LIGHT-INDUCED DEGRADATION OF POLYSACCHARIDES: FROM THE MODIFICATION OF THE CHEMICAL STRUCTURE TO THOSE OF THE NANOMECHANICAL PROPERTIES

<u>Pierre-Olivier Bussière</u>^{a,c}, Sebastien Berthumyrie^{a,b}, Sandrine Thérias^{a,b}, Jean-Luc Gardette^{a,b}

^aClermont Université, Université Blaise Pascal, BP 10448, F-63000 Clermont-Ferrand, France ^bCNRS, UMR 6505, Laboratoire de Photochimie Moléculaire et Macromoléculaire, F-63177 Aubière, ^cClermont Université, Ecole Nationale Supérieure de Chimie, Laboratoire de Photochimie Moléculaire et Macromoléculaire, BP 10448, F-63000 Clermont-Ferrand (<u>p-olivier.bussiere@univ-bpclermont.fr</u>)

The ageing of polymeric materials provokes dramatic modifications of the chemical structure of the macromolecules and induces a loss of the polymer engineering properties. For that reason, it is absolutely necessary to correlate changes in the chemical structure to changes in the properties. The modifications of the chemical structure result from several processes: rearrangement, fixation of oxygen, chain scission and cross-linking reactions. The main objective was to give evidence of the consequences of photochemical reactions on the macroscopic properties of the polymer and to qualitatively and quantitatively confirm the direct relationship between the modifications of the chemical structure and the modifications of the properties.

In this study, we analysed the consequences of photo-ageing in the presence and in the absence of oxygen on majors Polysaccharides: cellulose ether/acetate/nitrate, chitosan... We realised roughness and stiffness measurements by AFM in combination with the use of other techniques, such as infrared and UV visible spectroscopies, gel fraction, SEC, micro-Hardness, DMTA... This set of attractive complementary techniques allows us to propose a new mechanism of degradation for each king of cellulose derivatives. In order to quantify degradation, mechanical

analyses were done and it confirms that that the cross-linking reaction is ,in the most case, the predominant route.



Figure 1. Bottom: Δ micro-Hardness (\blacksquare) and conversion rate of the CO groups at 1740 cm⁻¹ (\bullet) versus exposure time. Top: image of the cellulose nitrate before(a) and after (b) 100 hours of irradiation, the right picture presents an important yellowing and the formation of cracks.

Then, for a better understanding, quantitative correlations were made between the main relevant criteria of degradation, from the chemical structure to the mechanical properties. The most outstanding result obtained is the quantitative correlation between the modification of the chemical structure and the variation of the physical properties at each scale of analysis.