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Show Me the Road to Hydrogen

UTC/Transportation Fuel Research and Development

by

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A University Transportation Center Program
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16. Abstract

Hydrogen-powered fuel is an emerging technology that provides an alternative source of fuel to fossil fuel. Commercially viable technologies are emerging that are expected to allow for consumer vehicles powered by hydrogen as part of a growing hydrogen economy. These vehicles and their supporting infrastructure, such as pipelines and filling stations, will be constructed using innovative materials and manufacturing techniques to improve system efficiency and enable the economic growth. It is critical that these new technologies are fully understood prior to widespread application. One key technical challenge is the maintenance and assessment of systems under service conditions to ensure public safety. It is critical that possible failure methods be thoroughly investigated and understood, such that preventative maintenance and procedures can be implemented effectively. Nondestructive Evaluation (NDE) technologies have an important role to play in evaluating the condition of materials in-situ. This report identifies engineering materials that can be expected to play a key role in the infrastructure and vehicles in the coming hydrogen economy. The report focuses on materials to be used in composite overwrapped pressure vessels (COPVs) that will be used to store hydrogen fuel. These materials will also be used in other infrastructure such as pipelines and filling stations. The goal of the report is to develop key information on materials to be used in a hydrogen economy such that NDE technologies can be developed. The report also identifies and documents the materials failure modes to develop an understanding of what NDT&E methods must be employed in their inspection to ensure public safety.

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UTC/Transportation Fuel Research and Development

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ABSTRACT

Hydrogen-powered fuel is an emerging technology that provides an alternative source of fuel to fossil fuel. Commercially viable technologies are emerging that are expected to allow for consumer vehicles powered by hydrogen as part of a growing hydrogen economy. These vehicles and their supporting infrastructure, such as pipelines and filling stations, will be constructed using innovative materials and manufacturing techniques to improve system efficiency and enable the economic growth. It is critical that these new technologies are fully understood prior to widespread application. One key technical challenge is the maintenance and assessment of systems under service conditions to ensure public safety. It is critical that possible failure methods be thoroughly investigated and understood, such that preventative maintenance and procedures can be implemented effectively. Nondestructive Evaluation (NDE) technologies have an important role to play in evaluating the condition of materials in-situ. This report identifies engineering materials that can be expected to play a key role in the infrastructure and vehicles in the coming hydrogen economy. The report focuses on materials to be used in composite overwrapped pressure vessels (COPVs) that will be used to store hydrogen fuel. These materials will also be used in other infrastructure such as pipelines and filling stations. The goal of the report is to develop key information on materials to be used in a hydrogen economy such that NDE technologies can be developed. The report also identifies and documents the materials failure modes to develop an understanding of what NDT&E methods must be employed in their inspection to ensure public safety.

1.0 INTRODUCTION

The automotive industry is one that affects all parts of the world, both as a manufacturing base in the production of vehicles to the transportation of people and goods. As the world continues to progress and advance technologically, it is becoming more necessary to examine how the conventional gasoline-powered vehicles will fare a few years down the road. The environmental impact of fossil fuels, combined with dwindling natural resources, are leading to the examination of alternative fuels. Hybred vehicles that combine the electric power sources with traditional gasoline powered engines to improve efficiency have become commercially available, but continue to rely on the gasoline-powered engine and as such have limited ability to reduce dependence on fossil fuel. Hydrogen-powered vehicles are at the forefront of alternate fuel technologies intended to completely replace fossil fuel as a power source for commercial vehicles. Many top automotive manufacturers are researching methods and creating new technology to develop hydrogen powered vehicles in order to remain competitive in the industry's future. In the near future, hydrogen as an alternative fuel source is expected to make significant advances in developing commercially viable technologies that can lead to consumer products that utilize hydrogen as the primary power source in automobiles. There is a significant effort underway nation-wide to develop these technologies and promote a "hydrogen economy" where hydrogen is the key power source for consumer and commercial automobiles. A supporting infrastructure of pipelines, filling stations, and hydrogen manufacturing facilities can be anticipated as key infrastructure to be developed to support the hydrogen economy.

The development of this new generation of vehicles is introducing new manufacturing materials and technologies. The drive to improve vehicle efficiency to reduce power consumption in vehicles is introducing innovative engineering approaches that will significantly alter the vehicles are operated and maintained. Significant advances in the utilization of light-weight materials such as composites are expected to meet the need for lighter weight vehicles. For hydrogen powered vehicles, pressure vessels on board the vehicle are required to store gaseous or liquid hydrogen. These vessels typically consist of a metallic liner overwrapped with composite materials to provide strength and reduce the weight of the vessels relative to vessels consisting of only metal. The pressure vessels are generally termed “composite overwrapped pressure vessels,” or “COPVs.” Tanks with plastic liners overwrapped with composite materials have also become available, and are being widely used in natural gas vehicles today. Additionally, composite materials and other light-weight materials are expected be used as key structural and aesthetic materials in hydrogen vehicles due to their high strength to weight ratios.

The infrastructure required to support the new hydrogen economy will also be constructed utilizing new materials and processes. Pipelines for transporting hydrogen fuels and materials for the production of hydrogen will be necessary to support filling stations similar to gas stations that are widespread today. Concern exist that hydrogen filling stations and supporting infrastructure may present safety issues due to the unstable nature of hydrogen. New materials including composites materials are expected to play a significant role in the constructed infrastructure, utilized to overwrapped pipelines, provide structural elements in filling stations, and store large amounts of hydrogen for distribution.

With the anticipated wide-spread application of these new materials, it is necessary to analyze how these materials are expected to perform under service conditions, and to develop testing and evaluation techniques to monitor materials behavior. The development of nondestructive evaluation (NDE) technologies is required to monitor and assess the performance of vehicles and infrastructure for the hydrogen economy. NDE technologies have a significant role to play in both ensuring the safety by detecting the precursors to failure, and also as maintenance tools detecting deterioration in its embryonic stages such that repairs can be made in a cost-effective manner. This section of the report is intended to provide an overview of the new materials that will be utilized in hydrogen vehicles, record their engineering properties, and evaluate potential failure modes. This information will provide data to support the development of NDE technologies in the future.

2.0 GOALS AND OBJECTIVES

The goal of this project is to develop key information on materials to be used in a hydrogen economy such that nondestructive evaluation technologies can be developed. This goal is addressed through two objectives:

1. Document the engineering properties and characteristic of materials that may be used in the hydrogen economy

2. Document key failure modes for these technologies such that appropriate NDE technologies can be developed to detect the precursors to failure.

To meet these objectives, a literature search has been conducted to assess the current knowledge about materials and failure modes for materials. The results of this literature search are reported herein in two primary sections. First, information on a wide variety of composite and key metals to be utilized in the hydrogen economy in reported. Second, a description of failure modes for the less traditional materials, i.e. composites, is reported to provide engineers with the requisite knowledge to identify potential NDE technologies that may have a role to play in supporting the coming hydrogen economy.

3.0 MATERIALS

The first section of the report identifies key materials that will be employed in hydrogen vehicles and supporting infrastructure. This includes metals and polymer composite materials that could be used in the construction of COPVs for storing and transporting hydrogen. Basic engineering properties of the materials are indicated to provide the reader with a general understanding of the strength, weight and stiffness of the material. Obviously, most materials are available in some range of properties, the values provided represent typical values and may not indicate maximum or minimum values for a particular property. The information is intended to provide the reader with general information about the characteristics of the materials such that a foundation exists for understanding both how the materials will be used in hydrogen vehicles, and what NDE technologies may be appropriate for further development.

3.1 Liner materials

This section discusses the various materials available and utilized for the liner of COPV's. This includes traditional materials such as metals, for example aluminum, as well as state of the art materials such as polymer liners.

