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## Argon Plasma Treatment of Polymers - Trapping of Radicals by Nitric Oxide Gassing

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Low temperatures plasmas comprise a wide range of applications like plasma polymerization, surface modification, microbial inactivation, etc. They contain many reactive species like UV photons, excited electrons, atoms, ions, etc., well suited to produce C radical sites in the near-surface layer of polymers. When polyolefins (PP, PE) and PMMA were exposed to plasma radiation, its short-wavelength (vacuum) UV radiation is not only absorbed by the chromophores in the polymers. UV radiation with wavelengths shorter than about 200 nm can attack the chemical bonds in each polymer. In polyolefins, for example, scissions of C-C and C-H bonds (>3.5 eV) by  $\sigma \rightarrow \sigma^*$  transitions are induced by the vacuum plasma irradiation. The generation of C radical sites is followed by the formation of peroxy and hydro-peroxy radicals after photo-oxidation. The peroxy radical formation is the starting point of photo-degradation of polymers. To analyse the type of radicals that is formed, radical trapping or derivatization method was chosen besides the direct detection of radicals using ESR spectroscopy. The derivatization and the ESR results are compared. For gassing of the plasma irradiated polyolefins with NO, the samples were exposed immediately after the argon plasma treatment to the NO gas for 15 min at 400 Pa. XPS measurements show the presence of nitrogen containing groups by appearance of the N1s peak. The nitroso (C-N=O), nitro (C-NO<sub>2</sub>), nitriles (C-CN), nitrates (C-ONO<sub>2</sub>) groups were identified. Trapping/derivatizing of these radicals was also helpful to stop the auto-oxidation or slowing down further degradation due to the prevention of peroxide formation and start of the auto-oxidation cycle characterized by formation of a broad variety of oxygen functional groups as well as branching and crosslinking.

### Keywords

Ar plasma  
NO gassing  
radical quenching