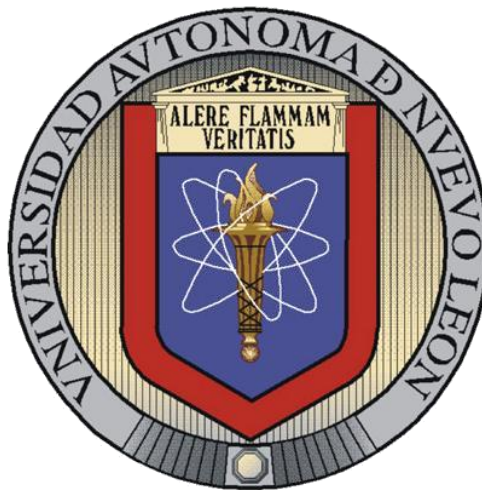# UNIVERSIDAD AUTÓNOMA DE NUEVO LEÓN

FACULTAD DE INGENIERÍA MECÁNICA Y ELÉCTRICA

DIVISION DE ESTUDIOS DE POSGRADO

CARBON FIBER RECOVERY USING SUBCRITICAL AND SUPERCRITICAL FLUIDS FOR CHEMICAL RECYCLING OF THERMOSET COMPOSITE MATERIALS

PRESENTA:

RODOLFO MORALES IBARRA

TESIS

EN OPCIÓN AL GRADO DE DOCTOR EN INGENIERÍA DE MATERIALES

CD. UNIVERSITARIA   SEPTIEMBRE 2014

UNIVERSIDAD AUTÓNOMA DE NUEVO LEÓN

FACULTAD DE INGENIERÍA MECÁNICA Y ELÉCTRICA

DIVISION DE ESTUDIOS DE POSGRADO

CARBON FIBER RECOVERY USING SUBCRITICAL AND SUPERCRITICAL FLUIDS FOR CHEMICAL RECYCLING OF THERMOSET COMPOSITE MATERIALS
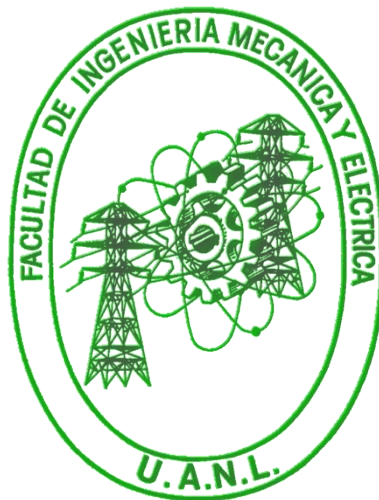
PRESENTA:

RODOLFO MORALES IBARRA

TESIS

EN OPCIÓN AL GRADO DE DOCTOR EN INGENIERÍA DE MATERIALES

CD. UNIVERSITARIA   SEPTIEMBRE 2014

UNIVERSIDAD AUTÓNOMA DE NUEVO LEÓN
FACULTAD DE INGENIERÍA MECÁNICA Y ELÉCTRICA
DIVISIÓN DE ESTUDIOS DE POSGRADO

Los miembros del comité de tesis recomendamos que la tesis *"CARBON FIBER RECOVERY USING SUBCRITICAL AND SUPERCRITICAL FLUIDS FOR CHEMICAL RECYCLING OF THERMOSET COMPOSITE MATERIALS"*, realizada por el alumno Rodolfo Morales Ibarra, matrícula 992276, sea aceptada para su defensa como opción al grado de Doctor en Ingeniería de Materiales.

El Comité de Tesis

Dr. Antonio Francisco García Loera
Asesor

Dr. Motonobu Goto
Co-Asesor

Dr. Mitsuru Sasaki
Co-Asesor

Dr. Juan Antonio Aguilar Garib
Co-Asesor

Dr. Martin Castillo Morales
Co-Asesor

Vo. Bo.

Dr. Simón Martínez Martínez
Subdirector de Estudios de Posgrado

Ciudad Universitaria, San Nicolás de los Garza, Nuevo León a Septiembre 2014

Carbon Fiber Recovery using Subcritical and Supercritical Fluids for Chemical Recycling of Thermoset Composite Materials

Abstract

Recovery of carbon fibers by recycling thermoset epoxy-matrix composites is highly desirable from both economic and environmental perspectives. This reduces waste disposal of scrap from production parts and end-of-life products. In this research, benzyl alcohol and water in subcritical and supercritical conditions, with and without addition of tripotassium phosphate (K_3PO_4) as a decomposition reaction catalyst, were used to recover carbon fibers from composite materials for potential reuse in high performance components; while, in the literature review, the composite materials and their manufacturing processes were revisited, as well as the legal implications of end-of-life composite components, justifying the need for a thermoset composite materials recycling research project. In the experimental section of this research, the reaction temperature and time duration were the experimental parameters. The methods were evaluated by measurement of the decomposition rate of epoxy resin, which reached up to 89.1% and 93.7% with supercritical water and subcritical benzyl alcohol, respectively. The samples were characterized by scanning electron microscopy (SEM). SEM analysis showed complete separation of the composites as indicated by the clean recovered carbon fibers.

Published Material

Several sections in this research have already been published as an original article by a peer-reviewed process in an indexed journal:

Material Submitted to for Revision

Acknowledgements

Table of Contents

1. Introduction

There are several main drivers for composite materials recycling: the sharp increase in the use of composite materials in aerospace, automotive and related industries; the number of aircraft and automotive components reaching end-of-life; environmental policy and legislation; the high intrinsical value of carbon fibers; and the development of a composite materials recycling industry. Decomposition of thermoset resins proceeds rapidly using supercritical fluids compared to conventional and experimental methods [1, 2]. Subcritical and supercritical fluids have the potential to be a new approach for recycling composite materials, since these materials are currently being confined or incinerated [3], which is not the ideal solution from an environmental standpoint. Moreover, very clean fibers can be recovered; for example, a 79.3% decomposition rate can be achieved using supercritical water; the decomposition reaction can be further improved to 95.4% by adding KOH as a catalyst [4] and to 95% with supercritical alcohols in semi-continuous flow systems [5, 6]. n-Propanol is also being used for this purpose [7]. While fibers can retain up to 98% of their tensile strength compared to virgin fibers [8], the use of different additives has shown that fibers could have even better properties after supercritical treatment [9].

1.1. Background

The composites industry has increased globally; in 2000, the European consumption of thermoset composites reached 106 tons per year [10]; in 2005, plastics production in Japan was over 6.1 million tons [3] and more than 210 million tons worldwide [1], and in 2008, the global demand of carbon fibers reached 20,000 tons per year [4]. The advantages of composite materials are many, including monolithic construction of components, lower density, high resistance and relatively good behavior in fatigue compared to metals in structural applications such as aerospace and automotive. Consequently, manufacturers are increasing the percentage of composite materials used in aircraft and automobiles, such that, the latest designs of commercial aircraft are being constructed with more than 50% in weight of composites, namely, carbon fiber and epoxy resin systems. Currently, the number of aircraft reaching end-of-life is more than 100 units per year, while automobile composites waste was more than 60,000 tons in 2011. All of this waste and scrap materials are being handled mainly by landfill and incineration. European Union legislation will demand, through the End-of-Life Vehicles Council Directive 2000/53/EC, that all vehicle manufacturers recycle end-of-life vehicles, aiming for all new vehicles to be 85% recyclable by 2015 [11]. Governmental legislation is being used, not just to provide financial incentives/penalties, but also to prohibit current practices (e.g., disposal, landfill). Thus, reuse and recycling are the only options going forward. Recycling composite materials is a developing industry since a very high value is invested in the manufacture of composites due to the costs of raw materials, certifications, and development of necessary technology.

The latest research has made possible the reuse of carbon fibers in several experimental applications with nonwoven short fiber fabric in new composite materials [12]. The high pressure and high temperature inside the decomposition reactor which is estimated according to Antoine equations and extrapolating according to Wagner equations leads the supercritical fluids to decompose the thermoset matrix materials [13]. Using supercritical water for decomposition in the presence of oxygen results in carbon fibers that can retain mechanical properties as high as the virgin fibers with DR between 94% and 96% [9]. Some other authors have found Young Modulus of 205 GPa retaining 85% of tensile strength compared to virgin fibers [4, 5] and 225 GPa retaining 98% of tensile strength compared to virgin fibers [7].

1.2. Scope

This research presents the recovery and characterization of carbon fibers from carbon-epoxy composite systems using subcritical and supercritical water and subcritical benzyl alcohol, with and without the use of tripotassium phosphate (K_3PO_4) as a decomposition reaction catalyst, as a medium for decomposition of the polymer matrix. Water and benzyl alcohol can be considered as eco-friendly solvents, due to their low potential toxicity and the ability to dissolve epoxy compounds. This research is focused in the decomposition rate of composite materials and the characterization of the resulting fibers by scanning electron microscopy.

1.3. Objective

1.3.1. General Objective

To develop an experimental method for carbon fiber recovery from carbon-fiber-epoxy-resin thermoset composite materials using subcritical and supercritical water and subcritical benzyl alcohol, with and without the use of tripotassium phosphate (K_3PO_4) as a decomposition reaction catalyst, as a medium for decomposition of the polymer matrix.

1.3.2. Specific Objectives

Extracted from the general objective:

- Development, through a design of experiments (DOE), of a method for carbon fiber recovery using subcritical and supercritical fluids.

