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Acid Resistant Organic Coatings for the Chemical Industry - A Review

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Abstract Industries that work with acidic chemicals in their processes need to make choices on how to properly contain the substances and avoid rapid corrosion of equipment. Certain organic coatings and linings can be used in such environments, either to protect vulnerable construction materials, or, in combination with fiber reinforcement, to replace them. However, degradation mechanisms of organic coatings in acid service are not thoroughly understood and relevant quantitative investigations are scarce. This review describes the uses and limitations of acid-resistant coatings in the chemical industry, with a comparison to alternative resistant materials based on metals or ceramics. In addition, coating degradation phenomena, caused by acid exposure, are mapped to the extent possible, and analysis methods for detecting coating degradation type and severity are listed and discussed. It is concluded that more knowledge on chemical and physical degradation mechanisms is required, and that improvements in resistance to elevated temperatures and abrasion would decrease the risk of use and increase the potential application areas of organic coatings exposed to acidic environments in the chemical industry.

Keywords: Protective coating, Acid resistance, Chemical industry, Degradation mechanism, Coating analysis.

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Introduction

Acidic solutions can be a challenge to process because of their ability to corrode common construction steels and concretes [1, 2]. Incorrect handling can result in incidents such as shown in Figure 1, where the acid-resistance of materials surrounding an acid bath was not taken into consideration, or as seen in Figure 2, where sulfuric acid produced by bacteria corroded a sludge tank, producing cavities in the tank [3, 4]. Many processes in the chemical industry consume or produce acidic substances, and often acid resistant alloys or ceramics are used as containment materials without considering the application of organic coatings as an option. This could be due to difficulties with the complex mechanisms of acid-resistance and a general lack of knowledge concerning the limitations and possibilities of organic coatings. This is unfortunate because cost savings can be achieved by coating inexpensive, but corrosion susceptible, construction material with a 0.8 to 3.8 mm thick acid resistant coating, or using fiberglass reinforced plastic (FRP) as the construction material, rather than making all the parts of costly alloy or ceramic material [5, 6]. The value of considering organic protection is evident by looking at some estimated expenses from 2010, where average cost of FRP material and installation is 1000 US\$/m^2, compared to 3000 US\$/m^2 for alloy material with similar acid-resistance [7].

Among the subcategories of organic materials, the chemically cured organic thermosets are of particular interest for harsh chemical exposure. Partly because the coating can be applied in liquid form without heating or excessive use of volatile organic solvents (VOC), but also because the hardened coating consists of a highly cross-linked network yielding good temperature resistance and excellent barrier properties. This makes thermosets the resin of choice when it comes to handling aggressive chemicals in industry [8, 9], and thus is the main focus of this review. Acid resistant organic materials is a topic that is only sporadically covered scientifically, and in

Figure 1: Damage on concrete flooring in a chemical etching plant. The floor was exposed to acid drips and spills. Reproduced from [3] with permission from NACE International, Houston, TX. All rights reserved. ©NACE International 2016.
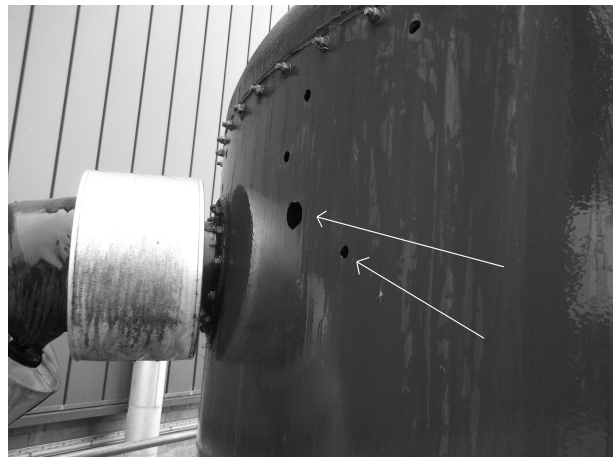
Figure 2: Damage on a sludge buffer tank for sewage treatment. The inside of the tank was exposed to sulfuric acid produced by bacteria. Reproduced from [4] with permission from Belzona International and NACE International, Houston, TX. All rights reserved. ©NACE International 2016.

contrast to previous thorough work in the field [10–12], the present paper aims at providing more background information. This includes an overview of current coating solutions, the limitations of acid-resistant organic coatings, the chemical compositions and uses of thermoplastics, thermosets, rubbers and FRP, and comparisons to ceramic and metal alloy alternatives. This is followed by an overview of coating degradation in acid service by molecular diffusion and chemical reactions, with specific focus on polyurethanes, epoxies, and vinyl esters. Finally, the methods used for testing and analyzing coating functionality are summarized.

Organic coatings in acidic environments

Acid-resistant organic coatings and linings are surface treatments capable of enhancing the acid-resistance of an underlying ceramic, metallic or organic substrate. These coating technologies can be used in chemical industries, or any other industrial process that involves the consumption, production or transport of acidic chemicals, to increase the lifetime and performance of vulnerable materials.

Organic coating materials can be self-supporting fiber-reinforced structures, or non-reinforced coatings. Fiber reinforced coatings have found use in wet flue gas desulfurization plants (FGD) [13], while non-reinforced coatings have, among others, been used to line rail-car tanks for acid transport, protect sewage pipes against microbial acids, and preserve stirred acid leach reactors in hydro-metallurgical processes [9, 14, 15]. Table 1 is a list of industries where acid resistant organic coatings are used or have potential use, as protective coatings. The use of organic coatings is not limited to acid protection, also caustic environments and organic chemicals can be handled [10].

Like any other material, organic coatings have limitations. Industrial process variables such as temperature, pressure, wear, acid type, and presence of additional chemicals, can limit the usability of an organic coating. This section will give a brief history of organic coatings in acidic environments and an overview of the general process limitation of organic coatings, usable for acid protection.

Table 1: Selected industries where acid resistant organic coatings are used or have potential use, as protective coatings.

Industry	Operation (temperature)	Acid types	Erosive particles present
Wet flue gas desulfurization [13, 16]	Absorber (45-55 °C) and stack (70-85 °C)	Sulfuric and hydrochloric acid	Limestone slurry
Pulp and paper production [17]	Acidic magnesium bisulfite pulping (125-135 °C) and Kraft pulping (20-170 °C)	Sulfuric, formic and acetic acid	None
Chemical transport [18]	Rail car tanks and piping (ambient to <90 °C)	Can vary greatly, both organic and inorganic acids	None
Metal refining [7, 19]	Acid leaching (25-80 °C) and electrowinning (65 °C)	Sulfuric and nitric acid	Slurry concentrates
Sewage treatment [14, 20]	Concrete piping (Ambient)	Sulfuric acid (Bacterial)	None
Metal surface treatment [21]	Pickling of low and high alloy stainless steels, aluminum, copper and zinc alloys (25-80 °C)	Sulfuric, hydrochloric, nitric, hydrofluoric, citric, tartaric and chromic acid	None
Inorganic acid production [10]	Depends on the acid in question	All inorganic acids	Not available
Fertilizer production [22, 23]	Production of ammonium nitrate, ammonium phosphate and ammonium sulfate (20-105 °C)	Sulfuric, nitric and phosphoric acid	None

History

Thermoplastics such as polyethylene (PE), discovered in 1933, and polytetrafluoroethylene (PTFE or Teflon^{TM}), discovered in 1938, are well known for their acid-resistance, particularly towards hydrochloric acid (HCl), which corrodes many steel alloys. This resistance is shared by many thermoset and thermoplastic materials. Since their invention, such plastics have been used as acid-resistant materials in equipment components, containers and tanks, and barrier coatings. Specially, the chemically hardened thermoset plastics, with their high cross-linking density have found uses in acidic environments. The most important ones are epoxy vinyl esters, phenolic epoxies, and polyurethane.

Polyurethane was invented in 1937 [24] and today is used in mattresses, tires, shoe soles, and many other applications. As protective coating in acidic environments, polyurethane is recommended by some manufactures in power plants, as well as the pulp and paper industry, though always in combination with epoxy based coatings [25].

Phenolic epoxies, such as bisphenol A epoxy, have been used commercially as protective coatings since 1947 [26, 27], and novolac epoxies are known as the resin within this category with the highest chemical resistance. Experience with use of epoxies in acidic environments is greater than for polyurethanes and it is more widely recommended for power plants and pulp and paper production [25].

Epoxy vinyl esters were discovered in the late 1960s, and succeeded the more brittle bisphenol A fumerate polyester as the resin of choice in aggressive chemical environments [28]. The vinyl ester found use as acid-resistant construction material as well as protective coatings in the chemical industry, and has reported lifetimes between 15 to 25 years in such environments [13]. Today all of the resins mentioned are used in industrial acidic environments, as long as the process

parameters fall within the coating limitations.

Process limitations of acid-resistant coatings

Temperature

A disadvantage of organic coatings is that they are only usable within a narrow temperature range. The glass transition temperature (T_g) of a hardened coating is a good indicator of how high temperatures it can handle. The higher the T_g, the higher process temperatures it can resist, but operating above T_g can cause rapid deterioration [29]. It should be noted that temperature resistance is reduced if a coating is immersed in a liquid [13]. This is due to plasticization effects, which is increased segmental mobility of the resin network also seen as increased material flexibility [30], that lowers the coating's effective T_g [31]. A vinyl ester resin can be usable up to 100-120 °C in fluids and 175-200 °C for gas service [7, 13], while application temperatures can reach around 260 °C at immersed conditions for PTFE [32]. The majority of organic coatings should not be used in environments where temperatures exceed approximately 150 °C [9].

Pressure

Effects of pressure on organic coatings in acidic environments has not been investigated in greater detail. However, decompression has been reported to damage coatings, by causing rapid expansion of gases or liquids dissolved in the coating, resulting in e.g. blister formation [29, 33]. An example of organic coatings in high pressure operations includes flouropolymer coatings, such as PTFE, that have found uses in autoclaves operating between 15 and 35 MPa [34].

Erosion and abrasion

Erosive wear occurs when particles flow against a coating surface, chipping or scratching away coating material. It is a subcategory of abrasive wear, which is defined as wear due to hard particles or hard protuberances forced against and moving along a solid surface [35]. Issues with erosion can occur whenever industrial operations process solid substances, it is a complex and diverse topic with entire journals based solely on the subject and will not be covered in depth in this article [36, 37].

Organic coatings can be used in processes with a low level of erosion or mild abrasion. This could be floor coatings for secondary containment where the coating is exposed to the abrasive sliding wear of pedestrians, or internal pipe coatings for transport of slurry material.

A particular property of some organic coatings, is the ability to deform if a force is applied, and reclaim the original shape when relaxed. This elastic property provides a high resistance towards impacts and related erosion, but organic coatings can also be hard and tough, making them useful in many types of abrasive conditions [38, 39].

Limitations in erosive environments depend on the severity of the erosive forces, which can be difficult to classify. Erosion has an overall dependency on both the erosive and the contact material, where factors, such as particle speed, shape, mass, hardness, impact angle and collision frequency are important [40–43]. As an example, a gas containing 0.2 wt% particles, moving at 76 m/s, is able to reduce the film thickness of a fiber reinforced coating by 3.18 mm a year in high angle impact zones, while slurries moving parallel to similar coatings at 1.8 to 3.7 m/s cause no issues in 10 years service [43]. Coating limitations are not straightforward when it comes to erosion, and proper testing methods have to be applied to asses potential uses.

Acids and pH

Acids can occur in industrial processes as reactants, solvents, pH regulators, and as desired or undesired products. The more common acids include sulfuric (H_2SO_4), hydrochloric and nitric acid (HNO_3) [5]. Industrial processes using acidic chemicals can vary from the use of weak to strong acids and low to high concentrations, in the pH range -1.25 to 7. It is possible to formulate coatings capable of resisting these low pH values, but pH is not the only important factor relevant for acid-resistance [15].

In general, organic coatings can have excellent resistance towards acids, but the type of acid(s) being processed is important to consider. An acids oxidative or reducing properties as well as organic or inorganic nature are important factors. A list of common organic, inorganic and oxidizing acids is given in Table 2. Very oxidative acids can be troublesome with their ability to cleave important chemical bonds in coating resins and causing irreversible damage. While organic acids can diffuse rapidly through an organic coating, due to chemical similarity with the resin [44], therefore a coating resistant to a reducing hydrochloric acid, might have poor performance in the oxidizing nitric or organic formic (HCOOH) acid.

Table 2: A selection of common inorganic acids, as well as the more troublesome organic and oxidizing inorganic acids. pKa values at 25 °C in aqueous solution are provided in parenthesis.

Organic	Inorganic	Oxidizing Inorganic
Citric (3.1)	Hydrochloric (-7.0)	Perchloric (-10)
Malic (3.4)	Phosphoric (2.1)	Hydrobromic (-9.0)
Formic (3.8)	Hydrofluoric (3.5)	Nitric (-2.0)
Benzoic (4.2)	Boric (9.1)	Sulfuric (-2.0)
Acetic (4.8)		Chromic (0.5)
Propionic (4.9)		Arsenic (2.19)

Acid concentration can also alter the properties of an acid. For example, sulfuric acid can chemically dehydrate vinyl ester, and char the surface, at concentrations above 76 wt%, while chromic acid is only non-oxidizing in very dilute concentrations [15]. The interaction of an acid with any given coating depends on the chemistry of both components. The limitations of organic coatings, with regard to acids, has more to do with the acids ability to react with, and rapidly diffuse through, the coating than it has to do with pH values [11].

In summary, the use of organic coatings in industrial processes is limited to low temperatures (< 260 °C, but for most coatings < 150 °C) and mild abrasive environments, but they can have exceptional resistance to acidic chemicals. Pressure limitation is not an area of much study. If an industrial process operates within these limits, organic coatings are an option, either to protect a vulnerable substrate, or to use with fiber re-enforcement as construction material.

Acid resistant materials

The need for protective measures against acid attack is a requirement for any industrial process using or producing such chemicals. Not only to create a safe environment, but also to allow a continuous production, without significant operational downtime due to damaged equipment. Choosing the correct material or surface treatment for unit operations in an aggressive environment is therefore vital.

The protective materials can be divided into two categories, *the inorganic*, using ceramics or metallic based protective measures, and *the organic*, including fiber reinforced plastic (FRP) and organic coatings. Though organic thermoset coatings are the main focus in this review, it is important to know of the alternatives. This section will give an overview of the chemical composition and use of metallic, ceramic and organic acid resistant systems.

Inorganic materials

Ceramic and metallic materials have also been developed to resist a wide range of acids. The advantages of utilizing these materials to prevent acid damage is a good abrasion and temperature resistance, properties that organic coatings cannot provide with the same reliability. Inorganic materials can also be applied as thin protective coatings or undergo surface treatment to enhance acid-resistance. These techniques include electroplating, physical or chemical vapor deposition, thermal spraying, and thermochemical diffusion processes, but are too extensive to be covered in this review [37, 45].

Metals are often prone to damage when in contact with acidic material, but it is possible to make alloys capable of resisting a large range of acids with varying concentrations. Small equipment components, as well as large constructions, such as pipes and vessels, can be made of steel alloys

[46]. These resistant alloys have the advantage of being very wear resistant, both to sliding and impact abrasion, though material and manufacture can be costly as the alloys are typically very expensive compared to low grade steels with high iron content, see Table 3 [47]. Metals are not inert in an acidic environment, but corrosion rates are often halted by the formation of passivating films on the metal surface. A list of acid resilient stainless steels and their compositions is also shown in Table 3, while Table 4 gives corrosion rates of these alloys immersed in sulfuric and hydrochloric acid solutions [48].

Metal alloys can be used at high temperatures and are resistant to erosion. However, with added contact to acidic substances, increasing temperatures will increase corrosion rates. Wear can also enhance corrosion rates, by inducing corrosive wear, a continuous removal of the passivating film [37]. Care must be taken if metals are to be used in acidic environments.

Table 3: An overview of metal costs in August 2015 as well as alloys and their general composition in wt.% [48–50].

