order to reclaim cotton fibres for regeneration of new fibres (Haule et al., 2014, Haule et al., 2012a). In such treatments the effectiveness of removal of nitrogen containing easy care finish was assessed by monitoring of the N(1s) atoms on the surface of stripped cotton fabrics. The stripping of poly-carboxylic acid- easy care finish was monitored by the –C(1s) peak intensity assigned to O=COOH. XPS was further used on determination of the effectiveness of sisal fibre modification by silane in order to improve fibre compatibility with the matrix during composite making (GonzÃ¡lez et al., 2012).

1.1 XPS spectral features

Normally during ESCA analysis two types of spectra are recorded; a wide scan/ survey scan spectrum and a high resolution scan spectrum. The wide scan spectrum is normally recorded in an energy range of 1000 eV and aims at getting general information about the sample composition. Once the general features about the specimen have been acquired, more detailed features are obtained by taking finite range (say 20eV) scans. Typical wide scan spectrum of cellulose material is presented on figure 1.

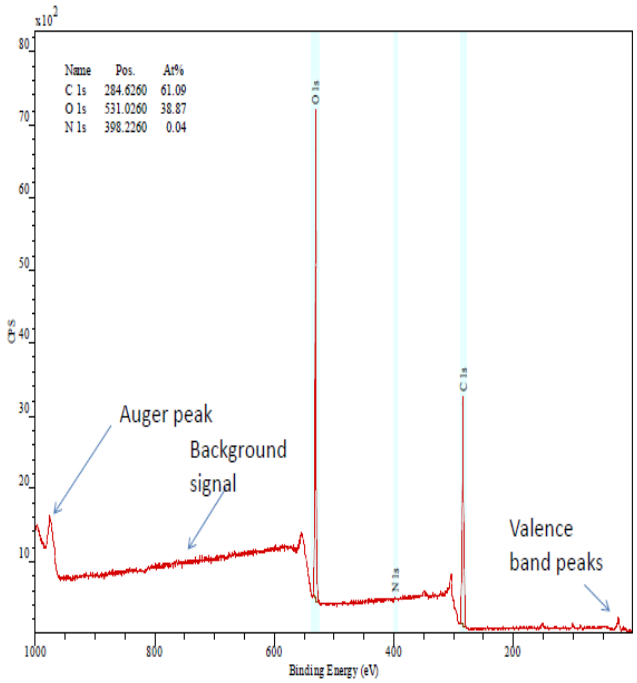


Figure1: Survey scan of cellulose fibre

Features common to all XPS spectra of organic material are the Auger electrons, Background signal and valence band peaks (Ratner. and Castner., 1997). The auger peaks are due to the release of atomic excess energy during re arrangement of electrons. The background signal is caused by accumulation of electrons which have lost kinetic energy thus contributing none to the spectral intensity.

In this paper the surface chemistry of the fibres regenerated from cotton based garments were analysed and compared to lyocell fibres using XPS.

2 Methodology

2.1 Preparation of material

The purification, dissolution of the pulp and spinning of fibres were done based on the previously reported work (Haule et al., 2016) and described hereunder.

In order to spin fibres the required spinning dope was prepared by mixing 300g of 50% NMMO solution with 27g pulp and 0.2g n-propyl gallate using a laboratory scale mixer The dissolution process was made possible by mixing the pulp and NMMO solution at increasing temperature and vacuum at suitable steps until the final spinning dope was composed of 9% cellulose, 13% water and 78% NMMO. For every sample the dissolution dope was checked for fibre solubility using a light microscope. The fibres were then spun from a laboratory scale spinning machine at Lenzing AG, Austria. The spinneret used had 19 holes of 100µm in size and the spinning temperature was 115ºC. The dope throughput was 0.03g/min per hole, the air gap conditions were set at 30mm, 24°C and 53% relative humidity.

The winding speed was 25.1m/min. and water was used to precipitate the fibres. The fibres were then oven dried at 60°C overnight prior to further analysis. The source and properties of the feedstock use for fibre making is presented in Table 1.