- Definition of experimental parameters, including, temperature, decomposition reaction duration, use or absence of catalysts.

- Quantitative characterization of the decomposition reaction.

- Qualitative characterization of recovered carbon fibers.

1.4. Hypothesis

Trough the experimental development of the decomposition reaction using subcritical and supercritical fluids it is possible to recover clean carbon fibers while reaching a high decomposition rate of the epoxy matrix for chemical recycling of thermoset composite materials.

2. Composite Materials

2.1. Introduction to Composite Materials

A composite material is a macroscopic combination of two or more distinct materials, having a recognizable interface between them. Fig. 2.1.1. Composites are used not only for their structural properties, but also for electrical, thermal, tribological, and environmental applications. Modern composite materials are usually optimized to achieve a particular balance of properties for a given range of applications. Given the vast range of materials that may be considered as composites and the broad range of uses for which composite materials may be designed, it is difficult to agree upon a single, simple, and useful definition. However, as a common practical definition, composite materials may be restricted to emphasize those materials that contain a continuous matrix constituent that binds together and provides form to an array of a stronger, stiffer reinforcement constituent. The resulting composite material has a balance of structural properties that is superior to either constituent material alone. The improved structural properties generally result from a load-sharing mechanism. Although composites optimized for other

functional properties (besides high structural efficiency) could be produced from completely different constituent combinations than fit this structural definition, it has been found that composites developed for structural applications also provide attractive performance in these other functional areas as well. As a result, this simple definition for structural composites provides a useful definition for most current functional composites.

Thus, composites typically have a fiber or particle phase that is stiffer and stronger than the continuous matrix phase.

| Reinforcement | Matrix | Composite |
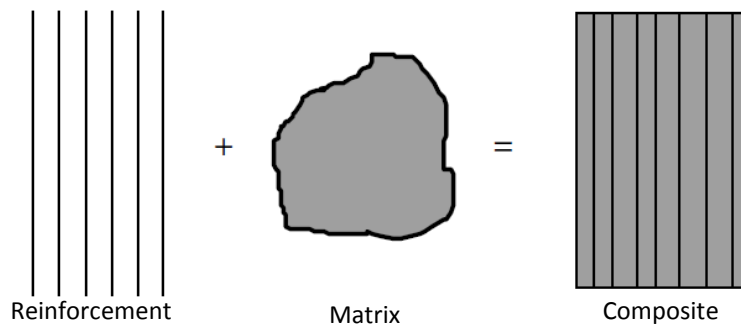
Fig. 2.1.1. - Formation of a composite material using reinforcement (fibers) and matrix (resin).

Composites are commonly classified at two distinct levels. The first level of classification is usually made with respect to the matrix constituent. The major composite classes include organic-matrix composites (OMCs), metal-matrix composites (MMCs), and ceramic-matrix composites (CMCs). The term "organic-matrix composite" is generally assumed to include two classes of composites: polymer-matrix composites (PMCs) and carbon-matrix composites (commonly referred to as carbon-carbon composites). Carbon-

matrix composites are typically formed from PMCs by including the extra steps of carbonizing and densifying the original polymer matrix.
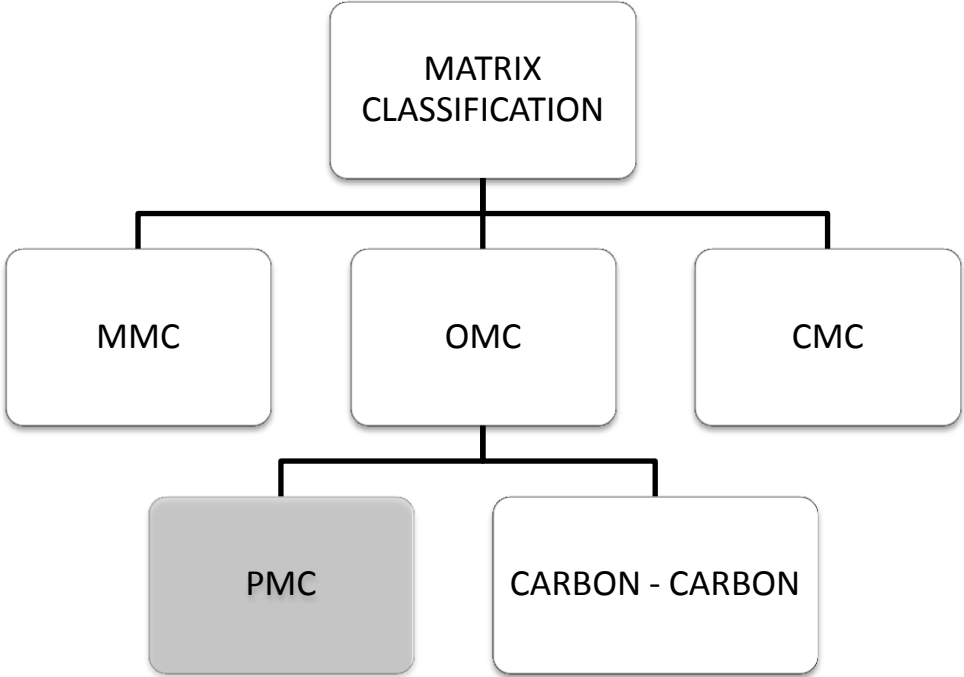
Fig. 2.1.2. - Common types of matrix used in composite materials; metal-matrix composites (MMCs), organic-matrix composites (OMC; subdivided in polymer-matrix composites PMCs and carbon-matrix composites), ceramic-matrix composites (CMCs).

In Fig. 2.1.2. Common types of matrix used in composite materials; metal-matrix composites(MMCs), organic-matrix composites (OMC; subdivided in polymer-matrix composites PMCs and carbon-matrix composites), ceramic-matrix composites (CMCs) are shown. Organic-matrix composites and particularly, polymer-matrix composites are of special interest for this thesis. As aerospace, automotive and general composites industry

revolves around this type of composites. Legislation and the recycling issue being studied in this research are also around the PMCs.

The second level of classification refers to the reinforcement form, particulate reinforcements, whisker reinforcements, continuous fiber laminated composites, and woven composites (braided and knitted fiber architectures are included in this category). Fig 2.1.3.

Continuous fibers   Discontinuous fibers, whiskers

Particles   Fabric, braid, etc.
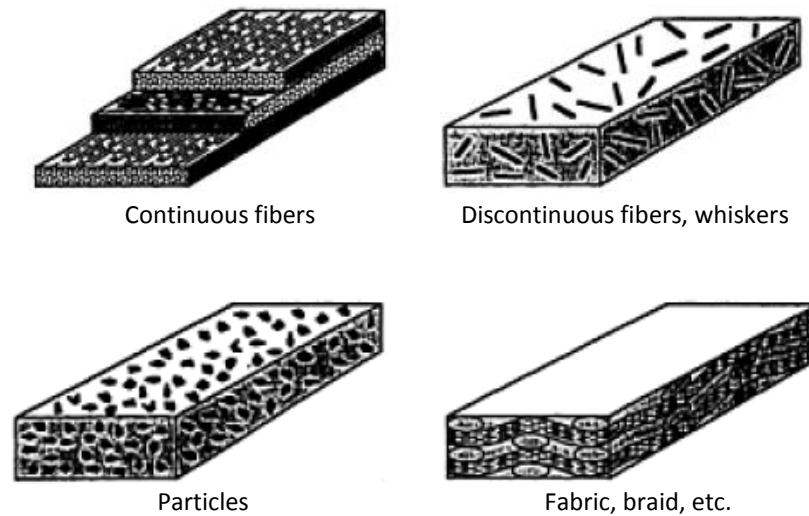
Fig. 2.1.3. - Common forms of fiber reinforcement. In general, the reinforcements can be straight continuous fibers, discontinuous or chopped fibers, particles or flakes, or continuous fibers that are woven, braided, or knitted.

Composites are designed and manufactured for high performance applications and light weight components. There are several advantages of high performance composite materials over traditional engineering materials:

- Part integration - Monolithic component

- Real-time monitoring - Stress, deformation, fatigue with embedded sensors

- High specific stiffness - High stiffness-to-density ratio

- High specific strength - High strength-to-density ratio

- High fatigue performance - High fatigue resistance relative to metals

- High corrosion resistance - High performance due to polymeric matrices

- Design flexibility - Due to materials and monolithic structures; complex parts

- Net-shape manufacturing - Eliminating need of post-processing

Composite materials have been utilized to solve technological problems for a long time but only in the 1960s did these materials start capturing the attention of industries with the introduction of polymeric-based composites. Since then, composite materials have become common engineering materials and are designed and manufactured for various applications including automotive components, sporting goods, aerospace parts, consumer goods, and in the marine and oil industries. The growth in composite usage also came about because of increased awareness regarding product performance and increased competition in the global market for lightweight components. Among all materials, composite materials have the potential to replace widely used steel and aluminum, and many times with better performance. Replacing steel components with composite components can save 60 to 80% in component weight, and 20 to 50% weight by replacing aluminum parts.

As of today, composite materials seem to be the best choice for engineering materials for high performance applications. Their several advantages, properties and the extensive research and interest in composite materials has created an ever increasing industry, replacing old metallic and ceramic materials and components with high performance, high technology, light weight composite materials.

