Université catholique de Louvain UCL

SECTEUR DES SCIENCES ET TECHNOLOGIES

Institut de la Matière Condensée et des Nanosciences

Invitation à la soutenance publique de thèse

Pour l'obtention du grade de Docteur en Sciences de l'Ingénieur

Madame Vanina CRISTAUDO

Master en chimie des matériaux

Surface and in-depth molecular characterization of plasma-treated polymers and plasma-polymers using SIMS

The use of plasma technologies under atmospheric pressure for the surface modification of polymers and the deposition of thin polymer films has expanded enormously since the last decade, finding countless applications in several sectors, such as material science, microelectronics and medicine. De facto, plasma-treated and plasma-synthesized polymers are systems extremely complex to characterize. Thanks to the latest advent of large noble gas clusters for 'damageless' sputtering of organics, time-of-flight secondary ion mass spectrometry (ToF-SIMS), a well-known surface-sensitive technique, is now able to *probe the detailed chemical structure of any organic material along the third dimension*. Moreover, statistical data treatment methods, such as principal component analysis (PCA), significantly improve the amount of information that can be extracted from the SIMS measurements.

This thesis focuses on the *development of new methodologies for the surface and in-depth chemical characterization of plasma-treated and plasma-synthesized polymers* under atmospheric pressure, by means of the application of the combined ToF-SIMS/PCA protocol and the use of large Ar cluster sputtering. Two different and challenging case studies involving plasma-treated and plasma-deposited polymer films, respectively, were defined for the development of novel characterization protocols.

The first study concerns the exposure of polyethylene films to the post-discharge of an atmospheric Ar-H_2O plasma torch. The recent use of H_2O as reactive gas in plasma treatments of polyolefins represents a new promising route of oxidative functionalization. However, tracing the reactivity of H_2O with the polyolefin is challenging, due to the inevitable intervention of the environmental humidity. Thus, exploiting the isotope sensitivity and selectivity of SIMS, deuterated water vapors were employed to investigate the hydrogen-deuterium exchange, oxygen/nitrogen-uptake, unsaturation, branching and/or cross-linking, as a function of the parameters "treatment time" and "sample-torch distance". For the first time, *the surface chemical characterization could be correlated with the in-depth modifications*, and rationalized on the basis of the lifetime of the reactive species present in the post-discharge.

The second investigation concerns the deposition of polystyrene-like films near atmospheric pressure by means of a dielectric barrier discharge. This plasma-polymer is widely used in the preparation of electronic devices, as protective films and in medical applications. The peculiar chemical and structural features of the deposited aromatic coatings were investigated as a function of the plasma power, after exposure to the ambient air but *in the inner layers*. This expedient permits to perform ex-situ characterization, even in presence of post-polymerization oxidation. This work demonstrated that SIMS can provide information about the unsaturation, branching and/or cross-linking, as well as the aromatic and aliphatic content of the plasma-deposited films. Insights about the polymerization degree could be derived thanks to fundamental studies on SIMS molecular depth-profiling of PS.

Vendredi 5 mai 2017 à 14h00

Auditoire SUD 08
Croix du Sud
1348 Louvain-la-Neuve

Membres du jury :

Prof. Arnaud Delcorte (UCL), promoteur
Prof. François Reniers (ULB), promoteur
Prof. Bernard Piraux (UCL), président
Prof. Jacques Devaux (UCL), secrétaire
Prof. Didier Léonard (Université Claude Bernard Lyon I, France)
Prof. Antonino Licciardello (Università degli Studi di Catania, Italie)