Element	Fe	C	Cr	Ni	Mo	N	Minor components
(Metal cost [€/kg])	(0.049)	-	(1.87)	(9.13)	(9.41)	-	-
Austenitic (S31600)	65	0.03	17	12.0	2.5	-	Si, Mn, P, S
Superaustenitic (N08020)	42.0	0.02	19.5	33.0	2.2	-	Cu
Duplex (S32550)	61.1	0.04	26.0	5.0	3.0	0.25	Si, Cu, Ti, Mn, P, S
Superferritic (S44660)	68.0	0.02	26.0	2.5	3.0	0.03	Ti, Cb
Nickel-Based (N06022)	4	0.01	21.0	57.5	13.5	-	Si, Cu, Mn, Al, S, P, W

Table 4: An overview of some relevant alloys and their corrosion rates in sulfuric and hydrochloric acids in mm per year. Concentration and temperature are provided in parenthesis [48].

Alloy family	Sulfuric acid	Hydrochloric acid
Austenitic (S31600)	>1.27 mm year^{-1} (10wt%, 15 °C)	>1.27 mm year^{-1} (20wt%, 15 °C)
Superaustenitic (N08020)	>0.51 mm year^{-1} (10wt%, boiling)	>1.27 mm year^{-1} (20wt%, 15 °C)
Duplex (S32550)	1.02 mm year^{-1} (10wt%, boiling)	0.003 mm year^{-1} (1wt%, boiling)
Superferritic (S44660)	>0.51 mm year^{-1} (10wt%, boiling)	-
Nickel-Based (N06022)	0.28 mm year^{-1} (10wt%, boiling)	0.06 mm year^{-1} (1wt%, boiling)

Ceramic bricks and coatings have found their uses as protective linings, also called refractories, in storage tanks, reaction vessels, fume ducts, and many unit operations in the chemical industry. They are often used for high acid concentrations and high temperature applications [51, 52]. Ceramics are prime candidates for anti-corrosive linings, the materials tend to be crystalline in nature and have a high melting point and chemical resistance, combined with a high resistance towards erosive wear [53, 54]. Ceramic protection also utilizes organic material, such as furan or vinyl esters for mortar adhesives, or organic membranes behind the lining to prevent leaks caused by cracks in the brittle material, an example is shown in Figure 3. Table 5 gives the composition of some acid resistant ceramic materials used in industry [55].

Table 5: An overview of acid resistant ceramics and their compositions in wt% [55, 56].

Ceramic type	SiO_2	Al_2O_3	Fe_2O_3	K_2O	TiO_2	Carbon	SiC	Other
Red Shale	64.0	20.6	6.2	4.2	1.6	NA	NA	MgO, Na_2O, CaO
Fire Clay	64.0	27.3	2.0	2.6	1.5	NA	NA	MgO, Na_2O, CaO
SiC	9.6	0.8	0.4	0.0	0.1	NA	87.9	MgO, Na_2O, CaO
Silica	98.4	0.8	0.4	0.0	0.1	NA	NA	MgO, Na_2O, CaO
Carbon	0.3	0.1	0.0	0.0	0.0	96.3	NA	MgO, Na_2O, CaO, S
High Alumina	8.5	85.6	0.3	0.1	0.1	NA	NA	MgO, Na_2O, CaO
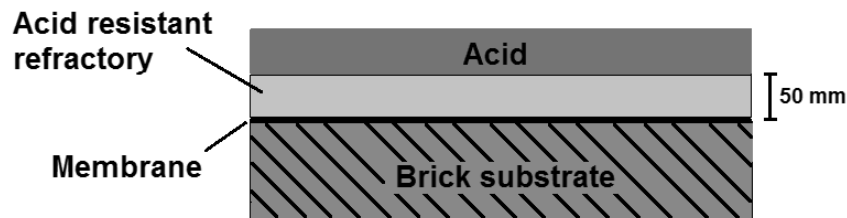
Figure 3: Build-up of a protective ceramic coating usable at high temperatures and in concentrated acid exposure from the refractory side. Typically around 50 mm thick coating. Figure modified after [52].

Ceramic linings are capable of resisting very high temperatures, abrasive wear and a wide range of acidic substances, while having lifetimes greater than 12 years [52]. So why would a metal alloy based protective system be preferable? The main reason is the cost. Metallic protective measures are considered higher risk than ceramic systems, they come at a lower total cost of installation. This consideration is important, as we discuss the uses of organic coatings as protective measures. Organic coatings are considered higher risk than the use of metal alloys, but can come at a an even lower cost [7, 46, 57].

Organic coatings

Organic coatings can be categorized into two major groups, thermoplastic and thermoset. In short, thermoplastics are physically cured, while thermosets are chemically cured via cross-linking reactions. The resin network of hardened thermosets or thermoplastics form the protective organic coating [39]. In between these groups are elastomers, or rubbers, which are cross-linked only to a small degree, see Figure 4 for comparison [58]. This section will give a short overview of the various organic resins that can be utilized in acidic environments to protect a vulnerable substrate.

The terms coating and lining are used for organic protective systems, but their meaning often overlap. The term coating is defined by ASTM as: "A liquid, liquefiable, or mastic composition that is converted by evaporation, cross-linking, or cooling to a solid or semisolid protective, decorative, or functional adherent layer after application" [59]. It often suggests a thin, up to 1 mm thick film on a substrate. Coatings are commonly thermosets as they are easily applied in thin layers, while linings are often a reference to thick, greater than 1 mm films, or coating systems reinforced with glass mats or likewise. Thermoplastic material that is attached to a surface via physical means or with the aid of an adhesive layer often goes by the term lining, and so do multi-layered coating systems and protective coatings on inner surfaces. The ASTM definition of lining is: "Coating or layer of sheet material adhered to or in intimate contact with the interior surface of a container used to protect the container against corrosion by its contents and/or to protect the contents of the container from contamination by the container material." [60]. In this paper, the term coating encompasses linings as well.
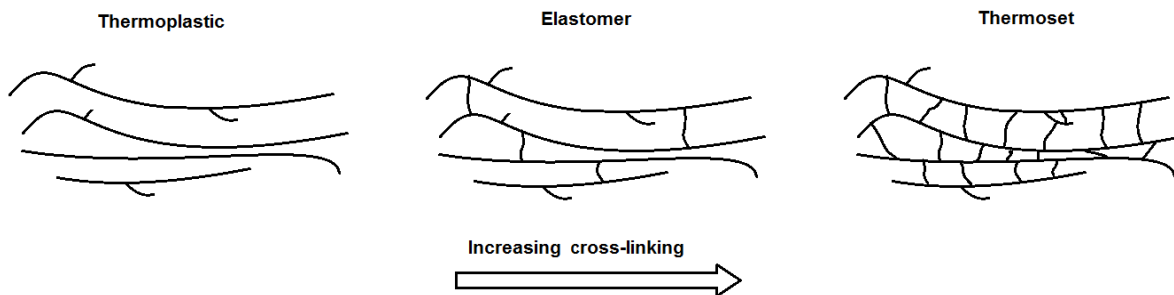
Figure 4: Comparison of polymer chain structure of thermoplastics, elastomers, and thermosets. Cross-linking density increases from left to right. For thermoset coatings, a 3D network is formed. Deduced from [39, 58].

Thermoset coatings

Thermoset coatings can be formulated in many varieties based on composition. From a formulation perspective there are many factors affecting the overall performance of a single coating or a coating system. Typically, thermosets are composed of binder, hardener, pigments/fillers, solvents and additives [39].

- Resins (binders) are polymers or network precursors which can cross-link with a curing agent to form the hardened coating film. The chemical structure of hardened polyurethane, amine and anhydride-cured epoxy, and vinyl ester resins are shown in Figures 5 to 8.

- Solvents are organic molecules added to dissolve the binder and/or alter the liquid coating viscosity to facilitate application.

- Additives are added in small amounts to control specific properties of the coating.

- Pigments and fillers are small, binder and solvent insoluble, particles.

The acid-resistance of a thermoset coating is a function of all the components as well as curing conditions, substrate pre-treatment, and application method. The most relevant thermoset resins

in use for acid-resistance include phenolic epoxy, vinyl ester and polyurethane [25]. The cross-linked structure and some general notes on these resins are given below. Particular attention should be paid to the various chemical bonds in the cured resins, which make up the backbone of the polymer matrix and play and important role in a coating's acid-resistance.

Polyurethanes are cured by reaction of an isocyanate with a polyol, forming a network with urethane linkages, see Figure 5. The polyol contains alchohol end groups and could be a polyester, polyether or polycarbonate. Polyurethanes have excellent impact and abrasion resistance but reduced acid-resistance in comparison to epoxy, and vinyl esters [39]. They are often used in combination with epoxies on secondary exposure (spillage) areas [61].
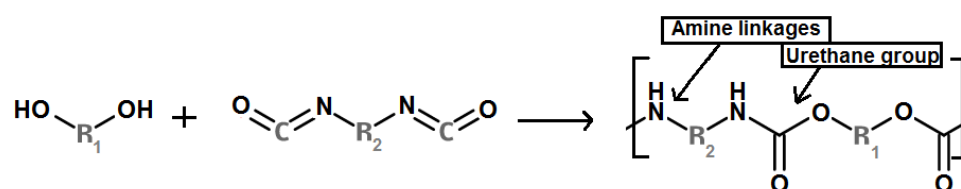
Figure 5: Formation of the repeating unit of a polyurethane coating. Chemical groups and linkages that could be involved in chemical degradation are highlighted [62].

Phenolic epoxies are based on resins containing epoxide (oxirane) groups and are known to be tough, non-brittle coatings. The choice of hardener is important for the acid-resistance of the cured resin. If the right hardener is chosen, epoxies can be used in acid service, but they are not recommended for oxidizing acids [10]. Amine and anhydride-cured epoxies, shown in Figure 6 and 7 respectively, can be used for acid service. Anhydride-cured epoxies are known to be more acid resistant, but due to slow curing and a need to postcure, the more practical amine-cured epoxies are more common as protective coatings [63].
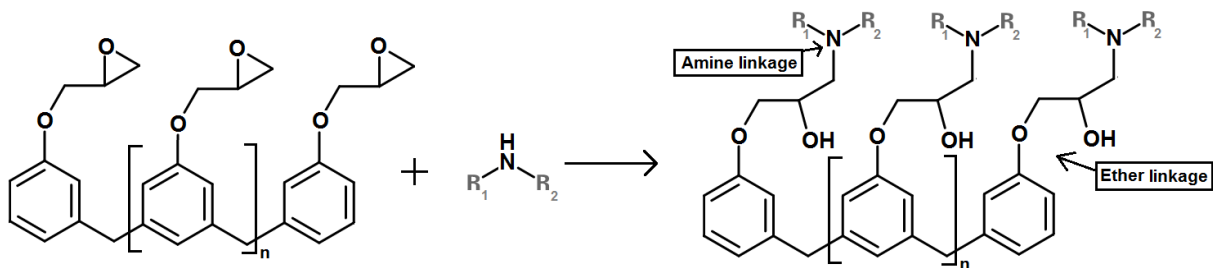
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Figure 6: The chemical curing and composition of amine-cured novolac epoxy. R groups can contain amines capable of cross-binding with more epoxy and n ≈ 0.2. Chemical groups and linkages that could be involved in chemical degradation are highlighted [63].

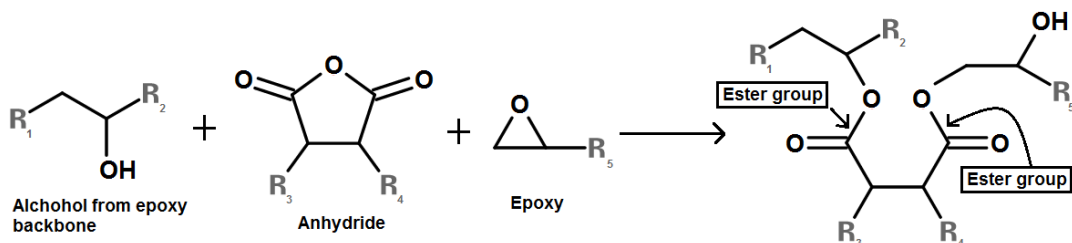**Figure 7:** The chemical curing and composition of an anhydride-cured epoxy. R_3 and R_4 will vary depending on the anhydride type, they can e.g. combine to make a benzene ring for phthalic anhydride. Not shown in this image is the epoxy backbone, which contains ether linkages [63].

Vinyl esters have high resistance towards both oxidizing and non-oxidizing acids [10, 64]. They can form highly cross-linked networks by radical initiated reactions with monomers such as styrene. Figure 8 shows a typical vinyl ester cross-linked with styrene. Vinyl esters have a good overall resistance to chemical exposure, due to ester-stabilizing methyl groups and the many aromatic groups in the resin. This, together with a sufficient degree of flexibility makes, the resin useful in many applications. Furthermore, they have been widely used together with fiber reinforcement to improved mechanical properties [15, 28, 65].
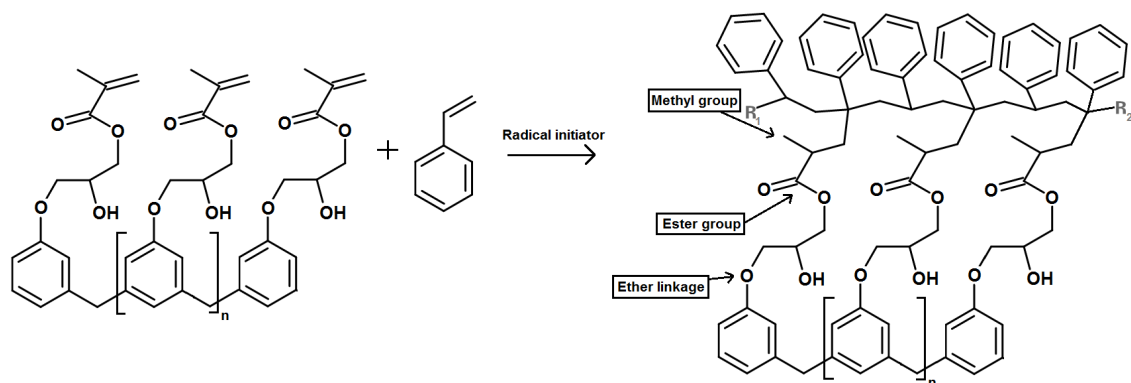
Figure 8: Vinyl ester cross-linked with styrene, using a radical initiator such as a peroxide. The vinyl ester shown is based on novolac epoxy reacted with methacrylic acid. R indicates a continuous chain, linking more components to form the resin network, n $\approx$ 0.2. Chemical groups and linkages that could be involved in chemical degradation are highlighted [63].

Acid resistant coatings based on polyurethane, epoxy or vinyl ester can be found with many small variations, depending on the particular environment they have to resist, leading to numerous brands as shown in Tables 6 and 7. The list is not exhaustive and does not include resin products, which can be supplied from companies like AOC, Ashland, DSM, Interplastic and Reichhold. It should be noted that sufficient caution and protective measures must be taken during the handling processes of these chemicals. Compounds like styrene, but also epoxy and isocyanates, can be harmful upon skin contact ingestion or inhalation. Details of health issues and correct handling can often be found in the safety data sheet of the selected product.

Table 6: Selection of commercial organic coating products with advertised usability in corrosive environments, often categorized under industrial and/or protective coatings. Vinyl esters are typically hardened using styrene and a radical initiator. See the companies' specific product data sheet for further details.

Resin	Company	Product Name	Application areas/environment
Vinyl ester	**Carboline** (carboline.com)	Plasite^{TM}	Highly aggressive environments
		Semstone^{TM}	Aggressive chemicals
	Corrocoat (corrocoat.com)	Corroglass^{TM}	Heavy duty equipment
	Hempel (hempel.com)	Hempaline^{TM}	High temperatures and acidic conditions
	International (international-pc.com)	Ceilcote^{TM}	High-performance corrosion control
	Jotun (jotun.com)	Chemflake^{TM}	Chemical tanks, cooling towers, pipes, water tanks
	Sauereisen (sauereisen.com)	NovolaK Vinyl Ester FibreLine^{TM}	Pulp and paper, superior chemical resistance
	Sherwin-Williams (protective.sherwin-williams.com)	Cor-Cote VEN^{TM}	FGD Systems, Chemical processing, Food and beverage, Metal and mining, Pharmaceutical, Pulp and paper, Water and wastewater, Petrochemical

Table 7: Selection of commercial organic coating products with advertised usability in corrosive environments, often categorized under industrial and/or protective coatings. Epoxies are typically amine-cured. See the companies' specific product data sheet for further details.

