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UNIQUE APPLICATIONS OF FLUOROEPOXY MATERIALS

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INTRODUCTION

Teflon has become essential in our daily life both at home and in industry. The trade name Teflon symbolizes a family of fluorocarbon thermoplastics that are known to have high thermal stability, good low temperature properties, low surface energy, low moisture absorption, excellent electrical properties, and particularly chemical inertness. Just because of its inertness and its high thermal stability, Teflon processing is very difficult. There is no good method to cure or crosslink Teflon yet.

It has been a challenge to develop a fluorinated thermoset material with properties similar to Teflon yet can be processed like regular thermosets. Let's imagine how nice it would be if our cars or boats could be spray-painted with Teflon paint. Our war ships would last longer at much lower maintenance cost and move faster without the nuisance of barnacle problem in the sea if they could be painted with Teflon-like epoxy paint. Indeed, Griffith and his coworkers in the U.S. Navy have worked hard toward this goal and have developed a basic fluorodiol structure from which a series of fluoroepoxies and fluoropolyurethanes can be prepared (1, 2). Although there is still a long way before we can see U.S. war ships painted with a fluoroepoxy paint, now fluoroepoxy resin may be commercially available in pilot-plant quantities, and its attractive potential can be demonstrated by a few unique applications presented in this paper.

Fluoroepoxy and curing agents. We at NASA are interested in this new material. We believe that fluoroepoxy resin could be formulated to make a good moisture vapor barrier coating. The first problem in formulating a fluoroepoxy material is to find a good compatible curing agent. Few fluorinated epoxy curing agents are commercially available. Figure 1 shows the fluoroepoxy resin I developed by the Navy and a few curing agents available that have been tried.

Fluoroepoxy I is a diepoxide functionally identical to the conventional epoxy resin. Its fluorine content may vary with the perfluoroalkyl group, R_f. For this work, the highly fluorinated epoxy C8F was generally used unless indicated otherwise. Fluorinated anhydride II was synthesized by the Naval Research Laboratory. Like other anhydrides. it needs elevated temperature curing. Siloxane diamine III, supplied by Silar Laboratories, Scotia, New York, could be made compatible with I-C6F at 50° C, but the system is handicapped by the high sensitivity of the amine to carbon dioxide in air as well as by the concern that the siloxane structure may compromise the low moisture permeation requirement. Fluorinated diamines IV and V are laboratory products. Unfortunately they are either sluggish or inactive in curing epoxy I. Polyamine VI is an adduct amine that can be conveniently prepared by reacting epoxy I-C6F with an excess of ethylenediamine. The unreacted diamine can be removed easily due to its relatively low boiling point. Curing with the adduct amine is equal to curing with ethylenediamine except that the ethylenediamine is pre-tied to epoxy I to minimize the compatibility problem. The liquid mix of epoxy I and adduct amine VI appears cloudy but compatible, and the cured products are transparent. The adduct curing agent may be less than perfect for many applications where more flexibility of the cured material is desired. Nevertheless, it gives room temperature gelation and the cured products can pass the stringent outgassing requirement that NASA emphasizes for space uses. Therefore, this paper presents applications basically using the adduct amine VI as the curing agent.

An excellent moisture vapor barrier coating. Fluoroepoxy I-C8F and adduct amine VI were formulated in stoichiometric amounts. For spray-coating, solutions of ca. 50% by wt. were made with a solvent mix of 1,1,1-trichloroethane, THF, methylene chloride, and methanol in a ratio of 20/20/30/30 by volume. Spraying was done with compressed helium as a carrier gas to avoid gas trapping as well as the appearance of orange peel which was observed when nitrogen was used. After room temperature gelation, curing was completed by heating at 80° C for 2 hours.

A low moisture vapor transmission rate is the key to a good moisture vapor barrier material. For the determination of the transmission rate, fluoroepoxy films were prepared by spray coating. Solvent trapping was a problem, a dilemma expected with a good vapor barrier material. To reduce trapping, a quite volatile solvent system was developed as given above. Film thickness was built with multiple light sprayings. Time was allowed for solvent evaporation between sprayings, and the curing temperature was programmed to facilitate the solvent release. With these precautions, it was possible to keep the 125° C vacuum outgassing level of the cured film at about 1.5% total weight loss. The level could be brought down to 1% or less by baking the film at 100° C in order to meet the NASA requirement.