2.2. Constituent Materials

As stated before, a composite material is formed by a reinforcement and a matrix. In our particular case of interest, which is that of OMC, moreover, PMC reinforced with fibers; we will talk and discuss about fibers as reinforcements and polymers as matrices. In order to develop a good understanding of composite materials, which has a combination of its constituent materials, is necessary to describe the roles of fibers and matrix in a composite. Also, their separate properties must be studied in order to select the best constituents for a composite material.

The functions of fibers in a composite are:

- To carry the load. In a structural composite, 70 to 90% of the load is carried by fibers.
- To provide stiffness, strength, thermal stability, and other structural properties in the composites.

- To provide electrical conductivity or insulation, depending on the type of fiber used.

The functions of a matrix in a composite are:

- The matrix material binds the fibers together and transfers the load to the fibers. It provides rigidity and shape to the structure.

- The matrix isolates the fibers so that individual fibers can act separately. This stops or slows the propagation of a crack.

- The matrix provides a good surface finish quality and aids in the production of net-shape or near-net-shape parts.

- The matrix provides protection to reinforcing fibers against chemical attack and mechanical damage (wear).

- Depending on the matrix material selected, performance characteristics such as ductility, impact strength, etc. are also influenced.

- A ductile matrix will increase the toughness of the structure. For higher toughness requirements, thermoplastic-based composites are selected. The failure mode is strongly affected by the type of matrix material used in the composite as well as its compatibility with the fiber.

2.2.1. Fibers

Fibers give the necessary strength to composite materials. Most common fibers are glass, carbon and aramid. Table 2.2.1.1.

Table 2.2.1.1 - Properties of fibers and conventional bulk materials.

Material	Diameter (μm)	Density (ρ) (g/cm³)	Tensile Modulus (E) (GPa)	Tensile Strength (σ) (GPa)	Specific Modulus (E/ρ)	Specific Strength	Melting Point (°C)	% Elongation at Break	Relative Cost
Fibers									
E-glass	7	2.54	70	3.45	27	1.35	1540+	4.8	Low
S-glass	15	2.50	86	4.50	34.5	1.8	1540+	5.7	Moderate
Graphite, high modulus	7.5	1.9	400	1.8	200	0.9	>3500	1.5	High
Graphite, high strength	7.5	1.7	240	2.6	140	1.5	>3500	0.8	High
Boron	130	2.6	400	3.5	155	1.3	2300	—	High
Kevlar 29	12	1.45	80	2.8	55.5	1.9	500(D)	3.5	Moderate
Kevlar 49	12	1.45	130	2.8	89.5	1.9	500(D)	2.5	Moderate
Bulk materials									
Steel		7.8	208	0.34–2.1	27	0.04–0.27	1480	5–25	<Low
Aluminum alloys		2.7	69	0.14–0.62	26	0.05–0.23	600	8–16	Low

Fibers for composite materials can come in many forms, from continuous fibers to discontinuous fibers, long fibers to short fibers, organic fibers to inorganic fibers. Composite-reinforcing fibers can be categorized by chemical composition, structural morphology, and commercial function. Natural fibers such as kenaf or jute are derived from plants and are used almost exclusively in PMCs. Oxide glass fibers are derived from a mixture of oxides; silica, or quartz, fibers are from a single oxide. They are amorphous and primarily used to reinforce thermoplastic and thermoset PMCs. Aramid fibers are crystalline polymer fibers and mostly used to reinforce PMCs. Carbon fibers are based on ordered planar structures; they are primarily used to reinforce PMCs. Ceramic fibers are polycrystalline. Oxide ceramic (e.g., silica-alumina and pure alumina) fibers and nonoxide ceramic (e.g., silicon carbide) fibers are used to reinforce CMCs and MMCs. Value-in-Use. In a PMC, the primary function of a reinforcing fiber is to increase the strength and

stiffness of a matrix material so that the resulting part can satisfy the design requirements or replace an existing part at equal strength, stiffness, and lower weight. In a CMC, the primary function of a reinforcing fiber is to facilitate the use of a given part at the highest possible ultimate-use temperature, offer superior fracture toughness, and prevent premature brittle failure. In a MMC, the primary function of a reinforcing fiber is to sustain the ultimate-use temperature of the part by preventing ductile failure. The value-in-use of a selected reinforcing fiber, whether based on a single property or on a combination of selected properties, depends on its cost as indexed to that property or combination of properties. Fig. 2.2.1.1.
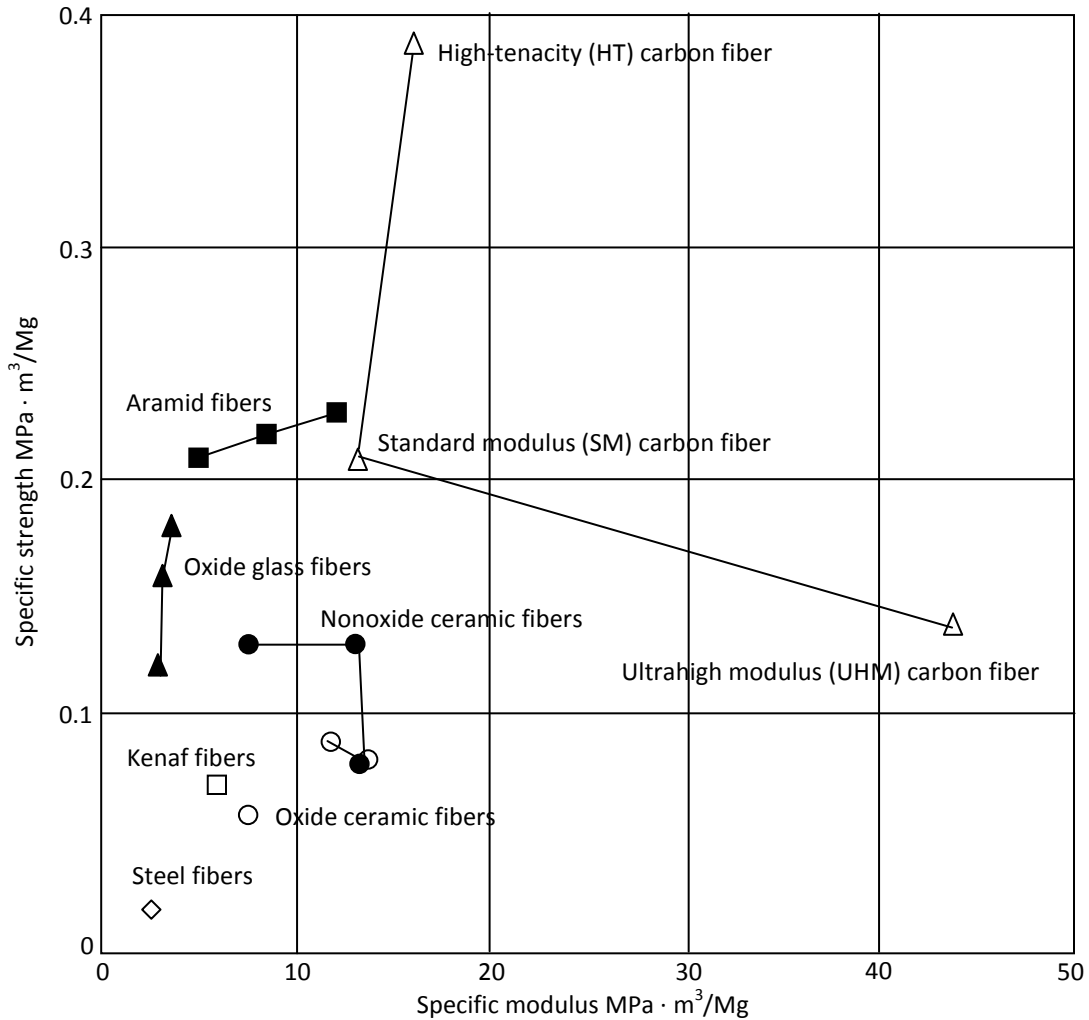
Fig. 2.2.1.1. - Specific properties of selected reinforcing fibers.

Polymeric-matrix composite reinforcing fibers have adequate strength and yield adequate composite strength. Their value-in-use, therefore, depends mostly on their stiffness or elastic modulus (GPa). In transportation, aircraft, and aerospace applications, value-in-use additionally depends on their density, g/cm3 (lb/in.3), and therefore on the specific modulus. Specific properties are material properties divided by the density of the material.

2.2.1.1. Glass Fibers

Glass fibers are among the most versatile industrial materials known today. They are readily produced from raw materials, which are available in virtually unlimited supply. Table 2.2.1.1.1. All glass fibers are derived from compositions containing silica. Table 2.2.1.1.2. They exhibit useful bulk properties such as hardness, transparency, resistance to chemical attack, stability, and inertness, as well as desirable fiber properties such as strength, flexibility, and stiffness.

Table 2.2.1.1.1 - Physical and mechanical properties of glass fibers.