Resin	Company	Product Name	Application areas/environment
Epoxy	**Belzona** (belzona.com)	Belzona 5811^{TM}	Excellent resistance to sulfuric and hydrochloric acid
	Carboline	Phenoline^{TM}	Chemically resistant coatings
	Corrocoat	Corrocoat^{TM}	Resistant to high concentrations of sulfuric acid
	Hempel	Hempaline^{TM}	Tank lining with excellent chemical resistance
	International	Enviroline^{TM}	Chemical attack, corrosion and leaks
	PPG (ppgpmc.com)	Phenguard^{TM}	Aggressive cargo such as methanol, ethylene dichloride and fatty acids
	Sauereisen	FibreCrete^{TM}	For processing and storage. Resists strong sulfuric acids
Polyurethane	**International**	Polibrid^{TM}	Corrosion protection for immersion, chemical, abrasion and impact resistant applications
	Sauereisen	ConoFlex Urethane^{TM}	Both primary and secondary containment. Highly impermeable, chemically resistant towards a wide range of acids

Thermoplastics

As protective coatings, thermoplastics can be applied as solid plastic sheets with an adhesive layer in between the substrate and plastic, or adhered via mechanical means. In liquid form, thermoplastics can be applied as a melt or dissolved in a solvent, where-after the plastic cools or solvent evaporates, resulting in a hardened coating [39]. When not protecting a substrate, thermoplastics are used as construction material such as containers or components for acid service. Among many thermoplastics, capable of acid service, the cheap polypropylene (PP) or polyethylene (PE) and the more expensive fluoropolymers are common examples [66]. Repeating polymer units of these thermoplastics are shown in Figure 9.

Poly propylene

Poly ethylene

Poly tetrafluoroethylene

Poly ethylene tetraflouroethylene
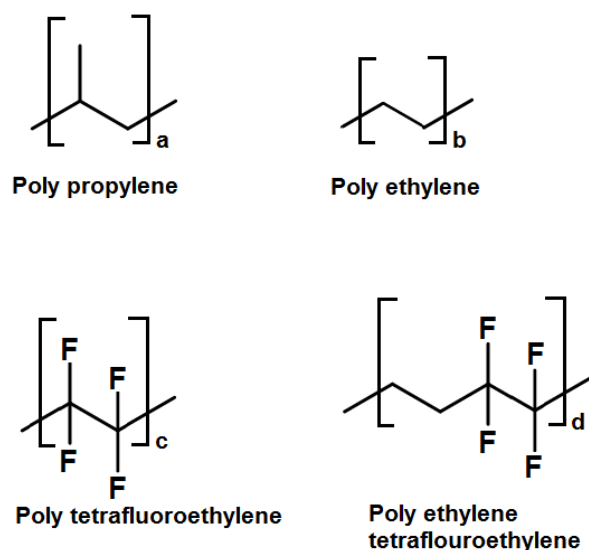
Figure 9: Repeating units of some thermoplastic polymers capable of acid immersion service. The common number of the repeating units are: a) 100 to 2400, b) 650 to 1580, c) 10^4 to 10^6, d) 3130 to 6140 [67–69].

PP is made of a pure hydrocarbon backbone and has a high resistance towards inorganic as well

as organic acids. It is also one of the cheapest thermoplastics available. It is, however, noted to oxidize slowly in highly oxidizing acids, such as nitric acid [66].

Fluoropolymers such as PTFE and polyethylene tetraflouroethylene (ETFE), have higher resistance towards acids and various solvents than any of the other thermoplastics mentioned. Most of these resins are unaffected by common organic solvents as well as hot concentrated oxidizing and non-oxidizing acids [32]. Flouropolymers are, however, challenging and costly to apply to surfaces, because the polymer resin often has to be applied as multiple thin (40 μm) films and baked above it's melting point, 327 °C for PTFE [69, 70].

Elastomers

Elastomers, also known as rubbers, are special kinds of plastics with unique physical properties. A rubber is able to deform when force is applied and reclaim the original shape when relaxed. This property gives rubbers a high resistance towards impacts, such as a hammer strike or particle impingement [37].

To form a rubber, a pre-polymer has to be partially cross-linked through curing or vulcanization reactions. The network formed is closely packed, and can have around 1 to 2 cross-links per 200 repeating polymer units, much less than for typical thermosets. The elastic properties of the rubber is a result of this low cross-linking density, while the close packing yields low permeability [71].

A rubber that has found use as protective lining in acid service is halogenated butyl rubber (HIIR). The rubber material is made by reacting isobutylene and isoprene into a high density polymer, followed by a halogenation of the polymer, shown as the reactant in Figure 10. It is then cured to produce the final product. HIIR such as chlorobutyl and bromobutyl rubber have good resistance towards inorganic acids and so does polychloroprene. For a more comprehensive

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view on rubbers for corrosion protection, see the book by Chandrasekaran [71] and the chapter by Webb et al. [72].
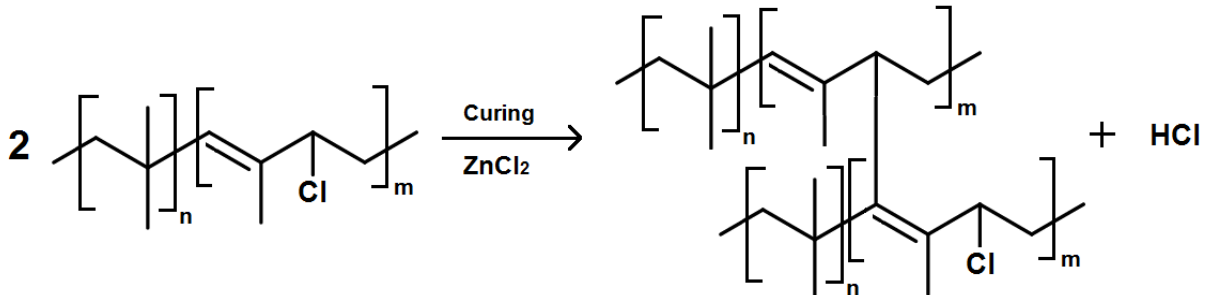
Figure 10: Curing of chlorobutyl rubber using zinc chloride catalyst [73]. The ratio n/m is around 200 to produce a low cross-linking density [58]. Typical rubber coating thickness is 6 mm.

FRP thermoset systems

Glass fiber reinforcement for thermoset resins can be either flake filled resin, fiber mat or woven fabric reinforced as shown in Figure 11. Glass fiber reinforcement of thermosets functions similar to steel reinforcement of concrete, by improving a number of mechanical properties of the material such as higher abrasion resistance, enhanced mechanical strength, and better elongation properties. Additionally, flake filled thermosets increase permeation resistance, while fiber mat and woven fabric reinforcement lower the thermal expansion coefficient of the coating close to that of steel, preventing stress cracking and damage from thermal shock [5, 9].

It is possible to use FRP as construction material to prepare pipes and vessels from a desired polymeric material instead of coating existing equipment [57], Figure 12 shows FRP cross-sections, and Figure 13 shows an example of a tank made out of FRP.

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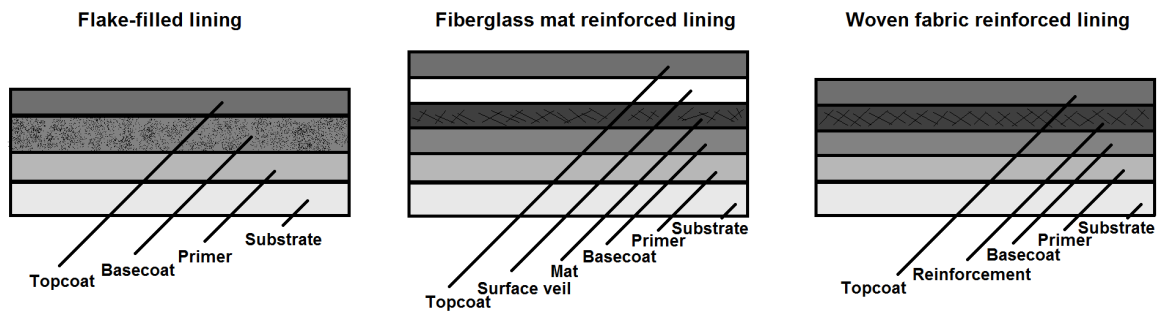
Figure 11: Flake filled, fiber mat and woven FRP linings on a substrate, typical lining thickness is 2, 4 and 3 mm from left to right [5].
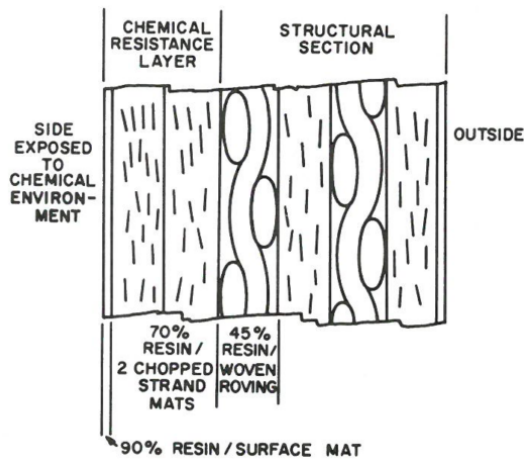
Figure 12: Cross-sectional build of a FRP structure without substrate support. The resin is present in the woven glass mat, and in greater quantities, combined with glass flakes, in layers closer to the exposed side to provide a chemical barrier. Reproduced from [57] with permission from NACE International, Houston, TX. All rights reserved. ©NACE International 2016.

Figure 13: Example of a FRP tank made of Derakane vinyl ester [74]. Courtesy of Ashland Inc. and Owens Corning

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Coating degradation in acid service

Acid and chemical resistance of organic coatings depend on two categories of degradation, physical and chemical [65, 75, 76]. Physical degradation entails the unavoidable diffusion of chemicals into and through a protective coating. Reactions of coating constituents with the environment are categorized as chemical degradation.

Physical and chemical degradation occur either separately or simultaneously, with a physical diffusion followed by chemical interactions. This section includes the current theories for both degradation mechanisms, with a more detailed look at important thermoset resins.

Physical degradation through diffusion

The diffusion of substances into organic coatings cannot be completely prevented, and coatings made to separate an aggressive solution from a given substrate, can fail due to this fact. The diffusion process enables contact between the coating and the diffusing species, and eventually the underlying substrate. This can cause film swelling, cracking and a loss of mechanical properties [5, 6, 13, 39, 65, 75–82], but it also allows chemical degradation to take place inside the coating. The movement of molecules through a coating film is dependent on the presence of free volume and cohesive forces in the resin matrix, and the frequency and distance with which penetrant molecules can "jump" from one void to another [83]. Penetrating molecules can exist in an unbound state in free volume or in a bound state, where cohesive forces attach the penetrant to the coating network [84]. It is also important to note that for a dissociated acid, the proton and anion likely move simultaneously to maintain charge neutrality [57].

Diffusion rates of molecules through a coating film depends on exposure conditions and choice of

coating system [65]. Important parameters for the coating are cross-linking density, crystallinity, pigments, and T_g, while for the penetrating molecule, molecular size and chemical similarity can have large effects on diffusion [85].

Diffusion coefficients are challenging to generalize, with recorded values for acid resistant resins ranging from 10^{-7} to 10^{-12} cm^2/s. Reducing the diffusion rate will prolong the time a coating is able to hinder contact between the aggressive substance and substrate, which, in turn, increases the coating's effective lifetime [86].

Cross-linking density and crystallinity

Increasing the cross-linking density of a thermoset resin typically leads to an increased solvent resistance, chemical resistance, and T_g, with reduced permeation speeds [5, 13, 15, 26, 28, 78, 87, 88]. The cross-linking density is defined as the number of moles of elastically effective network chains per sample volume or weight. Network chains are elastically effective when all ends are attached to the network [89]. Increasing cross-linking density reduces the segmental mobility of a resin network [30, 39] and decreases the free volume. This affects the above mentioned resistances, by limiting the diffusion rate of molecules through the coating. However, a higher degree of cross-linking will also make a coating more rigid and brittle, a property that can cause major issues in industrial applications.
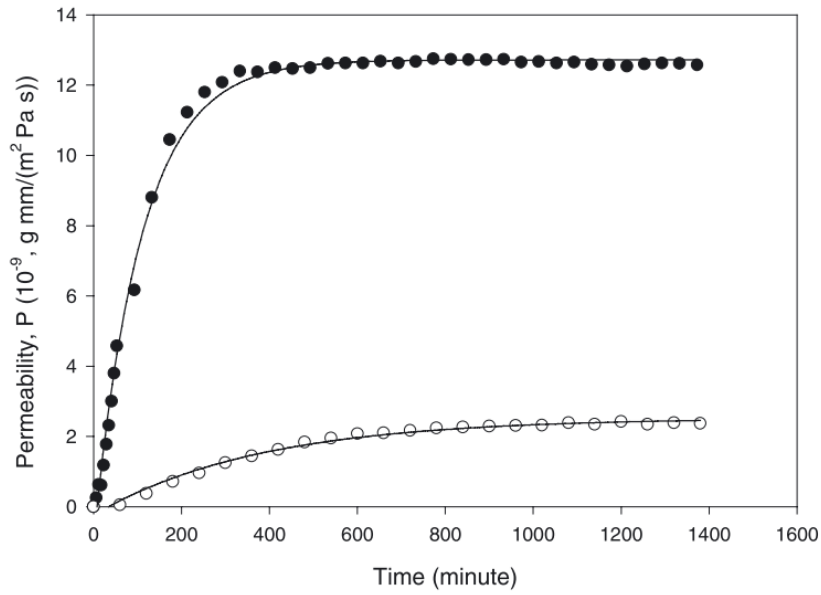
Figure 14: Permeation rates of water vapor through a liquid-crystalline (○) and non-crystalline (●) amine-cured epoxy at 37.8 °C. The solid lines are fits to the data points assuming Fickian diffusion. Reprinted from [90] with permission of Springer.
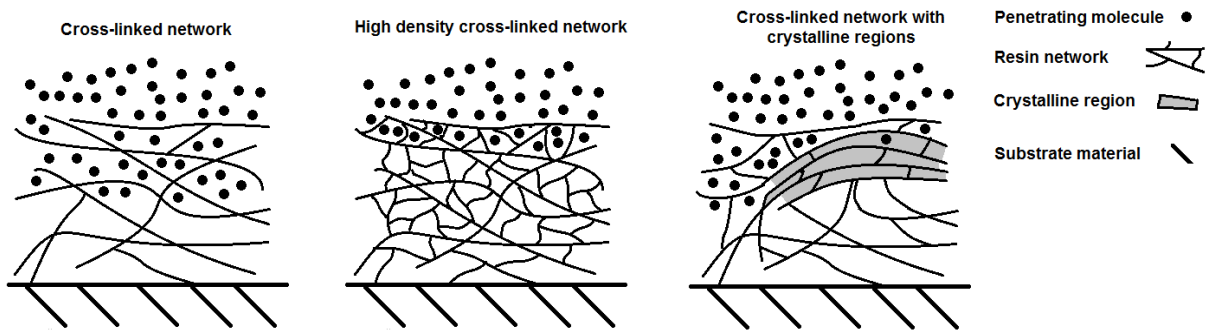
Figure 15: Increased rigidity and reduced free volume limits the diffusion rate of molecules through a coating film. Drawings based on [87, 90].

Similar reductions in diffusion rates can be obtained by having crystalline regions in a resin network, because crystalline structures have a closer chain packing than purely amorphous types [62]. Liquid crystal plastics (LCP) and liquid crystal thermosets (LCT) form crystalline domains

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in a melt or solution [91], and are made by including rod or disk like groups in the polymer backbone [92, 93]. As an example, Figure 14 shows the permeability of water through an LCT amine-cured epoxy, which was found to be much lower than the amorphous counterpart [90]. The effects of cross-link density and crystallinity on diffusion rates are visualized in Figure 15.

Cohesive and chemical factors

The type of chemical(s) a coating is exposed to can effect the coating's diffusion properties without breaking intra-molecular bonds in the resin. Cohesive interactions between the diffusing molecules and coating resin can account for this occurrence.