The moisture transmission rates of the fluoroepoxy film and the films of a number of reference materials were determined according to an ASTM method. The data collected are shown in Table 1. Generally, the rates are inversely proportional to the fluorine content of the materials. The transmission rate of the fluoroepoxy is higher than that of the highly fluorinated Teflon PFA and Teflon FEP, but is only about one twelfth of that of the four polyurethane coatings/potting materials popular in the market. Uralane and Conathane EN11 are polybutadiene-diol based polyurethane and are noted for their excellent moisture resistance.

Closely related to moisture transmission is moisture absorption. Three materials were compared in the moisture absorption experiment conducted at room temperature and 97% relative humidity (RH). The results shown by Figure 2 indicate the overwhelming superiority of the fluoroepoxy and polyurethane EN11 over epoxy Epon815/V140 (Epon815 and Versamid 140 in 50/50 ratio by wt.). Plotting on a different scale in Figure 3 illustrates that the moisture absorption of the fluoroepoxy had essentially leveled at 0.26% in 27 weeks, while that of EN11 was approximately two times higher and the difference increases continuously with time.

<u>As adhesives to bond Teflon without any surface treatment.</u> Teflon is non-polar, non-wettable, and consequently non-bondable with adhesives if its surface is not pre-treated. Since Teflon is noted for its chemical inertness, some special methods have to be used for the surface treatment. Up to now, the primary method is dependent on a special chemical etching agent which is a solution containing sodium-naphthalene complex. However, the reagent is corrosive and may be hazardous in use. In many cases, it is undesirable or simply impossible to conduct such an etching operation on an object to be bonded. Moreover, the etching action has to be drastic so that the Teflon surface can be converted from being non-polar to polar.

After the conversion, the surface layer is so much different from the bulk of the polymer that the molecular bond of the etched layer to the bulk of the plastic is seriously weakened. In fact, the layer becomes a weak interface subject to moisture penetration and layer separation even when it is bonded with a superb adhesive. The sensitivity of the etched layer to moisture makes it behave like an effective humidity sensor (4). Its sensitivity to air, oxygen, and ultraviolet light makes it necessary that either the etched Teflon be bonded without delay or be sealed from air and light in order to avoid rapid degradation. In view of all these shortcomings, people in the field have long sought after an adhesive that can bond Teflon or other fluoroplastics without any special surface treatment.

"Like dissolves like" is the old simple rule. The fluoroepoxy, like other epoxy resins, may be used as an adhesive, and especially it may be good to bond Teflon which is also a fluorinated plastic. To test its effectiveness, aluminum and Teflon PTFE rod adherends were made according to an ASTM method. One set was bonded with the fluoroepoxy adhesive formulated stoichiometrically with fluoroepoxy I-C8F and adduct amine VI, while the other set was bonded with a popular epoxy adhesive Epon828/V140 (50/50 by wt.) for comparison. The adhesive tensile strengths shown in Table 2 demonstrate that to bond aluminum, the strength of the fluoroepoxy is only 60% of that of Epon828/V140, yet to bond Teflon, its strength is 2 times that of the latter. The sodium naphthalene etching of Teflon improves the bond strength of the Epon828/V140, but only to a level 40% higher in average than that achieved by the fluoroepoxy without etching. The strength gained by the etching varied greatly with the degree of etching, and the etching led to a bond failure by separation of the etched surface layer. In contrast, the fluoroepoxy adhesive offers a new convenient way to bond Teflon without etching to achieve a considerable bond strength free from risk.

