5

Corrosion of Polymer (Plastic) Materials

As discussed previously, metallic materials undergo a specific corrosion rate as a result of an electrochemical reaction. Because of this, it is possible to predict the life of a metal when in contact with a corrodent under a given set of conditions. This is not the case with polymeric materials. Plastic materials do not experience a specific corrosion rate. They are usually completely resistant to chemical attack or they deteriorate rapidly. They are attacked either by chemical reaction or by solvation. Solvation is the penetration of the plastic by a corrodent, which causes softening, swelling, and ultimate failure. Corrosion of plastics can be classified in the following ways as to the attack mechanism:

1. Disintegration or degradation of a physical nature due to absorption, permeation, solvent action, or other factors
2. Oxidation, where chemical bonds are attacked
3. Hydrolysis, where ester linkages are attacked
4. Radiation
5. Thermal degradation involving depolymerization and possibly repolymerization
6. Dehydration (rather uncommon)
7. Any combination of the above

Results of such attacks will appear in the form of softening, charring, crazing, delamination, discoloration, dissolving, or swelling.

The corrosion of polymer matrix composites is also affected by two other factors: the nature of the laminate and, in the case of the thermoset resins, the cure. Improper or insufficient cure time will adversely affect the corrosion resistance, whereas proper cure time and procedures will generally improve the corrosion resistance.

All polymers are compounded. The final product is produced to certain specific properties for a specific application. When the corrosion resistance of a polymer is discussed, the data referred to are that of the pure polymer. In many instances, other ingredients are blended with the polymer to enhance certain properties, which in many cases reduce the ability of the polymer to resist attack of some media. Therefore it is essential to know the makeup of any polymer prior to its use.

5.1 Radiation

Polymeric materials in outdoor applications are exposed to weather extremes that can be extremely deleterious to the material, the most harmful of which is exposure to ultraviolet (UV) radiation, which can cause embrittlement, fading, surface cracking, and chalking. Most plastics, after being exposed to direct sunlight for a period of years, exhibit reduced impact resistance, lower overall mechanical performance, and a change in appearance.

The electromagnetic energy from sunlight is normally divided into UV light, visible light, and infrared energy. Infrared energy consists of wavelengths longer than the visible red wavelengths, and starts above 760 nm. Visible light is defined as radiation between 400 and 760 nm. UV light consists of radiation below 400 nm. The UV portion of the spectrum is further subdivided into UV-A, UB-B, and UV-C. The effects of the various wavelength regions are shown below:

Ultraviolet Wavelength Regions

Region	Wavelength (nm)	Characteristics
UV-A	400–315	Causes polymer damage
UV-B	315–280	Includes the shortest wavelengths at the Earth's surface Causes severe polymer damage Absorbed by window glass
UV-C	280–100	Filtered by the Earth's atmosphere Found only in outer space

Because UV is easily filtered by air masses, cloud cover, pollution, and other factors, the amount and spectrum of natural UV exposure is extremely variable. Because the sun is lower in the sky during the winter months, it is filtered through a greater air mass. This creates two important differences between summer and winter sunlight: changes in the intensity of the light and in the spectrum. During the winter months, much of the damaging shortwavelength UV light is filtered out. For example, the intensity of UV at 320 nm changes about 8 to 1 from summer to winter. In addition, the short-wavelength solar cut-off shifts from about 295 nm in summer to about 310 nm in winter. As a result, materials sensitive to UV below 320 nm would degrade only slightly, if at all, during the winter months.

Photochemical degradation is caused by photons of light breaking chemical bonds. For each type of chemical bond there is a critical threshold wavelength of light with enough energy to cause a reaction. Light of any wavelength shorter than the threshold can break the bond, but longer wavelengths of light cannot break it, regardless of their intensity (brightness). Therefore, the short-wavelength cutoff of a light source is of critical importance. If a particular polymer is sensitive only to UV light below 295 nm (the solar cutoff point), it will never experience photochemical degradation outdoors.