Molecules can diffuse through a coating using the free volume available, but they can also interact with the resin network via cohesive forces such as hydrogen bonding. A diffusing molecule can attach to a resin chain by cohesive forces and disrupt existing interchain bonds in the resin according to Vanlandingham [84]. This bonding can cause the network to expand in size, observed as swelling of the coating, and reduce the rigidity of the network, causing plasticization.

Plasticization is connected to increases in internal stress and cause cracks formation in a coating [90]. Swelling and plasticization effects can be caused by any diffusing molecules be they solvents or non-solvent, like water in amine-cured epoxy. Other side effects of plasticization include decreases in coatings T_g and increased diffusion rates [31, 94]. These enhanced diffusion rates do not only apply for the molecules that cause plasticization, other molecules such as acids can be carried more rapidly into a coating film, thereby facilitating diffusion of secondary chemicals [10].

However, cohesive forces such as hydrogen bonding between coating and the diffusing molecule do not always increase diffusion rates. If the disruption to the resin network is minimal, these interactions can actually decrease diffusion rates by holding on to the diffusing molecule and

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decreasing the frequency at which the penetrant can jump from one free volume to another. A known case is, once again, water into amine-cured epoxy resins, where the amine and hydroxyl groups in the resin are able to hydrogen bond with the water [90].

Cohesive factors are particularly strong for solvent molecules. A chemical works as a solvent if it has a solubility parameter close or the same of the coating. The Hilderand solubility parameter is defined as the energy required to vaporize a unit volume of liquid against the intermolecular forces between the molecules [95], and can be divided into the 3 previously mentioned cohesive forces, also called Hansens solubility parameters, hydrogen bonding, dipole-dipole and dispersion [96]. A solvent can cause greater swelling and plasticization in a thermoset than non-solvents, since the cohesive forces are similar to that of the coating. Solvent-like acids of particular trouble, are the smaller organic acids such as acetic ($C_2H_4O_2$), formic and propionic acid ($C_3H_6O_2$) [10], as shown by Kalenda [44], see Figures 16 and 19B.
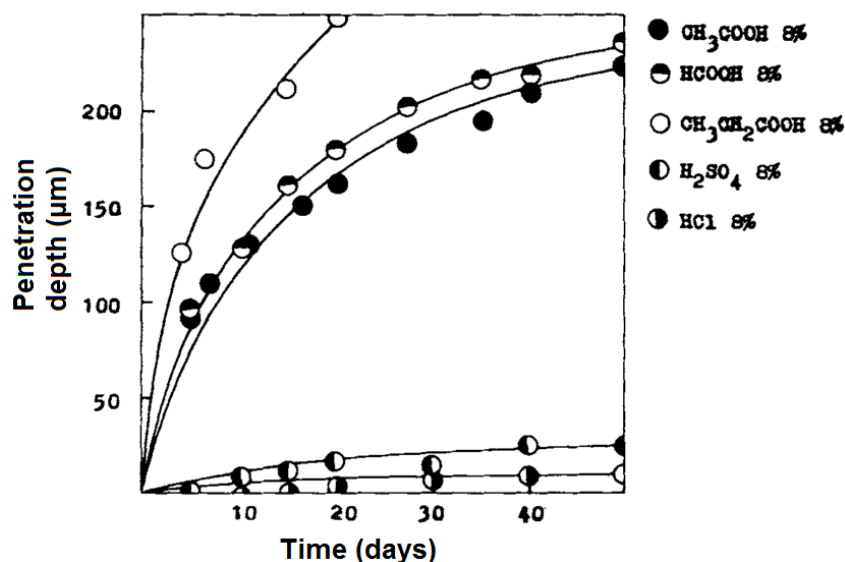
Figure 16: The penetration depth vs. time, of 8 wt% acidic solutions into an amine-cured epoxy resin at ambient temperature. The organic acids diffuse rapidly compared to the mineral acids. Reprinted from [44] by permission of John Wiley and Sons ©.

It is possible to determine which chemicals are particularly troublesome for a given coating using solubility parameters [65, 95]. Based on the parameters of various chemicals, and their effect on either physical attributes, such as flexural strength or degree of swelling, it is possible to map a solubility range for a given coating material. A rule of thumb states, that the closer a chemical's solubility parameter is to the material in question, the higher degree of swelling and loss of flexural strength [97]. Figures 17 and 18 show the relationship between the solubility parameter and swelling and flexural strength retention, respectively. A high swelling ratio or large drops in flexural strength indicate severe solvation is occurring when the coating is exposed to the given chemical.
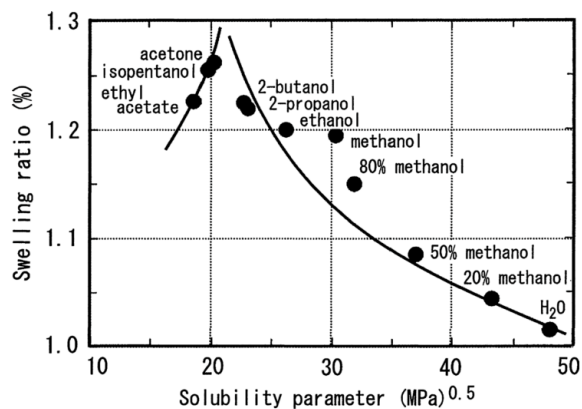
Figure 17: Changes in swelling ratio of a hardened polyester resin vs. solubility parameter of various solutions. Reprinted from [75] by permission of the Japan Petroleum Institute.
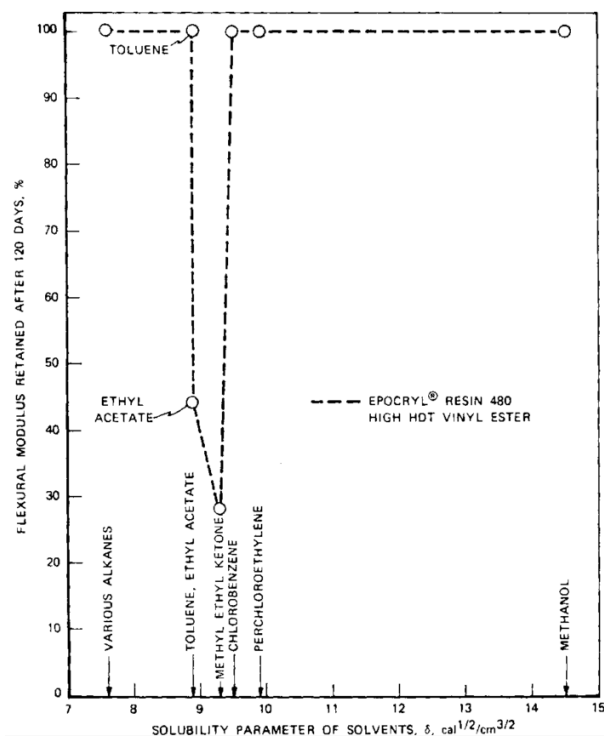
Figure 18: Changes in flexural modulus of a vinyl ester in various solutions. Reprinted from [65] by permission of John Wiley and Sons ©.

If there is a high degree of rigidity in a coating network, the diffusion can be described as

Fickian [44, 98–100]. Deviations from this behavior, also called non-Fickian diffusion, can be associated to relaxation of the network chains caused by the diffusing media [90, 101] and is seen often when the coating experiences extensive swelling [102], that is when cohesive factors are strong. According to a FRP material guide from Reichhold A/S [15], solvent penetration following Fickian diffusion, will eventually diffuse all the way through a coating and lead to failure, while for situations when non-Fickian diffusion is valid, an asymptote can be reached after a certain diffusing depth, limiting further penetration. Whether this phenomenon is valid for acidic environments is not stated.

Finally, acid concentration can also play a role in enhancing or even decreasing diffusion coefficients. Kalenda [103] noted that at increasing concentrations, the diffusion coefficient of acetic acid through amine-cured epoxy also increased. While in the same experiment, for sulfuric acid, a peak was reached at around 20-25 wt% acid, any reduction or increase in acid concentration caused a drop in diffusion coefficient value. No explanation was given for these trends, but it indicates that the diffusion coefficients were concentration-dependent.

Pigments

Fillers and pigments can be used to reduce diffusion rates of unwanted species through a coating, but one has to be careful and ensure the fillers themselves do not have antagonistic interactions with the diffusing medium and accelerate coating failure [12]. Pigments can play many protective roles in a coating system and using barrier pigments is common for reducing molecular and ionic diffusion. Adding pigments, that are inert to the diffusing solution, into a coating will create a physical barrier to diffusion and force the penetrant to take a longer, tortuous, path through the film [104, 105]. This increases the effective lifetime of a coating by delaying contact with the substrate. But pigments can also have the opposite effect, allowing rapid diffusion along the

filler-binder interface, and reducing the coating lifetime [106].

Optimizing the shape, orientation and concentration of pigments will enhance their positive functionality. Pigment volume concentrations(PVC) should be close, to but not above, the critical PVC value (CPVC) [39], and lamellar pigments oriented parallel to the surface, will provide a strong barrier to diffusion [105]. Figure 19A shows the diffusion path of unwanted species through a coating, comparing the effect of spherical and lamellar shaped pigments on the length of this path, while Figure 19B shows this effect with experimental data.

Forming a physical barrier is not the only way to reduce permeation by use of pigments. Reactive pigments have been investigated as an alternative or addition to the typical inert flake fillers. Reactive pigments work by partly reacting with, thus removing, and blocking the permeating substance [100, 107]. A combination of reactive and inert pigments is claimed to reduce the diffusion of aggressive species through a coating to a greater degree, than if used individually [104].
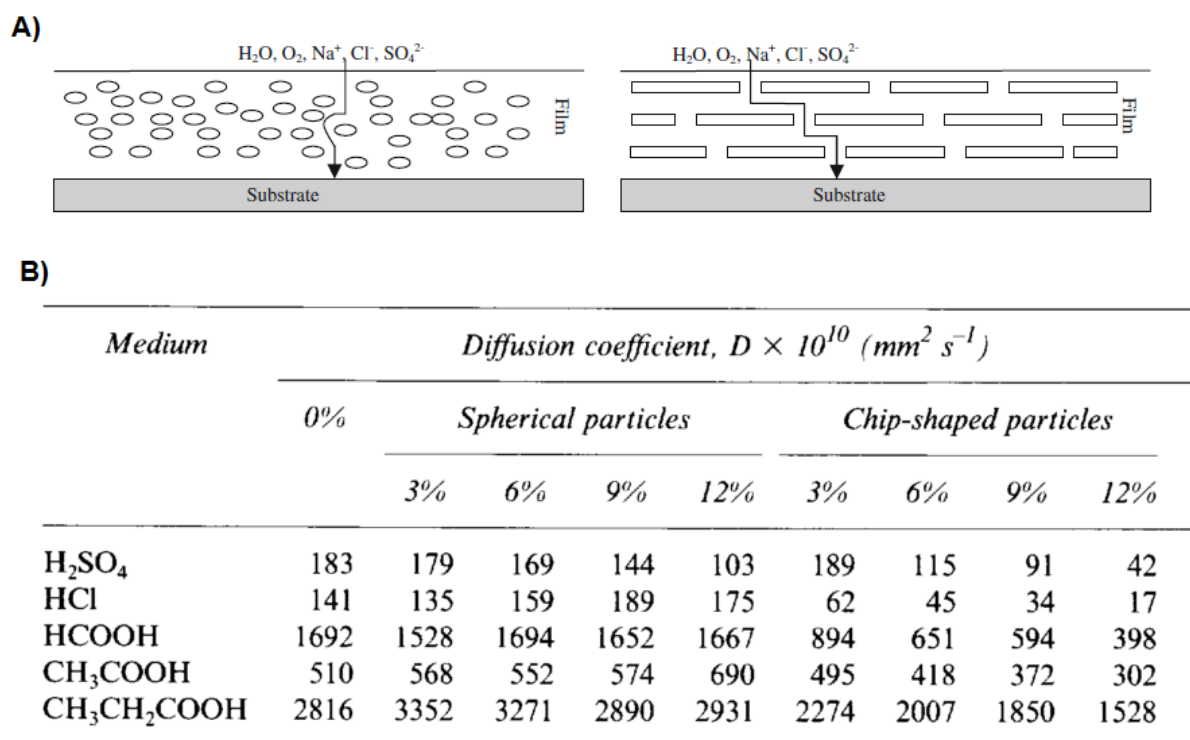
Figure 19: A: Idealized migration of species through a coating with spherical and lamellar barrier pigments. The lamellar pigments provide the longest most tortuous diffusion path of the two. Reprinted from [108] by permission of Springer. **B:** Diffusion coefficients of 8 wt.% acidic solutions through amine-cured epoxy coating with varying particle concentration [wt.%] and shape. No temperature has been provided in the reference. Reprinted from [107] by permission of Elsevier.

To summarize, physical degradation does not involve bond breaking or formation, but entails the effects caused by the diffusion of molecules into a coating film. Diffusion can be limited by increasing cross-linking density and crystallinity, using barrier pigments and avoiding contact with solvent molecules. The adverse effects on physical properties, caused by molecular diffusion, can be recovered, if the penetrants are removed, as long as no chemical reactions have taken place in the coating [109].

Chemical degradation

An important property of an acid resistant coating is to remain inert, any reaction with acidic substances or any other additives will damage the coating, causing premature failures, such as cracks in the film, and expose the substrate. Chemical degradation mechanisms are not plentiful in literature but some work can be found for coatings applied in severe acidic environments, and acid rain etching studies in the automotive industry.

The chemical composition and structure of a coating determines it's susceptibility to chemical exposure, and particular chemical bonds, or functional groups, in a resin network can be more or less reactive with the medium in which it is immersed. However, reactivity can be challenging to evaluate, and looking at functional groups and chemical bonds is not sufficient to determine a resins' chemical resistance. The molecular structure of the resin will determine the frequency of reactive sites and the presence of sterical obstructions to reaction. Furthermore, the reaction itself can be either harmless or damaging, and can involve changes in functionality, bond scissoring or bond formation.

This section considers the effects of chemical composition and structure of coating resins on the susceptibility to unwanted chemical reactions with the surrounding medium, and the possible mechanisms of this degradation.

Functional groups

As noted by Hare [10, 11], Allen [65] and Hojo [76], hydrolysis and chemical oxidation are two important reactions that can cause bond breaking in a resin. Acids are commonly found in aqueous solutions, and acid-induced hydrolysis is a reaction with water at low pH [11]. Oxidizing acids, such as nitric acid, are more prone to react with a resin, and can cause greater damage than

the stronger but non-oxidizing acids. Bond scission can severely damage a resin, but the same is true for additional bond formation in a cured resin. Additional cross-links can cause increases in internal stress and inducing cracks in a coating [75, 110]. Reactions that cause changes in functional groups in a resin, like the conversion of alcohol groups to ketones, has not been noted as an issue, unless it results in bond scissoring.

Functional groups such as esters, amides, ureas, urethanes and acetal are susceptible to acid hydrolysis, even ether, siloxanes and amino groups are said to be vulnerable, but to a lesser extent [11, 76, 111]. Linkages containing non-carbon atoms such as oxygen, nitrogen and sulfur atoms and their bonds with carbon, are susceptible to hydrolysis reactions, the fewer such weak linkages, the higher the hydrolysis resistance [11].

