



**ENVIRONMENTAL DEGRADATION
OF GLASS-FIBER REINFORCED
VINYL ESTER**

PUBLIC PART

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Bachelor's thesis
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ABSTRACT

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Environmental Degradation of Glass-fiber Reinforced Vinyl Ester

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The objective of this research was to study vinyl ester composite grating. Vinyl ester polymers are utilized in various chemically challenging environments. This thesis project focused on the chemical resistance of glass fiber reinforced vinyl ester resin. The material characteristics and its suitability to desired operating conditions were the key subjects of the research. To understand the characteristics of the composite product it is essential to understand the properties of the building blocks and their relations. This thesis determines the concept of composites and deals with resin materials and reinforcements.

The material properties were examined under diverse stress. The chemical environments effect on the material was tested with flexural property tests, moisture absorption tests and by visual observation tests. Flexural property tests and moisture absorption tests were exploited by ASTM standards the best way possible. With the designed series of experiments it was possible to understand the mechanical property degradation of vinyl ester composite in chemically challenging environment.

The bachelor's thesis is done from the request of Metso Power Oy. The thesis parts sample material, research methodology, results, discussion, conclusion and appendices are confidential.

Key words: composite, vinyl ester, chemical degradation, moisture absorption

TIIVISTELMÄ

Tampereen ammattikorkeakoulu
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Ympäristön aiheuttama lasikuituvahvisteisen vinyyliesterin hajoaminen

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Tämän tutkimuksen tarkoituksena oli tutkia ritilää, jonka materiaalina oli vinyyliesterikomposiitti. Vinyyliesteri-polymeerejä käytetään useissa kemiallisesti vaativissa ympäristöissä. Tässä opinnäytetyössä keskityttiin tutkimaan lasikuituvahvisteisen vinyyliesterihartsin kemiallista kestävyyttä. Tutkimus keskittyi materiaalin ominaisuuksiin ja sen soveltuvuuteen haluttuun käyttöympäristöön. Jotta on mahdollista ymmärtää komposiittituotteen ominaisuudet, on keskeisen tärkeää ymmärtää rakennusosien ominaisuuksia ja niiden välisiä suhteita. Tämä opinnäytetyö määrittää komposiittikäsitteen ja käsittelee hartsimateriaaleja sekä niiden lujittamiseen käytettäviä materiaaleja.

Materiaalin ominaisuuksia tutkittiin monipuolisen rasituksen alla. Kemiallisen ympäristön vaikutusta materiaaliin testattiin taivutuskokeiden, kosteusabsorptiotestien ja visuaalisten testien avulla. Taivutuskokeissa ja kosteusabsorptiotesteissä pyrittiin hyödyntämään ASTM-standardeja parhaalla mahdollisella. Suunniteltujen koesarjojen avulla oli mahdollista ymmärtää vinyyliesterikomposiitin mekaanisten ominaisuuksien heikkene- mistä kemiallisesti haastavassa ympäristössä.

Opinnäytetyö on toteutettu Metso Power Oyj:n pyynnöstä. Työn osiot opinnäytteen kuvaus, näytemateriaali, tutkimusmenetelmät, tulokset, päätelmät, johtopäätökset ja liitteet ovat luottamuksellisia.

Asiasanat: komposiitti, vinyyliesteri, kemiallinen hajoaminen, kosteusabsorptio

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ABBREVIATIONS AND TERMS

GRP or GFRP	Glass-fiber Reinforced Plastic
AR	Aspect Ratio
HDT	Heat Deflection Temperature
PMC	Polymer Matrix Composite
MMC	Metal Matrix Composite
CMC	Ceramic Matrix Composite
FRP	Fiber Reinforced Plastic
PC	Polycarbonate
PPM	Particles Per Million

1 INTRODUCTION

This thesis project is a composite material research. The objective of this study was to investigate mechanical properties of glass-fiber reinforced plastic (GRP) grating under combined chemical and thermal stress. Projects focus is on composite structure of vinyl ester resin matrix with glass-fiber reinforcement. The aim of the investigations was to examine the compatibility of material to the desired operating conditions.

GRP gratings are specially designed for worktops and flooring for industrial and public services. The advantages of GRP compared to the presently used grade stainless steel are its lower weight and cheaper price. Low weight cuts installation and shipping expenses. Corrosion resistance has made composite materials increasingly utilized in chemical industry and in other corrosive environments.

The research contains material property testing by two main laboratory experiments. Test focus is on monitoring materials mechanical properties and environmental degradation. Effects of combined thermal and chemical degradation are explored by moisture absorption tests and surface microscope observation. The sample material flexural properties and moisture absorption tests are exploited by applying ASTM standard tests.

The possibility of this research is to get results that support utilizing this material in desired chemical conditions. The goal is to replace grade stainless steel with tested composite material. If GRP grating can meet the mechanical performance, reliability and durability requirements, its utilization leads to major cuts in material expenses and makes the production more competitive.

2 COMPOSITE MATERIALS

A composite material is defined to be a combination of two or more separate materials combined as a structural unit. Composite is built of matrix and reinforcement. Matrix is the binding component, which is often a polymer. Reinforcement is the strengthening particle linked by the matrix. Typical reinforcements are glass- and carbon fibers but reinforcement can be also made of metals or other materials. The properties of a composite are a sum of its components. By changing the components and their concentrations composite may be tailored for various purposes.

Mankind has been using composites throughout the times as a construction material. Wood is a natural composite and has excellent strength properties because of its structure. Cellulose molecules form the wood fiber and lignin bonds the fibers as a matrix. As many other scientific inventions composite materials are inspired by nature's examples. Modern plastic composite utilization can be seen to start in the early 1900's. In 1930's composites started commercialize due to polyester and epoxy development. Glass-fiber production for commercial use began in the same decade. (Saarela ym. 2007, 13; Kulshreshtha & Vasile 2002, 1, 27.)

Industry of reinforced plastics began in 1940 mostly by the introduction of fiber glass as a reinforcement material. In World War II polyester resin composites were already in use for aircraft and boat material. In the early 1950s epoxy resin applications for glass-reinforced plastic gave a great boost for composite performance development. In 1951 first supplier of reinforced thermoplastics Fibrefil Inc. was formed. Practically all structural plastics were available with reinforcement by the year 1970. Research and development of reinforced plastics has been led mostly by military, aviation and aerospace industries. (Kulshreshtha & Vasile 2002, 207,208.)

Polymer composites worldwide market was estimated as; 3.24 million tons in 1997, 5.5 million tons in 1998 and in 2000 consumption reached 6 million tons. This development gives a clear vision of the composite material utilization growth. The consumption was distributed in 2000 between continents: 48% USA, 27% Europe, 23% Asia and 2% for South America. (Kulshreshtha & Vasile 2002, 208.)

Composite material markets are wide as can be seen in figure 1. Current uses of composites are mainly examples of metal material replacements in industries, where metals have been and still are in important role. This kind of development pushes composite markets ahead and new applications are found and researched continuously. The figure presents markets of United States but the data is similar worldwide. The figure is based on American Composites Manufacturing Association (ACMA) data from year 2000. The total shipments are estimated to be 1.8 million tons.

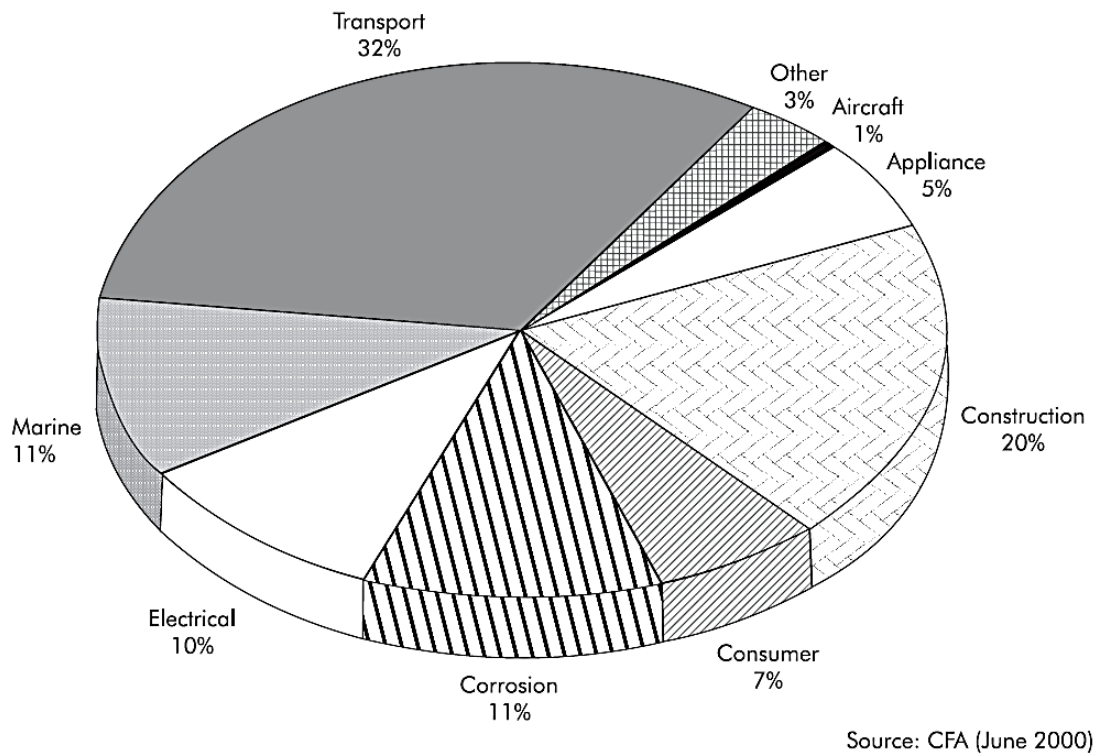


FIGURE 1. U.S. Composite Shipments by Industries (Strong 2008, 12, modified)

2.1 Composites Advantages and Disadvantages

Advantages of composite materials are many and most of all well individualized by tailoring composites to desired applications. Table 1 lists some of composites advantages and disadvantages. These characteristics help understanding composite properties and their competitiveness in material engineering.