The ability to withstand weathering depends on the polymer type and which grades of a particular resin. Many resin grades are available with UV-absorbing additives to improve weatherability. However, the higher-molecular-weight grades of a resin generally exhibit better weatherability than lower-molecular-weight grades with comparable additives. In addition, some colors tend to weather better than others. The resistance to UV degradation of selected polymers is shown below:

Polymer	UV Degradation	Polymer	UV Degradation	Polymer	UV Degradation
ABS	RS	PEEK	RS	UHMWPE	RS
CPVC	R	PEI	R	Epoxy	R
ECTFE	R	PES	RS	Polyesters:	
ETFE	R	PFA	R	Bis A–fum	RS
FEP	R	PI	R	Halogenated	RS
HDPE	RS	PP	RS	Bis A–Bis A	RS
PA	R	PPS	R	Isophthalic	RS
PC	RS	PSF	R	Teraphthalic	RS
PCTFE	R	PTFE	R	Vinyl ester	R
PVDC	R	PVC	R	Furan	R
				Silicone	R

Note: R = resistant, RS = resistant if stabilized with UV protector.

5.2 Permeation

All materials are somewhat permeable to chemical molecules, but plastic materials tend to be an order of magnitude greater in their permeability than metals. Gases, liquids, or vapors will permeate polymers.

Permeation is a molecular migration through microvoids either in the polymer (if the polymer is more or less porous) or between polymer molecules. In neither case is there any attack on the polymer. This action is strictly a physical phenomenon. However, permeation can be detrimental when a polymer is used to line piping or equipment. In lined equipment, permeation can result in:

1. Failure of the substrate due to corrosive attack
2. Bond failure and blistering resulting from the accumulation of fluids at the bond when the substrate is less permeable than the liner, or from corrosion/reaction products if the substrate is attacked by the permeant
3. Loss of contents through substrate and liner as a result of the eventual failure of the substrate (in unbonded linings it is important that the space between the liner and the support member be vented to the atmpsphere, not only to allow minute quantities of permeant vapors to escape, but also to prevent expansion of entrapped air from collapsing the liner)

Permeation is a function of two variables, one relating to diffusion between molecular chains and the other to the solubility of the permeant in the polymer. The driving force of diffusion is the partial pressure of gases and the concentration gradient of liquids. Solubility is a function of the affinity of the permeant for the polymer.

All polymers do not have the same rate of permeation; in fact, some polymers are not affected by permeation. The fluoroploymers are particularly affected. Table 5.1 depicts vapor permeation into PTFE, and Table 5.2 shows the vapor permeation into FEP. Table 5.3 provides permeation data for various gases into PFA and Table 5.4 gives the relative gas permeation into fluoropolymers.

TABLE 5.1

Vapor Permeation into PTFE[a]

	Permeation (g/100 in.²/24 h/mil)	
Gases	**73°F/23°C**	**86°F/30°C**
Carbon dioxide		0.66
Helium		0.22
Hydrogen chloride, anh.		<0.01
Nitrogen		0.11
Acetophenone	0.56	
Benzene	0.36	0.80
Carbon tetrachloride	0.06	
Ethyl alcohol	0.13	
Hydrochloric acid, 20%	<0.01	
Piperidine	0.07	
Sodium hydroxide, 50%	5×10^{-5}	
Sulfuric acid, 98%	1.8×10^{-5}	

[a] Based on PTFE having a specific gravity of 2.2.

TABLE 5.2

Vapor Permeation into FEP

	Permeation (g/100 in.^{2}/24 h/mil) at		
	73°F/23°C	**93°F/35 °C**	**122°F/50°C**
Gases:			
Nitrogen	0.18		
Oxygen	0.39		
Vapors:			
Acetic acid		0.42	
Acetone	0.13	0.95	3.29
Acetophenone	0.47		
Benzene	0.15	0.64	
n-Butyl ether	0.08		
Carbon tetrachloride	0.11	0.31	
Decane	0.72		1.03
Ethyl acetate	0.06	0.77	2.9
Ethyl alcohol	0.11	0.69	
Hexane		0.57	
Hydrochloric acid, 20%	<0.01		
Methanol			5.61
Sodium hydroxide	4×10^{-5}		
Sulfuric acid, 98%	8×10^{-6}		
Toluene	0.37		2.93

