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Plasma Advancement Expands Applications of Fluoropolymer Coatings and Linings

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Advanced plasma-surface technology permits combining nonstick, chemically inert, and temperature-resistant fluoropolymer coatings and linings with an unlimited variety of substrates and materials. This article discusses the surface modification science that creates reactive functionality on the surface of fluoropolymers and can covalently bond to appropriately selected substrates. The reaction creates an environmentally stable and permanent bond between adhesives and sealants and the fluoropolymer. Consequently, many cost-effective fluoropolymer-based materials are now available to protect equipment and facilities from extremely corrosive and high-temperature environments.

The chemical inertness and high-temperature resistance of fluoropolymers have long made them one of the best materials for service in harsh, elevated-temperature chemical environments. Achieving good adhesion to substrates from a class of materials that exhibits low-surface-energy, "nonstick" properties has long been a challenge. The serviceability and usefulness of fluoropolymers are severely limited because of the inability to achieve strong adhesive bonds between fluoropolymer surfaces and other materials such as adhesives, plastics, ceramics, metals, and glass.

Greater adhesion capabilities would expand the potential uses of fluoropolymers, making them a commercially feasible alternative to traditional coating and lining materials. Can this be achieved, however, without sacrificing any of the polymer's superior performance properties? This article describes a cold-gas plasma treatment that permanently bonds adhesives and coatings to thin films and sheets of fluoropolymers without degrading the performance of the material. The process enhances adhesive characteristics at the nexus of the treated fluoropolymers and various substrates.

Traditional Fluoropolymer Technology

Traditional fluoropolymer coatings and linings are applied in a powder, liquid, or sheet form. The powders are spray-applied and baked on in a multistep process.

Fluoropolymer sheet linings from 40 to 100 mils (1,016 to 2,540 µm) dry film thickness (DFT) are often manufactured by incorporating a glass fabric backing into the sheet during the extrusion process. The backing allows the sheet lining to be installed by mechanically adhering the fabric to a substrate with an adhesive—usually an epoxy. This process is expensive because of the high raw material costs associated with the thicker sheets and glass backing. Temperature usage must also be confined to the adhesive's thermal limits, typically <325°F (163°C). It is important to note, however, that the thicker sheets may be necessary to achieve permeability requirements in specific applications.

Other fluoropolymer sheets and films use alternative methods to promote adhesion to substrates. The films range from 1.5 (38 µm) to 40 or more mils DFT. They promote adhesion by using a less-fluorinated raw material or chemical etching with solvents such as sodium naphthalide. These processes adversely affect the chemical and morphological characteristics of the surface by physically altering and even destroying the fluorinated surface of the polymer to promote adhesion. The resultant surface is an oxidized carbonaceous oxide overlayer, which eventually degrades the adhesive bond when exposed to various forms of actinic radiation including ultraviolet (UV) radiation from sunlight. The adhesion characteristics are also compromised when the surface is exposed to chemicals and severe thermal cycling.

TABLE 1

ASTM AND CUSTOM TESTS

Test	Conditions
ASTM B117:[1]	2,000-h salt spray
ASTM G53:[2]	UV exposure
Nitric acid (HNO_3) immersion:	2,000 h
Humidity/temperature exposure:	168 h
Thermal shock testing:	50 cycles (–40 to 450°F [–40 to 232°C])
Thermal cycle testing:	500 cycles (–40 to 275°F [–40 to 132°C])
ASTM D 0903[3]	180-degree adhesive pull
ASTM D 4541[4]	Concrete pull

TABLE 2

RESULTS OF THERMAL-SHOCK AND THERMAL-CYCLING TESTING

Test	Plasma-Treated Fluoropolymer	Etched PTFE
Thermal-shock(A) acrylic adhesive	Passed	Failed
Thermal-shock(B) silicone adhesive	Passed	Failed
Thermal-cycle(C) silicone adhesive	Passed	Not evaluated