Advantages	Disadvantages
<ul style="list-style-type: none"> • Lightweight • High specific stiffness • High specific strength • Tailored properties (anisotropic) • Easily moldable to complex (net) shapes • Part consolidation leading to lower overall system cost • Easily bondable • Good fatigue resistance • Good damping • Crash worthiness • Internal energy storage and release • Low thermal expansion • Low electrical conductivity • Stealth (low radar visibility) • Thermal transport (carbon fiber only) 	<ul style="list-style-type: none"> • Cost of materials • Lack of well-proven design rules • Metal and composite designs are seldom directly interchangeable • Long development time • Manufacturing difficulties (manual, slow, environmentally problematic, poor reliability) • Fasteners • Low ductility (joints inefficient, stress risers more critical than in metals) • Solvent/moisture attack • Temperature limits • Damage susceptibility • Hidden damage • EMI shielding sometimes required

TABLE 1. Composite Advantages and Disadvantages (Strong 2008, 2)

Materials can be classified according to their loading properties in different directions. Isotropic and anisotropic materials behave differently when subjected to bending force from different directions. Isotropic material has symmetric properties from every direction and is normally a bulk material. Metals are a good example of isotropic materials; isotropic properties facilitate design and utilization. Composites in the other hand are anisotropic materials because of the fiber reinforcement. Fibers give composites strength and their orientation and alignment affect directional strength properties. (Campbell 2010, 4.)

The most important properties of composites are: low density, good fatigue life, corrosion resistance and great strength and stiffness properties. Strength and stiffness properties are great especially in relation of composites low weight. As mentioned before great advantage of composites is the ability to tailor the material to optimum properties desired. Tailoring the composition of composites components is common procedure to design the specified material. Tailoring composites structure affects strength and stiffness properties. Anisotropic properties of composites can be faded with laminate structure by varying laminas reinforcement angles. Lamina is a one ply with the same reinforcement orientation and laminate is constructed of stacked laminas to different angles

to reach less anisotropic properties. Continuous-fiber composites are normally laminated structures with multiple laminas with different reinforcement alignments. (Campbell 2010, 7.)

2.2 Comparison to Metals

Composite materials are often compared to metals and metallic alloys, even though the physical characteristics of these two materials are significantly different. Utilization and applications for these materials are closer to one another and composite materials often replace metals in many purposes. Composites anisotropic characteristics provide high in-plane strength and stiffness in certain direction, depending on the reinforcement orientation. Through-the-thickness tensile strength is weak because the stress subjects to the matrix instead of the high-strength fibers. Metals have higher ductility and tend to bend instead of cracking when reaching certain load. Benefits from this character are that it distributes the excess load to adjacent material, which improves static loading by stress relief, and it provides great energy absorption capacity. Composites are relatively brittle and have low ability to resist impact damage without matrix fracturing. Composites ability to withstand cyclic loading is superb compared to metals but their static strength is weak when damaged. The fatigue strength of composites is much higher than metals, and can be ignored unlike in metal structures where fatigue is normally a critical design consideration. (Campbell 2010, 10-14.)

Some of the important properties of metals and composites are compared in figure 2. All composites, steels and aluminum materials are combined into own groups but the data reflects general trends correctly. Figure 2 emphasizes composites superior characteristics over metals. (Strong 2008, 2.)

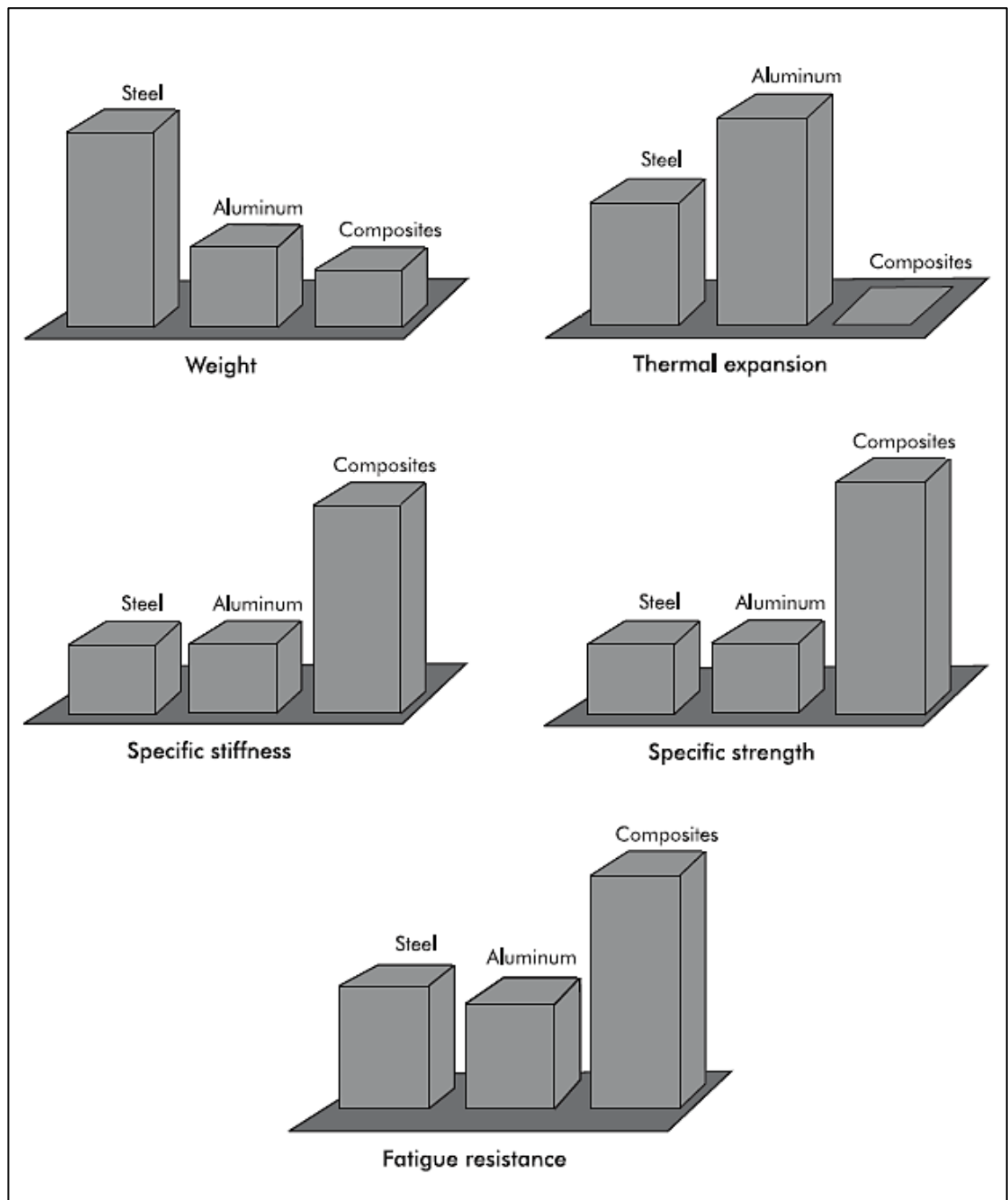


FIGURE 2. Property comparison between steel, aluminum and composites (Strong 2008, 3)

2.3 Polymer Matrix Composites

Composites are classified into four main categories based on their composition: Polymer matrix composite (PMC), metal matrix composite (MMC), ceramic matrix composite (CMC) and carbon matrix composite. Polymer matrix composites dominate the field due to their relatively low processing temperature and superior properties. The use

of polymer matrix composites has shown high growth and especially fiber-reinforced plastic (FRP) utilization has expanded continuously. (Ratna 2009, 281.)

As the expansion of the FRP utilization new applications for the material are researched constantly. This project is a basic example of a research to a new intended usage for composite material. FRPs high corrosion resistance and great strength properties lead to this study of FRPs ability to function in challenging corrosive environment.

Fiber reinforced plastic composites include two major constituents: resin matrix and the fiber reinforcement. Unlike blends, in composites its construction parts fibers and the matrix maintain their identities and together produce properties that could not be achieved with either acting alone. The fibers are high strength and are normally responsible of the load-bearing properties of composites. The matrix resin keeps the fibres orientated. The load on a FRP composite material is distributed into the fibres through the resin matrix. The matrix is responsible of the shear properties, maximum operating temperatures and the chemical resistance of the composite. Still the mechanical properties cannot be predicted straight from the components because the properties originate from various complex mechanisms. (Ratna 2009, 283, 284 & Military Handbook 1991, 1-2.)

Polymer matrix composites are classified to thermoset resin composites and thermoplastic resin composites due to the polymer matrix material. Thermosets are constructed of crosslinked polymer net. Thermosets are not possible to form more than once. Thermoplastics are made of long polymer chains, which have weak bonds. When heated, polymer chains are able to move which allows material re-forming. Thermoplastic is an amorphous material and it has no certain melting point, it softens as temperature rises. Thermoset composites dominate the field due to their availability, relatively easy processing, low material cost and lower cost of capital equipment for processing. Excellent flow properties of thermosets facilitate resin impregnation of fibre bundles and resins fiber surface wetting. Thermoset curing or crosslinking reaction converts them into a three-dimensional network form, which is infusible and insoluble. The crosslinked structure offers better creep properties and environmental cracking resistance compared with many thermoplastics. (Military Handbook 1991, 4-1 & Ratna 2009, 281.)

3 COMPOSITE COMPONENTS

Major changes in the properties of a composite can be done by adding special additives to reach certain performance specifications. Additives are solid fillers and reinforcements that differ from the polymer matrix with their composition and structure. Fillers basic role is to lower the cost of the polymer bulk. Reinforcing fillers are used to improve the physical and chemical properties of the polymer. Reinforcing fillers can improve properties like stiffness and strength, resistance to creep and fatigue failure. Non-mechanical properties like electrical properties, abrasion resistance and flammability can also be enhanced by reinforcing fillers. (Kulshreshtha & Vasile 2002, 39.)

Mechanical properties improving fibers and laminar structure are considered as reinforcements as ball type particles are count as fillers. Inert fillers are used to increase the bulk, ease the processing and to lower the price. With active fillers and reinforcements specific physical and mechanical improvements are produced to tailor modulus, tensile and impact strength, dimensional stability, electrical properties and heat resistance. Most fillers increase the weight of the compound but some have been developed to reduce it. Fillers and reinforcements improve properties but may reduce or degrade other performances at the same time. Tailoring composite properties is basically development of the specific mixture of polymer, reinforcements and fillers. (Kulshreshtha & Vasile 2002, 40.)