3.1.1 Aluminum

Aluminum is a widely used metal that can be found in many consumer products, from aluminum soda cans to automobile parts. Aluminum is derived from electrolytic processing of the ore bauxite. It is the third most common crustal element and most common crustal metal on earth. Pure aluminum is a silvery-white metal and possesses many of desirable properties as an engineering material[1-3].

Properties

Aluminum is remarkable for its resistance to corrosion and light weight (only one-third the density of steel). It is nontoxic, non-magnetic, and non-sparking. It is malleable and ductile, standing second among metals in the scale of malleability, and sixth in ductility. It can be cast, rolled or extruded into an infinite variety of shapes. Aluminum is an excellent conductor of heat and electricity. Due to the metal's natural coating of aluminum oxide, it is an effective barrier to the environmental degradation occurring from exposure to air, temperature, moisture and aggressive chemical attack. Aluminum can also be recycled without loss of quality or properties.

Alloys with small amounts of copper, magnesium, silicon, manganese, and other elements have very useful properties. The physical properties of aluminum are listed in Table 3.1.1.

Table 3.1.1 Typical Mechanical Properties of Aluminum.

	SI		**USCS**	
Property	**Value**	**Units**	**Value**	**Units**
Density	2.70	$g \cdot cm^{-3}$	0.0975	$lb \cdot in^{-3}$
Young's modulus	68	GPa	10,000	ksi
Tensile strength	280	MPa	40	ksi
Elongation at break	<60%		<60	
Poisson ratio	0.35	—	0.35	—
Thermal expansion	(25°C) 23.1	$\mu m \cdot m^{-1} \cdot K^{-1}$		
Thermal conductivity	(300 K) 237	$W \cdot m^{-1} \cdot K^{-1}$	1645	$BTU \cdot in \cdot hr^{-1} \cdot ft^{-2} \cdot {}^{\circ}F^{-1}$
Melting point	660	°C	1220	°F

Applications

Whether measured in terms of quantity or value, the use of aluminum exceeds that of any other metal except iron. Aluminum is used in many industries and is indispensable in our daily lives. Its wide applications are attributed to its properties such as lightweight, strength, recyclability, corrosion resistance, durability, ductility, formability and conductivity.

Pure aluminum has a low tensile strength, alloys with small amounts of copper, zinc, magnesium, silicon, manganese, and other elements have very useful properties. Today almost all materials that claim to be aluminum are alloys. Pure aluminum is encountered only when corrosion resistance is more important than strength or hardness.

Aluminum is primarily used in transportation, construction, packaging, electrical applications, and medicine & water treatment. Structural components made from aluminum and its alloys are vital to the aerospace industry and very important in other areas of transportation and building in which light weight, durability, and strength are needed. Aluminum is used extensively for the protection, storage and preparation of food and beverages. Aluminum foil finds its largest use in containers and packaging for food, cosmetics and pharmaceutical products. Aluminum cans are excellent containers: strong, light-weight, compact, impermeable, recyclable. Most beer and soft drink cans are now made of aluminum. Because of its high electrical conductivity, low weight and good resistance to corrosion, aluminum is particularly suited to the uses as overhead lines, electrical energy distribution and transport cables, and energy cables for industrial use.

Aluminum or Aluminum-based alloys can be used as liners for high pressure COPVs. Because of its light weight and formability, Aluminum can provide lightweight tank liners in a variety of shapes. The primary role of the liner in most COPVs is to contain the gaseous materials in the tank. A composite overwrap applied to the tank provides nearly all of the vessels strength. The low modulus of Aluminum allows for the liner to expand under pressure and transfer force to the composite wrap. The light weight of the material makes it ideal for aerospace applications. For space flight, where mass limitations are severe, Aluminum is frequently used as a linear material in carbon and Kevlar COPV's that hold a variety of critical gases. Hydrospin is the world's leader in thin-walled seamless aluminum liners for the high pressure composite cylinder market [4].

3.1.2 Titanium

Another key liner material is Titanium, a metal with high strength to weight ratio and significant ductility. It is the ninth most abundant element and the fourth most abundant structural metal after aluminum, iron, and magnesium in the crust of the earth. Titanium is almost always present in igneous rocks and in the sediments derived from them. It occurs in the minerals rutile (TiO_2), ilmenite ($FeTiO_3$), and sphene, and is present in titanates and in many iron ores. Titanium is present in ash of coal, in plants, and in human body. Titanium is also present in meteorites and the sun.

Properties

Interest in the properties of titanium started after the Second World War in the late 1940's and early 1950's. Pure titanium is a lustrous, white metal. It has a low density, good strength, is easily fabricated, and has excellent corrosion resistance. It is ductile when it is free of oxygen. Titanium is as strong as steel, but 45% lighter. It is 60% heavier than aluminum, but twice as strong. Titanium is resistant to dilute sulfuric and hydrochloric acid, most organic acids, most chlorine gas, and chloride solutions[5-6].

The physical properties of titanium are listed in Table 3.1.3.

Table 3.1.3 Typical Mechanical Properties of Titanium.

Property	SI		USCS	
	Value	**Units**	**Value**	**Units**
Density	4.5	$g\cdot cm^{-3}$	0.163	$lb\cdot in^{-3}$
Young’s modulus	100-120	GPa	14,500 – 17,500	ksi
Tensile strength	220	MPa	31.9	ksi
Elongation at break	<50	%	<50	%
Poisson ratio	0.32	—	0.32	—
Thermal expansion	(25°C) 8.6	$\mu m\cdot m^{-1}\cdot K^{-1}$		
Thermal conductivity	(300 K) 21.9	$W\cdot m^{-1}\cdot K^{-1}$	152	$BTU\cdot in\cdot hr^{-1}\cdot ft^{-2}\cdot {}^{\circ}F^{-1}$
Melting point	1668	°C	3034	°F

Applications

Although titanium has the highest strength to density ratio, it is used only for certain niche application areas because of its high price. Titanium is important as an alloying agent with aluminum, vanadium, molybdenum, manganese, iron, and other metals. Alloys of titanium are principally used for aircraft and missiles where lightweight strength and ability to withstand extremes of temperature are important. About 95% of titanium production is consumed in the form of titanium dioxide (TiO_2), an intensely white permanent pigment with good covering power in paints, paper, toothpaste, and plastics. Use of titanium in consumer products such as tennis racquets, golf clubs, bicycles, laboratory equipment, wedding bands, and laptop computers is becoming more common.

The much higher melting temperature of titanium as compared to aluminum, the main competitor in light-weight structural applications, gives titanium a definite advantage above application temperatures of about 150°C. Pure titanium is used primarily for applications where corrosion resistance is paramount.

Pressure vessels

Commercially pure (CP) titanium is also commonly used in pressure vessels because of strength, fabricability, and corrosion resistance [7]. Because of its thermodynamic feasibility as a storage host and lightweight, titanium is attractive in the application in hydrogen storage systems. There has been a modest continuing effort to develop a titanium based hydrogen storage medium and these efforts have been focused on the intermetallic compounds TiFe and TiMn. Titanium based hydrogen devices have great appeal in the area of hydrogen powered vehicles [7]. However, high cost associated with this material presents a barrier to widespread application in commercially-viable consumer products.

3.1.3. High density polyethylene (HDPE)

HDPE is a polymer commonly used in civil and environmental engineering applications for various types of piping. It is often used as a fuel tank liner due to its material characteristics such as resistance to corrosion, stress cracking, and cyclic fatigue. HDPE is also popular in fuel tank manufacturing due to the ability to connect different sections of HDPE pipe by way of fusion welding rather than bell and socket joints used for connecting sections of PVC pipe.

