

Fluorinated surfaces, coatings, and films

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1. Fluorinated coatings and films: motivation and significance

Historical perspective:

<1937: only three pure perfluorocarbons (CF₄, C₂F₄, C₂F₆) had been reported and characterized fully. Research in fluorine chemistry was focused primarily on fluoroarenes. Aliphatic fluorine chemistry, principally the work of Swarts at that time, had already been ostracized from the domain of mainstream organic chemistry.

1938: Plunkett first serendipitously discovered PTFE (Teflon).

1939: Simons reported amalgamated copper and mercury(II) fluoride yielded perfluorocarbons

other: GM worker's early search for new refrigerants among aliphatic fluorides; Manhattan Project secret efforts to use perfluorocarbons from Simons' lab as uranium derivatives in atomic bomb developments during World War II; post-World War II escalation of perfluorocarbon research in both the Western hemisphere and Russia

Perfluorocarbon properties derive from molecular structure and bonding:

Single fluorine bonds with carbon are the strongest known with carbon, some 25 kcal/mol stronger than C-Cl. Together with the poor leaving group ability intrinsic to fluorine, this makes alkyl fluorides 100-1,000,000 times less reactive than the corresponding alkylchlorides in certain solvolysis and displacement reactions.

Fluorination also influences adjacent bond energies. Addition of F strengthens adjacent aliphatic bonds: the CF₃-CF₃ bond is 10 kcal/mol stronger than the CH₃-CH₃ bond.

Fluorine's high ionization potential and low polarizability support a tendency for relatively weak intermolecular forces, low interfacial energies and low refractive indices in fluorinated materials.

Well-accepted Pauling van der Waals radius values (1.35Å for F and 1.2Å for H) are often-cited with the accompanying false conclusion that in fact these atoms are the same size. Actually, fluorine and oxygen are more closely isosteric and fluorine and the hydroxyl group are even more closely isosteric, with hydrogen's steric radius not even closely comparable.

Rotational barriers for various fluorine-substituted bonds are significantly higher than barriers in analogous hydrocarbon systems. The -CF₃ group is significantly larger than the -CH₃ group. Analysis supports more accurate comparison of -CF₃ with the isopropyl group.

Perfluorinated surfaces:

Two basic properties seem to be sought in the development of perfluorinated surfaces: low solid-state surface free energy, or surface tension, and chemical resistance and durability.

Perfluorocarbons, because of their intrinsically low intermolecular forces, exhibit the lowest surface tension values for all organic liquids and spread spontaneously

('wetting') over nearly all solid surfaces.

Fluorination imparts lower surface energies to solids. (PTFE: 18.5 mN/m (Zisman surface tension value γ_c); PVDF: 25; PCTFE: 31; HDPE: 31; n-pentane: 15.2; perfluorinated n-pentane: 9.4; n-hexane: 17.9; perfluorinated n-hexane: 11.4; n-octane: 21.1; perfluorinated n-octane: 13.6; decalin: 29.9; perfluorinated decalin: 17.6; benzene: 28.5; perfluorinated benzene: 22.6)

Fluorinated species prefer to reside on a material's surface for energetic reasons if allowed to assume the most thermodynamically stable position in a solid or liquid. This has particular importance in mixtures of components that have sufficient mobility (i.e., diffusivity, relaxation energy) to permit mass movement, migration, or reorganization: surface-enriched films of perfluorinated components are found to reside at surfaces even if present as dopants or minority components in bulk. This surface 'blooming' effect has origin in the surface activity (low interfacial tension) of perfluorocarbon species, as well as miscibility problems with components including hydrocarbons and monomer resins in bulk that favor surface partitioning.

Lowest surface free energies are generally attributed to ambient exposure of -CF₃ groups: the lowest γ_c value known was measured for closed-packed, organized monolayers comprising the nearly vertically aligned CF₃(CF₂)₁₀COOH molecule, a surface of closely packed -CF₃ groups. Substituting only one hydrogen for one fluorine in the terminal, exposed -CF₃ group increases the surface free energy to less impressive value of 15 mN/m.