Matrix resin is the protective cover for the fiber reinforcement. Matrix's basic role in composite is to bind the fibers together and protect them from the environment. Matrix material provides the composite with impact and abrasion resistance, toughness and damage tolerance. Individual properties of the matrix material determine the composites final properties including maximum usage temperature, moisture and fluid resistance, and thermal and oxidative stability. (Campbell 2010, 63.)

3.1 Particulate Fillers

Property improving effects of fillers are resulted by their chemical functions in the compound. Functions of active fillers can be attributed by three causes; chemical bond formation between the filler and the reinforced material, immobilization of polymer attached to the filler by valence bonds, uniform distribution of energy absorption caused by impact leading to increase impact strength. The most important characteristics of fillers in plastic are: chemical composition, diameter and shape, grain distribution, specific surface, surface energy, thermo-oxidative and UV-stability and moisture and water soluble compounds content. (Kulshreshtha & Vasile 2002, 40.)

Composites contain large volumes of particulate fillers. Non-reinforcing particulate fillers often lower the physical properties and increase water absorption of the matrix resin. Fillers are cheaper than the polymer matrix and that is why they are used with maximum volume possible. The goal is to lower the costs of the compound and by that improve production cost efficiency. Effects are shown as changes in glass transition temperature, modulus of elasticity and in composite hardness. Particulate fillers producing reinforcing effects are fillers with low aspect ratio and needle like shape, plate-like or roughly spherical particles. Aspect ratio (AR) is the ratio between length to thickness. These reinforcing fillers improve composites stiffness, hardness and heat deflection temperature. Heat deflection temperature (HDT) is the temperature at which polymer deforms under specified load, it is simplified to be the temperature where polymer starts softening. (Kulshreshtha & Vasile 2002, 43, 44.)

Most of the particulate fillers used in plastic composites are listed briefly. With a few exceptions these fillers are treated with silane coupling agents in a variety of plastic composites. (Kulshreshtha & Vasile 2002, 43, 44.)

- Silica
- Silicate
- Calcium Carbonate
- Metallic Oxides
- Metals, Fillers and Filaments
- Salts
- Other Fillers

Listed fillers have subclasses of different substances or structural forms of the chemical. Different fillers are used in specified particle sizes and shapes to receive desired effects.

Silica and silicates are both natural and synthetically produced. They are used to produce functions like: shrinkage reduction, reinforcement, dimensional stability improvement, electrical properties, increase hardness, thickening, rheological and thixotropic effects. (Kulshreshtha & Vasile 2002, 48.)

Calcium carbonates are the most used fillers in plastic because of their low price and property improving nature. Calcium carbonates mainly occur naturally in the form of chalk, limestone or marble. Filler is produced by fine milling or synthetically by precipitation. The synthetically precipitated filler is more expensive than the one milled of chalk. Properties of calcium carbonate fillers are: high degree of whiteness which can be utilized to substitute high cost white pigments, reduce shrinkage, increase stiffness and modulus of elasticity, improve the surface quality and improve stability and ageing resistance. (Kulshreshtha & Vasile 2002, 47.)

Metallic powders of aluminium, bronze, copper and nickel are used in thermoplastics in order to improve thermal or electrical conductivity. Metallic fillers are expensive. Metallic oxides are also supplied for selective changes such as aluminium oxide for improved electrical values, zinc oxide for weathering stability, beryllium oxide for thermal conductivity improvement, iron oxides for magnetic properties, lead oxides to increase density and magnesium oxide to increase stiffness. (Kulshreshtha & Vasile 2002, 48, 49.)

Salts are also used as fillers in composite polymer matrix. Calcium phosphate, calcium sulphate, barium sulphate and potassium titanate are the filler salts. Calcium sulphate is an extender to improve mechanical properties like impact, tensile and compressive strength. Barium sulphate increases chemical resistance, specific gravity and friction resistance. (Kulshreshtha & Vasile 2002, 46.)

Other fillers include silicon carbide, carbon black and graphite, carbon fibers, ceramic microspheres, organic fillers are wood flour, nut shells, corncobs, rice and peanut hulls. Polymer particles are also used as fillers as are cellulose fibres and whiskers. (Kulshreshtha & Vasile 2002, 46.)

3.2 Reinforcements

The reinforcing phase of the composite provides the material with strength and stiffness. Reinforcements are usually fibers or particulates. Normally the reinforcement is harder, stiffer and stronger than the matrix material. Particulate reinforcements are spherical, platelets or other shapes or forms; their aspect ratio is clearly smaller than that of fibers. Particulate reinforced plastics tend to be much weaker than fiber reinforced composites, but they are usually much cheaper. Fiber reinforcements are made of continuous fibers or discontinuous fibers. This research focuses on continuous fiberglass reinforced plastic composites. (Campbell 2010, 1.)

Reinforcement's type and quantity defines composites final properties. Highest strength and modulus of elasticity are reached with continuous fiber reinforcement. Discontinuous-fiber reinforcements have normally smaller aspect ratio and are randomly orientated. Random orientation and discontinuous-fiber reinforcement reduce strength properties but are much less expensive compared to continuous-fiber composites. Continuous-fiber composites are used when high strength and stiffness are needed and discontinuous-fiber composites are for applications where cost is more important than strength properties. Reinforcements can also be woven fabric of desired fibers. Different reinforcing types of fiber orientation are presented in figure 3. (Campbell 2010, 2.)

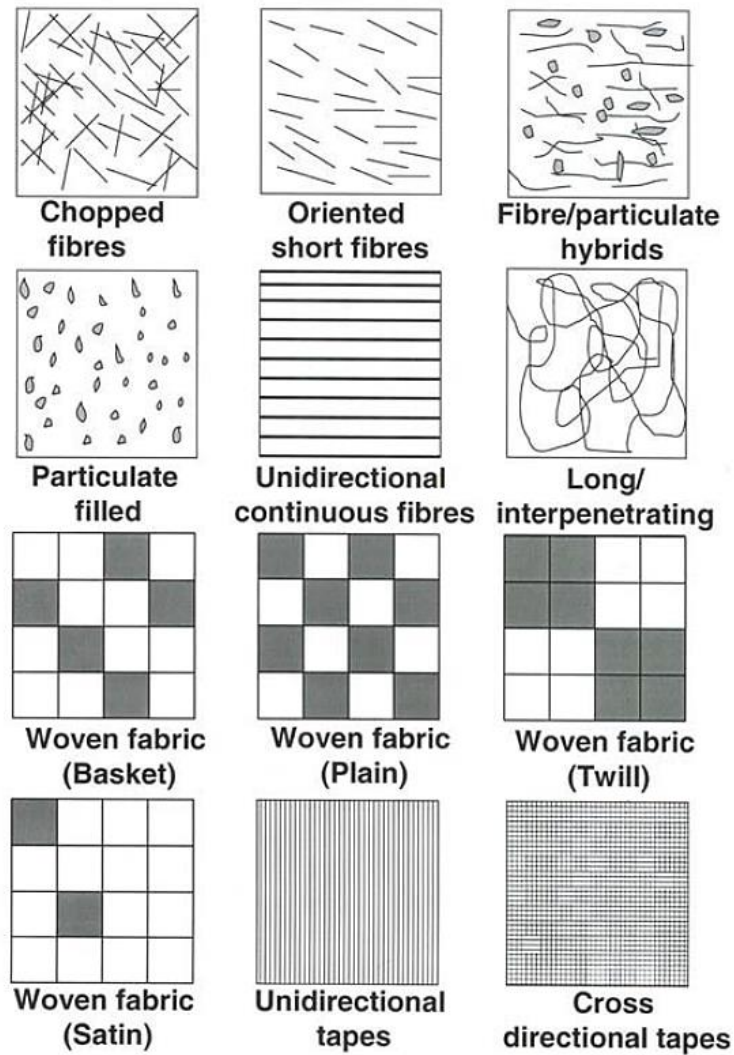


FIGURE 3. Various types of composite reinforcements (Ratna 2009, 283)

Reinforcing fibers can be used in composites with volume as high as 60 to 70 per cent. Above that level there is not enough matrix resin to fully wet the fibers and hold them in place. Reinforcement's type and volume determines strength and stiffness properties as well as the price of the product. This relation is shown in figure 4. Small diameter of fibers produces high strength properties because they contain few defects compared to traditional bulk material. Basically the smaller is the diameter of the fiber the higher is its strength, even though fiber comes more expensive as the diameter gets smaller. Small diameter fibers with high strength have great flexibility which eases most fabrication processes. Typical reinforcing fibers include glass, aramid and carbon. (Campbell 2010, 1.)