(A)Thermal shock:
Condition 1 for acrylic PSA: 50 cycles; 15 min at 275°F, transfer to –40°F; 15 min at –40°F, transfer to 275°F
(B)Condition 2 for silicone PSA: 50 cycles; 15 min at 450°F, transfer to –40°F; 15 min at –40°F, transfer to 450°F
(C)Thermal cycle test:
Conditions: 500 cycles; 70-min ramp to 275°F, 15-min hold at 275°F, 50-min ramp to –40°F, 15-min hold at –40°F

Plasma Surface Science

A process using a cold-gas plasma treatment has been developed to modify fluoropolymer surfaces to promote adhesion to materials such as other polymers, adhesives, ceramics, and metals. In the late 1980s, researchers discovered that a radio frequency (rf) glow discharge (cold-gas plasma) of hydrogen and vaporized liquids creates a distinctive surface modification at fluoropolymer surfaces. Using a hydrogen plasma as a fluorine scavenger in concert with vaporized liquids makes incorporating the oxygen into the surface matrix of a fluoropolymer material highly controllable. The researchers discovered that the plasma surface modification enables the subject material to retain levels of morphology, chemical resistance, and hydrophobic properties comparable to those of the original, unmodified fluoropolymer. Furthermore, the process effectively creates highly reactive sites where other materials can bond.

The research demonstrated that the oxygen functionalities created on these fluoropolymer surfaces were chemically reactive and permanent. It is this chemical functionality that allows various adhesives and polymers to form a covalent bond to the modified fluoropolymer surface. The treatment does not significantly affect the film's surface tension properties. The surface remains "nonstick" and easy-to-clean.

Plasmas consist of a low-temperature glow discharge or a low-pressure, partially ionized gas composed of a concentration of highly excited atomic, molecular, ionic, and free-radical species. Subjecting the gas mixture to an electrified field of rf energy in an enclosed vacuum chamber excites the gas molecules.

The imposed rf field creates free electrons. The free electrons collide with neutral gas molecules as their energy increases from the imposed field and transfer energy, forming numerous reactive species. The particles then interact with solid surfaces placed in the plasma, often causing dramatic modifications of the molecular structure of the solid surface. The desired effect can be controlled by judiciously selecting the process gas to create the desired surface properties required for the intended use of the material. Figure 1 shows traditional and plasma treatments.

In the application specific to halogenated polymers, a mixture of hydro-

TABLE 3

COMPARATIVE ADHESIVE PULL TESTS

Plasma-Treated Fluoropolymer Backbone				Peel Strength (oz./in.)		
Material	Thickness (mil)	Adhesive	Total (mil)	0°C	23°C	60°C
PTFE[A]	2	A[B] (4 mil)	6	26.2	163.2[C]	21.6[C]
MFA[D]	2	A (4 mil)	6	86	140.3[C]	29.8[C]
ECTFE[E]	2	A (4 mil)	6	98.9	249.6[C]	32.2[C]
PCTFE[F]	2	A (4 mil)	6	110.7	225.6[C]	26.2[C]

Commercially Available Etched Film					Peel Strength (oz./in.)		
Etched Film	mil	Adhesive	mil	Total	0°C	23°C	60°C
PTFE high modulus	1.5	Acrylic	2	3.5	NA	35.0	NA
PTFE high modulus	1.5	Acrylic	5	6.5	NA	45.0	NA

[A] Polytetrafluoroethylene
[B] A = acrylic
[C] Film tear, stretch (i.e., sample ripped in half or elongated prior to pulling free—actual value is higher than reported)
[D] Copolymer of tetrafluoroethylene and perfluoromethyl vinyl ether
[E] Ethylene-chlorotrifluoroethylene
[F] Polychlorotrifluoroethylene

gen and H_2O or MeOH vapor co-reactant is used to generate the plasma. This combination partially defluorinates the fluoropolymer surface and concurrently adds permanently stable –OH functionalities at the defluorinated sites. The –OH functionality adjacent to fluorinated carbon groups is extremely stable yet chemically reactive to various chemistries. The resultant reactivity is ideal for forming tenacious bonds with selective adhesives and polymers.

Advanced High-Performance Linings and Films

Although fluoropolymer films and linings that use chemical etching, flame, or corona treatments of the surface are suitable for many applications in ambient conditions, they are unsuitable for severely corrosive environments. Subjecting the material to repeated thermal cycling, external stresses, or UV radiation breaks down the carbonaceous overlayer between the film and adhesive and causes disbondment and delamination. This limits the use of thin films, linings, and sheets in high-temperature, atmospheric (UV), and harsh chemical environments.