The realization that the -CF₃ group could be the 'Holy Grail' of the low surface free energy contest has also brought recognition that what lies beneath it must not always be perfluorinated if the -CF₃ group surface presentation is optimal. Surface free energy is a coupled function of both chemistry and organization. (alignment of chains, organized monolayers, surface-blooming of -CF₃ groups)

Desirable low surface tension and chemical inertness associated with fluorinated and perfluorinated species might be imparted to surfaces, without requiring the entire bulk material to be fluorinated. This has significant cost advantages since fluorination costs and associated processing are expensive. Emphasis on fluorinated coatings and films has therefore increased as technological drivers to provide impetus for new, improved and less expensive methods to put this chemistry on surfaces.

While fluorinated coating materials comprise a wide variety of chemistries and physical embodiments, including surfactants, monomers, precursor chemicals and plasma depositions, fluorinated polymers are arguably the most well-known perfluorinated material coating.

PTFE is the largest volume commercial fluoropolymer. It is characterized by high molecular weight chains (1,000,000-10,000,000), high crystallinity, low solubility, high chemical inertness, high hydrophobicity, high creep or flow under stress, poor mechanical and machining properties, high opacity, poor processability, sensitivity to radiation and high bulk cost. Low polymer chain-chain cohesive energy imparts the slippery nature and surface lubricity characteristic of PTFE.

Chemical improvements to PTFE to achieve greater processing capabilities have diversified the markets for this material type. These strategies have introduced various copolymerizations with aliphatic monomers, deliberately induced branching, altered side chain chemistries, vinyl ether copolymers, and backbone alterations (e.g., vinylidene or perfluoroether copolymers) in attempting to reduce polymer bulk crystallinity while maintaining desirable PTFE properties. Many PTFE variants have resulted (PFA, PVDF, PCTFE, FEP, Teflon AF).

One option for polymers is to fluorinate their surfaces post-polymerization. Polyethylene, polysulfone, polystyrene, and cellulose have all been surface-treated to introduce fluorine for various applications.

Market issues:

World-wide consumption of fluorinated polymers in 1994 was about 70 million kg, with an annual growth rate of 3.2%.

A new class of amorphous thermoplastic fluoropolymer was introduced in 1989. DuPont introduced Teflon AF, a copolymer of TFE with the cyclic comonomer, perfluoro-(2,2-dimethyl-1,3-dioxole) (PDD). They are optically clear and exhibit excellent light transmittance from UV to near infra-red, low refractive index and low dielectric constant.

Surface enrichment as a coating strategy:

Perfluorinated liquids have long been known to exhibit non-ideal mixing behavior with their aliphatic analogs. This property, combined with the significantly lower solid state surface tension of perfluorinated chemistry over hydrocarbon chemistry at an air interface, comprise a substantial thermodynamic driving force for structuring films and surfaces. A mixture of hydrocarbons and perfluorocarbons cast together on a surface in air will spontaneously tend to phase separate, 'blooming' the lower interfacial energy components to the air interface and minimizing mixing energies between the two bulk component phases. The result then is a stratified film where the perfluorinated species have formed a layer useful to design stratified films of particular surface chemistry.

Small molecule perfluorinated component films as an alternative to fluorinated polymer coatings. The coating matrix is an inexpensive base coating material/resin and is doped with small amounts of the more expensive perfluorinated film former. A high value-added surface layer of perfluorinated chemistry is created with time if migration of components toward equilibrium distributions is allowed (e.g., solvent does not 'flash' off or viscosity is not too high). This migration time is less than the cure time of the coating, permitting full maturation of perfluorinated surface properties prior to film cure.

Small perfluorinated molecule film forming components include perfluoroalkanoic acids, perfluorinated amines, perfluoroethers, perfluoroalkylolefins and perfluoroalkylsulfonamides. Additionally, several cases exist where perfluorinated monomers (e.g., acrylates, epoxides) mixed with aliphatic resins readily form enriched stratified overlayers that can then be polymerized post-bloom.

Fluorinated plasma deposition:

In addition to more conventional solution-based methods to produce fluorinated coatings, gas-phase deposition of fluorinated precursors can proceed to confluent,

robust films via plasma polymerization process. This rather well-developed method of surface modification can be applied where solution coating is not technically feasible.

