

Superacidity of Hydroxyl Functionalized Polytetrafluoroethylene

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Introduction:

The functionalization of polytetrafluoroethylene (PTFE) with biological species is a critical need for the development of medical devices. Our laboratory has investigated methods for utilizing a proprietary radio frequency glow discharge modified PTFE coupled to EDC (1-Ethyl-3-[3-dimethylaminopropyl] carbodiimide hydrochloride) as the base material for blood contacting surfaces.

This hydroxylation process used to create the OH-PTFE material that we used is substantially different from that reported by other groups as it relies on strict control of the process to deposit strict hydroxyl concentrations on the surface. This allows for novel chemistry based in the acidity (or superacidity) of the hydroxyl group.

Here we show data suggesting that the covalent attachment of EDC to functionalized PTFE occurs. Further we show that the base material, OH-PTFE is a superacid capable of effecting novel chemistries.

Materials and Methods:

PTFE was hydroxylated at Integument and transferred to the University of Iowa for testing. It was exposed to 3.35 μ M EDC in dry acetone for one hour. After rinsing with dry acetone and allowing it to dry, the hydroxylated PTFE was first examined by ESCA. When examining our results, nitrogen concentration (three nitrogen atoms per EDC) was measured as a marker for EDC attachment.

We then performed a contact angle titration under the non-reactive spreading protocol as developed by Creager and Clarke to ascertain surface acidity of the OH-PTFE. The sample was prepared by being rinsed with deionized water, and fully immersed in the same buffer solution that was to be used to measure contact angle. After removal from the buffer solution, any adhering water droplets were air dried off the surface, and the sample was placed on a sterilized microscope slide. Contact angles were measured ten seconds after the droplet contacted the surface.

To ascertain more data suggesting superacidity, we performed hydroxylated PTFE dip into sulfuric acid. Taking 25 ml of sulfuric acid in a beaker, we first determined the pH of the solution using a Hanna instruments 209 pH meter. We then added a 2.5 x 2.5 cm piece of hydroxylated PTFE to the sulfuric acid and continued to measure the pH for twenty minutes, keeping the sulfuric acid at room temperature.

Results and Discussion:

When examining our results, nitrogen concentration (three nitrogen atoms per EDC) was measured and found to increase significantly after reaction with EDC suggesting a covalent linking between the EDC and PTFE base material.

This is an unexpected result in that EDC has been used extensively as a bifunctional coupler between carboxyl groups to primary amines (typically the N-terminus of proteins). Here, we propose that this reaction takes place with a reactive hydroxyl surface instead of carboxyls. We believe that this is possible due to the strong electron withdrawing capacity of the bulk PTFE material. This leads to suggestions of a superacidic material.

Using Craeger's technique, we found that there was no greater than a $\pm 5^\circ$ difference in testing from pH 1 to 12. This suggests that the -OH moiety is highly acidic. Further, preliminary experimentation suggests that the OH-PTFE is a net proton donor to sulfuric acid.

Conclusions:

The attachment of biological molecules including adhesion proteins is a critical need for the development of biomaterials. We have shown a method by which that can be affected using a novel, proprietary hydroxylation process.

References:

1. Creager, Stephen E., and James Clarke. "Contact-Angle Titrations of Mixed *w*-Mercaptoalkanoic Acid/Alkanethiol Monolayers on Gold. Reactive *us* Nonreactive Spreading, and Chain Length Effects on Surface pKa Values." *Langmuir* 10 (1994): 3675-3683.
2. Koloski TS, Vargo TG. Transition metalhalopolymers. U.S. Patent 525/326.2 (1996)
3. Ludwig NS, Yoder C, McConney M, Vargo TG, and Kader KN. Type IV Collagen Coupling to Hydroxylated PTFE. *Journal of Biomedical Materials Research*. 78A (2006):615-619.