To verify the effect of the fluorine content, fluoroepoxy adhesives were prepared with fluorine content varied from 56.4 to 45.9% by using fluoroepoxy I-C8F, -C6F, and -C0F, with adduct amine VI as the curing agent in stoichiometric amounts. The adhesive tensile strengths obtained in bonding Teflon PTFE without etching are given in Table 3. The trend shown is that the strengths decreases only slightly with the decrease of the F-content of the adhesives until the content drops to a level of around 46% where the bonding strength falls sharply to a value as low as that of the common adhesive containing no fluorine. It is important to note that here the 46% marginal level is for bonding Teflon PTFE which is a fully fluorinated plastic with the highest F-content of 76%. We have evidences to indicate that the novelty of the fluoroepoxy adhesives is limited to the application to the highly fluorinated plastics. For bonding Tefzel, a random copolymer of ethylene and tetrafluoroethylene made by DuPont with a F-content of 54%, there is little advantage to choose fluoroepoxy adhesives over a conventional adhesive (5, 6).

A new method to make thermosetting fluoropolymer foam. Teflon has been widely used for electrical insulation and as structural components due to its excellent electrical and other properties. For many applications, Teflon and other thermoplastic fluoropolymer foams are particularly desirable because they render reductions in weight, dielectric constant, and dissipation factor. There are many patented processes to make Teflon foam. However, all of them require a minimum temperature of 240° C and a pressure of up to 1500 psi or much higher. These methods employ volatile or chemical blowing agents and nucleating agents which may leave undesirable residues in the foam products. The main reason for the required extreme conditions is that the available thermoplastic fluoropolymers are processable only at such high temperatures and the high temperature dictates the use of high pressure to control foaming. Consequently, these requirements can constitute a prohibitive barrier to many applications.

With liquid fluoroepoxy resins, regular epoxy foaming processes should be practical. Particularly a new foaming method has been developed on the basis of a novel property of the fluoroepoxy observed. The highly fluorinated epoxy compound made of I-C8F and adduct amine VI is viscous but has minimal tendency to trap the air introduced in mixing the two components. In other words, the usual vacuum deaeration step following the mixing step is easy and fast. Just as it is easy to get the air out under vacuum, gas can also be readily dispersed in the fluoroepoxy compound under a moderate pressure. Perhaps this may be attributed to the low molecular forces between fluorinated molecules. It is this unusual property that offers a new foaming process for fluoroepoxy as well as other thermosetting fluoropolymeric materials.

The process is simple. A chosen unreactive gas is dispersed at or near room temperature in the fluoroepoxy compound before gelation by exposing the compound to the gas under a moderate pressure. The compound gas will be trapped in the compound upon gelation. The gelled clear compound will then expand to form a foamy or cellular structure when it is heat-cured to its completion (3, 7, 8). The process is contrary to the common pressure potting method, which removes trapped air and eliminates voids in the common potting compound by pressing the compound in a gas chamber under a moderate pressure for a period of time or until gelation.

The depth of the gas dispersion in the fluoroepoxy compound depends on the type of the gas and the magnitude of the gas pressure. The cellular structure may be controlled by the degree of gelation or cure and the temperature programming in the heat-cure step. Generally, a pressure of 3 atmospheres or 45 psi suffices to make a foam sheet 3 mm thick. The foam cell is essentially closed. The fact that one has the freedom to choose any unreactive gas for foaming is practically a freedom to store a chosen gas in the cellular material. Air and nitrogen may be used for ordinary purposes. Oxygen, argon, krypton, sulfur hexafluoride, and many others may be the choice when some special properties from the gas may be desired. The stored gas will remain in the cell for a long time because of the low permeation rate.

As a new antifoaming agent for epoxy material manufacturing and processing. The control or elimination of the foam that arises in many industrial processes can be a critical factor in their operation and their cost reduction. Antifoaming agents are therefore needed to inhibit and reduce foam formation or to rapidly knock down foam (to defoam) when it occurs. The annual world market for antifoaming agents probably exceeds a quarter of a million metric tons.