TABLE 5.3

Permeation of Gases into PFA

Gas	Permeation at 77°F/25°C (cc/mil thickness /100 in.^{2} /24 h/atm)
Carbon dioxide	2260
Nitrogen	291
Oxygen	881

TABLE 5.5

Water Absorption Rates of Polymers

Polymer	Water Absorption 24 h at 73°F/23°C (%)
PVC	0.05
CPVC	0.03
PP (Homo)	0.02
PP (Co)	0.05
EHMWPE	<0.01
ECTFE	<0.01
PVDF	<0.04
PVDC (Saran)	nil
PFA	<0.03
ETFE	0.029
PTFE	<0.01
FEP	<0.01

TABLE 5.6

Absorption of Selected Liquids by FEP[a]

Chemical	Temp. (°F/°C)	Range of Weight Gains (%)
Aniline	365/185	0.3–0.4
Acetophenone	394/201	0.6–0.8
Benzaldehyde	354/179	0.4–0.5
Benzyl alcohol	400/204	0.3–0.4
n-Butylamine	172/78	0.3–0.4
Carbon tetrachloride	172/78	2.3–2.4
Dimethyl sulfide	372/190	0.1–0.2
Nitrobenzene	410/210	0.7–0.9
Perchloroethylene	250/121	2.0–2.3
Sulfuryl chloride	154/68	1.7–2.7
Toluene	230/110	0.7–0.8
Tributyl phosphate	392/200[b]	1.8–2.0

[a] Exposure for 168 h at their boiling points.

[b] Not boiling.

TABLE 5.4

Relative Gas Permeation into Fluoropolymers[a]

Gas	PVDF	PTFE	FEP	PFA
Air	27	2,000	600	1,150
Oxygen	20	1,500	2,900	—
Nitrogen	30	500	1,200	—
Helium	600	35,000	18,000	17,000
Carbon dioxide	100	15,000	4,700	7,000

[a] Permeation through a 100-μm film at 73°F/23°C. Units = cm^3/m^2 deg bar.

There is no relationship between permeation and the passage of materials through cracks and voids, although in both cases migrating chemicals travel through the polymer from one side to the other.

Some control can be exercised over permeation, which is affected by:

1. Temperature and pressure
2. The permeant concentration
3. The thickness of the polymer

Increasing the temperature will increase the permeation rate because the solubility of the permeant in the polymer will increase and, as the temperature rises, polymer chain movement is stimulated, permitting more permeant to diffuse among the chains more easily. The permeation rate of many gases increases linearly with the partial pressure gradient, and the same effect is experienced with the concentration gradient of liquids. If the permeant is highly soluble in the polymer, the permeability increases may not be linear. The thickness will generally decrease permeation by the square of the thickness.

The density of the polymer as well as the thickness will have an effect on the permeation rate. The greater the density of the polymer, the fewer voids through which permeation can take place. A comparision of the density of sheets produced from different polymers does not provide any indication of the relative permeation rates. However, a comparision of the density of sheets produced from the same polymer will provide an indication of the relative permeation rates. The denser the sheet, the lower the permeation rate.

The thickness of a lining affects the permeation rate. For general corrosion resistance, thicknesses of 0.010 to 0.020 inches are usually satisfactory, depending on the combination of the lining material and the specific corrodent. When mechanical factors such as thinning to cold flow, mechanical abuse, and permeation rates are a consideration, thicker linings may be required.

Increasing the lining thickness will normally decrease permeation by the square of the thickness. Although this would appear to be the approach to follow to control permeation, there are disadvantages. First, as thickness increases, the thermal stresses on the boundary increase, which can result in bond failure. Temperature changes and large differences in coefficients of thermal expansion are the most common causes of bond failure. Thickness and modulus of elasticity are two of the factors that influence these stresses. Second, as the thickness of a lining increases, installation becomes difficult with a resulting increase in labor costs.

The rate of permeation is also affected by the temperature and temperature gradient in the lining. Lowering these will reduce the rate of permeation. Lined vessels, such as storage tanks, that are used under ambient conditions provide the best service.