Among all common polymers, polyethylene possesses the simplest molecular structure. The molecular structure is made up by two carbon and four hydrogen atoms arranged in a simple repeating pattern. Polyethylene is made from petroleum that is derived from natural gas or crude oil. They are classified by density. HDPE, by definition, are those that have a density ranging between 0.941 to 0.965 g/cm^3. Making HDPE attractive to manufacturers of fuel tanks is its high strength and elastic modulus, toughness, flexibility, high chemical resistance, light weight, easy installation, and low Manning coefficient of roughness [8]. Typical material properties associated with HDPE are shown in Table 3.1.4 [10].

Table 3.1.4 HDPE material properties.

Property	SI		USCS	
	Value	**Units**	**Value**	**Units**
Density	0.95	g·cm^{-3}	0.034	lb·in^{-3}
Flexural modulus	1.25	GPa	181	ksi
Tensile strength	32	MPa	4.64	ksi
Elongation at Break	100	%	100	%

3.2 Wrapping materials / Structural components

3.2.1 Glass Fibers (E-Glass/S-Glass)

Glass fibers used in structural applications are divided into two main types, E-glass and S-glass. E-glass, or fiberglass, as it is more commonly known, was developed for electrical uses, but has more recently been utilized as a fiber component of polymer matrix composites (PMCs). S-glass has higher silica content than E-glass, and is used primarily in aerospace applications [9].

Properties

Glass fibers are formed by passing liquid glass through very small cylindrical openings as it is cooled. Fibers range in diameter from 5 to 24μm, and are formed into strands or rovings. The different types of glass (E-glass and S-glass) are obtained by altering the base ingredients of the glass mixture. Table 3.2.1 lists the general properties of E-glass and S-glass. Properties that are beneficial in use as a structural reinforcement include:

- High strength, tensile and compressive
- Low cost
- High chemical resistance
- Excellent insulating properties

Some advantages of S-glass over E-glass include better strength retention at high temperatures, higher fatigue strength, and better wet strength retention. Factors that limit use in structural applications include low impact resistance, low modulus of elasticity, abrasion sensitivity, and lower fatigue strength than other fibers used in PMCs [9,11].

Table 3.2.1 Typical Properties of Glass Fibers.

	E-Glass				**S-Glass**			
	SI		**USCS**		**SI**		**USCS**	
Property	**Value**	**Units**	**Value**	**Units**	**Value**	**Units**	**Value**	**Units**
Density	2.54	$g \cdot cm^{-3}$	0.092	$lb \cdot in^{-3}$	2.49	$g \cdot cm^{-3}$	0.090	$lb \cdot in^{-3}$
Young's modulus	72.4	GPa	10500	ksi	85.5	GPa	12400	ksi
Tensile strength	3447	MPa	500	ksi	4585	MPa	665	ksi
Coefficient of Thermal Expansion	5.04	$\mu m \cdot m^{-1} \cdot K^{-1}$			5.58	$\mu m \cdot m^{-1} \cdot K^{-1}$		

3.2.2 Kevlar (Aramid fiber)

Kevlar is the DuPont Company's brand name for material made out of synthetic fiber of poly-paraphenylene terephthalamide which is constructed of para-aramid fibers. Kevlar is 5 times stronger than steel on an equal weight basis and is lightweight and flexible. It is also very heat resistant and decomposes above 400°C without melting [9,12,13].

Properties

Fibers of Kevlar consist of long molecular chains produced from poly-paraphenylene terephthalamide (PPPT). The chains are highly oriented with strong interchain bonding which result in a unique combination of properties. General features of Kevlar include:

- High tensile strength at low weight
- Low elongation to break high modulus (structural rigidity)
- Low electrical conductivity
- High chemical resistance
- Low thermal shrinkage
- High toughness
- Excellent dimensional stability
- High cut resistance
- Flame resistant, self-extinguishing
-

Table 3.2.2 gives the properties of Kevlar fibers.

Table 3.2.2 Typical Properties of Kevlar fibers.

	Kevlar 29				**Kevlar 49**			
	SI		**USCS**		**SI**		**USCS**	
Property	**Value**	**Units**	**Value**	**Units**	**Value**	**Units**	**Value**	**Units**
Density	1.44	g·cm^{-3}	0.052	lb·in^{-3}	1.48	g·cm^{-3}	0.053	lb·in^{-3}
Young's modulus	62	GPa	9000	ksi	131	GPa	19000	ksi
Tensile strength	3620	MPa	525	ksi	3620	MPa	525	ksi
Elongation at break	3.3	%	-	-	2.4	%	-	-
Tenacity	2.95	GPa	428	ksi	2.95	GPa	428	ksi

Applications

In the almost 40 years since its discovery, Kevlar has played a significant role in many critical and diverse applications. The many applications of Kevlar result from its light weight, resistance, hardness, strength and capability of absorbing vibrations. Kevlar is best known for its application in the field of bullet-resistant personal body armor. It is often used to protect cables and to reinforce linking structures under the sea. In the automobile design field it is an exceptional reinforcement for tires. It is also used instead of asbestos in the clutch, in the brakes, and in other parts of the engine. In combination with other materials it is used in the construction of air planes, ships, and sports equipment. In the telecommunications field it is a fundamental component for fiber optic cables, providing tensile strength when used to reinforce fiber cladding.

In structural applications, Kevlar fibers can be bonded to one another or to other materials to form a composite. Kevlar's main weakness are that it decomposes under alkaline conditions or when exposed to chlorine. While it can have a great tensile strength, sometimes in excess of 4.0 Gpa., like all fiber composite materials, it tends to buckle in compression. Kevlar was also used in the 1970's for COPV's, to overwrap the vessels to give the high strength at low weight. Some of first COPV's were constructed using Kevlar as the primary composite material, and a number of these vessels are still in service in the Space shuttle. The material is still used for certain personnel oxygen supplies such as those use in fire fighting or scuba diving. \

3.2.3 Graphite/Epoxy and Carbon/Epoxy

Polymer matrix composites (PMCs) [9]

The most common advanced composites are polymer matrix composites (PMCs) consisting of a polymer (e.g., epoxy, polyester, urethane) reinforced by thin diameter fibers (e.g., graphite, aramids, boron). The main drawbacks of PMCs include low operating temperatures, high coefficients of thermal and moisture expansion, and low elastic properties in certain directions.

Epoxy [9]

Epoxy resins are the most commonly used resins. They are low molecular weight organic liquids containing epoxide groups. The room temperature properties of a typical epoxy are given in Table 3.2.3.

Table 3.2.3 Room Temperature Properties of a Typical Epoxy.

Property	SI Units		USCS	
	Value	Units	Value	Units
Density	1.28	$g{\cdot}cm^{-3}$	0.046	$lb{\cdot}in^{-3}$
Young's modulus	3.79	GPa	550	ksi
Tensile strength	82.7	MPa	12.0	ksi

Epoxy has the advantages of high mechanical strength and good adherence to metals and glasses. The drawbacks are high cost and difficulty in processing. Although epoxy is costlier than other polymer matrices, it is the most popular PMC matrix. It has the properties of

- High strength
- Low viscosity and low flow rates, which allow good wetting of fibers and prevent misalignment of fibers during processing
- Low volatility during cure
- Low shink rates, which reduce the tendency of gaining large shear stresses of the bond between epoxy and its reinforcement
- Available in more than 20 grades to meet specific property and processing requirements

Graphite and Carbon fibers

Graphite fibers are very common in high-modulus and high-strength applications such as aircraft components, etc. The advantages of graphite fibers include high specific strength and modulus, low coefficient of thermal expansion, and high fatigue strength. The drawbacks include high cost, low impact resistance, and high electrical conductivity. Table 3.2.4 gives properties of graphite fibers obtained from two different precursors.

Table 3.2.4 Mechanical Properties of Two Typical Graphite Fibers.