The advanced plasma treatment process offers expanded applications of fluoropolymer materials because of four factors:

- The surface of the film is not degraded or destroyed by flame, corona, or etching to provide an adhesive bond.
- Thinner linings and films can be used without glass-backing to produce a mechanical-adhesive bond.
- The process allows the use of a variety of adhesives and sealants such as fluoroelastomers and silicones, epoxies, epoxy-novolacs, and vinyl esters.
- Sheets and linings can be easily field-repaired with alternative methods and materials.

The plasma treatment permits permanent chemical bonding of a variety of adhesives to the fluoropolymer. The bonds are not subject to failure from stresses such as thermal cycling, chemical attack, or UV degradation. When tested, the failure typically occurs at the adhesive-to-substrate interface rather than the adhesive-to-fluoropolymer interface. The surface modification allows adhesives to perform to their utmost, thereby greatly expanding the use of bondable fluoropolymers as easy-to-install, permanent paint-replacement films and linings.

The modification process can be used to treat both sides of a sheet or film. It allows the material to be wrapped back onto itself, layered, and overlapped to simplify field-seaming and permanent adhesion installation.

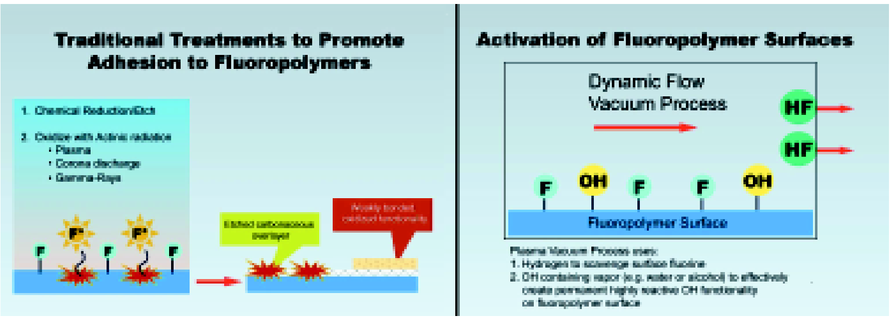
Testing and Evaluation

The tests identified in Table 1 produced results confirming the suitability of a new generation of treated fluoropolymer for new applications. Two evaluative tests are detailed below: thermal shock and cycling, and adhesive pull.

THERMAL SHOCK AND CYCLING

Temperature cycling is an established nemesis of fluoropolymer films and sheets treated with traditional methods. It typically causes surfaces to lose their treatment, leading to delami-

FIGURE 1



Traditional treatments and dynamic-flow plasma process for promoting adhesion to fluoropolymers.

nation of the adhesive from the fluoropolymer and disbondment of the film or sheet from the substrate.

The advanced plasma-treated material was tested side-by-side with a sodium naphthalene-etched PTFE. The films were surface-treated and laminated with either an acrylic-based pressure-sensitive adhesive (PSA) or silicone PSA. All samples were mounted on smooth carbon steel (CS) plaques. The plasma-treated samples were modified on both sides and overlapped to create a seam. Table 2 shows the results.

> *Combining the ability to bond adhesives, sealants, and other coating and lining materials has created a new generation of composite protective systems.*

Thermal-cycling the sodium-etched PTFE caused the surface to lose its modification. The bond between the adhesive and the film was broken. Thermal shocking and cycling had no effect on the samples with plasma surface modification. The seams themselves were also unaffected.

ADHESIVE PULL TESTS

Four fluoropolymers were plasma-modified and laminated to an acrylic PSA. The films were peeled per ASTM D0903. The average values were obtained for each of 10 samples of the plasma-modified film that were pulled at temperatures of 0, 23, and 60°C. The samples were prepared by applying the PSA-backed film with vigorous thumb pressure to a smooth panel of CS. After setting for 24 h, the PSA was subjected to a 180-degree pull at a crosshead speed of 152 mm/min.