Fiber	Log 3 forming temperature[a]		Liquidus temperature		Softening temperature		Annealing temperature		Straining temperature		Bulk density, annealed glass, g/cm³
	°C	°F	°C	°F	°C	°F	°C	°F	°C	°F	
General-purpose fibers											
Boron-containing E-glass	1160–1196	2120–2185	1065–1077	1950–1970	830–860	1525–1580	657	1215	616	1140	2.54–2.55
Boron-free E-glass	1260	2300	1200	2190	916	1680	736	1355	691	1275	2.62
Special-purpose fibers											
ECR-glass	1213	2215	1159	2120	880	1615	728	1342	691	1275	2.66–2.68
D-glass	...	...	...	...	770	1420	...	...	475	885	2.16
S-glass	1565	2850	1500	2730	1056	1935	...	...	760	1400	2.48–2.49
Silica/quartz	>2300	>4170	1670	3038	...	...	...	...	...	...	2.15

Fiber	Coefficient of linear expansion, 10⁻⁶/°C	Specific heat, cal/g/°C	Dielectric constant at room temperature and 1 MHz	Dielectric strength, kV/cm	Volume resistivity at room temperature, log₁₀ (Ω cm)	Refractive index (bulk)	Weight loss in 24 h in 10% H₂SO₄, %	Tensile strength at 23 °C (73 °F)		Young's modulus		Filament elongation at break, %
	10^{-6}/°C	cal/g/°C	and 1 MHz	kV/cm	$\log_{10}$ (Ω cm)	(bulk)	H_2SO_4, %	MPa	ksi	GPa	10^6 psi	
General-purpose fibers												
Boron-containing E-glass	4.9–6.0	0.192	5.86–6.6	103	22.7–28.6	1.547	~41	3100–3800	450–551	76–78	11.0–11.3	4.5–4.9
Boron-free E-glass	6.0	...	7.0	102	28.1	1.560	~6	3100–3800	450–551	80–81	11.6–11.7	4.6
Special-purpose fibers												
ECR-glass	5.9	...	...	...	...	1.576	5	3100–3800	450–551	80–81	11.6–11.7	4.5–4.9
D-glass	3.1	0.175	3.56–3.62	...	...	1.47	...	2410	349	...	...	...
S-glass	2.9	0.176	4.53–4.6	130	...	1.523	...	4380–4590	635–666	88–91	12.8–13.2	5.4–5.8
Silica/quartz	0.54	...	3.78	...	...	1.4585	...	3400	493	69	10.0	5

Glass fibers are used in the manufacture of structural composites, printed circuit boards and a wide range of special-purpose products. Glass melts are made by fusing (co-

melting) silica with minerals, which contain the oxides needed to form a given composition. The molten mass is rapidly cooled to prevent crystallization and formed into glass fibers by a process also known as fiberization. Nearly all continuous glass fibers are made by a direct draw process and formed by extruding molten glass through a platinum alloy bushing that may contain up to several thousand individual orifices, each being 0.793to 3.175 mm in diameter. While still highly viscous, the resulting fibers are rapidly drawn to a fine diameter and solidify.

Table 2.2.1.1.2 - Glass fiber composition.

Fiber	Ref	Composition, wt%												
		SiO_2	B_2O_3	Al_2O_3	CaO	MgO	ZnO	TiO_2	Zr_2O_3	Na_2O	K_2O	Li_2O	Fe_2O_3	F_2
General-purpose fibers														
Boron-containing E-glass	1, 2	52–56	4–6	12–15	21–23	0.4–4	...	0.2–0.5	...	0–1	Trace	...	0.2–0.4	0.2–0.7
Boron-free E-glass	7	59.0	...	12.1	22.6	3.4	...	1.5	...	0.9	...	...	0.2	...
	8	60.1	...	13.2	22.1	3.1	...	0.5	...	0.6	0.2	...	0.2	0.1
Special-purpose fibers														
ECR-glass	1, 2	58.2	...	11.6	21.7	2.0	2.9	2.5	...	1.0	0.2	...	0.1	Trace
D-glass	1, 2	74.5	22.0	0.3	0.5	...	...	...	...	1.0	<1.3	...	...	...
	2	55.7	26.5	13.7	2.8	1.0	...	...	...	0.1	0.1	0.1	...	...
S-, R-, and Te-glass	1, 2	60–65.5	...	23–25	0–9	6–11	...	...	0–1	0–0.1	...	...	0–0.1	...
Silica/quartz	1, 2	99.9999	...	...	...	...	...	...	...	...	...	...	...	...

Typical fiber diameters range from 3 to 20 μm. Individual filaments are combined into multifilament strands, which are pulled by mechanical winders at velocities of up to 61 m/s (200 ft/s) and wound onto tubes or forming packages. The marble melt process can be used to form special-purpose, for example, high-strength fibers. In this process, the raw materials are melted, and solid glass marbles, usually 2 to 3 cm in diameter, are formed

from the melt. The marbles are remelted (at the same or at a different location) and formed into glass fibers. Glass fibers can also be drawn from the surface of solid preforms.

Glass fibers fall into two categories, low-cost general-purpose fibers and premium special-purpose fibers. Over 90% of all glass fibers are general-purpose products. These fibers are known by the designation E-glass and are subject to ASTM specifications. The remaining glass fibers are premium special-purpose products. Many, like E-glass, have letter designations implying special properties. Table 2.2.1.1.3. Some have trade names, but not all are subject to ASTM specifications.

Table 2.2.1.1.3. - Designation of glass fiber types and characteristics.

Letter designation	Property or characteristic
E, electrical	Low electrical conductivity
S, strength	High strength
C, chemical	High chemical durability
M, modulus	High stiffness
A, alkali	High alkali or soda lime glass
D, dielectric	Low dielectric constant

Once the continuous glass fibers have been produced they must be converted into a suitable product form for their intended composite application. The major finished forms for glass fibers are continuous roving, woven roving, fiberglass mat, chopped strand, and yarns for textile applications.

2.2.1.2. Carbon Fibers

After a 40 year period of development and use in specialized applications, carbon fibers are now on the brink of broad commercialization. Their use is growing rapidly, fueled by significant price reductions during the 1990s and increasing availability. Changes in the performance/price ratio have resulted in the increased penetration of composites into applications formerly held by metals and has enabled their use in other applications previously not possible with existing materials. Additionally, market conditions increasingly favor designs for commercial products that are lighter, stronger, faster, and more fuel efficient—designs that are possible with carbon fibers. No longer relegated to aerospace, carbon fiber composites are now being adopted in fields such as automotive, civil infrastructure, offshore oil, and paper production.

Precursor sources used, in order of volume, are PAN, pitch, and rayon. Although the specific processing details for each precursor is different, all follow a basic sequence involving spinning, stabilization, carbonization, and application of a finish or sizing to facilitate handling, as shown in Fig. 2.2.1.2.1

PAN Process

PAN   Stretch   Thermoset   Carbonize   Graphitize

Pitch Process

Petroleum Pitch   Melt Spin   Thermoset   Carbonize   Graphitize

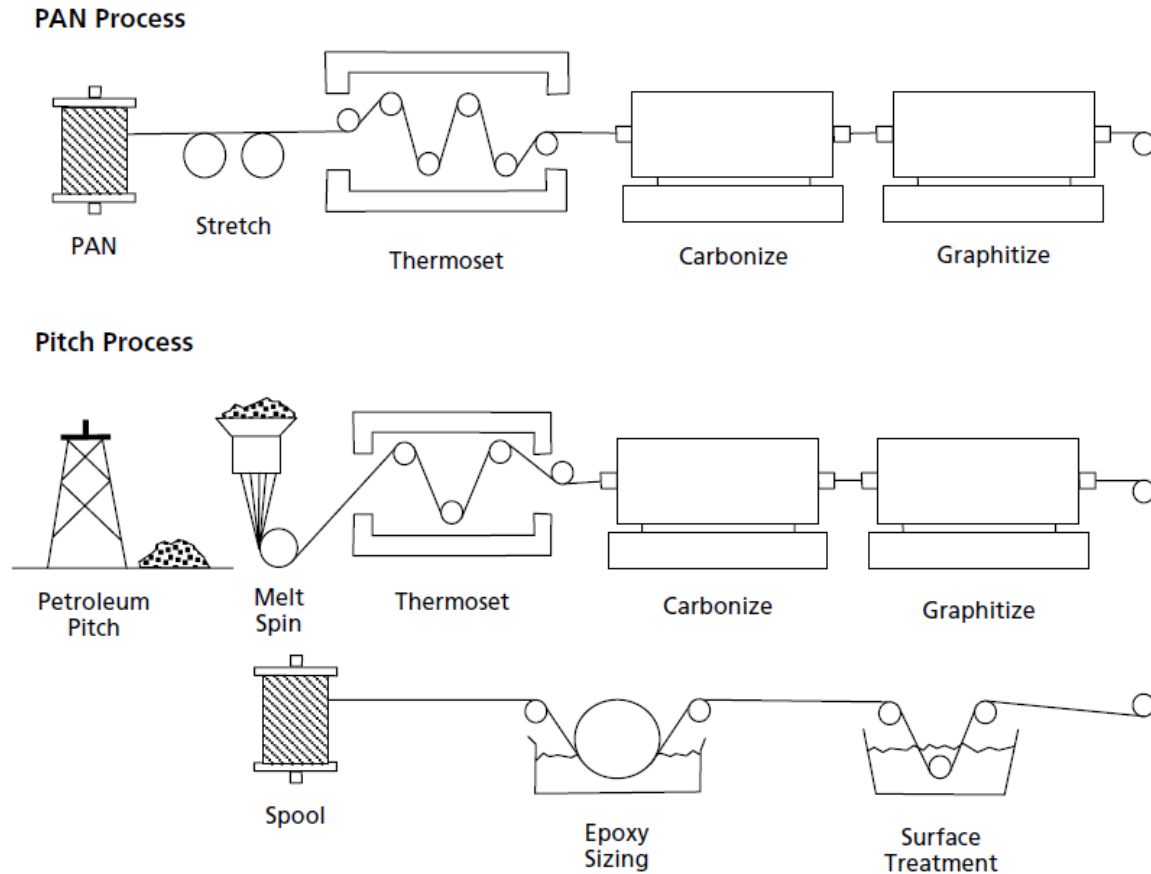Spool   Epoxy Sizing   Surface Treatment

Fig. 2.2.1.2.1 - PAN and pitch fiber manufacturing processes.