	PITCH				PAN			
	SI		**USCS**		**SI**		**USCS**	
Property	**Value**	**Units**	**Value**	**Units**	**Value**	**Units**	**Value**	**Units**
Density	1.99	g·cm^{-3}	0.072	lb·in^{-3}	1.78	g·cm^{-3}	0.064	lb·in^{-3}
Young's modulus	379	GPa	55000	ksi	241.3	GPa	35000	ksi
Tensile strength	1723	MPa	250	ksi	3447	MPa	500	ksi
Elongation at break	2-3	%	-	-	2-3	%	-	-
Axial thermal expansion	-0.54	µm·m^{-1}·°C^{-1}	-3.00E-07	in·in^{-1}·°F^{-1}	-1.26	µm·m^{-1}·°C^{-1}	-7.00E-07	in·in^{-1}·°F^{-1}

Graphite and carbon are different. Carbon fibers have 93 to 95% carbon content, but graphite has more than 99% carbon content. Also, carbon fibers are produced at 2400°F (1316°C), and graphite fibers are typically produced in excess of 3400°F (1900°C).

The advantages of carbon fibers include:

- High modulus
- Good strength
- Low density, giving good specific properties
- Good thermal stability in the absence of O_2
- High thermal conductivity, assisting good fatigue properties
- Low thermal expansion coefficient
- Excellent creep resistance
- Good chemical resistance and does not wick
- Low electrical resistivity
- Biocompatibility

- No significant inhalation problem with filament diameters down to 5µm

Graphite/Epoxy

Graphite/epoxy composites are promising materials for structures in which low weight to strength ratio is important. Table 1.8 gives typical mechanical properties of graphite/epoxy.

Table 3.2.5 Typical Mechanical Properties of a Graphite/Epoxy.

Property	SI Units		USCS	
	Value	**Units**	**Value**	**Units**
Density	1.6	$g\cdot cm^{-3}$	0.58	$lb\cdot in^{-3}$
Young's modulus	181	GPa	26300	ksi
Tensile strength	150	MPa	22.0	ksi
Thermal Expansion	0.02	$\mu m\cdot m^{-1}\cdot °C^{-1}$	1.11E-08	$in\cdot in^{-1}\cdot °F$

Carbon/Epoxy

Carbon/Epoxy has many applications in aerospace, automotive fields, sailboats, and modern bicycles, where the qualities of strength and lightness are of importance. It is becoming increasingly common in small consumer goods as well, such as laptop computers, tripods, fishing rods, racquet sports frames, stringed instrument bodies, classical guitar strings, and drum shells.

Applications

CNG storage cylinders [14]

Over 10% buses operating in the US are powered by compressed natural gas (CNG) and carbon fiber reinforced CNG cylinders are common. Light duty vehicles are generally fitted with two or three pressure vessels, whilst heavy duty vehicles tend to be fitted with four to six. The cylinder types are classified as follows:

1. Type II—metallic vessel body with composite hoop wrap (generally fiberglass)
2. Type III—metallic liner with full composite overwrap (mainly carbon fiber)

3. Type IV—all-composite construction (mainly carbon fiber)

All-composite construction CNG vessels are made by IMPCO Technologies, Lincoln Composites and Quantum Technologies Worldwide in the US and MCS Cylinder Systems GmbH and Ullit in Europe.

Dynatek Industries manufactures cylinders for CNG powered vehicles using carbon fiber/glass composite, offering great savings for transit buses. They are used for the Ford Focus Fuel-Cell Vehicle (FCV).

Lincoln Composites manufacture a range of on board vehicle tanks for CNG. The tanks are made by overwrapping a polymeric liner such as HDPE with a composite and a hybrid mix of glass and carbon fiber is used to improve impact resistance.

Dynatek Industries, based in Calgary, has found it advantageous to use a selected heat treatment to aluminum liners to provide higher strength and then overwrapping with high strength carbon fiber.

A conformable tank has been developed by ATK Thiokol Propulsion Co. for on-board storage of H_2 for fuel cell vehicles, comprised of a polymer lining, a carbon fiber inner layer and an impact resistant outer layer.

American Technical Center has used a seamless metallic liner overwrapped with carbon fiber for storing 5000 psi hydrogen in a fuel cell.

3.2.4 Zylon (PBO fiber)

Zylon is a high-performance fiber developed by Toyobo Corporation. It consists of rigid-rod chain molecules of poly(p-phenylene-2,6-benzobisoxazole) (PBO).

Properties

The following information is retrieved from Toyobo homepage [15].

Zylon (PBO fiber) is the next generation super fiber with strength and modulus almost doubles that of p-aramid fiber. Zylon shows 100°C higher decomposition temperature than p-aramid fiber. There are two types of fibers, AS (as spun) and HM (high modulus). HM is different from AS in modulus, moisture regain and etc.

Table 3.2.6 Typical Properties of Zylon Fiber.

	Zylon AS				**Zylon HM**			
	SI		**USCS**		**SI**		**USCS**	
Property	**Value**	**Units**	**Value**	**Units**	**Value**	**Units**	**Value**	**Units**
Density	1.54	$g\cdot cm^{-3}$	0.056	$lb\cdot in^{-3}$	1.56	$g\cdot cm^{-3}$	0.056	$lb\cdot in^{-3}$
Young's modulus	180	GPa	26100	ksi	270	GPa	39100	ksi
Tensile strength	5.8	GPa	841	ksi	5.8	GPa	841	ksi
Elongation at break	3.5	%	-	-	2.5	%	-	-
Decomposition Temperature	650	°C	1202	°F	650	°C	1202	°F

Compared with other high-performance fibers, Zylon has the highest tensile strength and tensile modulus among high-performance fibers, according to the manufacturers.

Applications

Zylon is used in a number of applications that require very high strength with excellent thermal stability. Zylon can be used as protective cloth such as protective clothing for fire fighter, safety gloves, heat-resistant clothing, body armor, and protective gloves for electric works. In sports field, it can be applied to tennis rackets strings, ski poles, fishing rods, racing suits, bicycle spokes, and racing cars. Zylon is also used in aerospace field as balloon, air-craft engine fragment barrier (see SRI International homepage), and satellite.

3.2.5 M5

M5 fiber is a high-performance synthetic fiber produced by Magellan Systems and DuPont Advanced Fiber Systems. It has properties such as high tensile and compressive modulus, high tensile and compressive strength, high damage tolerance, low specific weight, good adhesion to matrix materials (for composites) and a good temperature resistance[16].

Properties

The characteristics of M5 fiber include:

- Higher modulus and stronger than steel, on a volumetric basis
- Higher modulus than any other synthetic, polymer fiber
- Good ductility
- Outstanding adherence to resins
- Superior fire (flame and thermal) resistance
- Outstanding UV light stability
- Non-conductive and will not corrode

Table 3.2.7 Typical Properties of M5 Fiber.

		Value	
Property	**SI Units**	**Experimental**[a]	**Target**[a]
Young's modulus	GPa	> *350*	> *400*
Elongation at break	%	> 1.5	> 2.0

[a] Experimental & target performance criteria appearing in italics have been achieved already

Applications

M5 can be applied in the areas such as ballistic protection, fire protection, cables & ropes, signature education, and structural composites. Historically, fibers that perform well as a ballistic or fire protective fabric often lacked the compressive strength typically necessary to perform well as a composites material. Similarly, fibers that have been well-suited for use as a composites material were too brittle to serve as a ballistic protection material. M5's ability to provide superior performance in the personnel protection and composites marketplaces makes it a truly unique synthetic fiber. Testing conducted to date shows that M5:

- Adheres extremely well to resins
- Does not degrade when exposed to sea water, boiling water, acids, bases, humidity, or high/low temperatures
- Does not degrade when exposed to Ultra-Violet light
- Composite bars bent too far, fail in a ductile mode, like a super-metal, as opposed to failing catastrophically
- Can be shaped into load bearing struts, pressure vessels, rocket motor casings, armor plating, Battle helmets, airplane wing structures, automobile safety cages, golf clubs, Tennis rackets, ski poles, bicycle frames, and just about anything else imaginable.

