



The Hidden Radiation Chemistry in Plasma Modification and XPS Analysis of Polymer Surfaces.

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The surface modification of polymers using plasma treatments is being widely researched to achieve changes in the surface energetics and consequent wetting and reactivity for a range of applications.¹ These include i) adhesion for polymer bonding and composite material fabrication² and ii) biocompatibility of polymers when used as orthopedic implants, catheters and prosthetics.³ A low pressure rf plasma produces a variety of species from the introduced gas which may react with the surface of a hydrocarbon polymer, such as polyethylene. In the case of O₂ and H₂O, these species include oxygen atoms, singlet molecular oxygen and hydroxyl radicals, all of which may oxidise and, depending on their energy, ablate the polymer surface. In order to better understand the reactive species formed both in and downstream from a plasma and the relative contributions of oxidation and ablation, self-assembled monolayers of n-alkane thiols on gold⁴ are being used as well characterised substrates for quantitative X-ray photoelectron spectroscopy (XPS).

The identification and quantification of oxidised carbon species on plasma treated polymers from broad, asymmetric XPS signals is difficult, so derivatisation is often used to enhance sensitivity and specificity. For example, trifluoroacetic anhydride (TFAA) selectively labels hydroxyl functionality.² The surface analysis of a modified polymer surface may be confounded by high energy radiation chemistry which may occur during XPS analysis. Examples include scission of carbon-halogen bonds (as in TFAA adducts), decarboxylation and main-chain polyene formation. The extent of free-radical chemistry occurring in polyethylene while undergoing XPS analysis may be seen by both ESR and FT-IR analysis.

References:

1. See for examples, C-M. Chan, *Polymer Surface Modification and Characterisation*, 1994, Munich: Hanser, and references therein.
2. (a) G. A. George, G. A. Cash, T. T. Le, B. G. S. Goss, B. J. Wood, J. R. Brown, N. A. St John, *Polym. Adv. Technol.*, 1996, 7, 343
(b) G. A. George in, W. J. Feast, H. S. Munro. R. W. Richards ed, *Polymer surfaces and Interfaces II*, 1993, Chichester: John Wiley and Sons.
3. (a) B. D. Ratner, *Biosensors and Bioelectronics*, 1995, 10, 797
(b) J. Andrade ed, *Surface and Interface Aspects of Biomedical Polymers*, 1985, New York: Plenum Press and references therein.
4. C. D. Bain, E. B. Troughton, Y-T. Tao, J. Evall, G. M. Whitesides, R. G. Nuzzo, *J. Am. Chem. Soc.*, 1989, 111, 321