EUROPEAN ADHESIVE ENGINEER

MODULE 4.5

DURABILITY- CHEMICAL EFFECTS ON ADHESIVE JOINTS

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4.5 Chemical Effects on Adhesive Joints

Scope:

- ✓ Often encountered chemical agents
- ✓ Chemical resistance of adhesive by chemical family
- ✓ Chemical resistance of common adherends
- ✓ Methods of bonded joint protection (paints and coatings, water displacing materials, elastomeric sealants)
- ✓ Chemical resistance test methods

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Often enconutered chemical agents [1], [2]

Families of chemicals

- petroleum based fuels, oil, gasoline
- hydraulic fluids, refrigerants
- alkali solutions
- acids and acidic solutions
- salt water
- corrosive gases
- aliphatic and aromatic solvents
- esters and ketones

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Often enconutered chemical agents [2]

Adhesive joints can come into contact with a number of chemicals and organic solvents during service life, sometimes inadvertently through maintenance (e.g. cleaning fluids and paint strippers) and accidents.

Absorption of any fluid (liquids and gases) plasticizes the adhesive, lowering the glass-transition temperature T_g and reducing the stiffness and strength of the adhesive. Other physical changes that can occur include swelling and leaching of soluble constituents (additives) of the adhesive, thus compromising its chemical resistance. Exposure to chemicals and organic solvents will often result in degradation of the adherend-adhesive interface.

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Chemical resistance of adhesives by chemical family [1]

Some organic adhesives tend to be susceptible to chemicals and solvents, especially at elevated temperatures. Most standard tests to determine chemical resistance of adhesive joints last only 30 days or so.

Practically all adhesives are resistant to these fluids over short time periods and at room temperatures.

Some epoxy adhesives even show an increase in strength during aging in fuel or oil over these time periods. This effect is possible due either to postcuring or plasticizing of the epoxy by the oil.

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Chemical resistance of adhesives by chemical family [1]

There are two properties of adhesive joints that protect them from exposure to chemical or solvent environments:

1.) High degree of crosslinking: Most crosslinked thermosetting adhesives such as epoxies, phenolics, polyurethanes and modified acrylics are highly resistant to many chemicals at least at temperatures below their glass transition temperature T_g .

2.) Low exposure area: The adhesive bond-line is usually very thin and well protected from the chemical itself. This is especially true if the adherends are non-porous and non-permeable to the chemical environments in question.

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Chemical resistance of adhesives by chemical family [1]

Adhesive joint designers can take advantage of the low exposure area effect by designing the joint configuration for maximum protection or by specifying a protective coating and/or sealant around the exposed edges of the adhesive.

The temperature of the immersion chemical is a significant factor in the aging of the adhesive. As the temperature increases, more chemical is generally absorbed by the adhesive, and the degradation rate increases.

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Chemical resistance of adhesives by chemical family [2]

Each adhesive has specific attributes that provide protection against a range of chemicals.

The problem for designers and engineers is selecting an adhesive that will guarantee the required design life performance when exposed to the chemicals and solvents that the bonded product is expected to experience during its service life.

This includes secondary environments, such as maintenance activities involving chemical cleaners and paint strippers.

Chemical resistance of adhesives by chemical family [2]

There is no single adhesive that offers a universal solution and protection from all environments.

An adhesive with maximum resistance to acids generally has poor resistance to bases, and vice-versa.

Most thermosetting adhesives tend to be hydrolytically stable in the presence of most organic solvents and moderate acids and alkalis.

Thermoplastic adhesives can be appreciably degraded when exposed to a range of organic solvents, acids or alkalis.

Chemical resistance of adhesives by chemical family [1]

It becomes more difficult to find an adhesive that will not degrade in two widely differing chemical environments.

Generally, adhesives that are most resistant to high temperatures have good resistance to chemicals and solvents because of their dense crosslinked molecular structure resulting in relatively rigid adhesives that must be cured at elevated temperatures.