3.3 Brittle Matrix Composites

Brittle matrix composites comprise a group of high-performance, high-cost composite materials typically designed and manufacturer as very specific parts. High temperature resistance is commonly a goal for the brittle matrix composite, for example, the leading edge of the shuttle wing is a brittle matrix composite. The leading edge is intended to withstand the temperature of reentry, while mitigating those effects on the balance of the vehicle.

3.3.1 Carbon / Carbon

Carbon-carbon composites consist of carbon fibers embedded in a carbon matrix. They are frequently used because of their lightweight nature and ability to perform well at extreme temperatures. The composites exemplify superior performance in thermal shock, toughness, ablation, and high-speed friction properties [17].

The characteristics of carbon-carbon composites can vary greatly depending on how they are manufactured [17,18]. A wide variety of combinations can be produced depending on the method of heat temperature treatment of the composite. Therefore, a wide range of thermomechanical properties can be produced, and carbon-carbon should be viewed as a family of materials rather than a single one [18]. By varying production methods, carbon-carbon composites can range from glass-like and made up of small, randomly oriented crystallines (turbostatic carbon) to strongly oriented and highly graphitized in relatively large crystallines. Mechanical properties are determined by microstuctural features and the nature of the fiber/matrix interface. These microstructural features are a result of the type of fiber, matrix forming method, and factors such as temperature and pressure when creating the matrix. The interfaces between the carbon fibers and matrix are generally weak, which is beneficial, because the weak interfaces allow matrix cracking to take place without propagating through the fibers. The fibers, therefore, can continue to carry load [17].

Fabric weaving, braiding, winding, and multi-directional weaving are general methods for fabricating carbon-carbon composites with continuous fibers. The epoxy resin is implemented in order to rigidize the preform composite. Often, phenolic resins are used, because they are inexpensive and produce a high yield of carbon when decomposed by heating. Following this decomposition, the composites are somewhat porous, and these pores must be filled with carbon matrix by performing either liquid or vapor phase processing in order for the material to perform well. This process is commonly referred to as chemical vapor infiltration or chemical vapor deposition. After completion, non-destructive testing methods such as X-ray radiography, ultrasonic inspection, and electrical conductivity measurements determine how the carbon-carbon composite will perform [17].

3.3.2 Carbon / silicon carbide

An alternative to carbon-carbon composites is a carbon-fiber reinforced silicon carbide matrix (C/SiC) composite. The advantages of using a C/SiC composite are its superior performance in fracture toughness, flaw tolerance, and mechanical strength in comparison with other ceramics, especially in high-temperature situations [19, 20]. Compared to carbon-carbon composites, C/SiC composites exhibit higher mechanical properties as well as better resistance to oxidation of carbon fibers [19].

Often, ceramic materials are fabricated by means of hot-pressing the fibers and matrix in order to hybridize them. Unfortunately, the extreme temperatures and high stress accompanying hot-pressing may damage the carbon fibers and affect the performance of the material [20]. Chemical vapor infiltration is a common alternative procedure used in commercial construction. Similarly to carbon-carbon composites, C/SiC composites are somewhat porous following decomposition. During chemical vapor infiltration, these pores are filled with a carbon matrix in order to densify the composite [19, 20]. The matrix must be fully distributed throughout the pore structure in order for the composite to densify properly and perform effectively [18]. One of the biggest advantages of chemical vapor infiltration is that the process can be performed at relatively low temperatures (900-1100° C), and as a result, the carbon fibers remain unharmed during fabrication [20].

4.0 FAILURE MODES

It is apparent that manufacturers have a wide selection of engineering materials available to them when designing fuel tanks for hydrogen-powered vehicles. Choosing a material should be a result of the necessary mechanical properties and strength characteristics of the tank as well as evaluating what resources are most readily available to the manufacturer. Once the material or materials are selected, the typical processes that result in the degradation or failure of that material can be identified. Methods to mitigate the effects of that degradation can then be developed. This may include developing NDE technologies to detect or assess specific modes of degradation, design features to reduce the effect of the degradation, regular maintenance, etc.. This chapter of the report describes the typical failure modes for the primary materials that could be envisioned within a hydrogen infrastructure. As a result of the research conducted, and given the availability of information of many traditional engineering materials such as metals, this report will primarily focus on high-density polyethylene as a liner material and carbon fiber composite overwrapped pressure vessels. These are both very commonly used in hydrogen fuel tanks, and can be expected to be critical in the coming hydrogen economy. These materials also present a clear risk to consumers, given the proximity of the tanks to a vehicle user. Most of the failure modes are ubiquitous for the material whether used in a COPV or, for example, used as a pipe or other structural component, and as such these are summarized herein with respect to COPV's but with broader application.

4.1 Liners

This section addresses the COPV liner and its relevant failure or deterioration modes that might be expected to occur when utilized for hydrogen storage. The failure modes described in the following sections includes fatigue, creep, environmental stress cracking, Hydrogen embrittlement, and poor weld quality.

4.1.1 Fatigue

Failure due to fatigue loading is common in HDPE. A material experiences fatigue damage upon being cyclically loaded over long periods of time. The loads are often significantly lower than the material's ultimate tensile stress or yield stress. The fluctuating nature of the loading, however, is what eventually causes failure. A specimen's behavior under fatigue loading is often represented by a plot of cyclical stress range versus number of cycles to failure, or the S-N curve.

HDPE experiences either ductile or brittle failure in fatigue loading, depending on the conditions to which it is subjected. Ductile failure typically occurs at high ambient temperatures, low strain amplitudes, and surroundings with a low heat transfer coefficient. Brittle failure, however, typically occurs at low ambient temperatures, high strain amplitudes, and surroundings with a high heat transfer coefficient [21]. Other sources identify different characteristics to different stages in crack propagation. In another model, initial crack propagation is characterized by a brittle crack tip and damage zone. As the crack continues to grow over time, the crack tip and damage zone become increasingly ductile in nature [22]. The latter theory better accounts for the stepwise crap growth seen in HDPE.

At the onset of cracking, HDPE materials form a tough craze in the damage zone in order to resist further cracking. After a while, craze fibrils are temporarily incapable of supporting the cyclic loading, and the crack is allowed to increase in size. As a result, crack growth to rupture is a stepwise process in HDPE [23].

The rate at which cracks grow in any polymer in fatigue is best represented by the Paris equation $da/dt = A\Delta K^n$, where da/dt is the change in crack length over time, ΔK is the stress intensity amplitude, and the constant values A and n represent material properties of the polymer. The Paris equation can also be written substituting crack growth per cycle (da/dN) for crack length over time. Many other factors aside from stress intensity affect crack growth. Often, these effects are incorporated in the Paris equation by the addition of empirical factors in order to best predict behavior [23-26].

Factors affecting the fatigue lifetime and fatigue limit of HDPE include ambient temperature, environmental settings, imposed stress and strain amplitudes, sample shape, and testing frequency. Changes in ambient temperature are accompanied by changes in the behavior of polymer chains in HDPE. An increase in temperature will activate the polymer chains. Consequently, both the fatigue lifetime and fatigue limit are reduced. When the environmental media is characterized by a large heat transfer coefficient and high heat capacity, the heat generated from damping properties of the material is more easily transferred to these media. Therefore, this environment will increase the fatigue lifetime. An increase in imposed stress and strain amplitudes creates division in the polymer chains as well as plastic deformation. As a result, the fatigue lifetime will be reduced at increased imposed stress and strain amplitudes.

