The effect of washing on the surface chemistry of plasma coated textiles as studied by high resolution XPS

Keywords
XPS, high resolution, charge neutralisation, plasma polymerisation

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Overview

The performance of fluorinated textile treatment methods, in terms of wash resistance, was evaluated by XPS. Two different fluorination methods, solution based treatment and plasma polymer deposition, and four different textiles were studied with a view to producing long lasting, high performance clothing systems for outdoor activities. An important attribute of such textiles is the ability of the surface of the material to retain or regain its liquid repellent nature following conventional washing cycles.

XPS analysis revealed the degree of surface fluorination before and after wash cycles enabling the durability of the thin film coatings to be evaluated. Results indicated that for most materials the plasma polymer coated textiles exhibited better performance in terms of fluorine coverage and retention than the solution based fluorination method.

Introduction

The goal of this work was to evaluate the performance of fluorinated material treatment methods, in terms of wash resistance, by surface analysis techniques. Two different fluorination methods and four different materials were studied with the aim of producing long lasting, high performance clothing systems for outdoor activities. Fluorinated fabrics have long found applications in outdoor sports wear due to their liquid repellent nature[1] and breathability. Methods of imparting these properties on low cost textiles have been investigated for some time. An important attribute for any such textiles must be the ability of the material to retain or regain its liquid repellent nature following conventional washing cycles.

X-ray photoelectron spectroscopy was used to complement other techniques in the investigation of the surface properties of the treated materials. Detection of high amounts of fluorinated surface components indicated that the coating treatment was present on the test material. Samples of the test materials were first exposed to the fluorinated surface treatments, analysed by XPS to verify surface coverage of the fabrics, boil washed in conventional detergents, dried and re-analysed to determine the performance of the coating treatments.

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Experimental

Four different fabrics were chosen as test materials. These were cotton (c), nylon (ny), nomex (no) and polyester (p). Each fabric was coated with either a proprietary solution based treatment (named fluorosolvent) or a fluorinated plasma polymer (named plasma). An outline of the treatment processes is given below:

1. **Solution based treatment (fluorosolvent):** The fluorinated coating was simply applied in solution to the fabric surface. The fabric was rinsed in methanol and then dried in air.
2. **Plasma Polymer (plasma):** The fluorinated plasma polymer was applied to the fabric using an electrically pulsed, non-equilibrium, inductively coupled glow discharge.[2] Fabric was placed into a clean glass reactor vessel and the chamber evacuated using a trapped rotary pump. On the attainment of base pressure, the fluorinated monomer was introduced into the chamber at a fixed leak rate. A glow discharge was ignited in the chamber by means of a 13.56 MHz radio frequency source inductively coupled to the plasma chamber. Electrodes were situated on the outside of the reaction chamber to avoid unwanted contamination problems. Typically the discharge was maintained for 10 minutes treatment time. After extinguishing the plasma the monomer vapour was allowed to continue to flow into the reactor system for a further two minutes before it was isolated and the chamber pumped back down to base pressure.

   Following surface treatment the fabric samples were boil washed in water containing a readily available detergent between one and five times. Fabric samples were either allowed to dry in the air or ironed.

Analysis

Surface analysis of the treated fabric samples was performed on the AXIS Supra X-ray photoelectron spectrometer from Kratos Analytical. Due to the complex surface chemistry of these samples high energy resolution and efficient charge neutralisation was of particular importance. Kratos' patented[3] coaxial charge neutralisation system provided a reliable means to neutralise surface charge and is described elsewhere.[4]

Results

A typical survey spectra obtained from the plasma treated nylon sample is presented below, Figure 1.

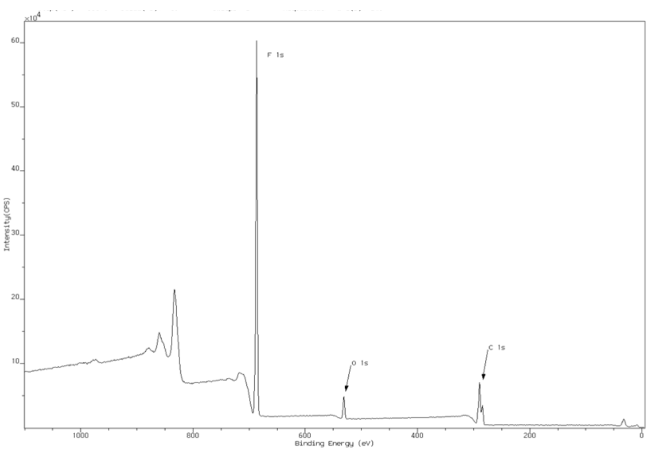

Figure 1: Survey spectrum of plasma treated nylon demonstrating a large amount of fluorine incorporation.