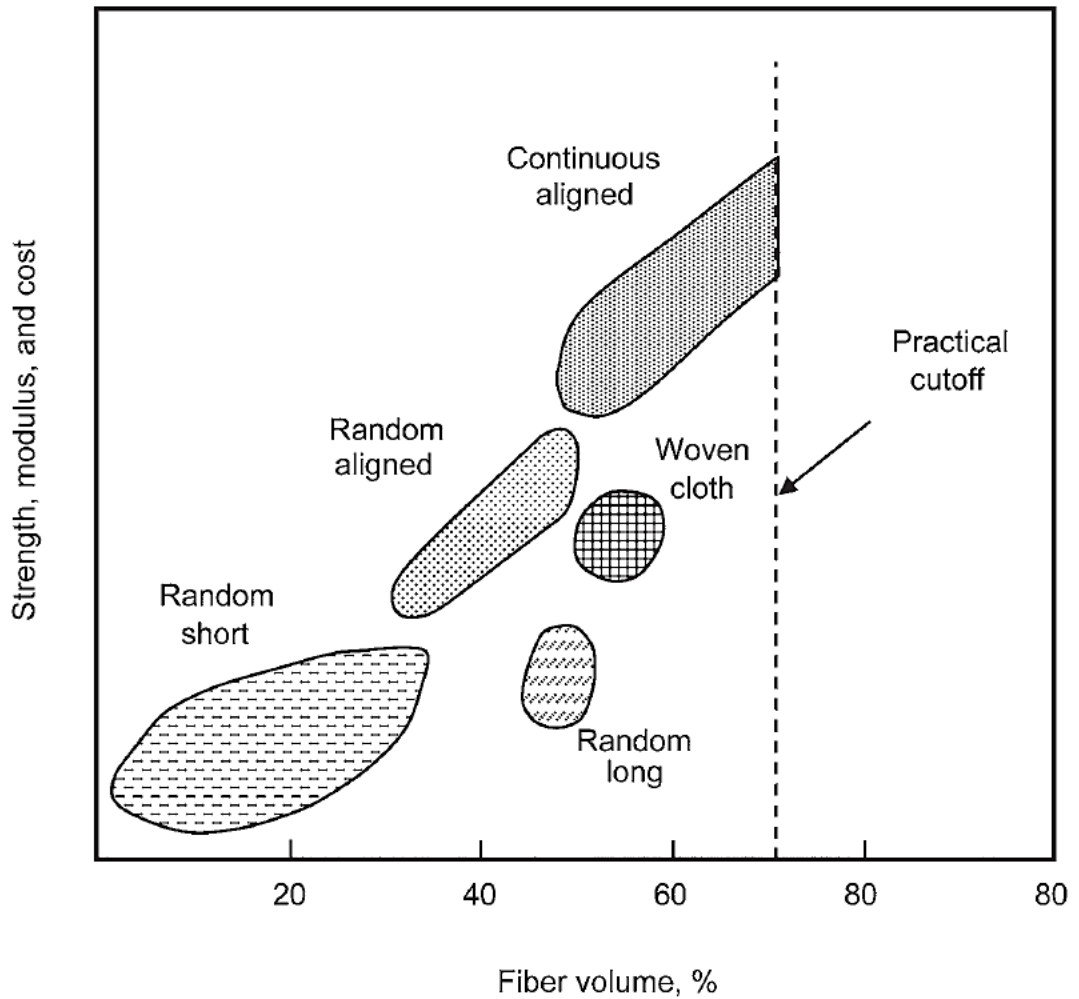


FIGURE 4. Composites performances relation to reinforcement type and volume (Campbell 2010, 3)

Fibers internal molecular structure is orientated in the lengthwise direction. This explains fibers exceptional strength and stiffness in the long direction compared to the other directions. Internal molecules are orientated usually by drawing the solid but pliable fiber in the long direction. This process orients the molecules uniformly along the length of the fiber. When the fiber is forced under a load, the force subjects to the molecular chains themselves rather than against a mere entanglement of the chains. Fibers lengthwise oriented molecule chains form a strong polymeric backbone to the fiber. (Strong 2008, 199.)

Inorganic fibers are utilized in composites because of their thermal resistance and compatibility with most matrix materials. Commercially used inorganic fibers are based on

silica, aluminum, boron, silicon carbide and high melting temperature metal fibers. Table 2 presents the chemical composition of inorganic fibers. (Campbell 2010, 61.)

Material	Components (%)						
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O + K ₂ O	B ₂ O ₃
A-glass	72.0	<2.5	≤0.5	5-10	0.4-4.0	<15.0	≤0.5
C-glass	60-66	<6.0	<0.3	≤14.0	<3.0	8-15	2-7
D-glass	72-75	<0.5	0.2	-	0.2	1.3	22
E-glass	50-56	12-16	0.3	16-25	<6.0	<2.0	6-13
R-glass	60	25	0.3	6-9	6-9	0.4	-
S-glass	65	22-25	0.2	<8.81	10-18	<1.1	<8.81
Quartz	>99.95						
C- 1 (Nextel 312)	24	62					14
C- 2 (Nextel 448)	28	78					2
Al-1	15	85					
Al-2 (Soffil)	3	97					
Al-3 (Fibre FP)		>99					

A-glass belongs to the group of alkaline-limestone glass (A-alkaline); C-glass belongs to the group of alkaline-limestone glass, but it has a higher proportion of boron trioxide (C-chemical corrosion endurance);
D-glass is a technical glass rich in silicon dioxide (D-dielectric properties);
E-glass has aluminium trioxide apart from silicon dioxide and boron trioxide (E-electrical applications);
ECR-glass, in addition to silicon dioxide and calcium oxide, has as main component aluminium trioxide (ECR – electro chemical resistance);
R-glass, apart from the standard main components of aluminium trioxide and silicon dioxide, has additions of calcium and magnesium oxides (R-resistance to fatigue, thermal shock and moisture);
S-glass belongs to the group of aluminosilicate glass (S-stiffness, for mechanical requirements);
C-1, ceramic 1 fibre;
C-2, ceramic 2 fibre;
Al-1, alumina 1 fibre;
Al-2, alumina 2 fibre;
Al-3, alumina 3 fibre.

TABLE 2. Inorganic fibers chemical composition (Campbell 2010, 62)

Fiber properties are generally compared in table 3. This table includes fibers commonly used in composites along with some metals that might compete in some applications. Density unit g/cc means grams per cubic centimeter and is equal to g/cm³. Strength and

modulus values are listed in American ksi and Msi units but SI-unit values can be found in brackets.

Fiber Type	Density, g/cc	Tensile strength, ksi* (MPa)	Tensile Modulus, Msi** (GPa)	Elongation to Break, %
Glass (E-glass)	2.5	500 (3,447)	10 (69)	4.9
Glass (S-glass)	2.5	665 (4,585)	12 (83)	5.7
Carbon/graphite (standard modulus)	1.8	600 (4,137)	33 (228)	1.6
Carbon/graphite (intermediate modulus)	1.8	780 (5,378)	40 (276)	1.8
Carbon/graphite (ultra-high modulus)	1.9	500 (3,447)	64 (441)	0.5
Aramid (high toughness)	1.4	523 (3,606)	12 (83)	4.0
Aramid (high modulus)	1.4	580 (3,999)	19 (131)	2.8
Aramid (ultra-high modulus)	1.5	494 (3,406)	27 (186)	2.0
Ultra-high-molecular-weight polyethylene (UHMWPE) (standard modulus)	0.97	375 (2,585)	17 (117)	3.5
UHMWPE (high modulus)	0.97	435 (2,999)	25 (172)	2.7
Boron (on tungsten)	2.5	500 (3,447)	56 (386)	0.9
SiC	3.0	500 (3,447)	60 (414)	1.8
Flax	1.5	116 (800)	9 (62)	2.5
Spider silk	1.3	145 (1,000)	14 (97)	35
Steel	7.8	145 (1,000)	29 (200)	30
Aluminum	2.8	70 (483)	10 (69)	20
Titanium	4.5	166 (1,145)	25 (172)	30
Magnesium	1.8	40 (276)	7 (48)	15
*ksi = psi × 10 ³ , **Msi = psi × 10 ⁶				

TABLE 3. Property comparison of several key fiber types (Strong 2008, 200)

The most commonly used fiber materials; glass, carbon and aramid have quite high tensile strength values, but not significantly high compared to other materials. Modulus properties of all listed fiber materials are also in quite small range. Elongation values of metals are clearly higher than most used fiber types. (Strong 2008, 199.)

It has to be noted that commercial utilization of materials focuses on all of the properties combined. In the bigger picture all of the properties are viewed in relation to each other. Mechanical properties are often in relation to density and this viewpoint benefits most common fiber materials. Manufacturing properties are also in great value. Maybe the most important property of any material nowadays is its cost. Availability, service life, maintenance, shipping expenses and installation are all properties that influence the material choice. In a broad perspective glass, carbon and aramid fiber reinforcements stand out from the mass of other materials.

When materials mechanical properties strength and modulus of elasticity are compared they are often combined with material density. These values are specific strength and specific stiffness and they are calculated by dividing tensile strength or tensile modulus by materials density. This gives better view of materials physical properties in applications where weight plays a part. Figure 5 presents various materials specific strength and specific modulus. These charts emphasize the reasons why traditional fiber types have achieved their position. (Strong 2008, 199, 203.)