FIGURE 2

Rail car for sodium hydroxide (NaOH) has center-band coated with clear 5-mil ECTFE for paint protection, ease of cleaning, and minimized product buildup.

The peel data (Table 3) indicate that the plasma-treated materials produced bonds significantly stronger than the traditionally etched materials. At 0 and 60°C, the new surface modification process created peel values nearly as high—and in some cases higher—than those for etched film at room temperature. The etched films disbonded from their adhesives, leaving the adhesive on the panel. Samples using the new modification process film either stretched or cohesively failed, or the adhesive peeled from the substrate panel. In no case did the fluoropolymer film peel from its adhesive.

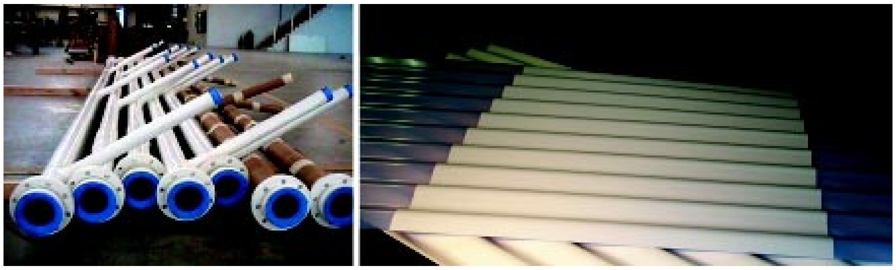
Technical and Commercial Feasibility

The plasma technology has increased the number and variety of technical and commercial applications for fluoropolymers commonly referred to as ECTFE, MFA, PTFE, perfluoroalkoxy-polymer (PFA), fluorinated ethylene propylene polymer (FEP), and polyvinylfluoroethylene (PVDF). The applications include secondary containment in concrete dikes, pits and sumps, and splash-and-spill exposures and primary containment of both dry- and aqueous-based materials. The new surface modification process creates fluoropolymer surfaces that permit combining various polymers to devise new solutions to coating and lining problems—nonstick properties are no longer constraints. The high-temperature and chemical resistance of fluoropolymers can be incorporated with other materials and polymers to expand the applications and uses of this material. The costs of thinner films and sheet fluoropolymers compete with costs of traditional high-performance coatings and linings on an installed basis.

Combining the ability to bond adhesives, sealants, and other coating and lining materials has created a new generation of composite protective systems. Even silicones can now bond to fluoropolymers.

The new material is suitable as a laminated coil coating for applications such as high-temperature ductwork in high-purity and harsh-chemical applications, equipment manufacturing, architectural (antigraffiti) coatings, and corrugated pipe. Coils of thin-gauge metals can be laminated with fluoropolymer films from 2 to 10 mils (51 to 254 μm) thick. They can later be formed into cor-

FIGURE 3



A 5-mil white and clear ECTFE film used to protect dual-laminate FRP piping and PVC panels from splash and spills of high-temperature liquid in a chlorine-caustic environment.

rugated building products, panels, and various components of process equipment where high temperature resistance, chemical resistance, or nonstick properties are demanded.

Surfaces subject to splashes and spills of aggressive chemicals can take advantage of the chemical resistance of the base material and the nonstick, easy clean-off properties of fluoropolymers. The railcar in Figure 2 was coated to protect against corrosives and facilitate cleanup of surfaces from splash and spillage during loading and unloading.

Joining the properties of fiberglass-reinforced plastics (FRP) and fluoropolymer films yields a composite material for construction that enhances flow characteristics and cleanability while optimizing corrosion protection (Figure 3). Typical applications include FRP paneling, corrugated panels, doors, and manufactured equipment.

Summary

Advanced plasma-surface technology permits combining a nonstick, chemically inert, and temperature-resistant coating and lining material with substrates and materials such as PSAs, polymers, and sealants. The unique surface modification creates a reactive functionality on the surface of fluoropolymers that can be covalently bonded to appropriately selected substrates, composites, adhesives, sealants, and coatings. The chemical bonds provide an environmentally stable and permanent bond between adhesives and sealants and the fluoropolymer lining or coating material. This advanced technology provides a new selection of cost-effective fluoropolymer materials.

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