Table 1: Source and properties of the feed stock used for fibre making

S/No	Source	Purification approach	Fibre name
1	Cotton fabric	Washed 50 times using detergent, Ground into pulp	ReCell-1
2	Cotton fabrics	Treated with easy care finish, washed 50 times stripped in acid-alkali solution blend with 80% high purity wood pulp	ReCell-2
3	Waste denim garments	Washed and ground into pulp	ReCell-Denim
4	Wood pulp	Chemical treated pulp	Lyocell

2.2 XPS Analysis

XPS analysis was performed using a Kratos Axis system spectrometer. The fibre bundles sample were cut from the middle of the specimen and attached to the sample holder using a double sided tape. Monochromatic AlKα x-rays (1486.69eV) with a power of 150W were used to irradiate the samples. A wide scan spectrum was recorded with pass energy of 160eV from which the surface composition (C, N and O) was determined. High resolution Carbon (1s) spectra were recorded with pass energy of 40eV. The binding energy (BE) values were calculated relative to the Carbon (1s) photoelectron at 285.0eV. Charge compensation for the samples was achieved using a 4-7 eV electron beam at a flood current of approximately 0.1mA, and an electrically ground 90% transmission nickel mesh screen adjacent to the fibre samples. Data analysis was performed using the CASA XPS software (Walton et al., 2010).

3 Results and Discussion

Examination of the wide scan surface elemental analysis of the ReCell and Lyocell fibres indicated that the surface of the fibres is rich in C and O and the ReCell-Denim fibres indicated some amount of nitrogen, Table 2, which can be assigned to indigo dyes present in the fibres.

Table 2: XP wide scan elemental atomic composition and C1(s) BE = 286.6/BE=288.0eV intensity ratio for Lyocell and ReCell fibres

Fibre	Wide Scan, atomic %			C1(s) high resolution component intensity		
	C	O	N	C-O	C=O	C-O/C=O
Lyocell	76.0	24.0	0.0	27.4	5.4	5.1
ReCell-1	72.9	27.1	0.0	34.3	7.9	4.3
ReCell-Denim	71.5	28.0	0.5	32.7	13.6	2.4
ReCell-2	76.0	24.0	0.0	32.5	9.0	3.6

The composition of carbonyl species (BE=288 eV) is increasing in the order of lyocell< ReCell-1<ReCell-2<ReCell-Denim. This trend implies that the fibres recovered from waste garments have suffered some oxidative degradation either during the first life cycle of the garment or during fibre regeneration.

Examination of the high resolution C1(s) spectra of the ReCell and Lyocell fibres indicated that the major chemical states occurred at 285.0eV, which was due to C-C, and C-H bonding, indicating that the surface was not pure cellulose, Figures 2 -5. The nature of these impurities was not ascertained

but some of it may be due to the dissolution and regeneration solvents.