Advantages to this technique include production of conformal and usually defect-free films in a one-step process. Disadvantages surround the requirement for volatile gas-phase perfluorocomponents, resulting crosslinked film product, lack of control of aspects of film chemistry, resultant film surface roughness in some cases and low deposition rates and throughput.

Future needs:

Increased radiation resilience.

Improved aftermarket coating applications.

Reduced bulk materials cost.

Improved perfluorinated materials processing.

Possible alternatives to perfluorinated surface chemistry that produce the same effects.

Direct evidence as to why a C-F bond (with associated higher dipole moment than a C-H bond) is in fact not attracted to polar liquids, including water, remains enigmatic.

Helical perfluoroalkyl chains occupy one and one-half times the volume of an all-trans hydrocarbon chain (28Å²/chain vs. 18Å²/chain, respectively). Additionally, a typical R_f chain available (e.g., 10 perfluorinated carbon units) comprises only one full helical turn (if assuming a PTFE-type helical structure). Such a structure standing on end might be considered as a stiff, short stump. Spontaneous surface orientation of these R_f stumps for structural self-avoidance and surface packing purposes is a logical consequence.

2. AFM study on lattice orientation and tribology of SAMS of fluorinated thiols and disulfides on Au(111): the influence of the molecular structure

3. Aggregation structure and surface properties of immobilized fluoroalkylsilanes and their mixed monolayers

4. Stabilizing colloids with fluorocarbon-hydrocarbon diblocks: example of vesicles made from single-chain fluorinated surfactants

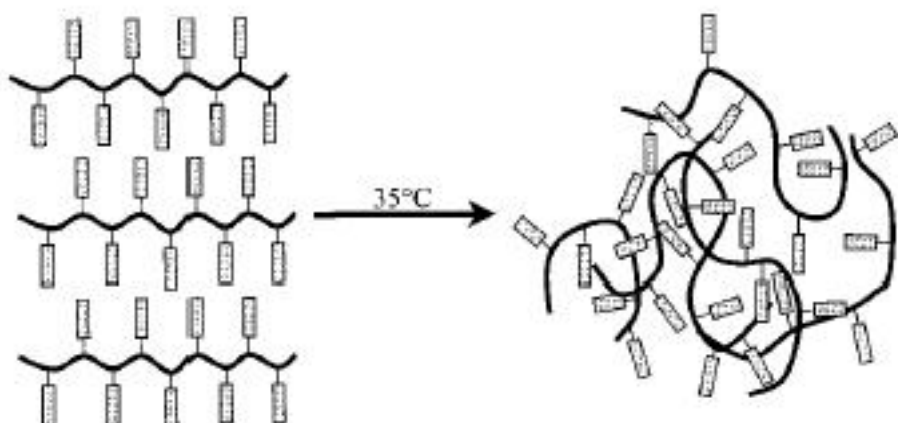
5. Adsorption and aggregation properties of a series of semifluorinated, unsaturated fatty acid esters from nonaqueous solution

6. Wetting behavior of thin films of polymethacrylates with oligo(hexafluoropropene oxide) side chains

Science 1999, 285, 1246

Switchable tackiness and wettability of a liquid crystalline polymer

Fig. 1. Schematic representation of the transition between the smectic and the isotropic phase.



7. Grand unified theory of fluorocarbon polymer mobility on disk surfaces
8. Fluorinated silicone coatings with controlled surface chemistry and microstructure
9. Wettability of fluorosilicone surfaces
10. Design of fluorinated acrylic-based polymers as water repellent, intrinsically photostable coating materials for stone
11. Fluorinated polymer claddings for optical fibers
12. Ultra water repellent thin films prepared by dc plasma polymerization of vinylidene fluoride
13. Surface interactions of CF₂ radicals during deposition of amorphous fluorocarbon films
14. Chemical and contact mechanical characterization of thin plasma-deposited hexafluoropropylene films
15. Fluoropolymer films deposited by rf plasma sputtering of PTFE using inert gases
16. Fluoropolymer films deposited by argon ion-beam sputtering of PTFE