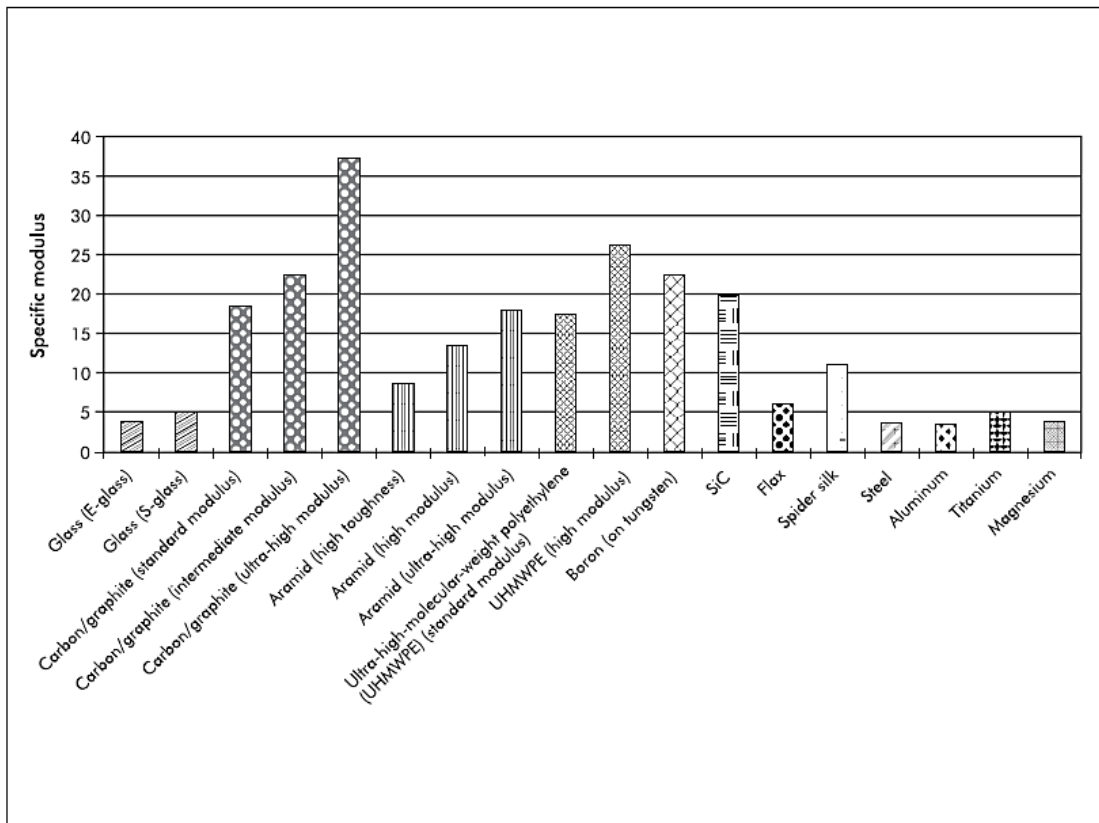
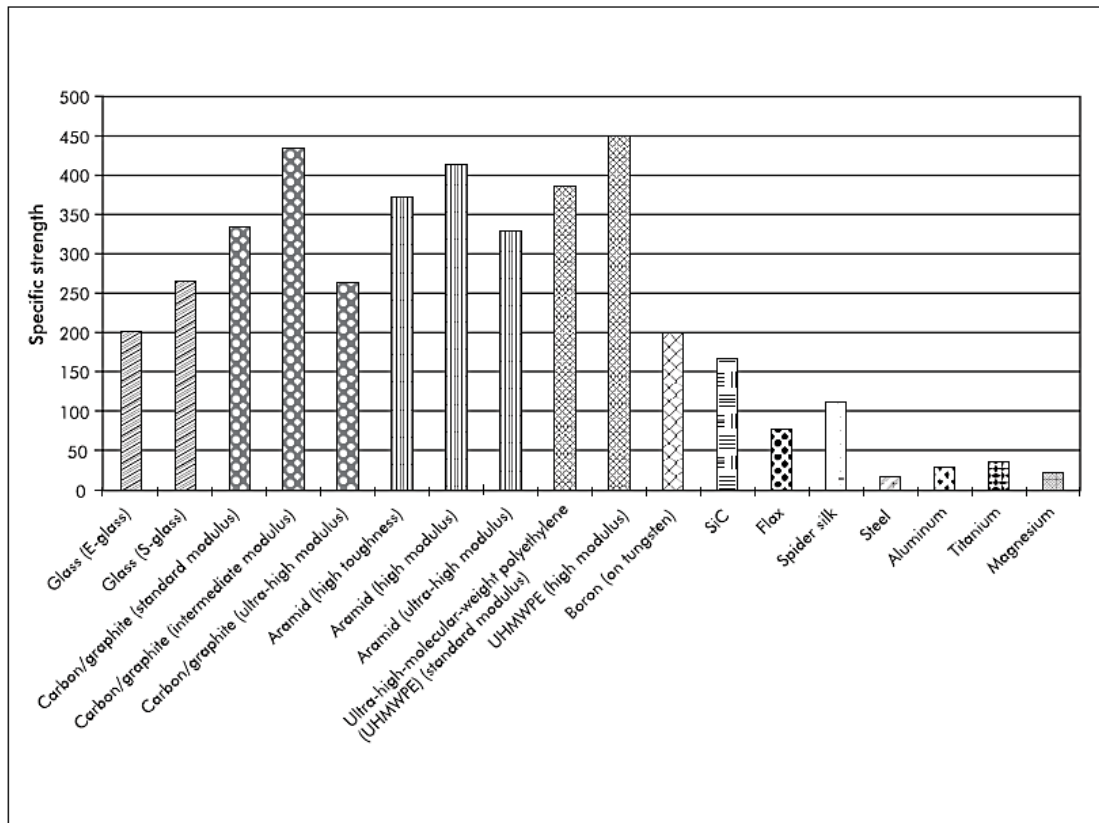


FIGURE 5. Specific strength and modulus of various materials (Strong 2008, 201, 202, modified)

3.2.1 Glass Fiber Reinforcement

Fiberglass dominates the reinforcing material industry due to its low price and excellent properties. The main advantages of glass fibers are low cost, highly crosslinked polymer, high tensile strength, great chemical resistance and excellent insulating properties. Because of the great insulating properties fiberglass was originally intended as an insulation material. Glass fibers disadvantages are: low tensile modulus, relatively high weight, relatively low fatigue resistance and high hardness. Glass fibers are sensitive to abrasion and with frequent handling it decreases tensile strength. High hardness causes excessive wear on moulding dies and cutting tools. (Strong 2008, 203 & Kulshreshtha & Vasile 2002, 64.)

Despite the great properties, glass fibers cannot match the high specific strength and specific modulus of carbon fibers, as can be seen in figure 5. Carbon fibers have the highest strength and modulus properties of all reinforcing fiber types. Because of the high cost of carbon fibers they are only used high performance applications.

Glass is an amorphous material and is based on silica backbone with many oxide components to improve specific properties. Glass fibers are made of silica sand, limestone, boric acid and smaller amounts of clay, coal and fluorspar. There are many types of glass fibers with specific properties and compositions. E-glass is the most commonly used type with good electrical and weathering properties, dimensional stability, good strength and stiffness, moisture resistance and most of all low cost. E-glass was originally used to get high strength and high electrical resistivity, though electrical properties are not important in most composite applications. S-glass has the highest strength and modulus of all glass fibers and high temperature resistance. S-glass was originally developed for aviation industry and has also a lower cost version S-2-glass. S-glass's manufacturing costs are higher which makes it more expensive than E-glass. S-glass is normally used in advanced composites where high strength is more important than increased expenses. (Kulshreshtha & Vasile 2002, 64.)

Less used glass fiber types are A-glass, C-glass and D-glass. A-glass is used in applications where the material is not subjected to stress and exposed neither to weathering or moisture. C-glass is a chemical glass type suitable for acidic environment with low strength requirements. Dielectric D-glass is only used in electric insulating materials.

There are also three glass fiber types for other special applications with high strength and good thermal and radiation stability: AR, M and R. These three types are very expensive. Table 4 presents some of glass fiber types discussed and their main properties. (Kulshreshtha & Vasile 2002, 64.)

Properties	A-glass	C-glass	D-glass	E-glass	R-glass	S-glass
Specific gravity, g/cm ³	2.48-2.50	2.49	2.16	2.54-2.60	2.5	2.49
Tensile modulus, GPa	45.5	70	55	72-75	88	87
Tensile strength, GPa	2.9	3	2.5	3.5	4.7	4.6
Maximum applied temperature, °C	785	749	763	600-846	928	760
Dielectric constant, 10 Hz	6.3	6.9	6.5	5.1	5.8	5.2
Thermal expansion, 10 ⁻⁶ m/m.K	8.6	7.5	6.8	8.2	5.6	5.6

TABLE 4. Glass fiber property comparison (Kulshreshtha & Vasile 2002, 63)

To help understanding the properties and behavior of glass fiber it is essential to know something about the components and the fabrication process. The manufacturing is basically just melting the right mixture of components and forming fibers from it. Just to understand this process it is useful to briefly go through the steps.

When pure silica is heated above 1720 °C and quickly cooled, it forms an amorphous or random orientated atomic structure of glass. High-strength glass fibers are fabricated by blending the components and melting them in a three-stage furnace, extruding the glass molt through bushings and cooling the formed filaments with water or air. After the cooling, the filaments are coated with chemical sizing in order to avoid mechanical abrasion and then gathered and packed. The fabrication process can be divided into five steps: batching, melting, fiberization, coating and packaging. Schematic model of the manufacturing process is presented in figure 6. (Campbell 2010, 34, 36.)

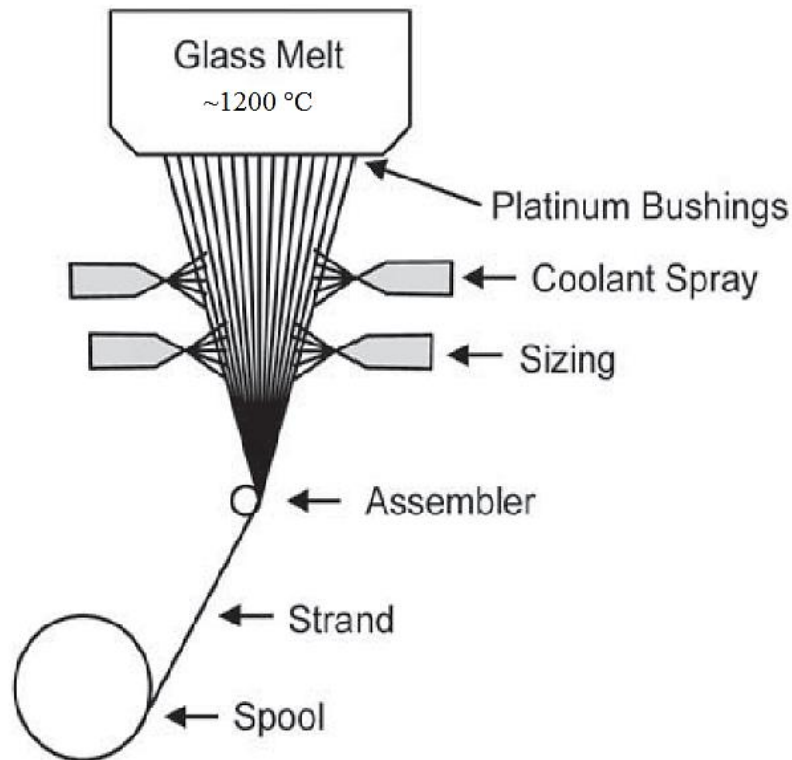


FIGURE 6. Glass fiber fabrication process (Campbell 2010, 37, modified)

Glass fiber coating is done to protect the brittle fibers from flaws and defects. Fibers high strength depends on the undamaged surface. Flaws are nanometer-size cracks and fibers tensile strength depends on the internal stresses at the surface. The surface layer is only one nanometer thick but it is in the control of the strength of the fiber. Untreated glass filaments are very vulnerable to degradation by mechanical abrasion. That is why sizing is done immediately after manufacturing to prevent scratch formation on the surface during spooling or other textile processes. Sizing is an extremely thin layer usually of starch or lubricant and may already contain coupling agent. The sizing can be removed from the fiber surface after all mechanical operations are completed. After the remove of the sizing, it is replaced with surface chemical which improves fibers adhesion to matrix. Basic idea of these coupling agents is to have one end group compatible to glass fibers silane structure and the other end compatible with the matrix. Coupling agents are critically important to the performance of glass-reinforced composites, strength properties can be improved over 100 per cent with its right usage. Coupling agents also protect the glass fiber surface form water. Final procedure in glass fiber fabrication is the packaging. The drawn and sized filaments are gathered into a bundle of

51 to 1624 filaments forming a glass strand. Then the strand is wound into a package roll and dried in oven. (Campbell 2010, 37-39.)