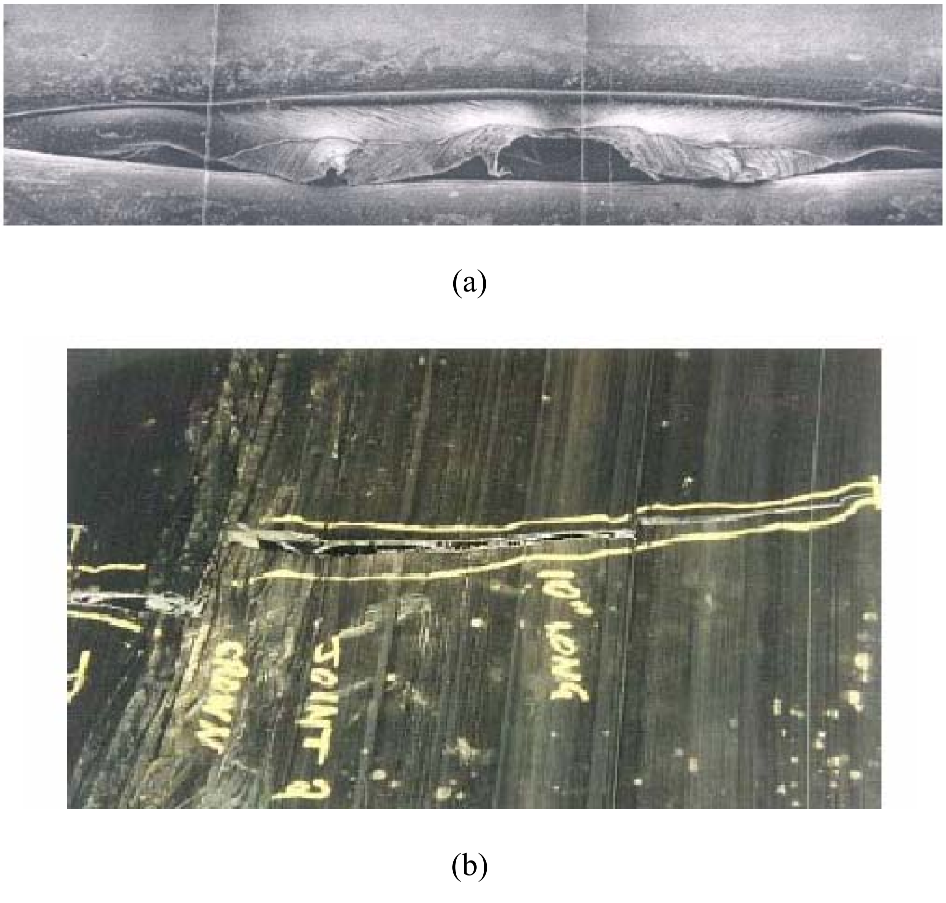
The sample shape affects how heat is transferred to the environmental media. To increase the effectiveness of how a specimen transfers heat to its surroundings, the ratio of its surface area to its volume can be increased [21].

4.1.2 Stress Rupture of HDPE Liners

Not all long-term failures at stresses below ultimate or yielding are a result of fatigue loading. Creep rupture is another common failure mode for HDPE. Creep, like fatigue, occurs at levels of stress below ultimate or yielding, however there is no cyclic component to the loading. Creep involves materials deforming permanently in order to relieve stresses. Creep rupture is commonly referred to as stress rupture, and the process of creep rupture is often called static fatigue.

Testing materials for resistance to static fatigue using field conditions is impractical due to the length of time it takes for it to take effect. It can take months for creep rupture to occur in HDPE. While it does not involve cyclic loading, a specimen's behavior of crack propagation and rupture in creep is closely related to its behavior in fatigue loading. As a result, an estimation of how HDPE will perform in static fatigue can be obtained from short-term dynamic fatigue testing or elevating the test temperature [22-24, 27]. Fatigue tests often use an R-ratio to characterize the minimum/maximum loads in the fatigue loading cycle. For example, an R-ratio of 0.1 will contain minimum loads that are 10% of the maximum. As R-ratios increase, the disparity between maximum and minimum peaks decreases until eventually R=1.0, and there is no fluctuation in loading (creep). By relating a specimen's behavior in fatigue to the R-ratio, the high end (R=1.0) can be used to characterize creep.

Long-term failure of HDPE can be categorized into two distinct failure modes, ductile creep rupture and brittle crack growth, depending on the stress level [8, 28]. Figure 1 shows an example of each.



(a)

(b)

Figure 4.1.1. Photographs from the literature showing (a) ductile failure in HDPE [8]. (b) brittle failure in HDPE [8].

Ductile creep rupture occurs when the HDPE is subject to high applied stresses. The material generally fails in a short amount of time in cases of ductile creep rupture. Brittle crack growth is more prevalent when the material is subject to low applied stresses. In this case, it takes a long period of time for cracks to propagate and the HDPE to fail. Information regarding the failure of HDPE under static fatigue loading can be best illustrated by plotting log (applied stress) versus log (time to failure). In Figure 2, a distinct discontinuity in the slope of the linear relationship distinguishing ductile and brittle failure is shown [8,28,29].

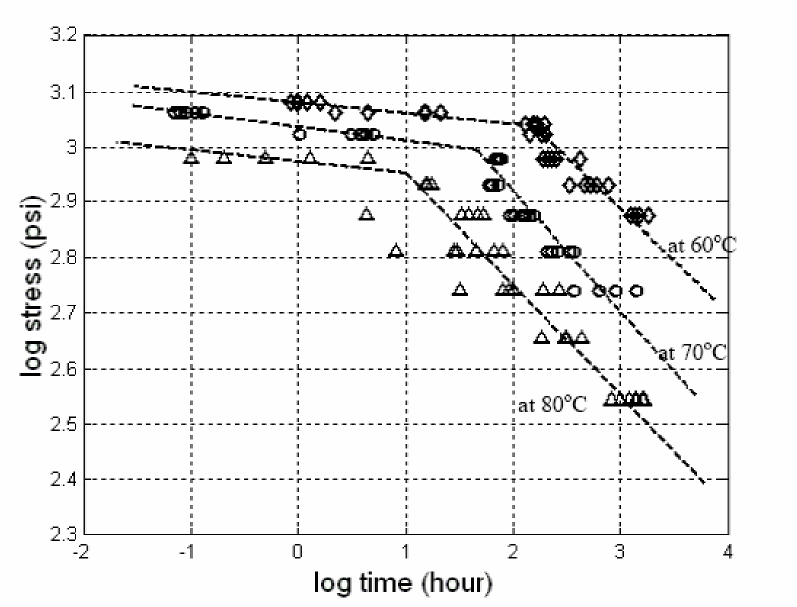


Figure 4.1.2. Log stress vs. log time for samples of HDPE in static fatigue at varied temperatures [8].

At the microscopic level, HDPE is made up of link (tie) molecules that intertwine giving the material its tensile strength. Link molecules are polymer chains that link two or more crystalline lamellae through the amorphous phase. These chains should contain both crystallizable, long sections of ethylene units, and non-crystallizable sections, containing comonomers or short chain branches [30]. The material fails when either the link molecules cannot support the applied stress, or they become untangled and slip past one another. The high stresses associated with ductile failure are too great for the link molecules to support. The act of link molecules relaxing and slipping past one another is exemplified in brittle failure.

A greater amount of link molecules will improve the resistance to crack growth. A higher molecular weight results in more link molecules and more effective entanglements. Consequently, a HDPE's molecular weight is the strongest indication of how it will perform under static fatigue. The comonomers in HDPE form short chain branches that also improve the material's strength, and increasing the short branch concentration can improve strength as well [8, 27].

4.1.3 Environmental Stress Cracking

In the previous section, stress cracking under creep loading conditions was discussed in detail. When HDPE is exposed to field conditions, further considerations must be accounted for. Field conditions often include exposure to moisture. The material becomes susceptible to small fluid molecules becoming distributed in the polymer molecular chains. This presence of moisture eases the mobility of the chains, and the material becomes more vulnerable to deformations. The addition of moisture in the polymer has the ability to act as both a plasticizer and a crazing agent, both of which can lead to a significant decrease in mechanical strength properties, specifically resistance to creep [31]. The surface-initiated failure of axially stressed polymers in the presence of surface-acting substances such as detergents (surfactants), leachate, polar vapor, or any other liquid which may accelerate stress cracking is defined as environmental stress cracking (ESC) [30-33]. It is important to note that the environmental agents do not chemically alter the material it is affecting. Instead, the agents accelerate the process of crack growth in the polymer. ESC has been estimated to be accountable for 30-40% of all premature in-service failures in plastic components [30].