Discontinuous carbon fiber whiskers are also now produced in a batch process from hydrocarbon gases using a vapor-liquid-solid growth mechanism. Both carbon and graphite fibers are produced as untwisted bundles called tows. Common tow sizes are 1k, 3k, 6k, 12k, and 24k, where k = 1000 fibers. Immediately after fabrication, carbon and graphite fibers are normally surface treated to improve their adhesion to the polymeric matrix. Sizings, often epoxies without a curing agent, are frequently applied as thin films (1% or less) to improve handleability and protect the fibers during weaving or other handling operations.

Composites made from carbon fiber are five times stronger than grade 1020 steel for structural parts, yet are still five times lighter. In comparison to 6061 aluminum, carbon fiber composites are seven times stronger and two times stiffer, yet 1.5 times lighter. Carbon fiber composites have fatigue properties superior to all known metals, and, when coupled with the proper resins, carbon fiber composites are one of the most corrosion resistant materials available. Certain mesophase-pitch-based carbon fibers possess thermal conductivity three times greater than copper. The electrical conductivity of PAN and pitch-based carbon fibers is used to dissipate static electricity in a wide variety of computer related products. They do not melt or soften with heat, allowing them to be used in such high temperature applications as rocket nozzles and aircraft brakes. In fact, their strength actually increases with temperature in non-oxidizing atmospheres. These unique properties are the result of the fiber microstructure, in both the axial and transverse directions. Envision a single carbon filament as a long cylinder with a diameter of approximately 7 μm. Packed within this cylinder are tiny undulating ribbon-like crystallites which are intertwined and oriented more or less parallel to the axis of the cylinder. The length and straightness of these crystallite "ribbons" determines the modulus of the fiber. A model of the axial structure of a PAN-based carbon fiber is shown in Fig. 2.2.1.2.2.
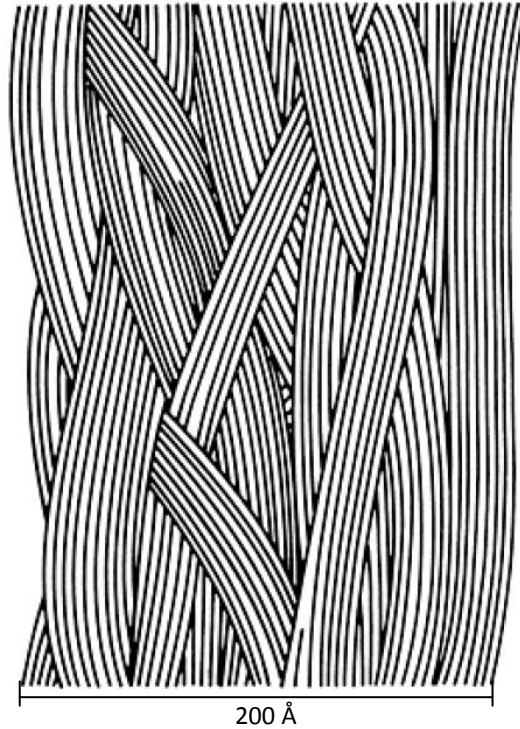
Axial Direction

Fiber Surface

200 Å
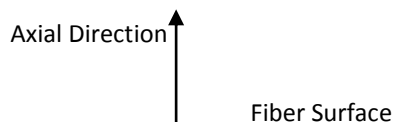
Fig. 2.2.1.2.2. - The undulating ribbon structure of the graphene layers for a PAN-based carbon fiber with a 400 GPa (600 × 106 psi) modulus. The ribbons at the surface have lower amplitude than in the core. There are about 20 graphene layers in the ribbons in the core and about 30 near the surface.

On a finer scale, each ribbon-like crystallite is comprised of multiple wrinkled layers. Fig. 2.2.1.2.3. Each layer is made of carbon atoms arranged like chicken wire in a hexagonal structure characteristic of graphite, called a graphene plane. Strong covalent CC bonds within the layer plane give the potential for high strength and stiffness. Weak van der Waals bonding between the layer planes gives rise to poor shear resistance, but also allows thermal and electrical conductivity. Loose electrons and thermal energy in the form of phonons take advantage of the weak bonding between layer planes and use the interplane space as a corridor to travel.
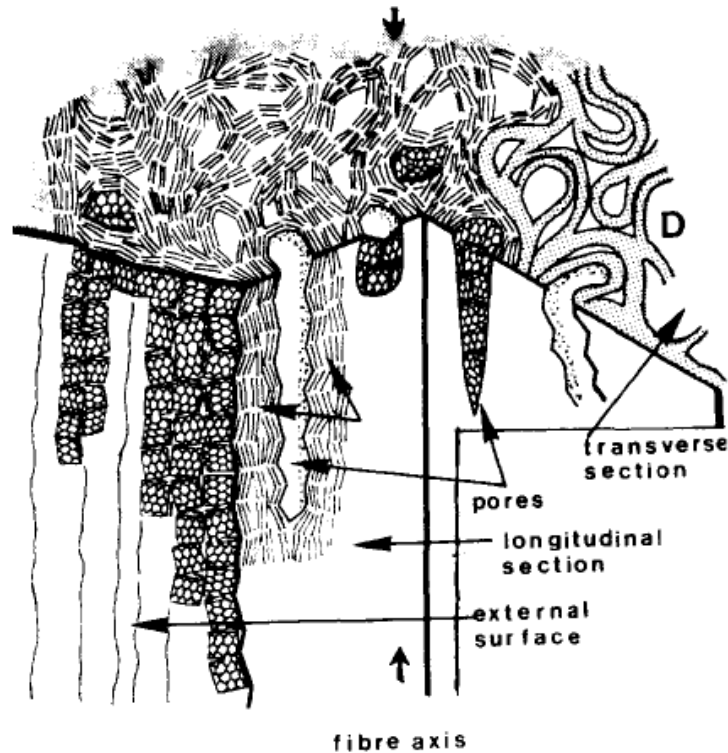
Fig. 2.2.1.2.3. - Model of microstructure within a high strength PAN-based carbon fiber.

The width of the ribbons, the number of graphene layers comprising their thickness, and the length of the ribbons help determine the electrical and thermal characteristics of the carbon fiber, as well as contribute to fiber modulus.

Typically, larger and more oriented graphene planes result in higher thermal and electrical conductivity. Improving the orientation of the microstructure can also increase filament tensile modulus, thermal conductivity, electrical conductivity, and density. This can be accomplished by plastic deformation (for example, stretching the fiber)and/ or heat treatment. Fig 2.2.1.2.4. shows x-ray diffraction results relating heat treatment temperature to the degree of preferred orientation of the microstructure. The degree of

preferred orientation represents the average angle at which the crystallites lie relative to the fiber axis; a zero degree angle means that the crystallites are perfectly aligned with the fiber axis. Transmission electron microscopy shows that the ribbons undulate, such that their amplitude is greater than their wavelength. Any reported measurement of preferred orientation is therefore only an average. The data clearly shows improved orientation with increasing heat treatment temperature. Fig. 2.2.1.2.4 also shows that for heat treatment temperatures above 1600 °C (2900 °F) the mesophase pitch-based fiber will orient more than the PAN fiber, a result of larger crystallite sizes that PAN precursors are not able to achieve.
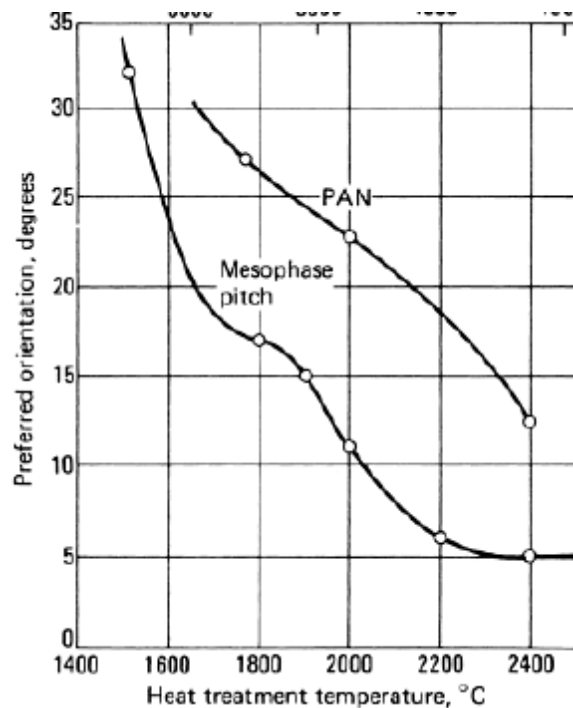

Fig. 2.2.1.2.4. - The preferred orientation of the graphene planes is determined by the heat treatment temperature and the precursor type.