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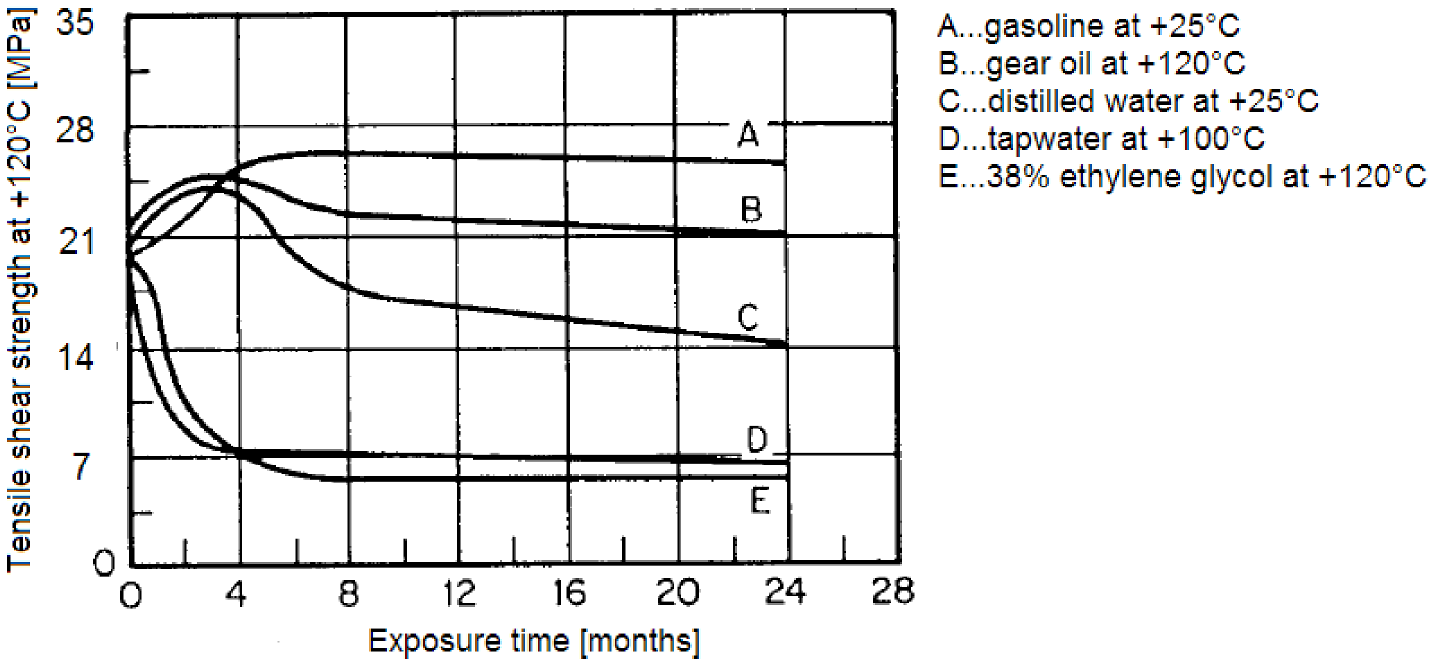
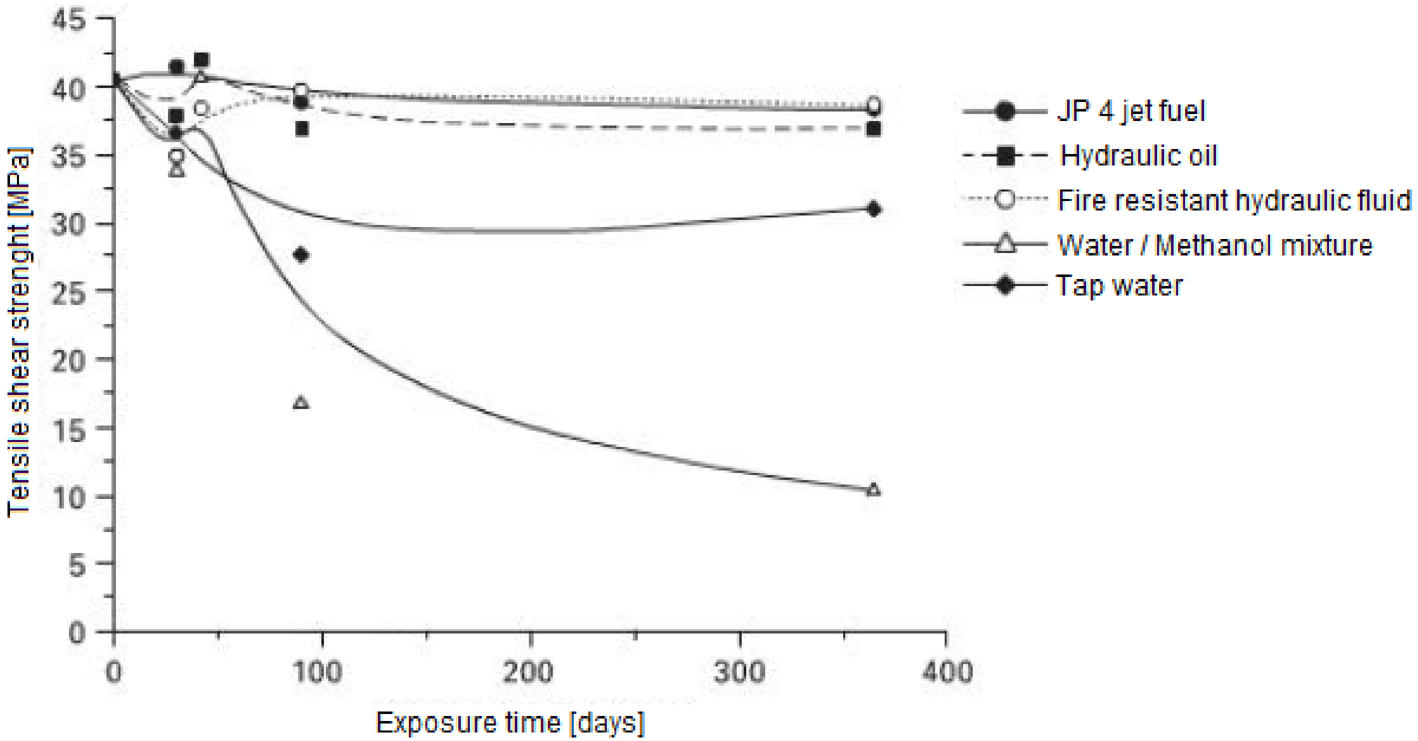
Chemical resistance of adhesives by chemical family [1]



