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## **Energetic ion surface modifications for the one step functionalisation of scaffolds and porous materials: fundamentals and applications**

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Over the last half-decade an opportunity to functionalise the surfaces of materials using radicals embedded in polymeric surface layers has emerged [1]. The radicals are created by plasma processes designed to direct energetic ions to the surface layers. Covalent immobilisation of functional (including biologically functional) molecules is then achieved by simple immersion or incubation of the surface in a solution containing the functional molecules to be immobilised. This eliminates the need for multiple stage linker chemistry and the associated solvent disposal and variable yield problems. To date this approach has been used to surface immobilise bioactive peptides, antibodies, enzymes, single stranded DNA and extra-cellular matrix proteins [2] onto the external surfaces of materials including three dimensional structures.

Increasingly, the materials of interest for many applications in biomedicine, sensing and enzymatic processing are porous three-dimensional structures and there is a need to functionalise their internal surfaces. Scaffold development in tissue engineering, for example, focuses on the use of natural and synthetic hydrogels as well as thermoplastic polymers such as PCL which allow structures to be printed in 3D using technologies often referred to as additive manufacturing. Combining these platforms shows promise in creating hierarchical structures that mechanically mimic in-vivo tissues.

In this presentation, we review recent work in which the diffusion of surface embedded radicals that underpins the direct single step covalent functionalisation of ion implanted surfaces is characterised in detail. Studies with radical traps in ion-implanted polyether ether ketone (PEEK), a polymer used increasingly for orthopaedic applications, are used to determine the diffusion coefficient and its activation energy. We will also describe a new plasma process we have developed to enable the energetic ion implantation of complex interconnected 3D polymeric networks, exploring the roles of flow rate, pressure and pulsed bias. This treatment enables direct covalent immobilisation of functional molecules on internal surfaces of the structures. Bioactive molecules are applied simply and safely by immersion, spotting or painting of the biomolecule containing solutions.

[1] M.M. Bilek, et. al., PNAS 108:14405-14410 (2011)

[2] M.M. Bilek, Applied Surface Science 310:3-10 (2014)