Other factors affecting permeation consist of these chemical and physiochemical properties:

1. Ease of condensation of the permeant: chemicals that condense readily will permeate at higher rates.
2. The higher the intermolecular chain forces (e.g., van der Waals hydrogen bonding) of the polymer, the lower the permeation rate.
3. The higher the level of crystallinity in the polymer, the lower the permeation rate.
4. The greater the degree of crosslinking within the polymer, the lower the permeation rate.
5. Chemical similarity between the polymer and the permeant: when the polymer and the permeant have similar functional groups, the permeation rate will increase.
6. The smaller the molecule of the permeant, the greater the permeation rate.

5.3 Absorption

Polymers have the potential to absorb varying amounts of corrodents with which they come into contact, particularly organic liquids. This can result in swelling, cracking, and penetration to the substrate of a lined component. Swelling can cause softening of the polymer, introduce high stresses, and cause failure of the bond on lined components. If the polymer has a high absorption rate, permeation will probably take place. An approximation of the expected permeation and/or absorption of a polymer can be based on the absorption of water. These data are usually available. Table 5.5 provides the water absorption rates for the more common polymers, Table 5.6 gives the absorption rates of various liquids by FEP, and Table 5.7 provides the absorption rates of representative liquids by PFA.

and (2) partially fluorinated polymers such as ETFE, PVDF, and ECTFE, called fluoropolymers. The polymeric characteristics within each group are similar but there are important differences between the groups.

5.5 Thermoset Polymers

Once formed, thermoset polymers, unlike the thermoplasts, cannot be heated to change their shape. Consequently, they cannot be recycled. These resins are initially liquid at room temperature and then by adding a catalyst or accelerator, they are changed into a rigid product that sets or cures into its final shape. The thermoset resins are high-molecular-weight polymers that are reinforced with glass or other suitable material to provide mechanical strength. The most commonly used resins are the vinyl esters, epoxies, polyesters, and furans.

For reinforcing these polymers, fibrous glass in the F and C grades is the most commonly used. Other reinforcing materials used include boron nitride, carbon fiber, ceramic fibers, graphite jute, Kevlar, metallic wire or sheet, monoacrylic fiber, polyester fiber, polypropylene fiber, quartz, sapphire whiskers, and S-grade glass.

The advantages of the thermosets are many; they

1. Are less expensive than the stainless steels
2. Have a wide range of corrosion resistance
3. Are light in weight
4. Do not require painting
5. May be formulated to be fire retardant

Unreinforced, unfilled thermoset polymers can corrode by several mechanisms. The type of corrosion can be divided into two main categories: physical and chemical.

Physical corrosion is the interaction of a thermoset polymer with its environment so that its properties are altered but no chemical reactions take place. The diffusion of a liquid into the polymer is an example. In many cases, physical corrosion is reversible; once the liquid is removed, the original properties are restored.

When a polymer absorbs a liquid or a gas resulting in plasticization or swelling of the thermoset network, physical corrosion has taken place. For a crosslinked thermoset, swelling caused by solvent absorption will be at a maximum when the solvent and polymer solubility parameters are exactly matched.

Chemical corrosion takes place when the bonds in the thermoset are broken by means of a chemical reaction with the polymer's environment. There

TABLE 5.7

Absorption of Liquids by PFA

Liquid[a]	**Temp. (°F/°C)**	**Range of Weight Gains (%)**
Aniline	365/185	0.3–0.4
Acetophenone	394/201	0.6–0.8
Benzaldehyde	354/179	0.4–0.5
Benzyl alcohol	400/204	0.3–0.4
n-Butylamine	172/78	0.3–0.4
Carbon tetrachloride	172/78	2.3–2.4
Dimethyl sulfoxide	372/190	0.1–0.2
Freon 113	117/47	1.2
Isooctane	210/99	0.7–0.8
Nitrobenzene	410/210	0.7–0.9
Perchloroethylene	250/121	2.0–2.3
Sulfuryl chloride	154/68	1.7–2.7
Toluene	230/110	0.7–0.8
Tributyl phosphate[b]	392/200	1.8–2.0
Bromine, anh.	–5/–22	0.5
Chlorine, anh.	248/120	0.5–0.6
Chlorosulfonic acid	302/150	0.7–0.8
Chromic acid, 50%	248/120	0.00–0.01
Ferric chloride	210/100	0.00–0.01
Hydrochloric acid, 37%	248/120	0.00–0.03
Phosphoric acid, conc.	212/100	0.00–0.01
Zinc chloride	212/100	0.00–0.03

[a] Samples were exposed for 168 h at the boiling point of the solvent. Exposure of the acidic reagents was for 168 h.