Glass fibers modulus and fatigue properties cannot compete with high-strength carbon fibers, but its tensile strength is comparable to carbon fibers. Under a static tensile load glass fibers lose their strength with time so their fatigue properties are weaker than carbon fibers. Still GRPs have significantly higher fatigue resistance than metals. Glass fibers do not absorb water into their bulk but when subjected to moisture, water molecules are attached to the surface forming a very thin softened layer. This layer can affect fiber strength because the water with other surface active substances can produce microcracks on the surface. As mentioned before the strength of the fiber is related to the surface structure and when its damaged fiber loses great deal of its strength. Humid conditions reduce glass fibers strength under continuous loading, as the moisture adsorbed onto the surface of the flaw reduces surface energy, thus promotes slow crack growth. (Campbell 2010, 39.)

3.3 Matrix Resin

Polymer matrices for composite materials are divided into thermosets or thermoplastics. Thermosets are monomers with low molecular weight and low viscosity. Curing converts them into three-dimensional crosslinked structure which is infusible and insoluble. Crosslinking is driven by heat generated externally or by the exothermic chemical reactions. As curing process progresses the reactions accelerate and the mobility of the molecules decrease leading to higher crosslinking and increase in viscosity. After the polymer resin gels and forms a rubbery solid it cannot be remelted. Further heating cures the resin fully and monomers are highly crosslinked forming a polymer. Thermoset curing is a thermally driven event requiring large amount of chemical reactions which makes their processing time-consuming. Thermoplastics are high molecular weight polymers that does not crosslink, thus they do not need long curing cycles. Thermoplastics can be melted, formed again and hardened by cooling, even though due to their high viscosity and high melting points, processing requires high temperatures and pressures. Difference of the structure between thermosets and thermoplastics is presented in figure 7. (Campbell 2010, 65.)



FIGURE 7. Thermosets have crosslinks all over the structure as thermoplastics are independent macromolecules tangled together (Architecture and Plastic, modified)

Thermoset matrices include polyesters, vinyl ester, epoxies, bismaleimides, cyanate esters, polyimides or phenolics. Common thermoplastic matrices include polyethylene, polypropylene, nylon, polycarbonate, polyethylene terephthalate, polyvinyl chloride, acrylic and acetal. Epoxy matrix materials are the dominant resin used in low and moderate temperatures. All of the listed matrix materials have their own polymeric characteristics and are used in various applications, epoxies and polyesters being the most

widely used in commercial applications. As discussed before, the composite properties are a combination of the reinforcement and the matrix, though there are some properties that are so called matrix-dominant. Most of all composites thermal properties are based on matrix resin properties. As the matrix is the protective shell for the reinforcement, it is in charge of environmental properties such as moisture- and chemical resistance, fire-retardant, electrical resistance and radiation properties. (Strong 2008, 28)

Vinyl esters are the researched matrix material of this study. Vinyl esters are highly chemical resistant and that is why they are used in chemical processes and other corrosive environments. They have a good strength properties and a low ability to moisture absorption. Vinyl esters are introduced fully in the following chapters.

4 VINYL ESTERS

Throughout many years scientists have been trying to find a composite matrix material for corrosive environments. Composite materials have been a great interest of chemical engineering industry and other industries with the need of great chemical resistance. Unsaturated polyesters, “standard” polyesters and bisphenol-A fumarate type polyesters have been studied to match the requirements of corrosive environment. All of these matrix materials have shown low stability under ageing. Standard cured polyesters have weak chemical resistance especially against hydrolysis, and epoxies are known for their challenging processing properties. Bisphenol-A fumarate type of polyesters have a good chemical resistance but their mechanical properties are poor. (Kulshreshtha & Vasile 2002, 365.)

As the advanced resin materials are discussed, their properties are examined and normally compared to convenient reference materials polyesters and epoxies. In some cases their properties are also compared to metals as they are competitors in some aspects. Some knowledge of material and polymer sciences will help understanding the property characteristics discussed. (Strong 2008, 115.)

Vinyl ester resins have been found to answer the need of composite matrix material in corrosive environments. Popularity of vinyl esters is resulted by their combination of good price and chemical properties. Vinyl ester is a thermoset resin which has great chemical resistance and good mechanical properties. They can be fabricated with the same mechanisms as conventional polyesters. The fabricator is able to combine epoxies mechanical properties with the easy processing in use of unsaturated polyesters. Vinyl esters low molecular weight allows a high volume of fillers added. Fillers can be used 60 to 70% by weight and this leads to lower price. Vinyl esters are a bit more expensive than unsaturated polyesters but not as expensive as epoxies. Furthermore, they have a good capability of wetting the reinforcing fibers. Another advantage is vinyl esters low styrene content that can be used; this alleviates some of the styrene emission problems occurring during polyester manufacturing process. (Kulshreshtha & Vasile 2002, 365 & Strong 2008, 115.)

Vinyl ester resin has been used in GRPs and FRPs for over four decades in chemically challenging environments. Traditional construction materials like steel, titanium and other metals cannot be used in construction of chemical plants which deal with aggressive chemicals. Vinyl ester resin composites can tolerate strong acids, bases, solvents, oxidizing agents, hypochlorite and very hot gasses. Chemical unit processes often combine challenging chemical environments with high temperature and major mechanical forces. As a construction material for process plants FRP has proved itself to be one of the most cost effective materials. High chemical resistance against wide range of chemicals and great temperature performance combined with relatively low price and excellent mechanical properties make vinyl ester resin FRP an outstanding material for chemical engineering. (Kulshreshtha & Vasile 2002, 366.)

4.1 Epoxy Vinyl Ester Resins

Bisphenol-A epoxy vinyl ester was found in the late 1960's to answer the need for corrosion resistant and mechanically good matrix resin. As polyester resins could not answer the need in chemical resistance and Bisphenol-A fumarate polyesters had problems with toughness, Bisphenol-A epoxy vinyl ester was both tougher and better in chemical resistance. This new type of resin improved FRPs mechanical and thermal properties and could be used in wider variety of chemical environments. Chemical resistance of Bisphenol-A epoxy vinyl ester was equal or better than more expensive high nickel alloys and superior compared to stainless steel. (Kelley, Graham & Johnson, 3.)

The chemical structure of Bisphenol-A "Vinyl Ester" is shown in figure 8. Polymers ester groups are chemically most active part of the molecule and because of that the most vulnerable to chemical attack. In Bisphenol-A epoxy vinyl ester there is only two ester groups per molecule, they are highlighted in the figure 8. This explains polymers great chemical resistance. The Bisphenol-A group in the brackets gives toughness to the resin and by that makes it more resistant to mechanical and thermal stress. Furthermore, resins multiple ether linkages add their chemical resistance. Also the backbone of the resin has several hydroxyl groups (OH^-) which provide more opportunities to hydrogen bonding and that improves adhesion to fibers and increases the total number of bonds. Bisphenol-A epoxy vinyl ester resin material has been so successful in chemical appli-

cations that it has become moreover the industry standard in the field of corrosion resistant composite matrix resins. (Kelley, Graham & Johnson, 4.)

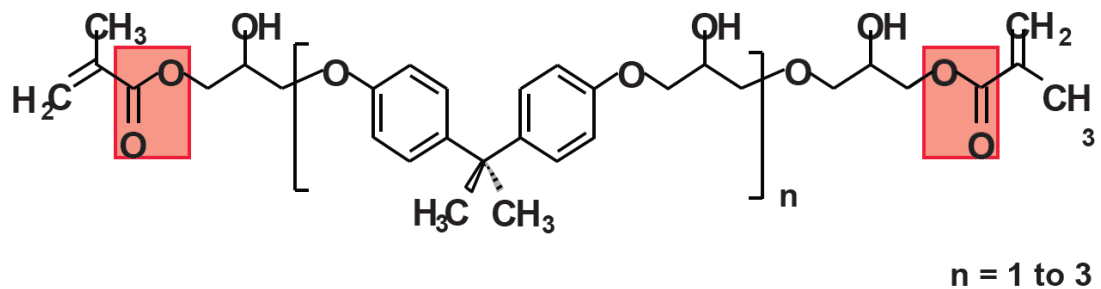


FIGURE 8. Molecule structure of Bisphenol-A Epoxy Vinyl Ester – Derakane 411 from The Dow Chemical Company (Kelley, Graham & Johnson, 4)

Epoxy based vinyl ester resins were improved with the incorporation of novolac chemistry. Novolac functionality changes the polymer structure to higher cross-linking polymer. This improves resins ability to withstand higher temperatures. Higher cross-linking decreases solvents penetrating the structure and by that makes epoxy novolac vinyl ester resin more resistant to organic solvents. Figure 9 presents the polymer structure of epoxy novolac vinyl ester resin. From the figure it can be noted that one molecule has three vinyl groups which form the high cross-linking structure in polymerization. Highly cross-linked structure also increases polymers glass transition temperature. (Kelley, Graham & Johnson, 5.)

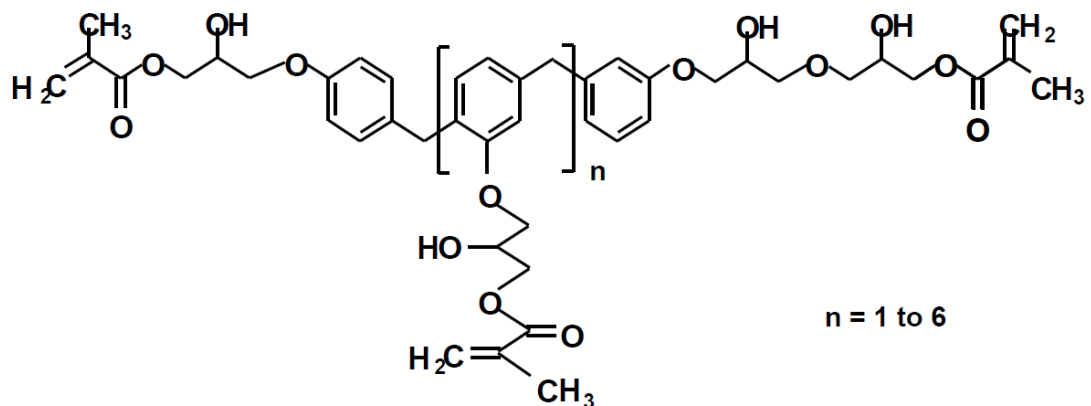


FIGURE 9. Molecule structure of Epoxy Novolac Vinyl Ester – Derakane 470 from The Dow Chemical Company (Kelley, Graham & Johnson, 5)

Another development of vinyl ester structure was the brominated epoxy vinyl ester resin. This polymer has bromine added to its backbone and it gives improvements to resins fire retardance and added more corrosion resistance. Bromine functionality in the molecule provides superior fire retardance which is important in many industrial applications. It also enhances the corrosion resistance of sodium hypochlorite. Brominated epoxy vinyl ester gives FRP enhances in toughness and fatigue resistance over standard epoxy vinyl esters. Structure of brominated epoxy vinyl ester resin is presented in figure 10. (Kelley, Graham & Johnson, 5.)