A high resolution C 1s spectrum, recorded at 10 eV pass energy, from the same sample demonstrates the excellent spectral resolution achieved by the spectrometer on these irregular, highly insulating samples, Figure 2.

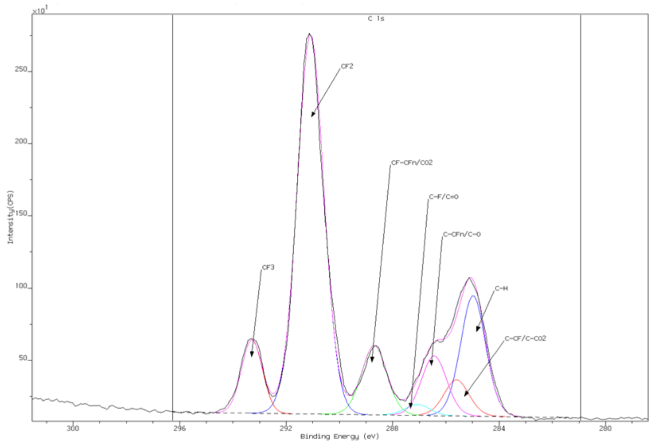

Figure 2: High resolution C 1s spectrum of plasma treated nylon showing excellent resolution and charge neutralisation.

The resolution allows confident identification of many of the chemical functionalities present: C-H; C-CF/C-CO_2; C-CFn/C-O; C-F/C=O; CF-CF_n/CO_2; CF_2; and CF_3

Comparison of the percentage fluorine detected on fluorosolvent and plasma treated fabric showed that in general plasma treated fabrics had greater fluorine incorporation, Figure 3.

Polyester treated material was an exception with comparable amounts of fluorine coverage on both samples. Figure 4 presents the relative amounts of the CF_2 chemical functionality found on the fabric surfaces. Plasma treatment provided the greatest amount of CF_2 incorporation and appears to be less substrate dependent that the fluorosolvent treatment. The C 1s spectra from all plasma treated textiles appeared very similar for all the textiles, Figure 5, overleaf.

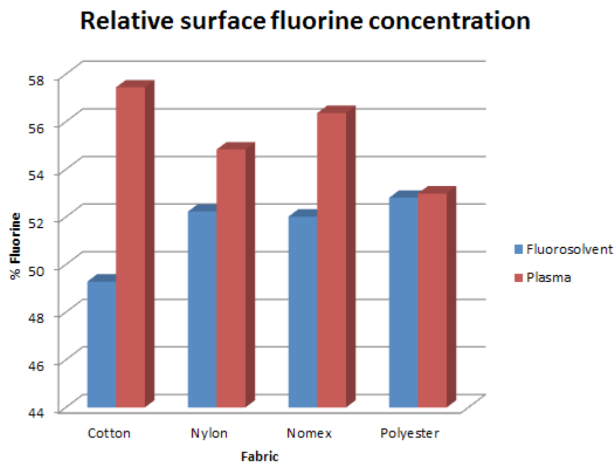

Figure 3: F content of treated fabrics, plasma treatment works best.

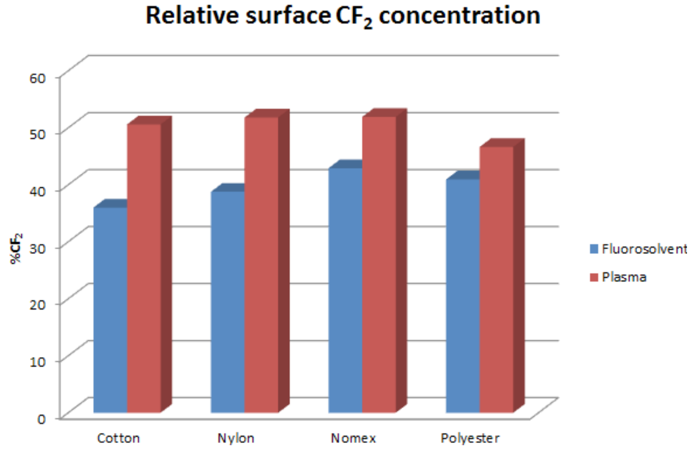

Figure 4: CF_2 content of treated fabrics.