[b] Not boiling.

The failure due to absorption can best be understood by considering the "steam cycle" test described in ASTM standards for lined pipe. A section of lined pipe is subjected to thermal and pressure fluctuations. This is repeated for 100 cycles. The steam creates a temperature and pressure gradient through the liner, causing an absorption of a small quantity of steam, which condenses to water within the inner wall. Upon pressure release or on introduction of steam, the entrapped water can expand to vapor, causing an original micropore. The repeated pressure and thermal cycling enlarges the pores, ultimately producing visible water-filled blisters within the liner.

In an actual process, the polymer may absorb process fluids, and repeated temperature or pressure cycling can cause blisters. Eventually, a corrodent may find its way to the substrate.

Related effects can occur when process chemicals are absorbed that may later react, decompose, or solidify within the structure of the polymer. Prolonged retention of the chemicals may lead to their decomposition within the polymer. Although it is unusual, it is possible for absorbed monomers to polymerize.

Several steps can be taken to reduce absorption. Thermal insulation of the substrate will reduce the temperature gradient across the vessel, thereby preventing condensation and subsequent expansion of the absorbed fluids. This also reduces the rate and magnitude of temperature changes, keeping blisters to a minimum. The use of operating procedures or devices that limit the ratio of process pressure reductions or temperature increases will provide added protection.

5.4 Thermoplasts (Thermoplastic Polymers)

A general rule as to the differences in the corrosion resistance of the thermoplasts can be derived from the periodic table. In the periodic table, the basic elements of nature are organized by atomic structure as well as by chemical nature. The elements are placed into classes with similar properties, that is, elements and compounds that exhibit similar behavior. These classes are the alkali metals, alkaline earth metals, transition metals, rare earth series, other metals, nonmetals, and noble (inert) gases.

The category known as halogens is of particular importance and interest in the case of thermoplasts. These elements include fluorine, chlorine, bromine, and iodine. They are the most electronegative elements in the periodic table, making them the most likely to attract an electron from another element and become a stable structure. Of all the halogens, fluorine is the most electronegative, permitting it to bond strongly with carbon and hydrogen atoms but not well with itself. The carbon–fluorine bond is predominent in PVDF and is responsible for the important properties of these materials. These are among the strongest known organic compounds. The fluorine acts like a protective shield for other bonds of lesser strength within the main chain of the polymer. The carbon–hydrogen bond, of which plastics such as PE and PP are composed, is considerably weaker. The carbon–chlorine bond, a key bond in PVC, is even weaker.

The arrangement of the elements in the molecule, the symmetry of the structure, and the degree of branching of the polymer chain are as important as the specific elements combined in the molecule. Plastics containing the carbon–hydrogen bonds such as PP and PE, and carbon–chlorine bonds such as PVC, ECTFE, and CTFE, are different in the important property of chemical resistance from fully fluorinated plastics such as PTFE.

The fluoroplastic materials are divided into two groups: (1) fully fluorinated fluorocarbon polymers such as PTFE, FEP, and PFA, called perfluoropolymers;

may be more than one form of chemical corrosion taking place at the same time. Chemical corrosion is usually not reversible.

As a result of chemical corrosion, the polymer itself may be affected in one or more ways. For example, the polymer may be embrittled, softened, charred, crazed, delaminated, discolored, dissolved, blistered, or swollen. All thermosets will be attacked in essentially the same manner. However, certain chemically resistant types suffer negligible attack or exhibit significantly lower rates of attack under a wide range of severely corrosive conditions. This is the result of the unequal molecular structure of the resins, including built-in protection of ester groups.

