High Doses Gamma Radiolysis of PVC: Mechanisms of Degradation

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PVC radiolysis leads to the formation of various degradation products: radicals, gas, oxidized products or polyenes... In order to predict the formation of the degradation products with regard to irradiation and ageing parameters, it is important to improve the understanding of the radiolysis mechanisms of PVC. Thus, we used several analytical techniques (Electron Spin Resonance, Fourier Transform Infrared spectroscopy, Nuclear Magnetic Resonance, Size Exclusion Chromatography) to get information on PVC samples irradiated at high doses (up to 4MGy) under different conditions.

Gamma irradiation induces the formation of various radicals into PVC. Older studies were generally focused on the effect of low dose and/or low temperature irradiations on PVC. We present here ESR signals of PVC irradiated at high doses and at room temperature. We show that peroxyl radicals are producted by radiolysis under aerobe conditions and that polyenyl radicals are formed under anaerobe conditions. PVC radiolysis induces gas production and especially hydrogen chloride. Production of hydrogen chloride is well known until 1 MGy. We have studied by FTIR, the evolution of the quantity of HCl produced until 4 MGy. We show that higher irradiation dose leads to the lower radiolytic yield of HCl (G(HCl)). Moreover, G(HCl) obtained in aerobe conditions is about fourfold as great as G(HCl) observed in anaerobe radiolysis.

Propagation and termination reactions induce degradation products: polyene sequences and crosslinking reactions are observed under anaerobe conditions; oxidized products with addition of chain scissions are formed under aerobe conditions. Although the literature about PVC radiolysis is rich, the main reacting pathways are not well established. Moreover the high doses studies are almost non-existent. We show by FTIR that aerobe radiolysis induces formation of ketons and acids. NMR experiments confirme these results but also focuse on small acids formed (with 2, 3 or 4 carbons). The main radiolysis product is an acid which derives from PVC macromolecule such as $-CHCl-CH_2-COOH$. According to radiolysis mechanisms, this acid is responsible for the formation of HCl and for scission reactions (which is confirmed by SEC). PVC samples irradiated under anaerobe conditions have been studied by NMR solid state techniques such as Cross Polarization Magic-Angle Spinning and Variable Contact Time. Thanks to these techniques, we show anaerobe radiolysis induces the formation of polyenes and also crosslinking reactions.

These results allow us to determine mechanisms of PVC radiolysis. We can also deduce what are the main reacting pathways, and explain hydrogen chloride production thanks to these mechanisms.