The relationship between preferred orientation of the microstructure and modulus is illustrated in Fig. 2.2.1.2.5. Increased orientation results in increased fiber modulus, as expected.
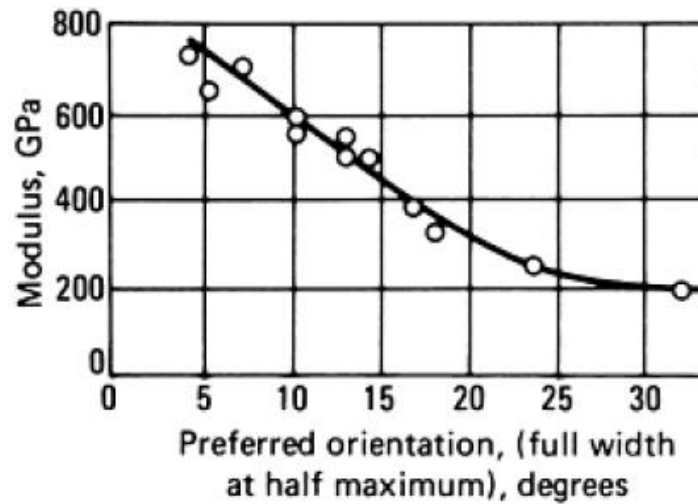

Fig. 2.2.1.2.5. - The modulus of a carbon fiber is determined by the preferred orientation, microstructure, and elastic constants. The relationship between modulus and preferred orientation for a pitch-based carbon fiber is shown.

PAN fibers used to be categorized into standard modulus, intermediate, and high modulus. New offerings by fiber producers have blurred these categories somewhat. The differences between the three categories for fibers made from a particular precursor are due to combinations of mechanical stretching, heat treatment, and/or precursor spinning. Distinctions are also made between aerospace and commercial-grade carbon fibers. The difference relates to the type of precursor used; commercial grades use a lower cost, modified textile-type PAN. Polyacrylonitrile chemistry is similar between the two, and

differences relate more to processing. Generalized properties for PAN-based fibers are presented in Table 2.2.1.2.1

Table 2.2.1.2.1 - Properties of PAN-based carbon fibers.

Property	Commercial, standard modulus	Aerospace		
		Standard modulus	Intermediate modulus	High modulus
Tensile modulus, GPa (10^6 psi)	228 (33)	220–241 (32–35)	290–297 (42–43)	345–448 (50–65)
Tensile strength, MPa (ksi)	380 (550)	3450–4830 (500–700)	3450–6200 (600–900)	3450–5520 (600–800)
Elongation at break, %	1.6	1.5–2.2	1.3–2.0	0.7–1.0
Electrical resistivity, $\mu\Omega \cdot$ cm	1650	1650	1450	900
Thermal conductivity, W/m $\cdot$ K (Btu/ft $\cdot$ h $\cdot$°F)	20 (11.6)	20 (11.6)	20 (11.6)	50–80 (29–46)
Coefficient of thermal expansion, axial direction, 10^{-6} K	−0.4	−0.4	−0.55	−0.75
Density, g/cm^3 (lb/in.^{3})	1.8 (0.065)	1.8 (0.065)	1.8 (0.065)	1.9 (0.069)
Carbon content, %	95	95	95	+99
Filament diameter, μm	6–8	6–8	5–6	5–8
Manufacturers	Zoltek, Fortafil, SGL	BPAmoco, Hexcel, Mitsubishi Rayon, Toho, Toray, Tenax, Soficar, Formosa		

One of the most beneficial properties of all carbon fibers is their superior fatigue resistance in composites. Unlike glass or aramid fibers, carbon fibers do not suffer from stress rupture, and demonstrate complete elastic recovery upon unloading. Creep is not observed in carbon fibers at temperatures below 2200 °C. The carbon content of low-modulus carbon fibers is less than 99%, largely because of retained nitrogen. Increasing carbon contents and densities are achieved through higher heat treatment temperature, which removes nitrogen and provides greater crystalline perfection.

Electrical and thermal conductivity also increase with increasing crystalline perfection and purity. The electrical conductivity of carbon fibers must be taken into account when

processing, since free-floating fibers can short out electrical equipment. Dust-proof, gasketed NEMA 12 enclosures (as specified by the National Electrical Manufacturers Association) are recommended for electrical cabinets, as are covers over electrical outlets.

Room temperature coefficients of thermal expansion (CTE) in the axial direction are slightly negative for low modulus carbon fibers, and grow increasingly negative for the higher modulus fibers. At temperatures above 700 °C, the axial CTE of all fibers turns positive. Composite designers are able to couple the negative CTE of high modulus fibers with appropriate matrix materials to make composites with a CTE of zero over limited temperature ranges.

Resins and molten metal do not easily wet carbon fibers, due to the relatively inert, non-polar fiber surface. Glass fibers depend upon coupling agents to chemically bond with resins; carbon fibers never achieve strong bonds. Instead, carbon fiber depends upon a combination of mechanical and weak chemical bonding with the matrix material. Surface treatments used by carbon fiber manufacturers populate the fiber surface with active chemical groups such as hydroxyls, carboxyls, and carbonyls. These form bridges between the fiber and resin, and depend upon the number of bonds rather than the strength of the bonds to achieve a strong interface.

As an inorganic material, carbon fibers are not affected by moisture, atmosphere, solvents, bases, and weak acids at room temperature. However, oxidation becomes a

problem at elevated temperatures. For low-modulus PAN-based fibers and high-modulus

PAN- or pitch-based fibers, the threshold for oxidation for extended operating times is 350

°C or 450 °C, respectively. Impurities tend to catalyze oxidation at these low temperatures

and somewhat improved oxidation resistance can be expected with higher purity fibers.

2.2.1.3.   Aramid Fibers

Aramid fibers held the distinction of having the highest strength-to-weight ratio of any

commercially available reinforcement fiber at the time of their first commercial

introduction in the early 1970s. The earliest aramid fibers, produced by E.I. Du Pont de

Nemours & Company, Inc., under the tradename of Kevlar, were initially targeted at

reinforcement of tires and plastics. The characteristics of light weight, high strength, and

high toughness have led to the development of applications in composites, ballistics, tires,

ropes, cables, asbestos replacement, and protective apparel. Table 2.2.1.3.1.

Table 2.2.1.3.1 - Kevlar 49 yarn and roving sizes.

Denier	Yield		Number of filaments
	m/kg	yd/lb	
55	163,636	81,175	25
195	46,155	22,895	134
380	23,684	11,749	267
720	12,500	6,200	490
1,140	7,895	3,916	768
1,420	6,388	3,144	1,000
1,860	4,877	2,400	1,000
2,160	4,225	2,097	1,000
2,450	3,673	1,822	1,333
2,840	3,169	1,572	1,333
4,560	1,973	980	3,072
5,680	1,585	786	2,666
7,100	1,268	630	5,000
8,520	1,056	524	3,999

The major fiber forms are continuous filament yarns, rovings, and woven fabrics, and discontinuous staple and spun yarns, fabrics, and pulp. Aramid is also available as textured yarn, needle- punched felts, spunlaced sheets, and wet-laid papers. Kevlar 49 is a high-modulus aramid fiber that is available in 11 yarn sizes and four roving sizes. Table 2.2.1.3.2. Yarns are multifilament products that are spun directly during fiber manufacture and range from a very fine, 25-filament yarn to 1333-filament yarns. Rovings are produced by combining ends of yarns in a process similar to that used to produce glass fibers. For example, four ends of 1140-denier yarn are combined to make 4560- denier roving. Denier, a textile unit of linear density, is the weight in grams of 9000 m of yarn or roving (1 denier = 1.111×10^{-7} kg/m).

Table 2.2.1.3.2. - Kevlar 29 yarn and roving sizes.

Denier	Yield		Number of filaments
	m/kg	yd/lb	
200	45,000	22,320	134
400	22,500	11,160	267
600	15,000	7,440	400
720	12,500	6,200	500
840	10,714	5,314	560
850	10,588	5,252	560
900	10,000	4,960	500
1,000	9,000	4,464	666
1,500	6,000	2,976	1,000
2,250	4,000	1,984	1,000
3,000	3,000	1,488	1,333
15,000	600	298	10,000

Because aramid yarns and rovings are relatively flexible and non-brittle, they can be processed in most conventional textile operations, such as twisting, weaving, knitting, carding, and felting. Yarns and rovings are used in the filament winding, prepreg tape, and pultrusion processes. Applications include missile cases, pressure vessels, sporting goods, cables, and tension members. Conventional woven fabric is the principal aramid form used in composites. Of the wide range of fabric weights and constructions available, those most commonly used are identified in Table 2.2.1.3.3.

Table 2.2.1.3.3. - Kevlar 49 fabric and woven roving specifications.