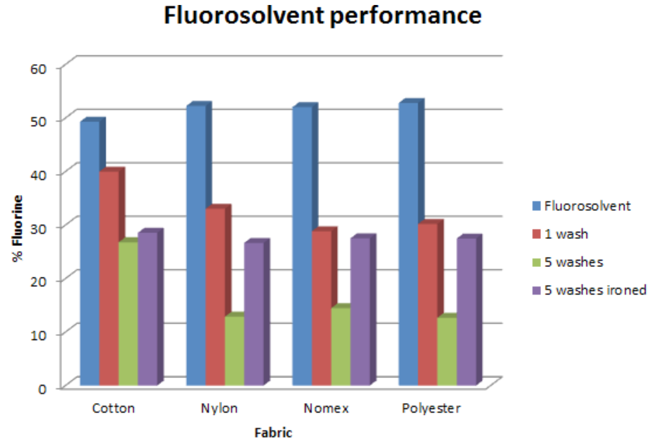

Figure 6: F content of fabric after fluorosolvent treatment, 1 wash, 5 washes and 5 washes and ironing.

Results showed that after 5 washes the fluorosolvent treated fabrics lost most of their surface fluorine coverage, Figure 6 and 7. Subsequent ironing reversed approximately half of this fluorine loss in all cases demonstrating that some of the reduction in surface fluorine is due to rearrangement of the water repellent fabric fibres in aqueous solution rather than permanent loss of coating. Heat treatment reversed this rearrangement to some extent.