The reaction rate of coatings undergoing hydrolysis was studied in the automotive industry, with a focus on acrylic-melamine clearcoats in acid rain conditions. By observing changes in absorbance, using Attenuated Total Reflectance (ATR), for important functional groups, reaction rates can be estimated [112], see Section "Analysis of chemical change" for more details. Such studies of reactivity are, however, rare. Reaction schemes of acid hydrolysis of the above mentioned functional groups and relative reactivities are shown in Figure 20.
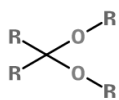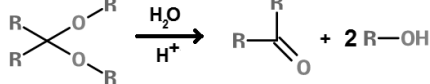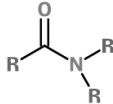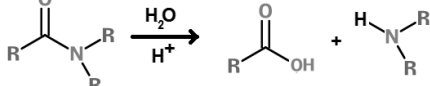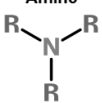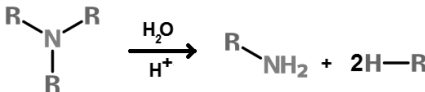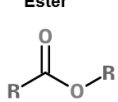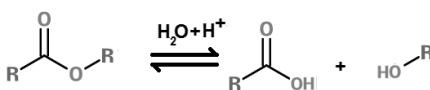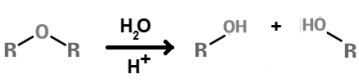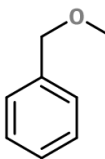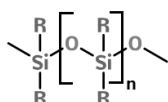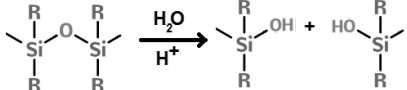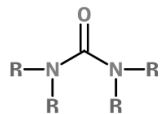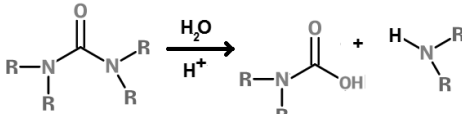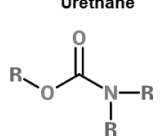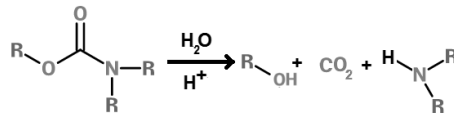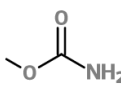
Figure 20: Name and structure of functional groups that can be present in coating resins and are vulnerable to acid induced hydrolysis. Proposed chain scissoring reaction schemes [11, 113, 114], and relative reactivity of similar molecules in acidic aqueous conditions are shown [115].

Oxidizing acids pose particular problems because the coating has to be resistant to both acidic and oxidizing environments, see Table 2 for examples of oxidizing acids. Where research on photo and thermal oxidation of organic coatings is extensive, information on purely chemical oxidation is rather scarce. Hare [11] and Allen [65] note that unsaturated carbon bonds as well as alcohol and aldehyde groups are vulnerable to chemical oxidation. Hojo [76] also mentions chemical oxidation as a typical corrosion reaction of resins, and specifies esters, aliphatics, phenols and ethers as vulnerable functional groups. Ono [109] observed chain scission of amine linkages in nitric acid.

The ability of an acid to act as an oxidizing agent shows that acid chemistry and not acid strength is of most importance when choosing a protective coating. Figure 21 summarizes the functional groups mentioned to be vulnerable to chemical oxidation along side example reactions.

The chemical structure of a cured film can have significant effects on oxidation resistance and/or hydrolytic susceptibility. An example of this is found in vinyl esters where steric hindrance brought by a methyl group near the ester linkage (see Figure 8) prevents contact between diffusing molecules and the vulnerable ester. The sterical effect also hinders the hydrolysis products from diffusing away from the reaction site, limiting reactions to the surface only [65, 116].

Induced cross-linking can also be detrimental to coating performance [75]. Chemical degradation through the formation of additional cross-links can be monitored by increasing T_g and E-modulus [110, 117], and causes increased brittleness and internal stress in a coating. However, chemical reactions responsible for increased cross-linking have not been mapped.

For an organic coating to be acid resistant, it should have either a slow or no reaction with the dissociated proton in aqueous solution. For a coating to be resistant to a specific acid, the same rule has to apply to the de-protonated anion in conjunction. Thus, the chemistry of a coating as well as the environment are of utmost importance, and if the resin, potential hardener or

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their cross-linking sites are susceptible to interaction with the acidic medium, the integrity of the coating could be compromised.

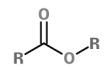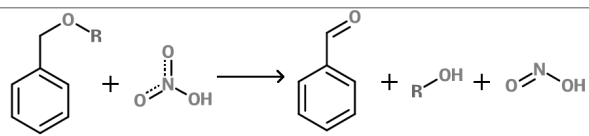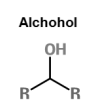

Figure 21: Name and structure of functional groups that are vulnerable to chemical oxidation [11, 65, 76, 109], as well as example reactions of organic molecules with oxidizing peroxy acids or nitric acid and comments from Trahanovsky [118].

Chemical degradation mechanism

Hojo et al. and Tsuda [75, 76] describe various chemical reaction scenarios of polymers, summarized in Figure 22. Whenever a coating is not completely inert towards the environment, one of these degradation mechanisms will occur. Each depends on the reaction and diffusion rate of aggressive media through the coating, as well as the frequency of chemical scissoring in the resin. The three mechanisms are described below:

- **Surface reaction** occurs when the penetrating solution is capable of rapid reaction with the coating film, i.e. reaction rate ≫ diffusion rate, and the susceptible linkages are abundant in the coating. This causes the binder to slowly break apart at the surface and a reduced film thickness can be observed. This is seen e.g. for amine-cured epoxy in nitric acid solutions.

- **Corroded layer** differs slightly from the previous mechanisms. Here the susceptible linkages in the coating are less frequent, leaving behind a degraded leached layer. Still the reaction rate ≫ diffusion rate. There are two types: in type 1 the leached layer provides no diffusion barrier, for type 2 the leached layer is partly intact and can act as a diffusion barrier, reducing the diffusion rate.

- A **penetration type** mechanism occurs when the reaction with the coating is very slow, i.e. reaction rate ≪ diffusion rate. The coating degradation is therefore dominated by the diffusion process rather than the rate of reaction. The solution diffuses into the coating film and then some time after a reaction is observed between the coating and penetrating molecules.
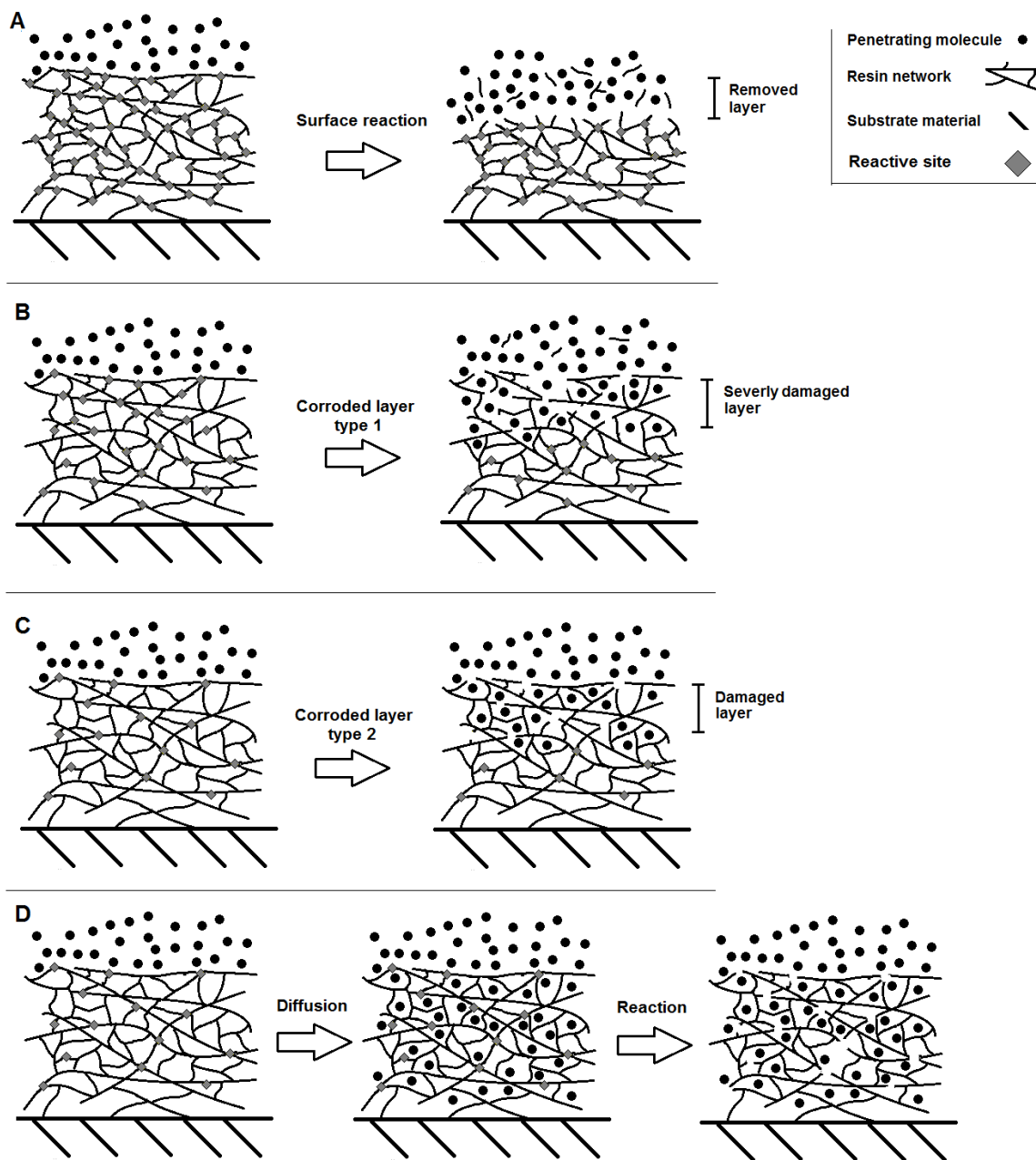
Figure 22: The three types of degradation mechanisms of an organic coating immersed in aggressive solutions. A: Surface reaction causes reduction in film thickness. B: Corroded layer type 1 leaves behind a severely weakened network. C: Corroded layer type 2, leaves behind a more intact network that still works as a diffusion barrier. D: Penetration type degradation is molecular diffusion in the presence of a slow reaction. Based on [76].

Hojo's corrosion mechanisms stress the important effects of both physical diffusion and potential chemical reactions in a coating with regards to a coatings overall chemical resistance. Diffusion can be accelerated by chemical interactions between the solution and coating, so chemical resistance is a function of a coating's ability to prevent diffusion of species through the film, as well as chemical inertness in the environment.

Acid degradation of commercial thermosets

Keeping the degradation processes in mind, it is possible to look at the most widely used commercial thermosets and discuss how they, specifically, degrade through chemical reactions in acidic solutions. According to the Journal of Protective Coatings and Linings' (JPCL's) coatings and linings buying guide, the most common coating systems for acidic environments are made of epoxy (novolac), vinyl ester and polyurethane resins [25], consequently these resins will be covered in the following. See Figures 5, 6 and 8 for resin formation chemistry.

Epoxy

Epoxy-based coatings have found uses in acidic environments, particularly novolac epoxies are commonly used due to the high cross-linking density compared to regular bisphenol A epoxies [26]. Nevertheless, no work has been found on acid degradation of novolac epoxies, so bisphenol A and F epoxies will serve as examples. The resin chemistry of a cured epoxy can vary greatly, because the epoxy end group can react with a host of chemicals, including itself when heated. Amine-curing systems are most common when a high acid-resistance is desired.

A cured epoxy film contains ether linkages, hydroxyl groups, unreacted epoxy groups or curing agent depending on curing stiochiometry, and a linkage dependent on the chosen curing agent. Figure 23 shows the cross-link chemistry of some curing agents with epoxy.
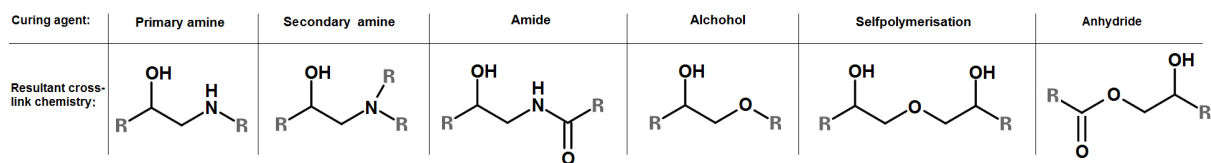
Figure 23: Curing agents and the resultant cross-link chemistry by reaction with epoxy groups. Deduced from [63].

Ether linkages are present in the backbone of epoxies and can be susceptible to acid-induced hydrolysis according to [11]. To the authors knowledge, no literature has confirmed this for epoxy resins. The only research available on this topic comes from Bauer [119] who showed that for melamine formaldehyde cross-linked co-polymer coatings, ether bonds can undergo hydrolytic cleavage in the presences of acids.

Amide-cured epoxies are vulnerable to degradation in acidic environments, and undergo chemical changes that yield increased concentrations of carbonyl groups as shown by Kotnarowska [117], while the amide linkages themselves have been shown to undergo hydrolytic cleavage for non-epoxy resins according to the reaction scheme shown in Figure 20 [80]. Non-oxidizing acids have also proved to cause increases in cross-linking densities for amide-cured epoxies. Kotnarowska [110, 117] noted an increase in cross-linking density in amide-cured epoxies when exposed to sulfuric acid, generating internal stress followed by blister formation in the coatings.

Amine linkages are not entirely inert either. Kalenda [44] investigated amine-cured epoxies in various acids and it was suggested that the amine bonds in the cured resin were susceptible to acid-induced degradation. Other publications have also noted amine linkages to be susceptible in acidic solutions [75, 101, 120]. Schmitz states that it is prone to hydrolysis, during examin-ations into Acrylic-melamine degradation in sulfuric acid, followed by conversion to an amine salt [111, 113]. The reaction sequence is reversed for Ono and Hojo [109, 120] who describe

the reaction product as an amine salt followed by C-N bond scissoring, shown in Figure 24. In opposition, Sembokuya [99] states that amine-cured epoxies exposed to sulfuric acid do not undergo a significant chemical change.

$$R_3N + HX \longrightarrow (R_3NH^+)X^-$$
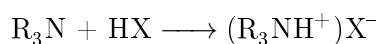
Figure 24: Production of amine salts from amine linkages and acid reactions in an epoxy network. This salt formation is followed by C-N bond scissoring according to Ono [109]. For which amine types this is valid is not provided.
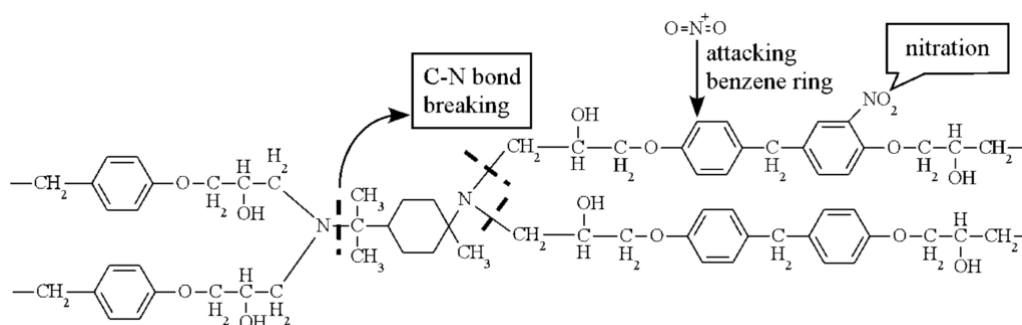
Figure 25: Acid-induced corrosion of amine-cured bisphenol F epoxy in oxidizing nitric acid. Reprinted from [121] by permission of Elsevier.

Ono [109] also investigated the behavior of amine-cured bisphenol A in an acidic oxidizing environment, using nitric acid and concluded that the amine and ether bonds were susceptible to cleavage in such an environment. It was observed that this degradation was rapid and highly destructive. Similar work was performed by Dang et al. [121, 122], who studied the degradation of amine cured bisphenol A and F in nitric acid. Dang notes the amine bonds as being susceptible to cleavage and observes a nitration of the benzene rings in both epoxy types, see Figure 25, yet no mention is made of the susceptibility of ether linkages to oxidative cleavage. The scissoring of both C-O in ethers and C-N and C-C bond in tertiary amines by nitric acid is mentioned by

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Trahanovsky [118].

To summarize, amide-cured epoxies perform poorly in acidic medium because they are susceptible to hydrolysis as well as induced cross-linking. Amine-cured epoxies perform better in acidic environments, but degrade in oxidizing acids due to amine (C-N) and ether (C-O) bond cleavage. The chemical cleavage of the amine bonds by non-oxidizing acids has been described [109], but the reaction must be slow since significant chemical alterations are not easily observed [99].