Style No.	Weave	Basis weight		Fabric construction		Yarn denier	Fabric thickness	
		g/m²	oz/yd²	ends/cm	ends/in.		mm	10⁻³ in.
Light weight								
166[a]	Plain	30.6	0.9	37 × 37	94 × 94	55	0.04	1.5
199[a]	Plain	61.13	1.8	24 × 24	60 × 60	55	0.05	2
120	Plain	61.1	1.8	13 × 13	34 × 34	195	0.11	4.5
220	Plain	74.7	2.2	9 × 9	22 × 22	380	0.11	4.5
Medium weight								
181	Eight-hardness satin	169.8	5.0	20 × 20	50 × 50	380	0.23	9
281	Plain	169.8	5.0	7 × 7	17 × 17	1140	0.25	10
285	Crowfoot	169.8	5.0	7 × 7	17 × 17	1140	0.25	10
328	Plain	230.9	6.8	7 × 7	17 × 17	1420	0.33	13
355	Crowfoot	239.9	6.8	7 × 7	17 × 17	1420	0.30	12
500	Plain	169.8	5.0	5 × 5	13 × 13	1420	0.28	11
Unidirectional								
143	Crowfoot	190.2	5.6	39 × 8	100 × 20	380 × 195	0.25	10
243	Crowfoot	227.5	6.7	15 × 7	38 × 18	1140 × 380	0.33	13
Woven roving								
1050	4 × 4 basket	356.6	10.5	11 × 11	28 × 28	1420	0.46	18
1033	8 × 8 basket	509.4	15.0	16 × 16	40 × 40	1420	0.66	26
1350	4 × 4 basket	458.5	13.5	10 × 9	26 × 22	2130	0.64	25

Many of these aramid fabrics of Kevlar were designed and constructed to be the volume equivalent to the same style number of fiberglass fabric. Generally, fabrics made of a very fine size of aramid yarn are thin, lightweight, and relatively costly, and they are

used when ultra-light weight, thinness, and surface smoothness are critical. Fabrics are available from weavers worldwide. Plain, basket, crowfoot, and satin weave patterns are available. Generally, crowfoot and satin weaves are recommended when a high degree of mold conformability is required. Heavy, woven roving fabrics are also available and are used in marine applications where hand lay-up is appropriate and for hard ballistic fabrics. Unidirectional fabrics are used when maximum properties are desired in one direction. Applications for high-modulus aramid fabrics include commercial aircraft and helicopter secondary composite parts, particularly facings of honeycomb sandwich constructions, boat hulls, electrical and electronic parts, ballistic systems, and coated fabrics.

Although continuous filament forms dominate composite applications, the use of aramid in discontinuous or short fiber forms is rapidly increasing. One reason for the increase is that the inherent toughness and fibrillar nature of aramid allows the creation of fiber forms not readily available with other reinforcing fibers. Kevlar is available in a unique short fiber form known as pulp. It is a very short fiber (2–4 mm) with many attached fibrils. These fibrils are complex in that they are curled, branched, and often ribbon like. They are a direct result of the inherent fibrillar structure of this fiber. The large surface area (40 times standard fiber) and high aspect ratio of the fibrils (greater than 100) can provide very efficient reinforcement. In general, pulp is more easily mixed into resin formulations than is staple fiber and is now used extensively in replacing asbestos in gaskets, friction products, sealants, caulks, and coatings

The dominant aramid paper used in advanced composites in honeycomb sandwich constructions is made from Nomex aramid fiber. It is chemically related to Kevlar, but its tenacity and modulus are considerably lower and are more like those of conventional textile fibers. A range of Nomex papers in varying thicknesses and weights are available. Honeycomb cores of Nomex are also available; densities range from 0.24 to 0.14 g/cm^3. Aramid chopped fibers and pulp can be processed into wet-laid papers on conventional fourdrinier machines. Applications include asbestos replacement, such as in gasketing and automatic transmissions. Straight, uncrimped fibers can be used to maximize stiffness and mechanical properties of the wet-laid papers. These thin, lightweight papers are readily impregnated and can be cost competitive with expensive, lightweight, thin, continuous filament fabrics. Composites that use these papers are being developed for printed circuit boards, aerospace, and industrial applications. The properties of para-aramid fibers are listed in Table 2.2.1.3.4.

Table 2.2.1.3.4. - Properties of para-aramid fibers.

Material	Density, g/cm^3	Filament diameter		Tensile modulus[a]		Tensile strength[a]		Tensile elongation, %	Available yarn count,
		μm	μin.	GPa	10^6 psi	GPa	10^6 psi		No. filaments
Kevlar 29 (high toughness)	1.44	12	470	83	12	3.6 2.8[b]	0.525 0.400[b]	4.0	134–10,000
Kevlar 49 (high modulus)	1.44	12	470	131	19	3.6–4.1	0.525–0.600	2.8	25–5,000
Kevlar 149 (ultrahigh modulus)	1.47	12	470	179	26	3.4	0.500	2.0	1,000

Kevlar 49 is the dominant form used today in structural composites because of its higher modulus. Kevlar 29 is used in composites when higher toughness, damage

tolerance, or ballistic stopping performance is desired. An ultrahigh-modulus fiber, Kevlar 149, is also available. Tensile modulus of para-aramid fibers is a function of the molecular orientation. As a spun fiber, Kevlar 29 has a modulus of 62 GPa. In composite form, it has a modulus 83 GPa that is slightly higher than that of E-glass (69 GPa). Heat treatment under tension increases crystalline orientation, and the resulting fiber, Kevlar 49, has a modulus of 131 GPa. Kevlar 149 has an even higher modulus (179 GPa) and is available on special order. This modulus approaches the theoretical maximum predicted for para-aramid fibers. The tensile strength of para-aramid fiber is in the range of 3.6 to 4.1 GPa). This is more than twice the strength of conventional organic fibers such as nylon 66 and is 50% greater than the strength of E-glass roving. It is believed that tensile failure initiates at fibril ends and propagates via shear failure between the fibrils. High-modulus para-aramid yarns show a linear decrease of both tensile strength and modulus when tested at elevated temperatures in air Fig. More than 80% of these properties are retained at 180 °C. Fig shows retention of room-temperature yarn strength after long exposures at elevated temperatures. More than 80% of strength is retained after 81 h at 200 °C.

2.2.2. Matrix

As discussed, composites are made of reinforcing fibers and matrix materials. Matrix surrounds the fibers and thus protects those fibers against chemical and environmental attack. For fibers to carry maximum load, the matrix must have a lower modulus and greater elongation than the reinforcement. Matrix selection is performed based on

chemical, thermal, electrical, flammability, environmental, cost, performance, and manufacturing requirements. Based on the performance expected from the composite, a proper matrix material can be selected, basically, thermoplastics and thermoset materials, as shown in Fig. 2.2.2.1. Comparison of thermoset and thermoplastic polymer structures.
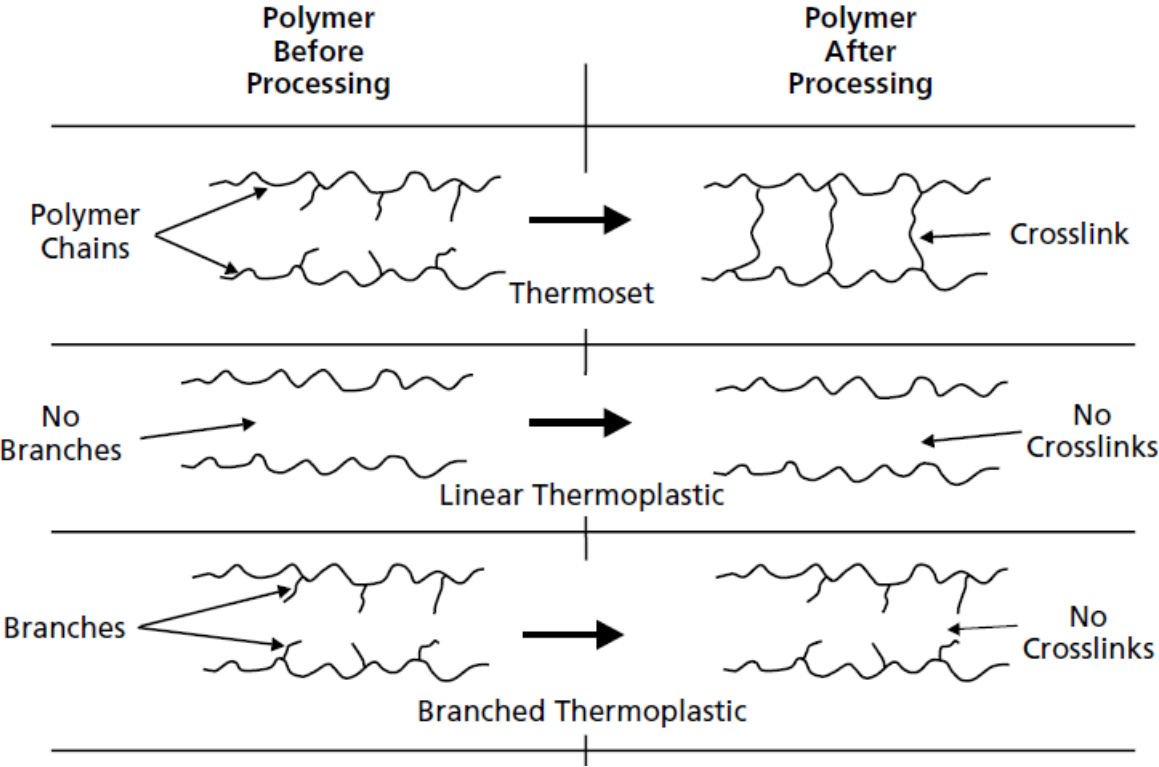
Fig. 2.2.2.1. Comparison of thermoset and thermoplastic polymer structures.

The matrix determines the service operating temperature of a composite as well as processing parameters for part manufacturing.