Since the addition of moisture only accelerates the stress cracking process of HDPE during ESC, the manner in which cracking occurs is unaltered from the description given in the previous section of the report. Crack growth is still a stepwise process, tie molecules and short branch chains resist cracking, and molecular weight remains the greatest indicator of performance in creep loading.

4.1.4 Hydrogen Embrittlement

One danger for engineering materials exposed to a hydrogen environment is the possibility of hydrogen embrittlement. Hydrogen embrittlement is generally more of a concern in metals. When materials are exposed to hydrogen, it sometimes causes them to become more brittle and experience brittle crack growth. This process is an understandable concern for hydrogen vehicle manufacturers. HDPE is unsusceptible to hydrogen embrittlement. Tests ranging from 30 years of natural gas distribution to service in the chemical industry have shown that HDPE has performed well in hydrogen environments. It is also of note that aluminum is one of very few metals with little vulnerability to hydrogen embrittlement [34].

4.1.5 Weld quality

Fuel tank liners are manufactured by way of fusing a HDPE pipe of variable length to standard end caps similarly to the way HDPE pipe sections are connected. Many welding methods exist for joining similar HDPE specimens that include various thermal, friction (mechanical), and electromagnetic implementations. Fusion (butt-fusion) welding is a common method for manufacturing fuel tanks, and that is the method that will be examined in this report.

Before the fusion welding begins, pipes are properly trimmed and prepared to be welded together. Once they are ready to be worked with, a four-phase welding process entails [35-37]. First, the HDPE ends to be fused together are subjected to a heated plate at a specific temperature and pressure. The pressure is kept constant until molten plastic begins to flow from the ends. Next, the heating and melting continue, but at a reduced pressure. Reducing the pressure lets the molten film grow. Once the film has reached a workable size, the next step can take place, which involves removing the heater plates and fusing the ends together. Finally, the ends remain in contact with one another at a specific pressure as joint cools and homogenizes. Variables of time, pressure, and temperature depend on specimen material properties, diameter, and wall thickness.

The quality of the weld depends on how well the process was executed. If executed correctly, joint sections should have nearly identical mechanical properties in comparison to a section of material at the pipe wall. Otherwise, the welding site could be the most vulnerable section [35,36]. Potential circumstances leading to poor weld quality include factors such as cold joints during excessively long removal time during phase three, inadequate heating temperatures and pressures, and joint misalignment. It is important that the material is at the correct temperature to form a good weld. If the manufacturer waits too long after the heating plate has been removed to join the fused ends, the temperature can decrease significantly resulting in poor weld quality. Some less obvious contributors to poor weld quality are environmental elements in the air such as dust, soil, water, and grease, all of which may be present on the material or welding plate. These factors are more pertinent in outdoor construction situations, but are not irrelevant in factory conditions. The presence of any of these elements in a fusion weld may lead to contamination at that site and affect the material's tensile yield stress, plastic deformation energy, maximum energy, and tensile energy to break [35,36].

4.2 Overwrapped pressure vessels

This section addresses the damage and deterioration modes for the overwrapping composite materials for COPVs. This includes the common form of damage from impact for which many of the initial NDE techniques and approaches have been developed. Other degradation modes, such as creep rupture, matrix erosion and UV damage, which has received typically less attention, are also discussed.

4.2.1 Impact damage

Carbon fiber composites are commonly used as a structural shell for fuel tanks due to their outstanding toughness, durability, and high strength and stiffness to weight ratios [38]. The brittle epoxy matrix renders carbon composites particularly susceptible to significant damage caused by a low-velocity impact like dropping a hammer on the pressure vessel [38-40]. The effects of a low-velocity impact are especially dangerous, because the damage is located opposite the side that the impact occurred rendering it invisible from the outside of the pressure vessel in some cases.

When a carbon fiber composite is subject to impact loading, the fibers absorb the majority of the energy and the remainder is distributed across an area or through the laminate thickness [38]. If the load exceeds the composite's ability to carry it, a combination of internal delamination and back-face tension driven failure will take place [39]. Internal delamination refers to the separation of composite layers, and it is a result of interlaminar shear and tension and laminar cracking. Back-face tension driven failure begins as matrix cracking or splitting between fibers. Eventually, fibers fracture and further delamination if the bending strains are high enough. These damages have the capability of significantly reducing the compressive strength of the composite [38-40]. Unfortunately, the delamination areas are more prominent in the interfaces opposite the impacted side, which makes them invisible when viewed from outside of the pressure vessel [38]. The combination of the complexity of low-velocity impact damage and the inability to visually detect flaws makes it difficult to attribute specific failure mechanisms to their contribution to overall strength reduction and hence predict the effects of impact damage [40].

Delamination plays the greatest role in compressive strength reduction for carbon fiber composites. Prior to failure the composite layers near the delamination buckle out of plane. As a result, bending and compressive loading occurs in the remaining undelaminated part of the laminate. Final failure is believed to occur due to the superposition of stresses resulting from bending and in-plane compression [40].

Glass fiber composites are more resistive to low-impact damage due to their low modulus, comparable strength, and weaker fiber/matrix interface. However, their overall performance in compression in general is not good due to their flexibility. Hybridization of carbon and glass can improve the material's performance in impact loading while maintaining the necessary compressive strength [39].

4.2.2 Stress Rupture

The effects of creep on HDPE were discussed in section 4.1.2. of this report. Carbon fiber composites are also susceptible to creep (stress) rupture when loaded in static fatigue. Matrix creep in shear alters a composite's stress-distribution from broken to surviving fibers, and it is a key component of time-dependent failure in a carbon fiber composite [41-43]. The process for creep rupture involves initial microstructural failures at surface flaw sites in the material. As a result, the stress that is usually carried by the damaged fibers is picked up by nearby fibers that are still intact. Eventually, clusters of overstressed fibers become localized and can no longer support the loading. At that point, creep rupture occurs resulting in the formation of a catastrophic crack in the composite [41, 42]. While creep in the matrix near fiber breaks (surface flaws) is a major factor in long-term composite failure, creep rupture can also be a result of progressive debonding at the fiber-matrix interface of a combination of thermally activated flaw growth and failure in the fibers [42]. Also, a high variability in the strength of fibers in a given composite material attributes to why stress-redistribution often results in failure [41].

4.2.3 Matrix erosion

Carbon fiber composites possess both a polymer matrix and a fiber-matrix interface. The polymer matrix allows applied loads to be transferred to the reinforcing carbon fibers as well as providing interlaminar shear strength for the material. The fiber-matrix interface, on the other hand, controls the load transfer characteristics and damage tolerance [44]. Damage, deterioration, or erosion to either component of the composite contributes significantly to its long-term failure. When polymers are exposed to environmental factors, matrix erosion may be experienced due to moisture, temperature, ultraviolet (UV) radiation, thermal cracking, and mechanical fatigue. The primary factors responsible for matrix erosion discussed here in this report include moisture absorption and UV radiation damage. Figure 3 shows a sample of carbon fiber-reinforced epoxy matrix that has been exposed to 2000 hours of cyclic exposure to 100% relative-humidity and UV radiation [45].