Antifoaming agents are widely used in the production of monomers and polymers, in the textile industry, in the paint and latex industry and other polymer coating processes, and in the manufacture and application of adhesives. In our investigation of copolymerizing the fluoroepoxy with Epon828, it was found that the use of I-C8F in a very small amount could effectively break the foam bubbles and cut tremendously the vacuum deaeration time in the preparation of the epoxy compound. Air entrainment almost always occurs when the components of an epoxy compound are mixed either manually or with a mechanical stirrer. The mixing is normally followed with vacuum deaeration to remove the entrained air from the viscous liquid compound. The deaeration process is time-consuming and involves fighting patiently with foaming-up. Any residual air in the compound may be the cause of a weakened bond when used as an adhesive or a composite matrix, or may be an electrical insulation failure when used for embedding or impregnation.

The antifoaming effect of fluoroepoxy I-C8F was tested with both commercial epoxy materials and our laboratory formulated epoxy compounds as shown in Table 4. Evidently, I-C8F shows excellent antifoaming effect when applied at a level of as low as 0.1 to 0.5% by weight in the epoxy compounds .

Many antifoaming agents are commercially available, but those which have little side effects are limited for epoxy compounds. The novelty of the fluoroepoxy is that it is reactive and can copolymerize with a conventional epoxy resin at the same time in the same way in forming an inter-crosslinking polymer network. Consequently, the antifoaming agent is not a free additive left in the cured material. Our experimental data indicate that as an antifoaming agent used only in small amount, I-C8F does not have any adverse effect on outgassing property and adhesive strength of either commercial adhesives tested or epoxy compounds formulated in our laboratory. Table 5 shows the adhesive tensile strength data with and without I-C8F added.

It is reasonable to expect that fluoroepoxy resins can be used as an effective antifoaming agent in the early stage of the epoxy manufacturing. It is known that foaming is usually a problem when excess reactants or solvents are stripped. Also, the antifoaming application may not be limited to epoxy processing either. A similar advantage will exist when the fluoroepoxy is applied to polyurethane and other thermoset polymers' processing where the functional groups of the pre-polymers are reactive to the epoxide. Their reaction will also tie up the fluoroepoxy to the crosslinked polymer network.

Conclusion. The four unique applications presented above are just examples to demonstrate the attractive potential of the fluoroepoxy. There may be many other novel properties waiting to be explored. Individually, epoxy resins and fluoropolymers are two known classes of important, wonderful materials. Their "married" product, fluoroepoxy material, is bound to possess novel properties. At this time, fluoroepoxy resin is still an exotic material in terms of cost. But when more novel properties and applications are identified, increased interest in the material may create a market demand that can make the fluoroepoxy cost effective. High tech competition is intensifying as we march toward the twenty-first century. Today's exotic material should be seriously considered in order to meet the future challenge.

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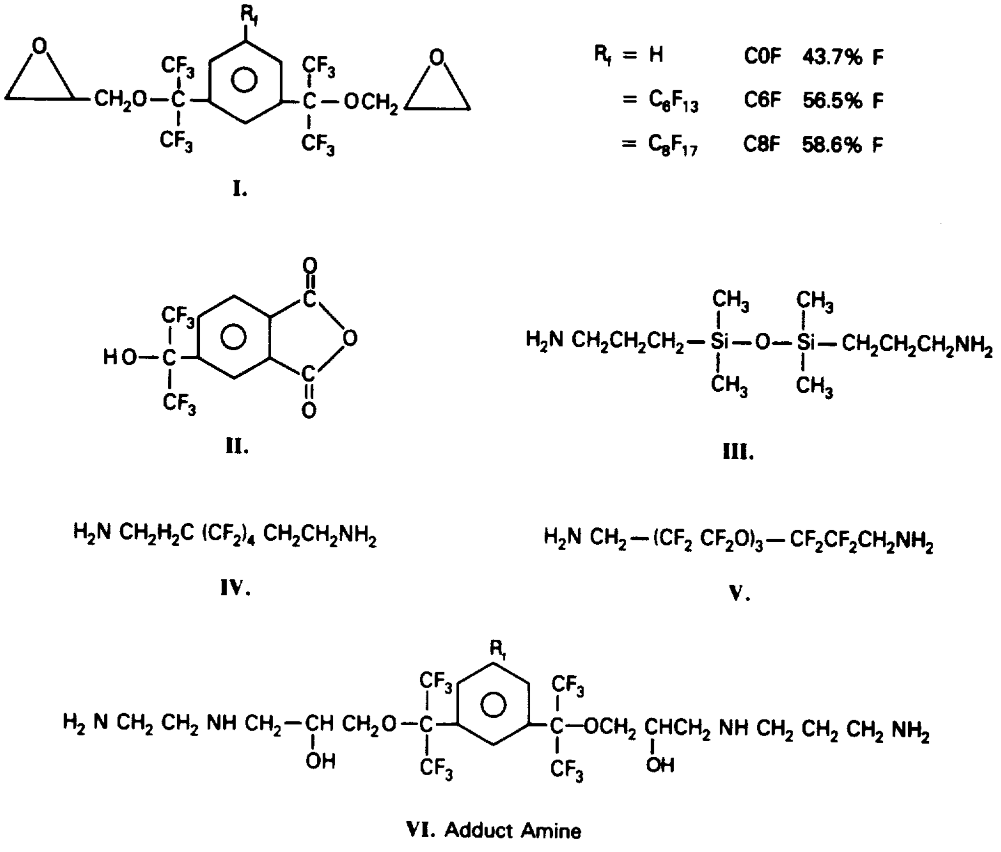