Curing the resin plays an important part in the chemical resistance of the thermoset. Improper curing will result in a loss of corrosion-resistant properties. Construction of the laminate and the type of reinforcing used also affect the corrosion resistance of the laminate. The degree and nature of the bond between the resin and the reinforcement also play an important role.

The various modes of attack affect the strength of the laminate in different ways, depending on the environment, other service conditions, and the mechanism or combination of mechanisms at work.

Some environments may weaken primary and/or secondary polymer linkages with resulting depolymerization. Other environments may cause swelling or microcracking, while still others may hydrolyze ester groupings or linkages. In certain environments, repolymerization can occur, with a resultant change in structure. Other results may be chain scission and decrease in molecular weight or simple solvent action. Attack or absorption at the interface between the reinforcing material and the resin will result in weakening.

In general, chemical attack on thermoset polymers is a go/no-go situation. With an improper environment, attack on the reinforced polyester will occur in a relatively short time. Experience has indicated that if an installation has operated successfully for 12 months, in all probability it will continue to operate satisfactorily for a substantial period of time.

Thermoset polymers are not capable of handling concentrated sulfuric acid (93%) and concentrated nitric acid. Pyrolysis or charring of the resin quickly occurs, so that within a few hours the laminate is destroyed. Polyesters and vinyls can handle 70% sulfuric acid for long periods of time.

The attack of aqueous solutions on reinforced thermosets occurs through hydrolysis, with water degrading bonds in the backbone of the resin molecules. The ester linkage is the most susceptible.

The attack by solvents is of a different nature. The solvent penetrates the resin matrix of the polymer through spaces between the polymer chains. Penetration between the polymer chains causes the laminate surface to swell, soften, and crack.

Organic compounds with carbon–carbon unsaturated double bonds, such as carbon disulfide, are powerful swelling solvents and show greater swelling action than their saturated counterparts. Smaller solvent molecules can penetrate a polymer matrix more effectively. The degree of similarity between solvent and resin is important. Slightly polar resins, such as polyesters and vinyl esters, are attacked by mildly polar solvents.

Generally, saturated long-chain organic molecules, such as the straight-chain hydrocarbons, are handled well by the polyesters.

Orthophthalic, isophthalic, bisphenol, and chlorinated or brominated polyesters exhibit poor resistance to such solvents as acetone, carbon disulfide, toluene, trichloroethylene, trichloroethane, and methyl ethyl ketone. The vinyl esters show improved solvent resistance. Heat-cured epoxies exhibit better solvent resistance. However, the furan resins offer the best all-around solvent resistance.

Stress corrosion is another factor to consider. The failure rate of glass-reinforced composites can be significient. This is particularly true of composites exposed to the combination of acid and stress.

Under stress, an initial fiber fracture occurs, which is a tensile type of failure. If the resin matrix surrounding the failed fiber fractures, the acid is allowed to attack the next available fiber, which subsequently fractures. The process continues until total failure occurs.

5.6 Environmental Cracking

Stress cracks develop when a tough polymer is stressed for an extended period of time under loads that are small relative to the polymer's yield point. Cracking will occur with little elongation of the material. The higher the molecular weight of the polymer, the less likelihood of environmental stress cracking, other things being equal. Molecular weight is a function of the length of individual chains that make up the polymer. Longer chain polymers tend to crystallize less than polymers of lower molecular weight or shorter chains, and they also have a greater load-bearing capacity.

Crystallinity is an important factor affecting stress corrosion cracking. The less crystallization that takes place, the less likelihood of stress cracking. Unfortunately, the lower the crystallinity, the greater the likelihood of permeation.

Resistance to stress cracking can be reduced by the absorption of substances that chemically resemble the polymer and will plasticize it. In addition, the mechanical strength will also be reduced. Halogenated chemicals, particularly those consisting of small molecules containing fluorine or chlorine, are especially likely to be similar to the fluoropolymers and should be tested for their effect.

The presence of contaminents in the fluid may act as an accelerator. For example, polypropylene can safely handle sulfuric or hydrochloric acids, but iron or copper contamination in concentrated sulfuric or hydrochloric acid can result in the stress cracking of polypropylene.