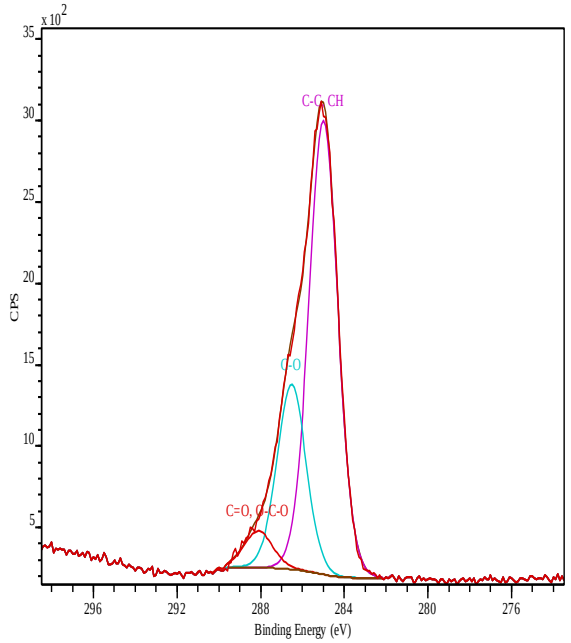


Figure 2: C(1s) XP spectrum of Lyocell fibres

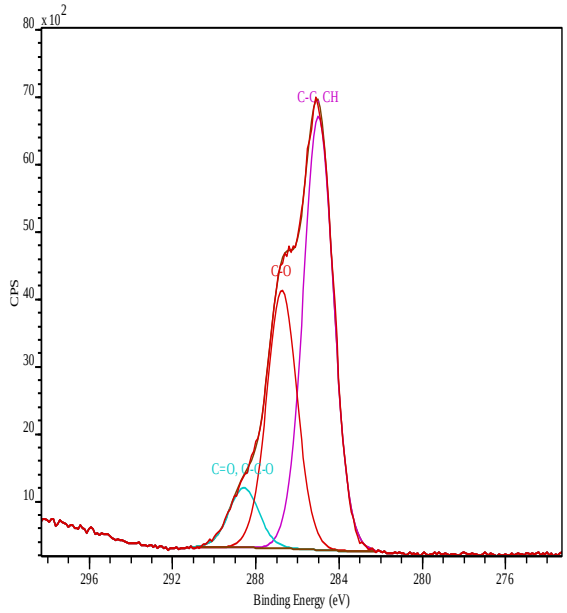


Figure: 3 C(1s) XP spectrum of ReCell-1 fibres

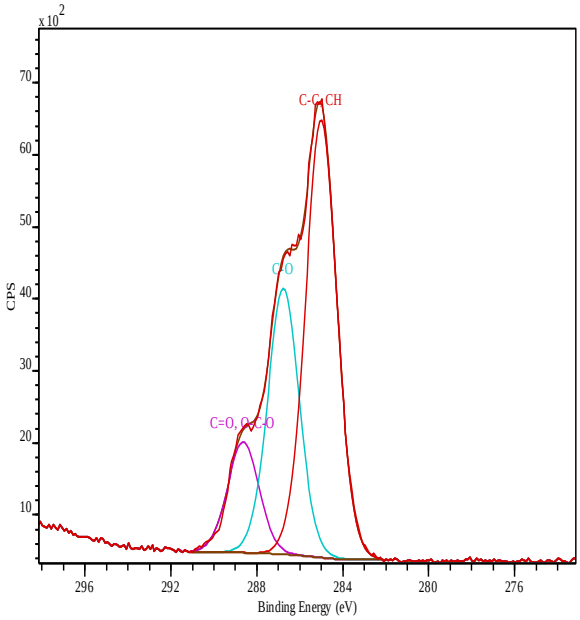


Figure: 4 C(1s) XP spectrum of ReCell-Denim fibres

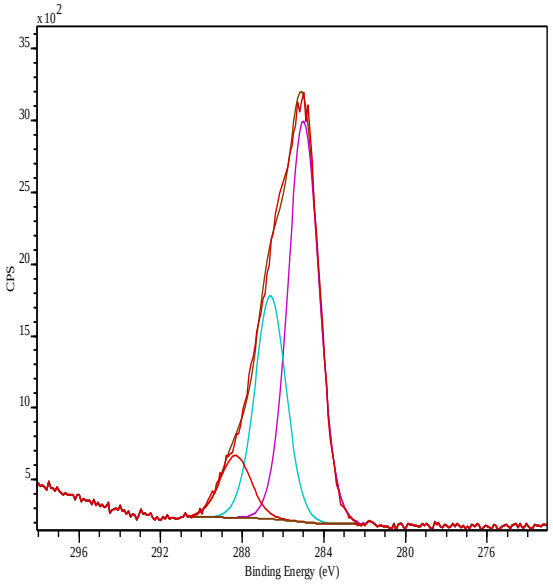


Figure 5: C(1s) XP spectrum of ReCell-2 fibres

The nature of chemical states occurring at 285.0eV for natural cellulose have been investigated and reported (Mitchell et al., 2005, Soignet et al., 1976, Buchert et al., 2001, Haule et al., 2012a) and information for regenerated fibres. Re-examination of Table 2 indicated that the C(1s) peak intensity ratio of 286.6eV (C-O) to 288.0eV (C=O, O-C-O) was highest for Lyocell fibres (5.1) and lowest for ReCell-Denim fibres (2.4). Theoretically the relative spectral intensity for the C1(s), BE 286.6eV to BE 288eV is supposed to be 5:1 (±10%). The lower peak intensity ratio for ReCell-Denim fibres was due to the residual indigo dye present in the fibres. The peak intensity ratio of

286.6eV (C-O) to 288.0eV (C=O, O-C-O) of ReCell-1 and ReCell-2 fibres was reasonably within the required range.

4 Conclusion

The XPS analysis was carried out for fibres regenerated from cotton waste garments, blends of waste pulp and wood pulp and standard lyocell fibres. Results indicated that the fibres regenerated from indigo dyed waste denim (ReCell-denim) contain traces of dyes as confirmed by the presence of nitrogen on the surface. The fibres reclaimed from waste garments demonstrated some oxidative degradation incidental to first life environment.

Acknowledgment

The first version of this article was published on the Journal of Textile Science and Technology, 2016, 2, 37-45.http://dx.doi.org/10.4236/jtst.2016.22006

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