Figure 1. Fluoroepoxy Resins and Curing Agents

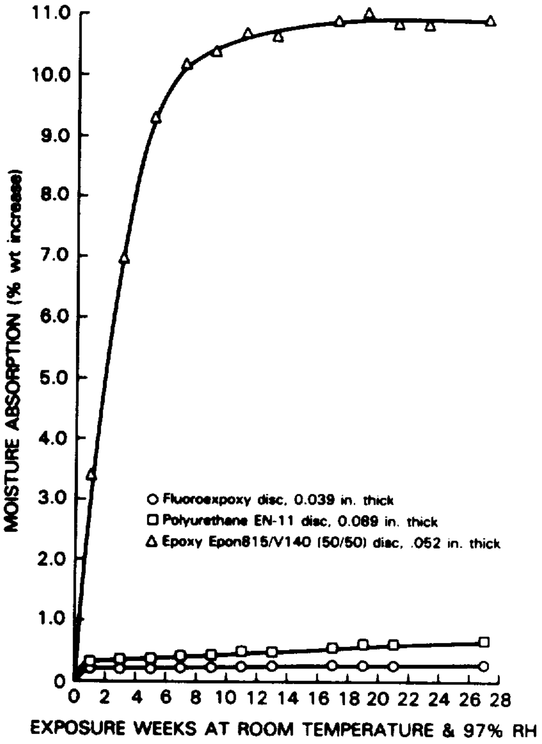

Figure 2. Moisture Absorption (Plastic Disk Specimens, 2.284-in. Diameter).

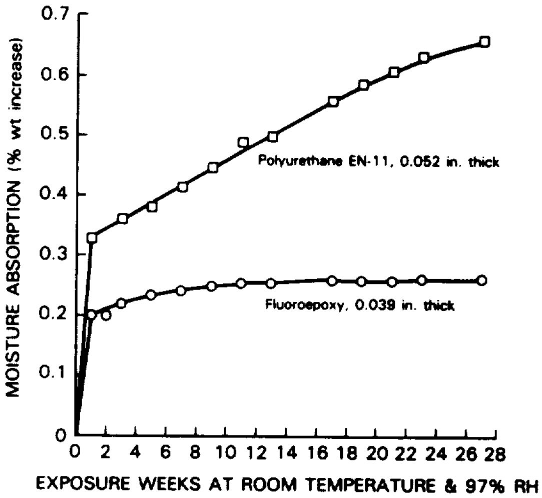

Figure 3. Moisture Absorption (Plastic Disk Specimens, 2.284-in. Diameter).

TABLE 1.