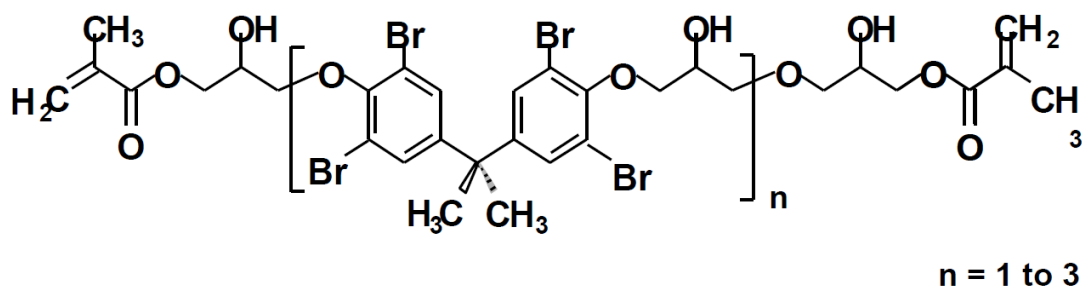


FIGURE 10. Molecular structure of Tetrabromo Bisphenol-A Epoxy Vinyl Ester - Derakane 510 from The Dow Chemical Company (Kelley, Graham & Johnson, 5)

4.2 The Chemistry of Epoxy Vinyl Ester Resins

The vinyl ester molecule structure is a combination of epoxy backbone with vinyl ester groups. Epoxy vinyl ester polymers are formed by a reaction between epoxy and acrylic acid. The acrylic acid opens the epoxy ring and forms a new bond with the oxygen and carbon in the end. Because of the acrylic acids unsaturated carbon-carbon double bond the molecule is attached to the end of the chain. So the epoxy based vinyl ester molecule is formed having epoxy backbone and unsaturated vinyl ester group at the end. Schematic model of the synthesis is presented in figure 11. (Strong 2008, 117.)

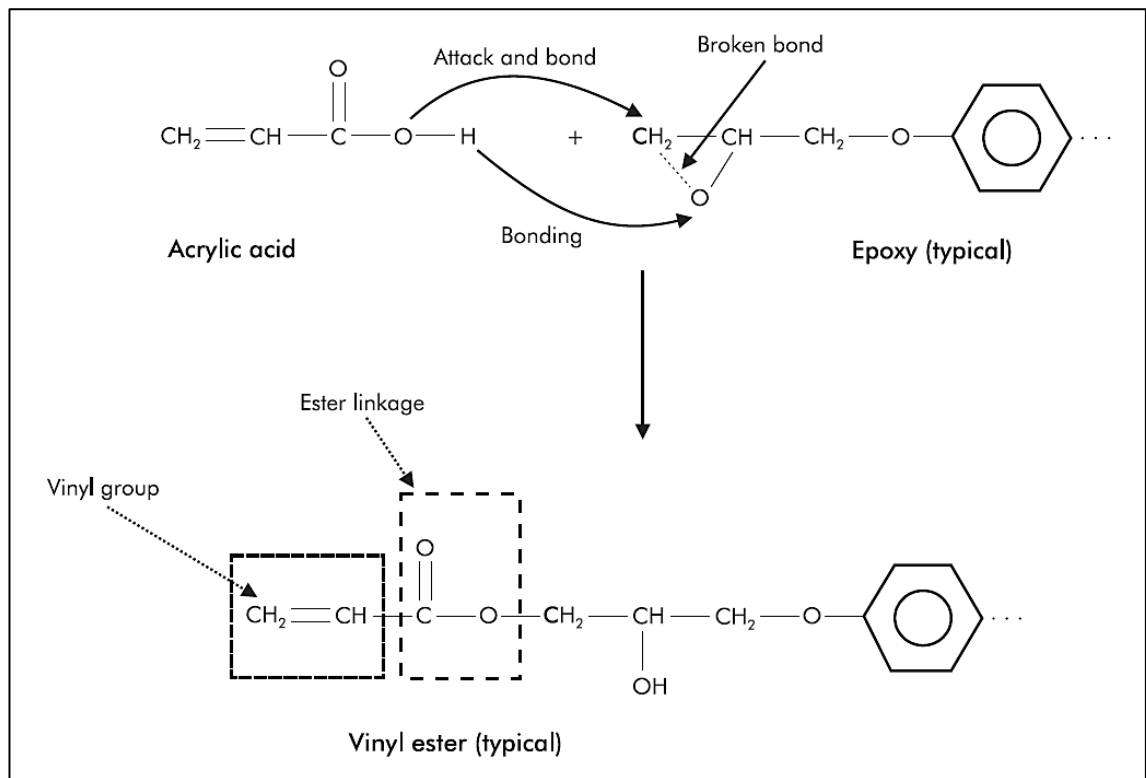


FIGURE 11. Synthesis of epoxy and acrylic acid forms a vinyl ester molecule (Strong 2008, 117, modified)

The formation of vinyl ester molecule explains the properties by functional groups. Epoxy backbone gives the molecule great mechanical properties of epoxies and vinyl ester group has the characteristics of unsaturated polyesters which make the processing easier and the cross-linking similar to polyesters. Highly aromatic and thus strong backbone is one of the basic characteristics of epoxies but is retained in vinyl ester molecule. Epoxy based vinyl ester resin is a combination of polyesters and epoxies beneficial characteristics and properties.

The cross-linking reactions begin as an initiator breaks the bond in the end of the chain activating a free-radical. Cross-linking reaction is based on the presence of styrene. Styrene molecule bonds with the free-radical and links it with another vinyl ester molecule which has also a free-radical to bond to. Styrene bridge links two molecules together and this bridge can contain several consecutive styrenes. Cross-linking reaction goes on forming more bonds and result a large cross-linked structure. (Strong 2008, 120.)

Vinyl ester molecules hydroxyl (OH^-) groups increase bonding in the polymer. These functional groups are very beneficial for the properties of vinyl ester in composites. They react with the surface of the glass fiber which leads to excellent wetting of the

fibers and good adhesion between fiber and the matrix. This increases composites strength properties overall. This is also a good property from the aspect of corrosion resistance, because corrosion is most likely to attack the point where the resin is attached to the fiber. (Strong 2008, 121, 122.)

5 ENVIRONMENTAL DEGRADATION

Environment affects the composites properties over time. The process is called ageing or environmental degradation and it is normally divided into physical and chemical degradation. Polymers that are subjected to liquid environment can face changes in the material characteristics. When environmental degradation occurs it is usually the matrix that is damaged. The stage of materials degradation is dependent on its characteristics and the conditioning environment. Before utilizing certain material in a new environment, its behavior has to be studied under the conditions.

5.1 Physical Degradation

As polymers are conditioned in a liquid environment the liquid molecules always penetrate the material surface. Smaller water molecules are able to get through the surface of polymers long molecule chains. Moisture absorption mainly covers physical degradation. Liquid penetrates the plastic matrix differently according to polarity properties of the liquid and the polymer. If the liquid and the polymer have the same polarities (polar to polar or non-polar to non-polar) after the liquid penetration and matrix swelling, the solvation phenomenon occurs and the polymer molecules are dissolved physically by loosening of the molecular chains bonds. If the polarities are different, liquid only causes swelling after its penetration to the polymer. (Kulshreshtha & Vasile 2002, 107.)

Moisture absorption is the primary concern in terms of environmental degradation. Moisture affects mainly the matrix dependent properties. Besides the polarity of the polymer matrix water absorption is also dependent on; degree of crosslinking, degree of crystallinity and presence of fillers in the resin. High crosslinking density and high degree of crystallinity decrease the liquid absorption ability. Generally vinyl esters absorb 0, 15- 0, 20 mass percent of liquid. (Kulshreshtha & Vasile 2002, 118, 126.)

As polymer matrix absorbs moisture, its glass transition temperature is reduced. This means that the temperature where solid polymer changes to softer more viscous state decreases. With increasing moisture absorbed matrix resins strength properties also decrease. Increased temperature adds liquids ability to penetrate the material faster but the

degree of moisture absorption stays the same. Mechanical stress in a humid environment also increases moisture absorptions speed. The point where material has absorbed the maximum amount of moisture is called the moisture equilibrium content. Each material has its own characteristic time to reach this point. Moisture equilibrium content is calculated using equation 1. (Campbell 2010, 402.)

$$\Delta M = \text{Mass change, \%} = \left| \frac{W_i - W_b}{W_b} \right| * 100 \quad (1)$$

where:

W_i = current specimen mass, g, and

W_b = baseline specimen mass, g

The water molecule is known to have a strong propensity to create intermolecular hydrogen bonds with polymers negative atoms. Water molecules can penetrate the material in different ways: by diffusion, by capillary action through the matrix-reinforcement interface and by filling of internal defects. (Martin 2008, 477.) The absorption process is controlled by diffusion phenomenon. Moisture diffusion occurs either by Fickian or non-Fickian model. Fickian term comes from a material behaving in accordance of Fick's law. Composites matrix resins diffusion behavior is Fickian which means that the moisture uptake reaches an asymptotic value as approaching the moisture equilibrium content. (Campbell 2010, 404.)