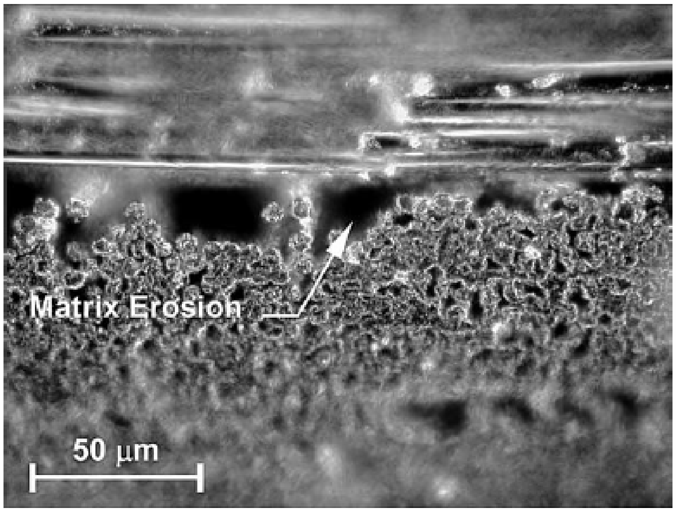


Figure 4.2.1. Carbon fiber-reinforced epoxy matrix exposed to 2000 hours of cyclic exposure to 1000% relative-humidity and UV radiation [45].

The sun emits UV radiation that is received on earth at wavelengths of 290-400 nm. The photons associated with UV radiation possess an energy level similar to the dissociation of polymer covalent bonds, 290-460 kJ/mol. This similarity is what renders exposure to UV radiation dangerous for carbon fiber composites. Absorption of the UV photons into the polymer matrix causes photo-oxidative reactions to take place thus altering the material's chemical structure and causing matrix erosion. The photo-oxidative reactions often result in chain scission and chain crosslinking. Chain scission involves a decrease in the molecular weight of the polymer, which in turn causes a decrease in strength and heat resistance. Chain cross-linking involves the matrix becoming extremely brittle and can cause microcracking in the material. In addition to chain scission and chain crosslinking, photo-oxidative reactions can also cause chromophoric chemical species. Chromophoric chemical species allow polymers to absorb visible light waves, which will result in a discoloration in the material [44].

In order to prevent UV damage, photostabilizers that aim to slow down the process can be utilized. Unfortunately, the photostabilizers can only slow down the rate at which UV damage occurs, and long-term stability of the material is still a concern when exposed to environmental surroundings, especially at high ambient temperatures. Carbon fiber composites affected by UV damage will experience a decrease in interlaminar shear strength, flexural strength, and flexural stiffness, all of which are matrix dominated mechanical properties. Mechanical properties relative to the undamaged fibers, tensile modulus and tensile strength, will remain generally unaffected [44].

The effects of moisture absorption are less significant than those of UV damage on polymers, but it is still important to cover when discussing matrix erosion. Upon exposure to humid environments, carbon-epoxy composites absorb moisture and experience dilatational expansion. The moisture absorption occurs prominently in the epoxy resin; the strength-providing carbon fibers absorb very little or no moisture at all. Despite the fact that these carbon fibers remain unaffected, deterioration in the epoxy matrix alone will greatly contribute to inferior performance over time [44]. Aside from deterioration, the event of moisture absorption solely in the matrix results in a significant mismatch in the volumetric expansion between the matrix and fibers. As a result of the material property mismatch, irreversible damage occurs at the fiber-matrix interface and along the interlaminar boundaries, thus creating localized stress and strain fields in the composite [44,46].

In addition to the volumetric change, the epoxy resin undergoes changes in its thermophysical, plastic, and chemical characteristics by undergoing plasticization and hydrolysis, both of which cause reversible and irreversible changes in the polymer structure [44-47]. Plasticization refers to a material becoming softer and more flexible at the introduction of moisture. Hydrolisis causes stress corrosion in fiber-reinforced plastics due to chemical bonding with a hydrogen environment, an obvious concern when dealing with hydrogen-powered vehicles. The plasticization is usually reversible upon desoprtion, the removal of moisture from the material; hydrolysis, however, involves irreversible chemical bonding or permanent damage [44]. The reversible and irreversible processes create a decrease in the value of both the elastic modulus and glass transition temperature of the material [44-47]. Finally, moisture wicking, absorption of liquid into a material via capillary action, along the fiber-matrix interface can degrade the fiber-matrix bond, resulting in loss of microstructural integrity [44,46]. The comprehensive effect of matrix deterioration as a result of moisture absorption is performance loss in matrix-dominated properties such as compressive strength, interlaminar shear strength, fatigue resistance, and impact tolerance [44].

Studies have shown that UV damage and moisture abosption act in a synergistic manner, resulting in microcracking and matrix erosion at an accelerated rate compared to when they act individually [44,46]. The microcracking caused by UV radiation allows moisture and other harmful chemical agents to enter the epoxy matrix much more easily. Also, moisture exposure may accelerate photo-oxidative reactions, thus accelerating the processes of chain scission and chain crosslinking. Condensation can also remove soluble products of photo-oxidation reactions from a matrix that has experienced UV damage. As a result, fresh surfaces are exposed, and the matrix is prone to further UV damage [44]. Figure 4 shows how exposure to UV radiation and moisture affect a fiber reinforced composite individually and combined.

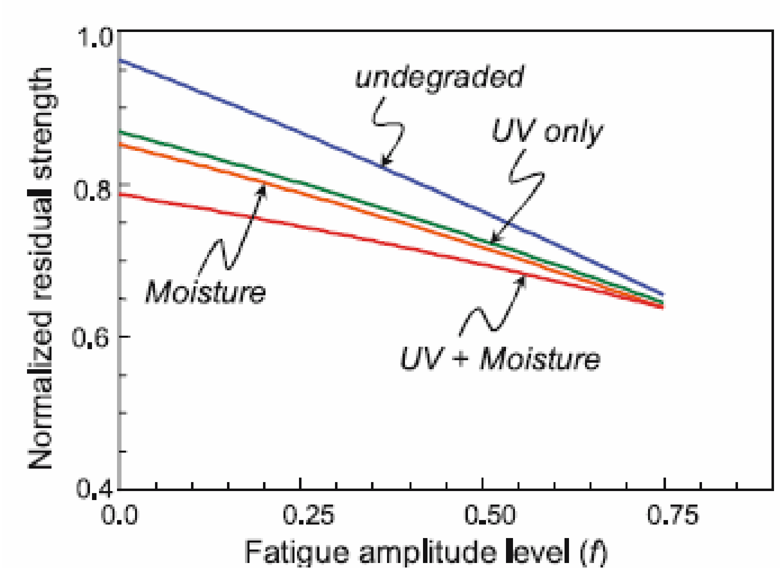


Figure 4.2.2. Performance of a fiber reinforced composite in environmental settings [46].

5.0 CONCLUSION

A wide array of engineering materials will be utilized in the coming hydrogen economy, including traditional engineering materials such as metals like aluminum and steel. For these materials, the failure and degradation modes are well documented and researched. New materials, such as carbon-based composites and polymer materials like HDPE will likely play a key role in the hydrogen infrastructure, the COPV's, pipelines, and storage facilities. For these materials, degradation modes are not as well documented, and there is significantly less experience in how to utilize and maintain these materials. This report has included a literature review of the basic material properties for many of the materials that can be anticipated for hydrogen vehicles and infrastructure. The common failure and degradation modes for COPV's liners of HDPE and overwrapped carbon composite materials were reviewed based on information provided in the literature, in many cases adopted from basic research that was not specific to COPV's but rather characterized the materials itself. This data is intended to provide guidance for the development of NDE technologies in two areas; first, what are the degradation modes that might afflict materials in a hydrogen infrastructure? These represent the target of the NDE inspection, and as such must be fully understood to begin to develop effective NDE technologies. Second, what are the typical materials properties for these materials, such that one can understand which NDE technologies might be most appropriate and develop a basic knowledge of the materials anticipated behavior in the field. This report has provided this guidance to assist in the development of NDE technologies and condition assessment methodologies for the future hydrogen economy.

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