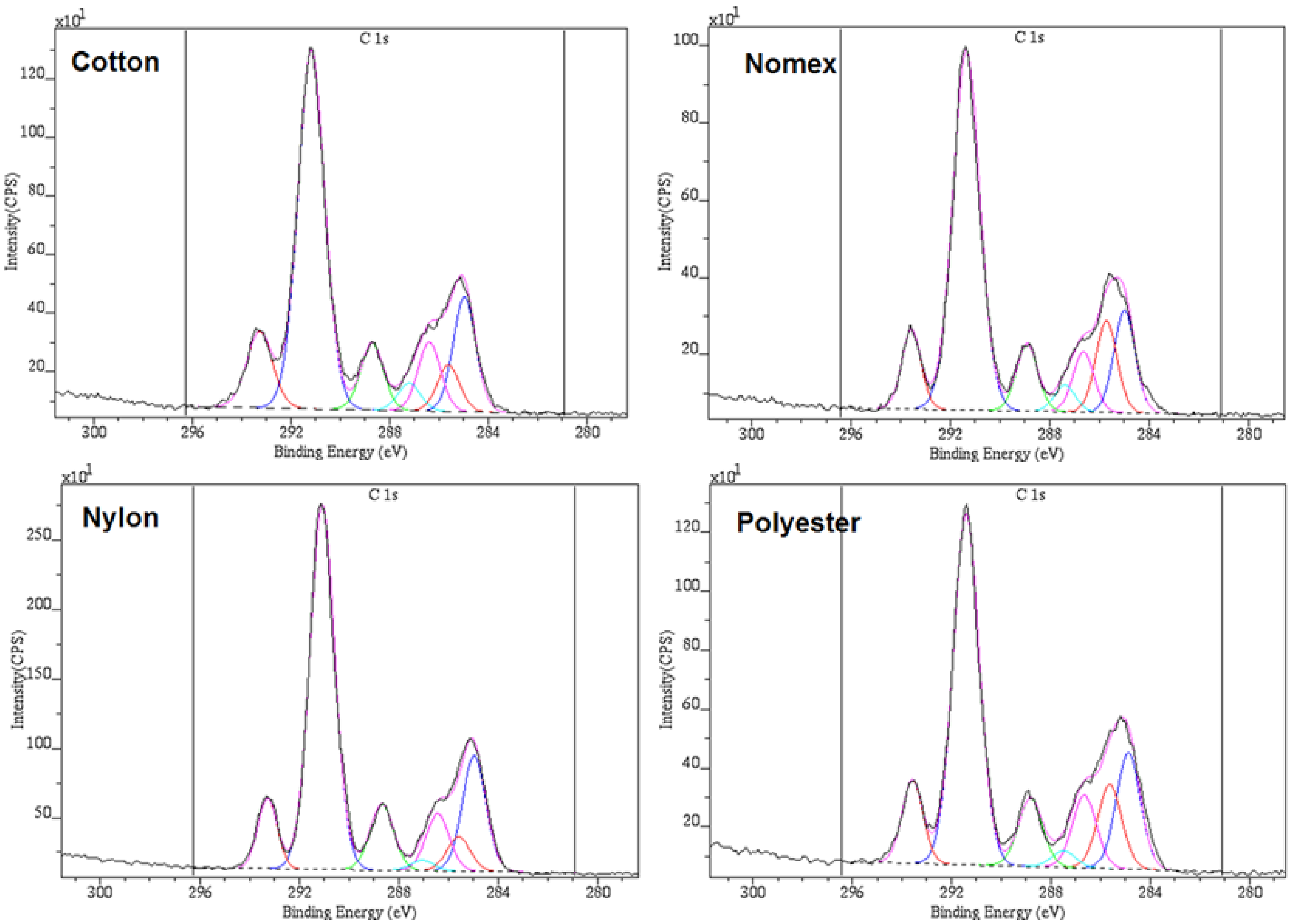

Figure 5: High resolution C 1s spectra of plasma treated fabrics demonstrating the substrate independent nature of the plasma coating process.

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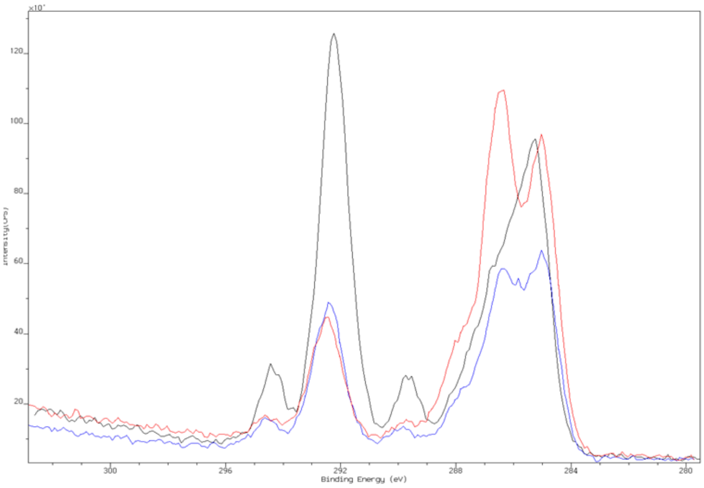

Figure 7: High resolution C 1s spectrum of fluorosolvent treated nylon (black) after 1 wash (blue) and 5 washes (red) demonstrating loss of surface coating.

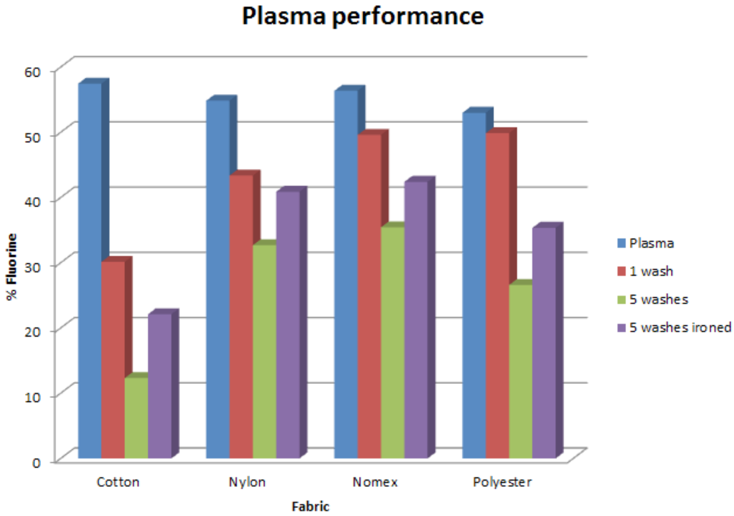

Figure 8: F content of fabric after plasma treatment, 1 wash, 5 washes and 5 washes and ironing.

The XPS results for the plasma coated textiles demonstrated better fluorine group retention than seen in the case of fluorosolvent treatment after washing for all fabrics except for cotton, Figure 8. Furthermore, ironing plasma coated Nylon, Nomex and polyester reversed almost all the fluorine group losses observed following the washing cycle.

Conclusion

XPS surface analysis has been used to assist in the development of fabric surface treatments. Plasma polymerisation of a fluorinated monomer molecule was shown to be a viable method of producing a long lasting, durable fluorine surface coating on several different textiles.

References

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4. Kratos Charge Neutraliser Technical Note MO222.

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