5.2 Chemical Degradation

Polymers tend to degrade by some environmental conditions and especially in the presence of liquids. Polymers functional groups are typical to react with the chemicals that they are subjected to. Chemical degradation on polymers is often discussed as corrosion, which is familiar from metal materials corresponding behavior. Polymer corrosion can be divided by the chemical reaction, which causes the degradation. Most known corrosion reactions are: hydrolysis, oxidation and transesterification. Depending on the polymer molecules functional groups it can be expected which kind of degradation the matrix material is prone to. The most typical reactions are hydrolysis and oxidation. (Kulshreshtha & Vasile 2002, 110.)

Hydrolytic corrosion is a reaction that occurs in polymer resins including ester bonds in their main chain or in the crosslinking chain. Researched vinyl ester resins are vulnerable to this type of degradation but they only have a few ester bonds, which makes them highly chemical resistant. Hydrolysis reaction occurs if the resin is in contact with acid or alkali and it leads to polymer chains scission. Reaction of ester group and acid is presented in figure 12 and is reversible. Hydrolysis reaction by alkali is presented in figure 13 and this reaction is irreversible. (Kulshreshtha & Vasile 2002, 111- 113.)

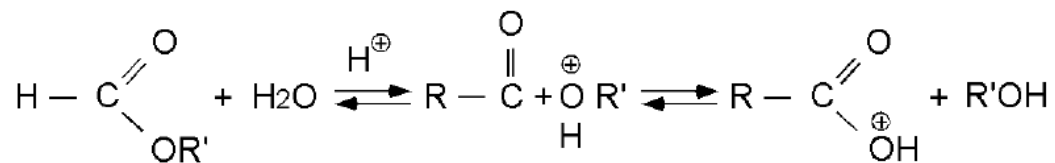


FIGURE 12. Hydrolysis reaction between ester group and acid (Kulshreshtha & Vasile 2002, 112)

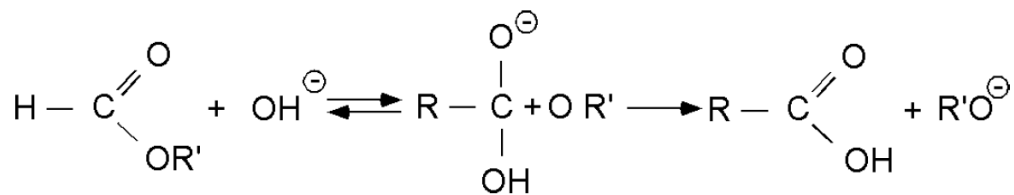


FIGURE 13. Hydrolysis reaction between ester group and alkali (Kulshreshtha & Vasile 2002, 113)

Hydrolytic corrosion decreases the amount of ester bonds in the resin. Because of the fewer bonds in the resin its properties deteriorates. Weaker bonding allows more liquid to penetrate the resin and it also decreases composites strength properties. Hydrolysis starts a cycle, which accelerates the chemical and physical degradation. Hydrolysis reaction also occurs in ether, amide and urethane bonds.

Oxidative corrosion occurs when polymers have double bonds or ether bonds in their structure. Also methyl and methylene groups in fatty acids or phenyl groups are vulnerable to oxidation by O_2 , O_3 , H_2O_2 and strong oxidizing acids like: H_2SO_4 , HNO_3 , H_2CrO_4 and H_3PO_4 . Oxidizing agents NaClO , KMnO_4 , and ClO_2 attack the unsaturated

double bonds in the resin structure and cause serious oxidative corrosion. Vinyl esters are not susceptible to oxidative corrosion even though they have unsaturated vinyl group. (Kulshreshtha & Vasile 2002, 114, 115.)

Tranesterification reaction based corrosion occurs in the presence of alcohol to polymers including ester bonds.

5.3 Corrosion Types

Polymer resin immersion to chemical environment is proved to form corrosion that is divided into three types such as surface reaction type, corrosion layer forming type and penetration type. Figure 14 presents a schematic picture of these three corrosion types. (Kulshreshtha & Vasile 2002, 130.)

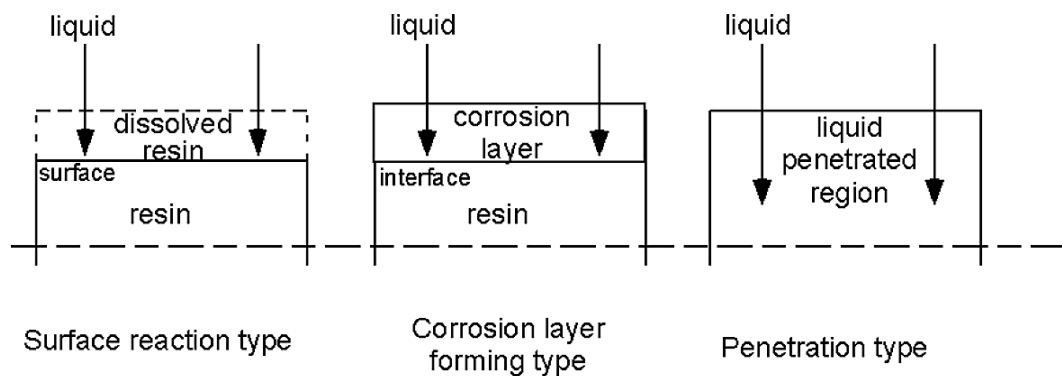


FIGURE 14. Three corrosion types (Kulshreshtha & Vasile 2002, 130)

The surface reaction type of corrosion occurs when the polymer can be dissolved into the liquid on the contact surface and the corrosion development is uniform over the whole surface. Corrosion reaction happens by this scenario when the liquid reacts with both the main polymer chain and the cross-linking chain producing low molecular weight compounds. These corrosion products are dissolved from the surface straight to the solution. This type of corrosion occurs for example to PC (Polycarbonate). (Kulshreshtha & Vasile 2002, 131.)

The corrosion layer forming type occurs in alkaline solutions to novolac type vinyl ester and isophthalic unsaturated polyester. Corrosion reaction dissolves part of the resin out

and the residual part remains as a corrosion layer where the initial bonds stay. The cross-linking molecular chain stays the same due to the highly stable C-C bonds, even though the ester bonds are hydrolysed. Hydrolysis of the ester bonds form corrosion products, which form the layer on the remaining surface. This layer works as a resistant layer for the penetration of solution by diffusion. (Kulshreshtha & Vasile 2002, 131, 133.)

The penetration type corrosion is characterized by a two-step process in diffusion and reaction. As the solution penetrates the resin, it reaches an equilibrium state, which causes the decreasing of the strength. Strength decrease leads to initiation of a corrosive reaction. (Kulshreshtha & Vasile 2002, 133, 134.)

5.4 Interface Corrosion

As discussed previously the corrosion resistance of GRP is mostly determined by the matrix material. However, it has to be noted that the interface of a matrix resin and the reinforcement is also vulnerable to corrosion. Glass fiber surface is treated with coupling agent to increase the adhesion to the matrix. The interface is vulnerable to hydrolysis, and liquid penetrates into the material by capillary action. Liquid absorption is higher parallel to fiber orientation. (Kulshreshtha & Vasile 2002, 139.)

The interface can be considered a very important factor related to GRP corrosion. The reaction between the coupling agent and the penetrated liquid results interface degradation. As the interface degrades, reinforcing fibers and the matrix are detached from each other, leading to blistering of the composite. To prevent interface degradation, the cut ends that have a surface of fibers with perpendicular orientation, are treated with protective resin material.

6 FLUE GAS SCRUBBING

Flue gas scrubbers are pollution control devices for industrial exhaust gases. Their purpose is to wash out the environmentally harmful components from the exhaust streams. The process is based on absorption reactions inside the scrubber. Typical applications that use flue gas scrubbers are industrial boilers, industrial combustion units, metal smelters, petroleum refineries and glass furnaces. Scrubbers are used to remove solid particles and neutralize various pollutants from the gas. The process is designed for certain gas stream and optimized to remove the typical components in this particular stream.

The primary pollutants that are removed from the flue gases are inorganic fumes and gases, volatile organic compounds and particulates. Scrubbing process concentrates on removing compounds like chromic acid, hydrogen sulfide, ammonia, chlorides, fluorides and sulfur dioxide. Flue gas scrubbers are typically wet scrubbers but also semi-dry and dry types of scrubbers are utilized. Wet scrubbers can reach the highest efficiencies of pollutant removal. However, wet scrubbers are the most expensive to maintain because of the continuous water circulation.

Wet scrubbers use a liquid to absorb the pollutants, in order to enhance the absorption, the contact area between the liquid and the gas is maximized. Packed-bed scrubbers provide a large contact surface for the liquid-gas contact. Packed-bed scrubbers are column like chambers with layers of packing material. Packing material varies but the basic idea is to provide large reaction surface, packing can be plastic or metal. Berl saddles, Raschig and spiral rings are common types of packings. The packing beds are held in place by metal gratings. Packed-tower scrubbers spray the absorbing aqueous liquid above the packing and it flows gravitationally downwards as the gas enters the scrubber from the bottom. The absorption occurs during this countercurrent flow. (U.S. EPA 1998)

The basic idea of flue gas treatment is to dissolve the contaminants to the washing liquid. Water is the most known solvent and it is used to remove inorganic pollutants from the exhaust stream. Acid gases are treated with caustic scrubbing liquid so that as the acid is absorbed to the solution it reacts with alkaline compounds producing neutral

salts. The physical absorption is dependent on the properties of the liquid and the gas stream. Density and viscosity of the liquid and specific characteristics of the pollutant like diffusivity and equilibrium solubility affect the reaction rate and efficiency. These properties are dependent on the temperature and generally lower temperatures improve the scrubbing liquids ability to absorb. Larger contact area and higher concentrations in the gas stream also enhance the absorption. (U.S. EPA 2003, 3)

Typically the hot exhaust gases are cooled from 150 – 200 °C to 60 – 70 °C before the input to the scrubber. Scrubber washes it with caustic liquid and the purified gas flow goes to droplet eliminator. The heat energy is collected during the scrubbing process by individual heat exchangers. Before releasing the washed gas to flue it goes once more through another droplet eliminator.

7 STUDY DESCRIPTION

This section is not included in the public version of the research.

8 SAMPLE MATERIAL

This section is not included in the public version of the research.

9 RESEARCH METHODOLOGY

This section is not included in the public version of the research.

10 RESULTS

This section is not included in the public version of the research.

11 DISCUSSION

This section is not included in the public version of the research.

12 CONCLUSIONS

This section is not included in the public version of the research.

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APPENDICES

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