Energy Dependent Electron Induced Modification of PTFE: Bulk Degradation and Surface Defluorination

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Purpose: A direct pathway for C–F bond cleavage in fluoropolymers induced by ionizing radiation was investigated. This study distinguished energy-dependent mechanisms of electron-induced decomposition in polytetrafluoroethylene (PTFE), focusing on bulk degradation under MeV irradiation and surface defluorination under sub-keV irradiation, where penetration depth and interaction volume were governed by electron energy.

Methods: PTFE powder was irradiated with 2 MeV electron beam in air at absorbed doses in the MGy range to evaluate bulk structural modification. Ni/NiO nanoparticles were incorporated to examine catalytic effects, and selected experiments combined irradiation with elevated-temperature conditions to assess thermally assisted pathways. Bulk decomposition behavior was quantified by thermogravimetric analysis (TGA), and evolved gaseous products were identified by gas chromatography–mass spectrometry (GC-MS). Complementary structural analyses, including functional group evolution and crystallographic characterization, were performed. In addition, PTFE films were irradiated with sub-keV electrons (10–500 eV) under ultra-high vacuum to investigate surface-limited modification. X-ray photoelectron spectroscopy (XPS) characterized surface chemical-state evolution and fluorine loss as a function of irradiation time and electron energy.

Results: MeV irradiation lowered the decomposition temperature of PTFE and increased low-temperature mass loss, with effects becoming more pronounced at higher absorbed doses. These changes were further enhanced by elevated temperature and Ni/NiO incorporation. GC-MS results indicated the formation of oxidized species that decomposed during low-temperature heating, consistent with the TGA results. High-temperature irradiation reduced lattice distortion and accelerated the decomposition of oxidized PTFE components. The presence of Ni/NiO nanoparticles was associated with an increased oxidative response under the present conditions. In contrast, sub-keV irradiation induced surface defluorination, leading to the formation of F-related defect species, including CF, C–CF, and CF_3. At identical irradiation flux, 10 eV electrons exhibited higher defluorination rates than 70 eV electrons, suggesting that dissociative electron attachment may have played a dominant role in C–F bond cleavage in the low energy regime.

Conclusions: Electron-induced PTFE modification exhibited clear energy-regime dependence. MeV irradiation drove bulk oxidative transformation, whereas sub-keV irradiation produced surface-localized defluorination through DEA-related processes. These findings link electron energy to C–F bond scission pathways in fluoropolymers and provide insight into radiation–material interactions relevant to PFAS-related systems.