

# Surface Acidity of Hydrous Ultrafine Plastics Particles in Simple Electrolyte

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## Abstract

The widespread use of plastics in modern society has brought about emerging plastic pollution because of high persistency and low biodegradability. Several environmental stresses ultimately render plastic debris to ultrafine plastics particles (UFP,  $d < 1 \mu\text{m}$ ), thereby threatening the eco-environment because of large specific surface area, increasing affinity toward contaminants thus elevated nanotoxicity. Surface chemistry, specifically surface acidity, governs the transport, biotic and abiotic transformation of UFP in the environment, by mechanisms such as interactions with natural colloids, adsorption of contaminants, and adhesion of microbes. Nevertheless, the origin of surface acidity of UFP and its role in pollutant transport in the aquatic environment has not been explored fully.

The surface charge of UFP was first studied in simple electrolytes to establish the surface acidity. The UFP of six major polymers, including low-density polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC), polystyrene (PS), and polyethylene terephthalate (PET), were reconstructed to submicron size. Optical photothermal infrared spectrometry (o-PTIR) and X-ray photoelectron spectrometry (XPS) revealed the presence of oxygen-rich functional groups on the surface of UFP. The chemical structure of UFP was estimated by the mass balance on carbon and oxygen atom. Results suggested that the



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UFP surface was comprised of polar and nonpolar functional groups. The zeta potential of UFP in simple electrolyte was dependent on pH, which suggested that proton was the potential determining ion. The surface acidity of UFP was described in two Brönsted acid sites with different intrinsic acidity constants ( $pK_a^{int}$ ). The first surface acidity site,  $pK_{a1}^{int}$ , was proportional to the abundance of non-polar functional groups, while the second site,  $pK_{a2}^{int}$ , was correlated to polar functional groups. Results showed that the acidity constants,  $pK_{a1}^{int}$  and  $pK_{a2}^{int}$  were between 4.5 and 6.0, and between 1.3 and 2.0, respectively, for the six plastics particles studied. Therefore, the surface charge of UFP was originated from the binding of deprotonated water molecule onto both polar and nonpolar sites, which can be predicted from the chemical structure of the plastics surface. The finding can be applied to estimate the surface charge density of microplastics in the environment and its interactions with other aquatic pollutants.