MOISTURE VAPOR TRANSMISSION RATES OF POLYMER FILMS (ASTM D1653-72, at 33°C)

Material	F-Content % by wt.	Av. film thickness mm (mil)	Transm. rate mg·mm/(cm2·24h)	Remarks
Fluoroepoxy	56	0.045 (1.8)	0.101	Spray coating
DuPont Teflon PFA	72	0.045 (1.8)	0.018	290°C softening
FEP	76	0.045 (1.8)	0.011	240°C sodtening
Solithane 113/300	0	0.28 (11)	1.19, 1.28	RT 7 days cure
Uralane 5750LV	0	0.34 (13)	1.18	65°C 10 h cure
Uralane 5753LV	0	0.18 (7)	1.21	55°C 24 h cure
Conathane EN11	0	0.32 (13)	1.33	45°C 48 h cure

Note: Fluoroepoxy compound was formulated with I-C8F and adduct amine VI. The last four materials are popular polyurethane coatings.

TABLE 2. TENSILE STRENGTH OF ADHESIVES (ASTM D2095)

	Fluoroepoxy I C8F/VI		Epoxy Epon 828/V140	
Rod adherend	Strength, psi	Failure mode	Strength, psi	Failure mode
Aluminum	3470±330	Adhesive	7030±258	Adhesive/cohesive
Teflon	640 ±48	Adhesive	330 ±16	Adhesive
Teflon, etched			912±180	(a)

(a) All failed by the separation of the etched surface layer. Strength varied from 710 to 1120 psi. Teflon PTFE was used.

TABLE 3

ADHESIVE TENSILE STRENGTH OF FLUOROEPOXY COMPOUNDS IN BONDING TEFLON PTFE WITHOUT ANY SURFACE TREATMENT (ASTM 2095)

Resin/Adhesive	F-content in the compound	Tensile strength psi
Fluoroepoxy I-C8F	56.4%	550 ± 46
I-C6F	54.6%	601 ± 87
I-C6F/COF	50.2%	567 ± 163
I-C6F/COF	46.9%	610 ± 55
I-C6F/COF	46.7%	590 ± 78
I-COF	45.9%	358 ± 51
Epon828/V140 (50/50)	---	330 ± 16

Note: All the fluoroepoxy compounds were formulated stoichiometrically with adduct amine VI as the curing agent, and cured at 80°C for 2 hours after room temperature gelation. The F-content of compounds I-C6F/COF was varied by changing the ratio of C6F to COF.

TABLE 4

ANTIFOAMING EFFECT OF FLUORODIEPOXIDES

Epoxy compound	Fluoroepoxy content by wt.	Number of foam-up in vac. deaeration
Epon828/V140 (50/50)	----	>25
Epon828/V140/C8F (4)	1.09%	1/2
(5)	0.55%	1
(6)	0.23%	4
(7)	0.10%	4
Epon828/TETA (14 phr)	----	13
Epon828/TETA/C8F (8)	0.23%	1
(9)	0.096%	1
Thermoset 321	----	22
Thermoset 321, +C8F	0.19%	1/2
Scotchweld 2216	----	34
Scotchweld 2216, +C8F	0.14%	2
Epon 828/TETA/C6F	0.23%	1/2

Notes: 1. Containers used in the experiments are PE cups, 180 ml size, 6 cm depth. Epoxy compounds weighed about 30 gms and took 2 cm or less in depth in the cup. The number of foam-up means the cycle number of foaming up to ther cup top and breaking it down.
2. V140 is Versamid 140. TETA is triethylenetetramine. Thermoset 321 and Scotchweld 2216 are the products of Thermoset Plastics and 3M Company respectively.
3. Fluorine content of the fluorodiepoxides: C8F 58.6%; C6F 56.5%.

TABLE 5

ADHESIVE LAP SHEAR TENSILE STRENGTH (ASTM D1002)

Epoxy compound	Fluoroepoxy content by wt.	Lap shear strength psi
Epon828/V140 (50/50)	---	2390 ± 211
Epon828/V140/C8F	0.10%	2293 ± 297
	0.50%	2599 ± 297
Scotchweld 2216	----	3186 ± 301
Scotchweld 2216, +C8F	0.20%	3036 ± 169

Note: Scotchweld 2216 is a product of 3M Company.