Vinyl ester

Vinyl ester resins do not contain amine linkages as the amine-cured epoxies, instead the weak linkages in vinyl esters include ether and ester bonds. The ester bonds would be expected to undergo rapid hydrolysis in acidic conditions as shown in Figure 20, a reaction that would cause chain scissoring and a chemical degradation of the resin network. Hojo and Tsuda [123] observed such a reaction for vinyl ester resins in HCl, but due to sterical effects discussed in Section 4.2.1, the extent of reaction was limited to the surface.

Vinyl esters have high acid-resistance but the formation of micro-cracks when exposed to acidic environments has been observed. The cause of these cracks has not been studied in depth, but could be due to induced cross-linking. Figure 26 depicts surface images before and after exposure to a sulfuric acid solution, where the appearance of micro-cracks or crazing is observed [82].
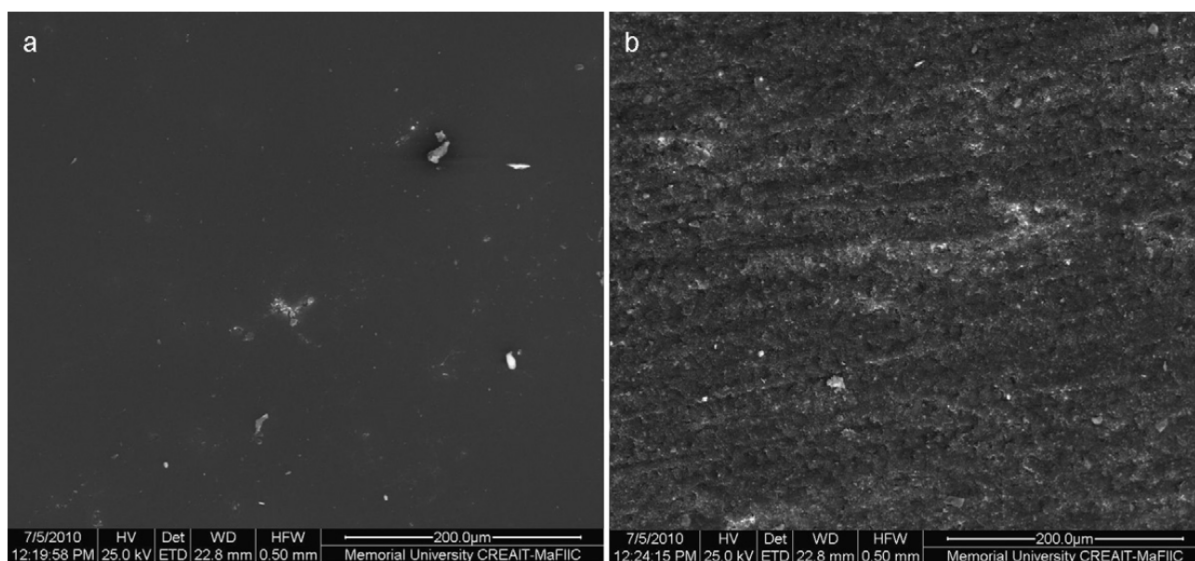
Figure 26: Scanning electron microscope image of an epoxy vinyl ester coating (a) unexposed, and (b) exposed to 1 M H_2SO_4 for 4 weeks (temperature was not stated). Reprinted from [82] by permission of Elsevier.

When it comes to acid-induced oxidation reactions, work is rather scarce. The ether groups in vinyl ester are vulnerable bonds shared with epoxies. However, vinyl esters are usable in oxidizing nitric environments [15], likely due to steric hindrance. The ether bond is noted to be cleaved for epoxies in oxidizing environments [109], but no studies have been made to determine the ether bond's part in vinyl ester degradation in oxidizing acid environments.

Polyurethane

Polyurethane resins are not as frequently used in acidic environments as epoxies and vinyl esters, but some manufactures still recommend the use of polyurethanes in combination with epoxy coatings [25].

The stability of polyurethanes depends in part on the monomer that provides the alchohol group. If this monomer is a polyester, the resultant resin becomes vulnerable to hydrolysis, due to the

ester linkages, specifically for strong acid immersion [124]. If the monomer is a polyether, the polyurethane becomes hydrolytically stable according to Stevenson [125]. Being stable, however, does not necessarily mean inert, the urethane groups themselves have been noted as vulnerable to hydrolytic cleavage in acidic conditions by Hare [11] as shown in Figure 20. Huisman [124] also reported the urethane bond as being susceptible to chemical cleavage in acidic solutions. However, acidic exposure can also induce cross-linking in polyurethanes [125]. A polyether-based polyurethane will form new cross-links in acid, causing a unique case where both formation and cleavage of chemical bonds takes place. The cross-linking is said to occur at the urethane linkages. Oxidizing nitric acid has been observed by Tanzi [126] to cause chain scissoring in polyether and polycarbonate-based polyurethanes. This was seen through decreasing molecular weight of the polyurethane, though the specific position of this chain scission was not specified.

The chemical degradation of acid resistant resins is a complicated process to generalize as it varies with resin and acid chemistry. It is not a subject of extensive research and potential reaction mechanisms have not been properly mapped. There is room for improvement and research, on the physical and chemical effects of acid exposure to chemically-resistant coating materials. Research, that can improve the understanding of underlying reactions and mechanisms, which in turn allows the formulation of improved products.

Experimental testing and analysis

The American Society for Testing and Materials (ASTM) has a wide range of testing methods coupled with analytical observations of relevance to cured organic coatings, see Table 8. These tests are often used to classify commercial coating systems, while researchers tend to use self tailored test methods for evaluation. This section covers a variety of analytical methods used to test diffusion characteristics, chemical reactions or degradation of organic coatings in acidic environments.

The most common method for testing organic coatings in acidic environments is by immersion [6, 18, 44, 77, 99–101, 109, 117, 120, 127–131]. The coating is immersed in a solution and analyzed periodically to monitor physical and/or chemical changes over time. It is a simple set-up to perform while yielding usable results when coupled with the correct analytical methods. It lacks, however, the ability to simulate actual process environments, which often involves cyclic stresses from maintenance shut-downs and environmental fluctuations. This is an old problem also encountered in accelerated tests for anti-corrosive coatings [132].

Table 8: ASTM procedures of relevance for testing and analyzing chemical resistance, diffusion, and mechanical properties of organic coatings.

Procedure Title	ASTM number	Notes
Chemical resistance		
Chemical resistance of thermosetting resins used in glass-fiber-reinforced structures intended for liquid service	C581	Immersion followed by weight, thickness and mechanical property analysis
Chemical resistance of protective linings	C868	Exposure followed by visual and mechanical property analysis
Standard practices for evaluating the resistance of plastics to chemical reagents	D543	Immersion tests followed by weight and mechanical property analysis
Water absorption of plastics	D570	Immersion followed by weight change analysis
Water vapor transmission of organic coating films	D1653	Exposure to water followed by weight change analysis
Sulfuric acid-resistance of polymer linings for flue gas desulfurization systems	D6137	Exposure followed by visual and adhesion analysis
Mechanical properties		
Tensile properties of plastics	D638	Tensile test and analysis
Flexural properties of un-reinforced and reinforced plastics and electrical insulating materials	D790	Flex test and analysis

Another common test set-up is the diffusion cell, often used when diffusion of substances through a coating system is of importance. The principle is to separate a chamber containing the aggressive substance(s) from one containing de-mineralized water using a free coating film, see Figure 27. It is possible to analyze the concentration development of the aggressive substance in the

pure water solution as time passes, giving a transient analysis of the diffusion process. A diffusion cell can also measure the mass flow between the two chambers by observing volume increase or decrease in either chamber as shown in Figure 28 [65, 80, 105, 133, 134].
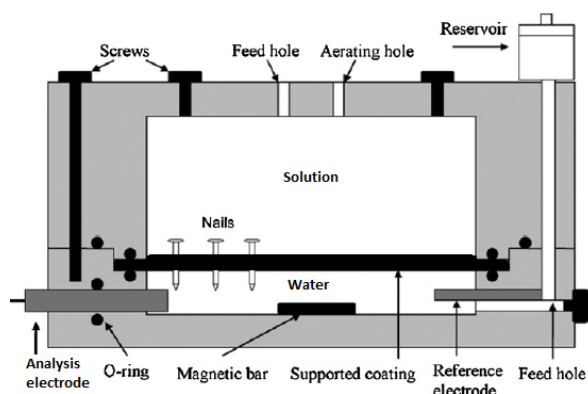
Figure 27: A diffusion cell used to monitor the permeation of ionic species across a free coating film or membrane. In this case, the interface diffusion of ionic species along a nail penetrating the film. Reprinted from [135] by permission of Elsevier.
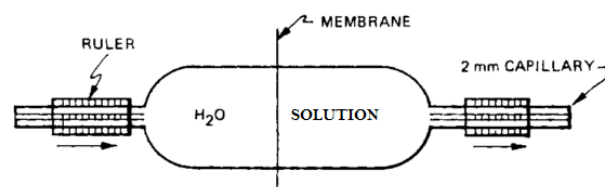
Figure 28: Diffusion cell, measuring the change in volume in either chamber as caused by mass flux through the center membrane. Reprinted from [65] by permission of John Wiley and Sons ©.

Analyses of coating chemistry, diffusion behavior, surface morphology and mechanical properties, can all assist in determining chemical stability, performance, possible degradation mechanisms and lifetime of a protective system. Table 9 gives an overview of analyses and testing methods with their uses. The following sections provide more details on how both physical and chemical degradation have been determined and analyzed for thermoset coatings exposed to acids.

Table 9: Analyses and test methods, what they detect, and the evidence they provide with regard to physical and chemical degradation.

Analysis or test method	will detect	which provides evidence of
Optical microscope	surface defects	visual degradation
	cross-section defects	visual degradation
SEM	surface defects and topography	visual degradation
SEM combined with **EDS**	cross-section elemental composition	molecular diffusion
Flexural strength	plastization	solvation
	cross-linking	chemical change
	bond cleavage	chemical change
Infra-red (IR) spectroscopy	functional groups	chemical change
Weight analysis	weight increases	diffusion and solvation, but not excluding chemical changes
	weight loss	diffusion and chemical changes
Diffusion cell	solution flux through a coating film	diffusion and possibly chemical changes

Diffusion analysis

Monitoring the permeation rate of molecules into and through a coating film determines the ability of a coating to function as a barrier. Three of the most common methods for diffusion analysis include the use of a Scanning Electron Microscope (SEM) coupled with elemental X-ray analysis (EDS), using specialized diffusion cells, or monitoring weight change for immersion experiments.

SEM coupled with EDS can be used to make a qualitative elemental analysis of a coating cross section [6, 99, 101, 136], thus detecting the depth of penetrating elements which are not originally

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found in the coating. This could for example be a sulfur element analysis as performed by Sembokuya [99] on the cross-section of an amine-cured epoxy, exposed to sulfuric acid, see Figure 29. The penetration depth can be approximated from the image and knowing the immersion time, a plot like the one shown in Figure 30 can be generated.
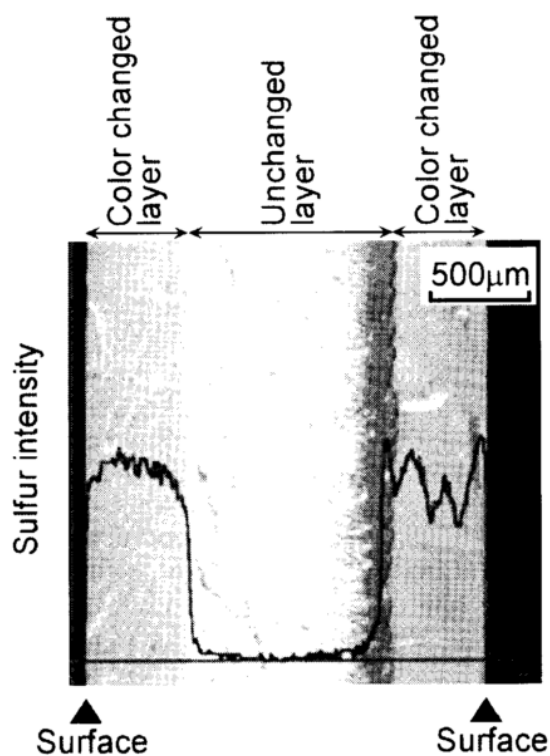
Figure 29: Cross-sectional EDS (X-ray) S-element analysis of a free coating film, made of amine-cured epoxy. Immersion in H_2SO_4 for 300 hours at 80 °C. No statement was made on the differences between the two color changed layers [99]. Courtesy of the Journal of the Society of Materials Science, Japan.
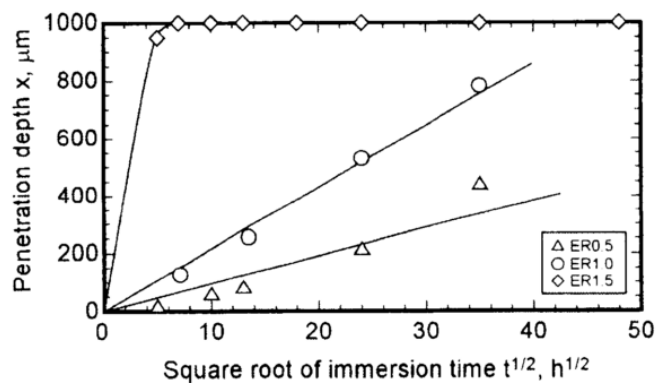
Figure 30: Sulfur element penetration depth vs. immersion time of amine-cured epoxies with varying hardener content. Legend refers to: 0.5=0.9 wt%, 1.0=17.9 wt% and 1.5=26.9 wt% hardener at 80 °C [99]. Courtesy of the Journal of the Society of Materials Science, Japan

One of the simplest methods for observing diffusion characteristics is immersion tests followed by weight change analysis. Weight change of a coating provides information relating to both chemical stability and diffusivity [75, 76, 99, 101], but does not necessarily separate the two effects. Therefore, weight change analysis should not be a stand-alone test. Molecular diffusion into a coating causes a weight increase, while leaching of solvents or chemical scissoring of network bonds, can cause a decrease in weight. Figure 31 shows the weight change over time of a glass reinforced amine-cured epoxy resin exposed to a large variety of chemicals at 80 °C. The rapid weight-losses for HNO_3 and H_2O_2 are due to a chemical degradation of the resin in oxidizing environments.

Drying a coating sample after immersion, makes it possible to remove the water content and measure actual changes in weight. For example, if a coating is partly degraded with an increased porosity, the submerged weight will be high, due to the diffusing liquid, while the dry weight might show an overall decrease, see Figure 32.

Analysis of chemical change

Changes in weight and flexural strength of a coating are not only caused by diffusion and solvation effects, but also of chemical changes in the resin network. IR analysis of a coating surface, known as Attenuated total reflectance (ATR), and SEM coupled with EDS can also be used to provide information on changes in chemistry within a coating.

A loss in weight during immersion can be caused by unreacted components or solvents diffusing out of the coating, but it can also be due to cleavage of chemical bonds within the film, releasing resin segments over time. One has to be careful when making conclusions based on weight change. Bond scission can occur without a weight loss, if the reaction sites are few and no resin segments are removed. Also, the occurrence of weight loss does not determine the time it takes
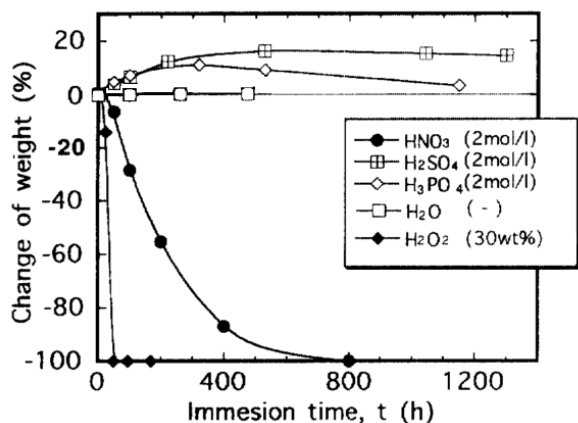
Figure 31: Weight change diagram of a glass reinforced amine-cured epoxy resin immersed in various aqueous environments at 80 °C. Reprinted from [76] by permission of Springer.
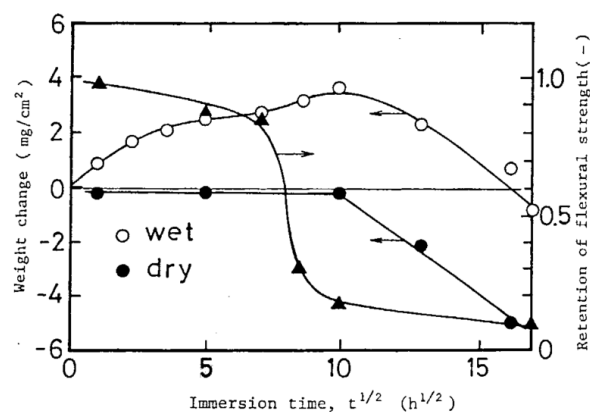
Figure 32: The wet and dry weight change of a polyester immersed in boiling water, showing water penetration and subsequent hydrolysis of ester bonds causing weight and flexural strength loss. Reprinted from [120] by permission of Taylor and Francis.

for reaction to take place because resin segments in cross-linked thermosets can require multiple bond scissions to be completely released. This is shown by Hojo [120] in Figure 32, where a drop in flexural strength, indicating bond cleavage, occurs before the observed weight loss.