Effect of immersion in various automotive chemicals (adhesive: one part heat curing epoxy ; adherend: Alclad 2024-T3; curing: 20 minutes at +200°C)

Chemical resistance of adhesives by chemical family [2]



Effect of immersion in various aviation chemicals (adhesive: one part heat curing epoxy film ; adherend: Alclad 2024-T3; curing: 60 minutes at +175°C)

Chemical resistance of adhesives by chemical family [2]

Adhesive	Chemical environment					
	Aliphatic solvents	Aromatic solvents	Esters and ketons	Strong oxidants	Strong acids	Strong alkalis (bases)
Acrylics	H	L	L	L	L	M-H
Bismaleimides	H	H	L-M	M	M	M
Epoxies	M-H	M-H	M-H	L	M	M
Phenolics	H	H	M-H	L-M	H	M
Poyimides	H	H	M-H	M	M	M
Polyurenthanes	M-H	L-M	M	M-H	M-H	L-M

L=low resistance; M=moderate resistance; H=high resistance

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Chemical resistance of adhesives by chemical family [1]

Epoxy adhesives:

Generally are more resistant to a wide variety of chemicals and solvents than other structural adhesives. Resistance to a specific chemical agent is strongly dependent on the type of epoxy curing agent used.

Aromatic amine curing agents are generally recommended in preference to other curing agents in epoxy systems for long-term chemical resistance applications. There are exceptions, such as exposure to oxidizing acids (concentrated perchloric acid, chromic acid, nitric acid) and the glass cleaning mixture of chromium trioxide.

Their chemical resistance is usually superior to that of polyesters. Vinyl esters are derivatives of epoxy resins and provide improved chemical resistance over the standard unsaturated polyester adhesives.

Chemical resistance of adhesives by chemical family [1], [2]

Phenolic adhesives:

Nitrile-, vinyl- and neoprene phenolics have outstanding resistance to solvents, salts and non-oxidizing mineral acids.

Acrylic adhesives:

Acrylics are highly sensitive to paint strippers, such as methylene chloride, a common ingredient in many paint strippers used on aircraft.

Polyurethane adhesives:

Chemical resistance to most chemicals, solvents, oils, greases. They are not recommended for use with strong acid or alkali solutions.

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Chemical resistance of adhesives by chemical family [1], [2]

Polyimide adhesives:

These adhesives are vulnerable to chemical attack by chlorinated solvents and ketones. Thermoplastic polyimides are susceptible to environmental stress cracking when exposed to organic solvents, such as acetone, methylethyl-ketone (MEK), toluene, ethylene glycol (deicing fluid), and aircraft fuels. Chemical resistance to strong acids and alkalis is moderate.

Bismaleimide adhesives:

They have very high resistance to solvents even at elevated temperatures, although like other adhesive systems, chemical resistance decreases at elevated temperatures.