Flexural strength changes can show both increases and decreases in cross-linking density. Increases in cross-linking density through induced cross-linking will increase flexural strength and vise-versa for bond scissoring reactions. Plastization also decreases flexural strength and samples should be dried and solvents removed to properly monitor changes in cross-linking density [75]. ATR allows determination the chemical composition of simple and complex molecules [137]. It is a useful tool in analyzing the chemical degradation, if any, that is occurring within the coating, Figure 33 is an example of this [18, 65, 99, 120, 121]. The figure shows the IR spectra of an amine-cured epoxy before and after immersion in nitric acid and was used to derive the

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degradation of amine-cured epoxies in oxidizing acids shown previously in Figure 25. The appearance or disappearance of absorption peaks provide indications of new functional groups or the disappearance of others. This change in absorption peaks is useful if one wants to determine the chemical reaction rate of species in the film, as was performed by Rodgers [112]. He related disappearance rates of ester and triazine in an automotive melamine-acrylic coating to the rate of hydrolysis caused by acid rain and subsequent scissoring of chemical bonds in the resin. Finally, Dang [121] showed the use of size exclusion chromatography (SEC). It is rather limited for thermosets, because these materials cannot be dissolved, but if resin segments are cleaved from the main body, it is possible to analyze the products in terms of molecular weight distributions as well.
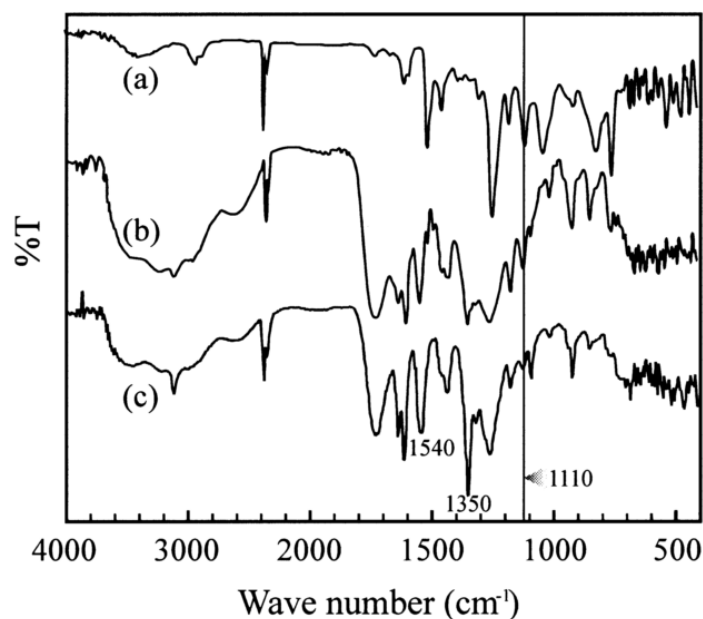
Figure 33: IR spectra of a amine-cured epoxy coating before immersion (a), after 150 h (b), and 500 h (c) of immersion in 4 M nitric acid at 80 °C. Wavenumbers at 1350 and 1540 cm^{-1} correspond to nitro and aromatic nitro groups, while the disappearance at 1110 cm^{-1} corresponds to C-N bonds. Reprinted from [121] by permission of Elsevier.

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Visual alterations

Coating performance can also be monitored by simply looking at a sample surface. Phenomena such as blistering, cracking, delamination, or color change, all of which are caused by physical and/or chemical degradation may be detected. This in itself does not require specialized equipment, but sometimes an optical or electron microscope can provide an enhanced picture and give information that the eye cannot capture.

Images using an optical microscope is a simple, non-destructive method for observing surface defects. Figure 34 is an example showing crack formation in an amide-cured epoxy coating exposed to sulfuric acid, as observed through an optical microscope [110].
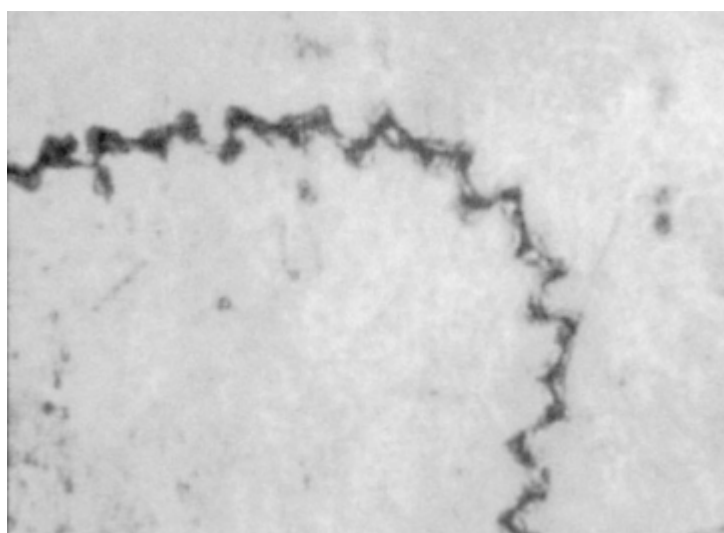
Figure 34: Cracks in an amide-cured epoxy coating exposed to 5 wt % sulfuric acid for 1008 h. The image was taken using an optical microscope at 100 times magnification. Neither a scale bar nor exposure temperature was provided. Reprinted from [110] by permission of Elsevier.

With SEM images it is possible to obtain a very high resolution, magnification as well as depth of field [138]. This allows detailed images of a coating surface for detecting small changes in a coating such as micro-cracks in a vinyl ester exposed to sulfuric acid as seen in Figure 26 [82].

By utilizing combinations of the previously mentioned analytic techniques it is possible to gain an all-around understanding of a coatings performance in immersed media, including knowledge of penetrant diffusion speeds, possible reactions and resultant chemical and physical changes to the coating.

Conclusions

This paper has discussed the use of organic coatings in acidic environments in the chemical industry, where resistant thermoplastics, thermosets and elastomers can, though limited by exposure conditions, replace expensive metal alloys and ceramic linings. Flouropolymers have the highest degree of acid and temperature resistance, rubbers have the highest impact resistance, while thermosets, based on vinyl ester and epoxy resins, have been extensively used as protective coatings and construction material combined with glass fiber reinforcement, due to their lower costs.

Acid-resistance in organic coatings is not strait forward to achieve as it varies with coating formulation and the industrial process environments. Acid, and general chemical resistance, are divided into two main categories, physical and chemical degradation. Physical degradation involves diffusion of molecules into the coating film and the effects that follow, while chemical degradation entails bond breaking and formation due to chemical exposure. The severity of these degradation mechanisms determine the degree of acid or chemical resistance of a coating.

Physical degradation is well understood and mathematically described, as it depends on well known diffusion behavior of polymers. Though deviations from Fickian diffusion behavior can occur. Chemical degradation is not as well understood. This paper has attempted to map acid-resistance with respect to thermoset resins and their functional groups, but even for coatings often used in acidic media, specific information on potential chemical reactions and the rate

of known reactions is lacking. The sole attempt to describe combined physical and chemical degradation was done by Hojo [76], who relates reaction rate with diffusion rate as shown in Figure 22.

Finally, the methods used to determine chemical and physical degradation have been discussed. Diffusion characteristics and chemical changes in a coating film are readily determined, while the rate of reaction between a resin and diffusing molecules has only been observed for bond cleavages by measuring flexural strength changes, and even there, specific reaction rates cannot be determined.

Higher degrees of abrasive and temperature resistance would expand the application areas of organic coatings in the chemical industry, and improved knowledge of the combined physical and chemical degradation mechanisms would reduce the risk of use. Research in the field of organic coatings for acid protection is progressing, but by no means complete.

References

[1] Allahverdi, ALI, Škvára, F, "Acidic corrosion of hydrated cement based materials part 1.-Mechanism of the phenomenon", Ceramics 44 (3) 114–120 (2000)

[2] Policastro, S, Martin, F, Natishan, P, Moran, P, "Corrosion and corrosion control", in: Kirk-Othmer Encyclopedia of Chemical Technology, pp. 1–31, John Wiley and Sons (2011)

[3] Harvey, C, "Delta air lines flying high with containment coatings", Coatings Pro Magazine (2014)

[4] Silva, M, "Cold bonding eliminates tank's through-wall corrosion", Coatings Pro Magazine (2014)

[5] Moukwa, M, Barkey, T, "The performance of thermoset polymers in mineral and organic acid service", J. Prot. Coat. Linings 13 (7) 58–69 (1996)

[6] Banna, MH, Shirokoff, J, Molgaard, J, "Effects of two aqueous acidic solutions on glass reinforced vinyl ester resins tubes", Canadian Metallurgical Quarterly 51 (1) 91–100 (2012)

[7] Kelley, D, "How to reduce construction and maintenance costs in metal extraction and refining processes", in: SME Annual Meeting and Exhibit, pp. 326–329 (2010)

[8] Hare, CH, "Corrosion control of steel by organic coatings", in: Uhlig's Corrosion Handbook, pp. 971–983, John Wiley and Sons (2011)

[9] Khaladkar, PR, "Using plastics, elastomers, and composites for corrosion control", in: Uhlig's Corrosion Handbook, pp. 915–970, John Wiley and Sons (2011)

[10] Hare, CH, "Chemically induced degradation", J. Prot. Coat. Linings 16 (12) 17–25 (1999)

[11] Hare, CH, "Chemically induced degradation of coatings: Part II", J. Prot. Coat. Linings 17 (1) 63–75 (2000)

[12] Hare, CH, "Chemically induced degradation of coatings: Part 3, Pigments", J. Prot. Coat. Linings 17 (2) 58–64 (2000)

[13] Hag, N, Harrison, P, "Experience with the use of Derakane vinyl ester-based GRP in flue gas desulphurization plants", Anti-Corros. Method Mater. 43 (2) 15–19 (1996)

[14] Shing, CK, Wu, CML, Chen, JWJ, Yuen, CS, Ricky, YC, "A review on protection of concrete for sewage installations and an accelerated test on protection systems", Hong Kong Inst. Eng. Transactions 19 (3) 8–16 (2011)

[15] Reichhold Inc., "FRP material selection guide: An engineer's guide to FRP technology", Tech. rep. (2009)

[16] Cooper, CD, "Air pollution control", in: Kirk-Othmer Encyclopedia of Chemical Technology, John Wiley and Sons (2007)

[17] Ragnar, M, Henriksson, G, Lindstrom, ME, Wimby, M, Blechschmidt, J, Heinemann, S, "Pulp", in: Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH (2014)

[18] Compère, C, Hechler, J, Cole, K, "Behavior of phenolic-coated steel in concentrated sulfuric acid", Prog. Org. Coat. 20 (2) 187–198 (1992)

[19] Duby, P, "Metallurgy", in: Kirk-Othmer Encyclopedia of Chemical Technology, John Wiley and Sons (2005)

[20] De Belie, N, Monteny, J, Beeldens, a, Vincke, E, Van Gemert, D, Verstraete, W, "Experimental research and prediction of the effect of chemical and biogenic sulfuric acid on

different types of commercially produced concrete sewer pipes", Cement Concrete Res. 34 (12) 2223–36 (2004)

[21] Hacias, K, "Metal surface treatments, pickling", in: Kirk-Othmer Encyclopedia of Chemical Technology, pp. 1–3, John Wiley and Sons (2000)

[22] Taylor, AW, "Fertilizers", in: Kirk-Othmer Encyclopedia of Chemical Technology, pp. 111–128, John Wiley and Sons (2004)

[23] Dittmar, H, Drach, M, Vosskamp, R, Trenkel, ME, Gutser, R, Steffens, G, "Fertilizers, 2. types", in: Ullmann's Encyclopedia of Industrial Chemistry, pp. 200–246, Wiley-VCH (2009)

[24] Bayer, O, "Polyurethane", Angewandte Chemie 59 (9) 257–288 (1947)

[25] Staff., J, "Coating systems for concrete in severe service: A brief discussion", J. Prot. Coat. Linings 23 (1) 50–57 (2006)

[26] Watkins, MJ, "Epoxy resins in coatings", in: Paint and Coating Testing Manual, 15th edn, pp. 87–92 (2012)

[27] Gannon, JA, "History and development of epoxy resins", High Perfor. Poly.: Orig. Devel. pp. 299–307 (1986)

[28] Kelley, D, Graham, J, Johnson, T, "Different FRP resin chemistries for different chemical environments", Tech. rep., Ashland Perfomance Materials (2010)

[29] Thomson, B, Campion, RP, "Testing of polymeric materials for corrosion control", in: Uhlig's Corrosion Handbook, pp. 1107–16, John Wiley and Sons (2011)

[30] Sonawala, SP, Spontak, RJ, "Degradation kinetics of glass-reinforced polyesters in chemical environments. Part 1 Aqueous solutions", J. Mater. Sci. 31 (18) 4757–65 (1996)

[31] Marais, S, Metayer, M, Nguyen, TQ, Labbe, M, Saiter, JM, "Diffusion and permeation of water through unsaturated polyester resins - influence of resin curing", European Poly. J. 36 (3) 453–462 (2000)

[32] Miller, WA, Schlanger, LM, Baumgaertner, ER, "Fluoroplastics", Managing Corros. Plastics 5 98–102 (1983)

[33] Koga, A, Yamabe, T, Sato, H, Uchida, K, Nakayama, J, Yamabe, J, Nishimura, S, "A visualizing study of blister initiation behavior by gas decompression", Trib. Online 8 (1) 68–75 (2013)

[34] Byrappa, K, "Hydrothermal processing", in: Kirk-Othmer Encyclopedia of Chemical Technology, John Wiley and Sons (2005)

[35] ASTM Commitee G02, "G40 - Standard terminology relating to wear and erosion", Tech. rep. (2013)

[36] Takadoum, J, "Tribology", in: Kirk-Othmer Encyclopedia of Chemical Technology, pp. 1–18, John Wiley and Sons (2012)

[37] Møller, P, Nielsen, LP, Advanced surface technology: volume 1, Moeller and Nielsen (2013)

[38] Zhang, S, Dam-Johansen, K, Nørkjær, S, Bernad, PL, Kiil, S, "Erosion of wind turbine blade coatings - Design and analysis of jet-based laboratory equipment for performance evaluation", Prog. Org. Coat. 78 103–115 (2015)

[39] Wicks, ZW, Jones, FN, "Coatings", in: Kirk-Othmer Encyclopedia of Chemical Technology, pp. 1–88, John Wiley and Sons (2013)

[40] Khruschov, M, "Principles of abrasive wear", Wear 28 (1) 69–88 (1974)

[41] Wu, L, Guo, X, Zhang, J, "Abrasive resistant coatings - A review", Lubricants 2 (2) 66–89 (2014)

[42] Hojo, H, Tsuda, K, Yabu, T, "Erosion damage of polymeric material by slurry", Wear 112 17–28 (1986)

[43] Mallinson, JH, "Abrasion of fiber-reinforced plastics in corrosive environments", Chem. Eng. 89 (11) 143–144 (1982)

[44] Kalenda, P, "Diffusion of acids into epoxy resin compositions", Appl. Poly. Sci. 45 (12) 2235–38 (1992)

[45] Møller, P, Nielsen, LP, Advanced surface technology: volume 2, Moeller and Nielsen (2013)