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Chemical resistance of adhesives by chemical family [1], [2]

With regard to aging of adhesive joints in chemicals it can be summarized that:

- Organic solvents (acetone, ethyl acetate, toluene) tend to have softening effect on the aircraft adhesives and can cause crazing or cracking of the adhesive.
- Chlorinated solvents (methylene chloride) and ketones are severe environments.
- High boiling point solvents, such as dimethylforamide and dimethyl sulfoxide, are severe environments.
- Acetic, chromic, hydrochloric, hydrofluoric, nitric and sulphuric acids are severe environments.
- Amine curing agents for epoxies are poor in oxidizing acids. Anhydride curing agents are poor in alkalis.
- Aviation fluids (gasoline, JP fuels, hydraulic fluids) can soften some structural adhesives, but far less than most other chemicals and solvents.

Chemical resistance of common adherends [2]

Many structural adhesives are far more resistant to strong acids, salt solutions and oxidative agents than stainless steel or aluminium alloys. It is not unusual in environmental trials for the adhesive to outlast the adherend, with the adhesive remaining unaffected whilst the adherend has degraded.

Certain combinations of adhesive and adherends may pose chemical incompatibility problems with constituents in either the adhesive or adherend migrating to the interface and chemically reacting with the other material, or the service conditions can trigger chemical reactions at the interface.

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Chemical resistance of common adherends [3]

Carbon and low alloy steels:

- resistant in: acetone, alcohols, ammonia, aniline, benzene, chlorine gas, deionized water, Diesel fuels, ethanol, ethylene glycol, gasoline, hydraulic oils, jet fuels, methanol, natural gas

- not resistant in: acetic acid, chlorides, freons, hydrazine, hydrogen sulfide, methane, milk, mineral acids and alkalis, nitrates, organic oils, petroleum, sea water, salt, fresna and distilled water, sulfur dioxide, sulfates

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Chemical resistance of common adherends [3]

Stainless steels:

- resistant in: acetone, alcohols, alkali solutions, ammonia, aniline, benzene, chlorine gas, Diesel fuels, distilled, deionized, fresh and salt water, ethanol, ethylene glycol, freon, gasoline, hydraulic oils, hydrogen peroxide, milk, nitric acid, organic acids, organic and hydrocarbon oils, phenol, urea

- not resistant in: acetivc acid, bromides, chlorides, fluorides, nitrates, sea water, some strong mineral acids, sulfides, sulfue dioxide

Chemical resistance of common adherends [3]

Aluminium and aluminium alloys:

- resistant in: acetic acid, acetone, alcohols, ammonia, benzene, Diesel fuels, ethylene glycol, fluorine, gasoline, heptane, hydrogen peroxide, jet fuels, methane, milk, organic and hydrocarbone oils, pheno, water (distilled, deionized, fresh, salt, sea)

- not resistant in: alkali hydroxides (Ca, K, Mg, Na), aniline, calcium chloride, chlorine, freon, mineral acids

Chemical resistance of common adherends [3]

Polymers:

	ETFE	FEP/PTFE/PFA	FLPE	FLPP	HDPE	LDPE	PC	PETG	PP	PVC
Acids, dilute or weak	E	E	E	E	E	E	E	G	E	E
Acids,** strong / concentrated	E	E	G	G	G	G	G	N	G	G
Alcohols, aliphatic	E	E	E	E	E	E	G	G	E	G
Aldehydes	E	E	G	G	G	G	G	G	G	G
Bases/Alkali	E	E	F	E	E	E	N	N	E	E
Esters	G	E	G	G	G	G	N	G	G	N
Hydrocarbons, aliphatic	E	E	E	G	G	F	G	G	G	G
Hydrocarbons, aromatic	G	E	E	N	N	N	N	N	N	N
Hydrocarbons, halogenated	G	E	G	F	N	N	N	N	N	N
Ketones, aromatic	G	E	G	G	N	N	N	N	N	F
Oxidizing Agents, strong	E	E	F	F	F	F	F	F	F	G

*not for tubing chemical resistance (except pvc)
**except for oxiding acids (see Oxidizing Agents, strong)

E	30 Days of constant exposure causes no damage. Plastic may tolerate for years.
G	Little or no damage after 30 days of constant exposure to the reagent.
F	Some effect after 7 days to the reagent. The effect may be crazing, cracking, loss of strength or discoloration.
N	Not recommended. Immediate damage may occur. Depending on the plastic, the effect may be severe crazing, cracking, loss of strength, discoloration deformation, dissolution or permeation loss.