[46] Lawrence, GCK, "New developments in reinforced corrosion-resistant thermosetting plastic lining materials", Australasian Corros. Eng. 19 (4) 25–28 (1975)

[47] Campbell, JL, "Metals resist hot sulfuric acid", Ind. Eng. Chem. 53 (11) 125–126 (1961)

[48] Schweitzer, PA, Fundamentals of metallic corrosion, vol. 825 (2006)

[49] MetalPrices.com, "MetalPrices.com", URL `www.metalprices.com`, [accessed 16-10-2015] (2015)

[50] Infomine.com, "Infomine.com", URL `www.infomine.com`, [accessed 16-10-2015] (2015)

[51] Hall, GR, "Improved corrosion protection for flue gas systems utilizing a dual liner concept", Energy in the 90's pp. 100–108 (1991)

[52] Hall, GR, Sauereisen, CK, "Restoration of a brick chimney with a dual lining system and polymer concrete", Mater. Performance 45 (11) 34–38 (2006)

[53] Sergent, JE, "Ceramic materials", in: Ceramic Interconnect Technology Handbook, pp. 163–197 (2007)

[54] Morrell, R, "Ceramics, structural", in: Kirk-Othmer Encyclopedia of Chemical Technology, John Wiley and Sons (2011)

[55] Bennett, JP, "Corrosion resistance of ceramic materials to hydrochloric acid", Tech. rep., bureau of mines (1983)

[56] Leigh, HD, "Refractories", in: Kirk-Othmer Encyclopedia of Chemical Technology, John Wiley and Sons (2000)

[57] Regester, RF, "Behavior of fiber reinforced plastic materials in chemical service", Corrosion 25 (4) 157–167 (1969)

[58] Morton, M, "Elastomers, synthetic, survey", in: Kirk-Othmer Encyclopedia of Chemical Technology, pp. 1–20, John Wiley and Sons (2009)

[59] ASTM Commitee D01, "D16 - Standard terminology for paint, related coatings, materials, and applications", Tech. rep. (2015)

[60] ASTM Commitee J01, "G193 - Standard terminology and acronyms relating to corrosion", Tech. rep. (2013)

[61] Praw, M, "Polyurethane coatings: A brief overview", J. Prot. Coat. Linings 30 (8) 34–39 (2013)

[62] Stevens, MP, Polymer chemistry: An introduction, Addison-Wesley (1975)

[63] Pham, HQ, Marks, MJ, "Epoxy resins", in: Ullmann's Encyclopedia of Industrial Chemistry, pp. 155–244, Wiley-VCH (2005)

[64] Hall, GR, "Understanding the basics of chemical-resistant polyesters and vinyl esters", J. Prot. Coat. Linings 30 (11) 34–45 (2013)

[65] Allen, RC, "Some corrosion mechanisms in attack of resin and resin-glass laminates", Poly. Eng. Sci. 19 (5) 329–336 (1979)

[66] Mills, CC, Day, FB, "Application of thermoplastics for corrosion control", Managing Corros. Plast. 5 1–12 (1983)

[67] Gahleitner, M, Paulik, C, "Polypropylene", in: Ullmann's Enclyclopedia of Industrial Chemistry, pp. 1–44, Wiley-VCH (2014)

[68] Jeremic, D, "Polyethylene", in: Ullmann's Enclyclopedia of Industrial Chemistry, pp. 1–42, Wiley-VCH (2014)

[69] Hintzer, K, Zipplies, T, Carlson, DP, Schmeigel, W, "Fluoropolymers, organic", in: Ullmann's Enclyclopedia of Industrial Chemistry, pp. 1–55, Wiley-VCH (2013)

[70] Chapman, FM, "Fluoropolymer linings for corrosion protection of chemical process equipment", Managing Corros. Plastics 5 121–127 (1983)

[71] Chandrasekaran, VC, Rubber as a construction material for corrosion protection: A comprehensive guide for process equipment designers, Scrivener Publishing LLC (2010)

[72] Webb, RN, Shaffer, TD, Tsou, AH, "Butyl rubber", in: Kirk-Othmer Encyclopedia of Chemical Technology, John Wiley and Sons (2003)

[73] Visakh, P, Sabu, T, Arup, KC, Mathew, AP, Advances in elastomers I, vol. 11, Springer (2013)

[74] Ashland Inc., "Design engineers depend on FRP for corrosion challenges in chemical processing", Tech. rep. (2015)

[75] Tsuda, K, "Behavior and mechanisms of degradation of thermosetting plastics in liquid environments", J. Japan Petroleum Inst. 50 (5) 240–248 (2007)

[76] Hojo, H, Tsuda, K, Kubouchi, M, Kim, DS, "Corrosion of plastics and composites in chemical environments", Met. Mater. 4 (6) 1191–97 (1998)

[77] Abeysinghe, H, Edwards, W, Pritchard, G, Swampillai, G, "Degradation of crosslinked resins in water and electrolyte solutions", Poly. 23 (12) 1785–90 (1982)

[78] Sobrinho, LL, Ferreira, M, Bastian, FL, "The effects of water absorption on an ester vinyl resin system", Mater. Res. 12 (3) 353–361 (2009)

[79] Sonawala, SP, Spontak, RJ, "Degradation kinetics of glass-reinforced polyesters in chemical environments. Part 2 Organic solvents", J. Mater. Sci. 31 (18) 4757–65 (1996)

[80] Abastari, Sakai, T, Sembokuya, H, Kubouchi, M, Tsuda, K, "The reciprocal influence between ion transport and degradation of PA66 in acid solution", Polym. Degrad. Stabil. 91 (11) 2595–604 (2006)

[81] Kootsookos, A, Burchill, PJ, "The effect of the degree of cure on the corrosion resistance of vinyl ester/glass fibre composites", Composites Part A: Appl. Sci. Manuf. 35 (4) 501–508 (2004)

[82] Banna, MH, Shirokoff, J, Molgaard, J, "Effects of two aqueous acidic solutions on polyester and bisphenol A epoxy vinyl ester resins", Mater. Sci. Eng.: A 528 (4-5) 2137–42 (2011)

[83] Crank, J, Park, GS, Diffusion in polymers, Academic Press (1968)

[84] Vanlandingham, MR, Eduljee, RF, Gillespie, JW, "Moisture diffusion in epoxy systems", J Appl. Poly. Sci. 71 787–798 (1998)

[85] George, SC, Thomas, S, "Transport phenomena through polymeric systems", Prog. Poly. Sci. 26 (6) 985–1017 (2001)

[86] Romhild, S, Bergman, G, Hedenqvist, MS, "Transport and adhesion properties of an unlined and a liquid-crystalline polymer-lined vinyl ester thermoset exposed to severe environments", Appl. Poly. Sci. 95 (4) 797–806 (2005)

[87] Wang, Z, Han, E, Liu, F, Ke, W, "Effect of different curing agents on cure reaction and exposure resistance of phenolic-epoxy resins in hot acid solutions", Corrosion 66 (7) 750011–19 (2010)

[88] Blankenship, LT, White, MN, Puckett, PM, "Vinyl ester resins: versatile resins for composites", Int. SAMPE Symp. Exhibition (Proc.) 34 (1) 234–245 (1989)

[89] Miller, DR, Macosko, CW, "A New Derivation of Post Gel Properties of Network Polymers", Macromole. 9 (2) 206–211 (1976)

[90] Feng, J, Berger, KR, Douglas, EP, "Water vapor transport in liquid crystalline and non-liquid crystalline epoxies", J. Mater. Sci. 39 (10) 3413–23 (2004)

[91] English, LK, "Liquid-crystal polymers: in a class of their own", Mater. Eng. 103 (3) 36–41 (1985)

[92] Hoyt, AE, Benicewicz, BC, "Rigid rod molecules as liquid crystal thermosets", American Chem. Soc., Poly. Preprints 30 (2) 536–537 (1989)

[93] Grebowicz, JS, "On the formation of liquid crystalline texture in epoxy resins", Macromol. Symp. 104 191–221 (1996)

[94] Kiil, S, "Model-based analysis of photoinitiated coating degradation under artificial exposure conditions", J. Coat. Technol. Res. 9 (4) 375–398 (2012)

[95] Bansal, RK, Sahoo, JC, "Determination of cohesive energy densities of bisphenol-A and epichlorohydrin epoxy resins from swelling measurements", Die Angewandte Makromolekulare Chemie 82 (1265) 149–156 (1979)

[96] Hansen, CM, Hansens solubility parameters. A user's handbook, CRC Press, 2 edn. (2007)

[97] Fried, JR, Polymer science and technology, Prentice Hall Professional Technical Reference, 2 edn. (2003)

[98] Kamaitis, Z, "Structural design of polymer protective coatings for reinforced concrete structures. Part I : Theoretical considerations", Civ. Eng. Management 13 (1) 11–17 (2007)

[99] Sembokuya, HK, Negishi, Y, Kubouchi, M, Tsuda, K, "Corrosion behavior of epoxy resin cured with different amount of hardener in corrosive solutions", Soc. Mater. Sci., Japan 9 (3) 230–234 (2003)

[100] Kalendova, A, "Spinels - reactive pigments affecting the diffusion of corrosive substances through the coatings", Pigm. Resin Technol. 29 (4) 215–221 (2000)

[101] Abacha, N, Kubouchi, M, Sakai, T, Tsuda, K, "Diffusion behavior of water and sulfuric acid in epoxy / organoclay nanocomposites", Appl. Poly. Sci. 112 (2) 1021–29 (2009)

[102] Crank, J, The Mathematics of Diffusion, Clarendon press - Oxford, 2 edn. (1975)

[103] Kalenda, P, "Chemical-resistance values of epoxy resins hardened with polyamines", Pigment Resin Technol. 30 (3) 150–157 (2001)

[104] Moggridge, GD, Lape, NK, Yang, C, Cussler, EL, "Barrier films using flakes and reactive additives", Prog. Org. Coat. 46 (4) 231–240 (2003)

[105] Pajarito, B, Kubouchi, M, "Flake-filled polymers for corrosion protection", J. Chem. Eng. Japan 46 (1) 18–26 (2013)

[106] Choudalakis, G, Gotsis, aD, "Permeability of polymer/clay nanocomposites: A review", European Poly. J. 45 (4) 967–984 (2009)

[107] Kalenda, P, Kalendova, P, "Improved chemical resistance of epoxy resin-based coating compositions", Dyes Pigments 27 (4) 302–312 (1994)

[108] Sørensen, PA, Kiil, S, Dam-Johansen, K, Weinell, CE, "Anticorrosive coatings: a review", J. Coat. Technol. Res. 6 (2) 135–176 (2009)

[109] Ono, S, Tsuda, K, Kubouchi, M, Hojo, H, Nishiyama, T, "Degradation behavior of amine cured epoxy resin and FRP in acid solutions", Proc. ICCM-10 4 215–222 (1995)

[110] Kotnarowska, D, "Influence of ultraviolet radiation and aggressive media on epoxy coating degradation", Prog. Org. Coat. 37 (3-4) 149–159 (1999)

[111] Schmitz, P, Holubka, J, Xu, Lf, "Mechanism for environmental etch of acrylic melamine-based automotive clearcoats: identification of degradation products", J. Coat. Technol. 72 (904) 39–45 (2000)

[112] Rodgers, W, Garner, D, Cheever, G, "Study of the attack of acidic solutions on melamine-acrylic basecoat/clearcoat paint systems", J. Coat. Technol. 70 (877) 83–95 (1998)

[113] Schmitz, P, Holubka, J, Xu, Lf, "Acid etch of automotive clearcoats II. comparison of degradation chemistry in laboratory and field testing", J. Coat. Technol. 72 (902) 53–61 (2000)

[114] Anderson, E, Capon, B, "Intermolecular general-acid catalysis in acetal hydrolysis", J. Chem. Soc. B-phys. Org. (8) 1033–1037 (1967)

[115] Greene, TW, Peter, GMW, Protective groups in organic synthesis, 5 edn, John Wiley and Sons (2014)

[116] Pritchard, G, Reinforced plastics durability, CRC Press (1999)

[117] Kotnarowska, D, "Epoxy coating destruction as a result of sulphuric acid aqueous solution action", Prog. Org. Coat. 67 (3) 324–328 (2010)

[118] Trahanovsky, W, Oxidation in organic chemistry. Part C: Organic chemistry 5C, Academic Press (1978)

[119] Bauer, DR, "Degradation of organic coatings. I. Hydrolysis of melamine formaldehyde/acrylic copolymer films", Appl. Poly. Sci. 27 (10) 3651–62 (1982)

[120] Hojo, H, Tsuda, K, Ogasawara, K, "Form and rate of corrosion of corrosion-resistant FRP resins", Adv. Composite Mater. 1 (1) 55–67 (1991)

[121] Dang, W, Kubouchi, M, Sembokuya, H, Tsuda, K, "An approach to chemical recycling of epoxy resin cured with amine using nitric acid", Poly. 43 (10) 2953–58 (2002)

[122] Dilafruz, K, Kubouchi, M, Dang, W, Sembohya, H, Tsuda, K, "Chemical recycling bisphenol a type epoxy resin based on degradation in nitric acid", 3rd Int. Symp. Env. Conscious Design Inverse Manufact. pp. 333–338 (2003)

[123] Hojo, H, Tsuda, K, "Effects of chemical environments and stress on corrosion behaviors of glass fiber reinforced plastics and vinyl ester resins", Soc. Plast. Ind., Annual Conf. Proc. (1979)

[124] Huisman, HF, van der Linden, JT, "Degradation of polyurethanes in organic solvents", Org. Coat., Sci. Techn. 6 167–182 (1984)

[125] Stevenson, JS, Kusy, RP, "Structural degradation of polyurethane-based elastomeric modules", J. Mater. Sci.: Mater. Medicine 6 (7) 377–384 (1995)

[126] Tanzi, MC, Mantovani, D, Petrini, P, Guidoin, R, Laroche, G, "Chemical stability of polyether urethanes versus polycarbonate urethanes", J. Biomedical Mater. Res. 36 (4) 550–559 (1997)

[127] Vecera, M. and Mleziva, J., "The influence of molecular structure on the chemical resistivity of solventless and high-solid epoxy resins", Prog. Org. Coat. 26 251–263 (1995)

[128] Aguiar, JB, Camões, A, Moreira, PM, "Coatings for concrete protection against aggressive environments", J. Adv. Concrete Technol. 6 (1) 243–250 (2008)

[129] Liu, J, Vipulanandan, C, "Modeling water and sulfuric acid transport through coated cement concrete", J. Eng. Mech. 129 (4) 426–437 (2003)

[130] Valix, M, Mineyama, H, Chen, C, Cheung, WH, Shi, J, Bustamante, H, "Effect of film thickness and filler properties on sulphuric acid permeation in various commercially available epoxy mortar coatings.", Water Sci. Technol. 64 (9) 1864–69 (2011)

[131] White, ML, Leidheiser, HJ, "Laboratory studies of organic coatings in FGD environments", Mater. Performance 24 (11) 9–16 (1985)

[132] Appleman, BA, "Survey of accelerated test methods for anti-corrosive coating performance", Coat. Technol. 62 (787) 57– 67 (1990)

[133] Carniero, C, Oliveira, F, Nogueira, J, "Permeability of paint film towards chloride ion", J. Coat. Technol. Res. 3 (2) 2–5 (2006)

[134] Kubouchi, M, "Evaluation method of degradation of anti-corrosion epoxy lining for concrete structures", in: Third international conference on sustainable construction materials and technologies

[135] Sørensen, PA, Dam-Johansen, K, Weinell, C, Kiil, S, "Cathodic delamination: Quantification of ionic transport rates along coating-steel interfaces", Prog. Org. Coat. 68 (1-2) 70–78 (2010)

[136] Nazemi, MK, Valix, M, "Evaluation of acid diffusion behaviour of amine-cured epoxy coatings by accelerated permeation testing method and prediction of their service life", Prog. Org. Coat. 97 307–312 (2016)

[137] Stuart, B, "Infrared spectroscopy", in: Kirk-Othmer Encyclopedia of Chemical Technology, pp. 1–20, John Wiley and Sons (2005)

[138] Goodhew, PJ, Humphreys, J, Beanland, R, Electron microscopy and analysis, Taylor and Francis Books (2001)