Chemical resistance of common adherends [3]

Abbreviations of polymers from Slide 22:

ETFE…Ethylene Tetrafluoroethylene
FEP…..Fluorinated Ethylene Propylene
PFA…..Perfluoroalkoxy Alkene
PTFE…Polytetrafluoroethylene
FLPE…Fluorinated High density Polyethylene
FLPP…Fluorinated Polypropylene
HDPE..High density Polyethylene
LDPE..Low density polyethylene
PC…… Polycarbonate
PETG..Polyethylene Teraphalate Gycol-modified
PP…….Polypropylene
PVC….Polyvinyl Chloride

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Methods for bonded joint protection [2], [4]

Chemical resistance of the bonded joint can be enhanced through the application of a protective coating and/or elastomeric sealant around the edges of the adhesive joint.

Elastomeric sealants: The primary function of a joint sealant is to prevent ingress of water or chemical agent to the adhesive bonded joint. They must withstand the effects of changing environmental conditions throughout its effective service life, including the effect of joint movements. To do this, it is required to maintain adhesion to the adjoining joint surfaces. Sealants are not adhesives, having entirely different functions.

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Methods for bonded joint protection [1], [2]

Most important elastomeric sealants:

- Polyurethanes (PUR): particularly suited to harsh environments at sub-zero and elevated temperatures. The operating temperature range is typically – 250°C to +250°C. Movement capacibility in the bonded joint is (+40/-25%).
- Silicones: particularly suited to harsh environments at sub-zero and elevated temperatures. The operating temperature range is typically – 160°C to +250°C. Movement capacibility in the bonded joint is (+100/-50%).
- Polysulfides (PS): Because of their solvent resistance, these materials find use as sealants to fill the joints in pavement, automotive window glass, and aircraft structures. The operating temperature range is typically – 50°C to +1000°C. Movement capacibility in the bonded joint is (+25/-25%).

Methods for bonded joint protection [2]

- Fluorosilicones: are able to offer improved chemical resistance compared with silicones and resistance to aviation fluids (including oils, fuels and greases), oxidation, ozone and weathering is excellent. In a functional temperature range of -60° C to +200° C these materials seem well suited for applications involving harsh environments, but the high costs and special nature of these materials has restricted their use to specific applications, such as seal materials in jet fuel components.

Methods for bonded joint protection [2]

Water displacing materials (corrosion inhibitors): can be either brushed or sprayed onto corrosion-susceptible areas of the bonded joints. However, because of the low surface tension and lubricating properties of these chemicals, concern has been expressed as to their potential side-effects on the fatigue performance of adhesive bonded joints. They can creep under existing water films, displacing the moisture and eliminating the corrosive environment.

Most important chemicals for water displacing materials:

- Calcium sulfonate ($CaSO_3$)
- Barium sulfonate ($BaSO_3$)
- Monoester of boric acid and monoethanolamine-Ethalomine borate ($C_2H_8BNO_3$)

Chemical resistance test methods [1], [5]

ASTM D896-04:

Standard Practice for Resistance of Adhesive Bonds to Chemical Reagents

This practice is designed to determine the general effects of chemical reagents on the strength of the bonded system. It cannot distinguish between adsorption in the bulk adhesive or penetration at the adhesive/adherend interface.

Specimens are immersed in selected chemical for a specified time and temperature. The specimens are recovered, dried, and tested in accordance with selected methods for determining shear strength of a single lap adhesive bonded joint.

Normal testing temperature: 23°C ± 3°C

Normal duration of test: 7 days

Chemical resistance test methods [5]

Standard chemicals for determination of adhesion joints chemical resistance (ISO 175):

Acetic acid, acetone, aniline, benzene, citric acid, distilled water, ethanol, ethylene glycol, hydrocloridic acid, hydrofluorodic acid, heptane, hydrogen peroxide, isooctane, kerozine, methanol, mineral oil, nitric acid, sodium chloride, sodium hydroxide, sulfuric acid, toluene

Supplementary chemicals for specific applications (automotive, aviation, military):

- isooctane/toluene blends (70/30, 60/40, 50/50)
- Diesel fuel grade No. 2 (automotive Diesel fuel)
- JP-4 jet engine fuel (according to MIL-T-5624)
- automotive hydraulic fluids (brake fluid, power steering fluid)
- fire resistant aircraft hydraulic fluid (according to MIL-H-83282)
- aviation anti-icing fluids – Isopropanol (FED TT-I-735A) and Propylene glycol (ISO 11075)

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[2]	D.A. Dillard, Ed.: Advances in Structural Adhesive Bonding, CRC Press, 2010
[3]	https://www.calpaclab.com
[4]	D.E. Packham, Ed.: Handbook of Adhesion, 2. nd ed., J. Wiley & Sons, 2005
[5]	ASTM D896-04: Standard Practice for Resistance of Adhesive Bonds to Chemical Reagents

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