2.2.2.1.   Thermoset Resins

Thermoset materials once cured cannot be remelted or reformed. During curing, they form three-dimensional molecular chains, called cross-linking, as shown in Fig. 2.2.2.1. Due to these cross-linkings, the molecules are not flexible and cannot be remelted and reshaped. The higher the number of cross-linkings, the more rigid and thermally stable the material will be. In rubbers and other elastomers, the densities of cross-links are much less and therefore they are flexible.
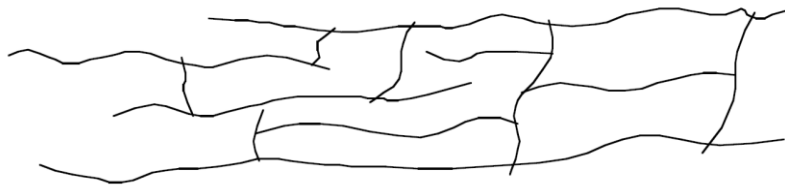
Fig. 2.2.2.1. Cross-linking of thermoset molecules during curing.

Thermosets may soften to some extent at elevated temperatures. This characteristic is sometimes used to create a bend or curve in tubular structures, such as filament-wound tubes. Thermosets are brittle in nature and are generally used with some form of filler and reinforcement. Thermoset resins provide easy processability and better fiber impregnation because the liquid resin is used at room temperature for various processes such as filament winding, pultrusion, and RTM. Thermosets offer greater thermal and dimensional stability, better rigidity, and higher electrical, chemical, and solvent resistance. The most common resin materials used in thermoset composites are epoxy, polyester, vinylester, phenolics, cyanate esters, bismaleimides, and polyimides. Some of the basic properties of selected thermoset resins are shown in Table. 2.2.2.1.

Table 2.2.2.1. - Typical unfilled thermosetting resin properties.

Typical Unfilled Thermosetting Resin Properties

Resin Material	Density (g/cm³)	Tensile Modulus GPa (10^6 psi)	Tensile Strength MPa (10^3 psi)
Epoxy	1.2–1.4	2.5–5.0 (0.36–0.72)	50–110 (7.2–16)
Phenolic	1.2–1.4	2.7–4.1 (0.4–0.6)	35–60 (5–9)
Polyester	1.1–1.4	1.6–4.1 (0.23–0.6)	35–95 (5.0–13.8)

Maximum continuous-use temperatures of the various types of thermoset and thermoplastic resins are shown in Table 2.2.2.2.

Table 2.2.2.2. - Maximum continuous-use temperatures for various thermosets and thermoplastics.

Maximum Continuous-Use Temperatures for Various Thermosets and Thermoplastics

Materials	Maximum Continuous-Use Temperature (°C)
Thermosets	
Vinylester	60–150
Polyester	60–150
Phenolics	70–150
Epoxy	80–215
Cyanate esters	150–250
Bismaleimide	230–320
Thermoplastics	
Polyethylene	50–80
Polypropylene	50–75
Acetal	70–95
Nylon	75–100
Polyester	70–120
PPS	120–220
PEEK	120–250
Teflon	200–260

2.2.2.2. Thermoplastic Resins

Thermoplastics have attractive mechanical properties for many supersonic aircraft requirements and for most commercial aircraft requirements. They also offer dimensional stability and attractive dielectric characteristics. Good flame-retardant and wear-resistant characteristics also are common.

Table 2.2.2.2.1. Qualitative comparison of current thermoplastics and thermosets.

Table 1   Qualitative comparison of current thermoplastics and thermosets

Characteristic	Thermoplastics	Thermosets
Tensile properties	Excellent	Excellent
Stiffness properties	Excellent	Excellent
Compression properties	Good	Excellent
Compression strength after impact	Good to excellent	Fair to excellent
Bolted joint properties	Fair	Good
Fatigue resistance	Good	Excellent
Damage tolerance	Excellent	Fair to excellent
Durability	Excellent	Good to excellent
Maintainability	Fair to poor	Good
Service temperature	Good	Good
Dielectric properties	Good to excellent	Fair to good
Environmental weakness	None, or hydraulic fluid	Moisture
NBS smoke test performance	Good to excellent	Fair to good
Processing temperatures, °C (°F)	343–427 (650–800)	121–315 (250–600)
Processing pressure, MPa (psi)	1.38–2.07 (200–300)	0.59–0.69 (85–100)
Lay-up characteristics	Dry, boardy, difficult	Tack, drape, easy
Debulking, fusing, or heat tacking	Every ply if part is not flat	Typically every 3 or more plies
In-process joining options	Co-fusion	Co-cure, Co-bond
Postprocess joining options	Fastening, bonding, fusion	Fastening, bonding
Manufacturing scrap rates	Low	Low
Ease of prepregging	Fair to poor	Good to excellent
Volatile-free prepreg	Excellent	Excellent
Prepreg shelf life and out time	Excellent	Good
Health/safety	Excellent	Excellent

Table 2.2.2.2.1. qualitatively compares current-generation thermoplastics and thermosets.
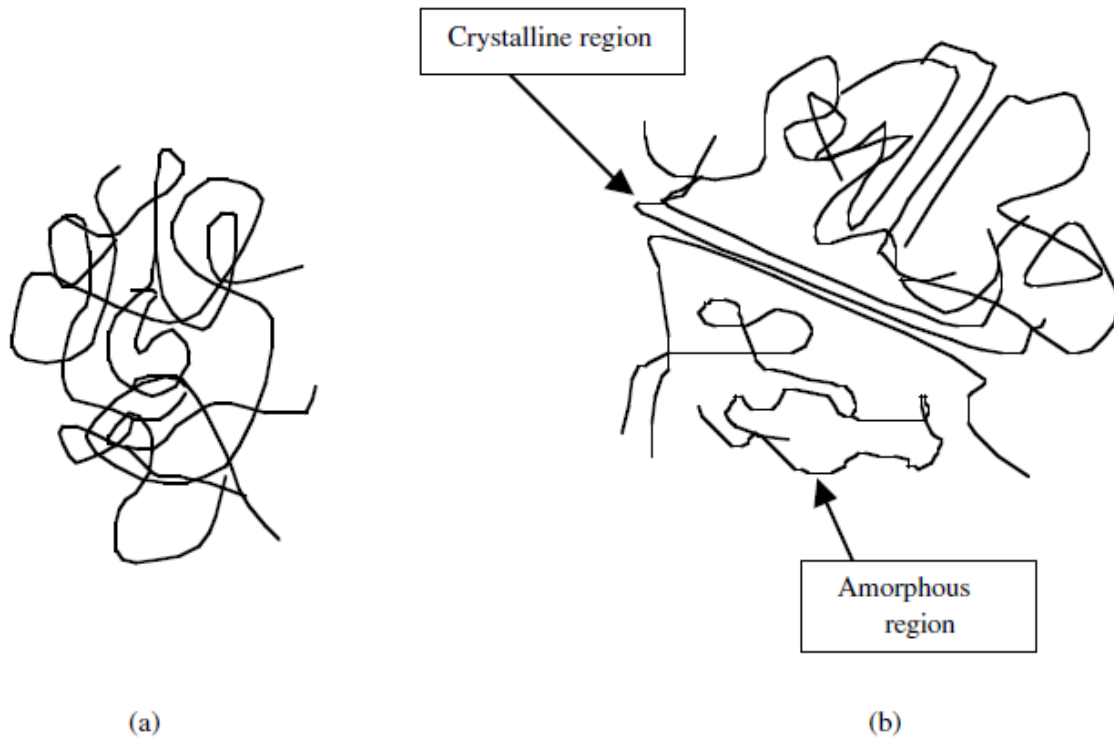
Fig. 2.2.2.2.1 - Molecular arrangements in thermoplastics (a) amorphous and (b) semi-crystalline polymers.

Thermoplastic materials are, in general, ductile and tougher than thermoset materials and are used for a wide variety of nonstructural applications without fillers and reinforcements. Thermoplastics can be melted by heating and solidified by cooling, which render them capable of repeated reshaping and reforming. Thermoplastic molecules do not cross-link and therefore they are flexible and reformable. Thermoplastics can be either amorphous or semicrystalline, as shown in Figure 2.2.2.2.1. In amorphous thermoplastics, molecules are randomly arranged; whereas in the crystalline region of semi-crystalline plastics, molecules are arranged in an orderly fashion. It is not possible to have 100% crystallinity in plastics because of the complex nature of the molecules. Their lower stiffness and strength values require the use of fillers and reinforcements for

structural applications. Thermoplastics generally exhibit poor creep resistance, especially at elevated temperatures, as compared to thermosets. They are more susceptible to solvents than thermosets. Thermoplastic resins can be welded together, making repair and joining of parts more simple than for thermosets. Repair of thermoset composites is a complicated process, requiring adhesives and careful surface preparation. Thermoplastic composites typically require higher forming temperatures and pressures than comparable thermoset systems. Thermoplastic composites do not enjoy as high a level of integration as is currently obtained with thermosetting systems. The higher viscosity of thermoplastic resins makes some manufacturing processes, such as hand lay-up and tape winding operations, more difficult. As a consequence of this, the fabrication of thermoplastic composite parts have drawn a lot of attention from researchers to overcome these problems.

2.2.2.3. Epoxy Resins

By the reaction of bisphenol-A with epichlorohydrin. The families of epoxy resins commercialized first were used as casting compounds and coatings. The same resins are now commodity materials that provide the basis for most epoxy formulations. Epoxy resins are a class of thermoset materials used extensively in structural and specialty composite applications because they offer a unique combination of properties that are unattainable with other thermoset resins. Available in a wide variety of physical forms from low-viscosity liquid to high-melting solids, they are amenable to a wide range of

processes and applications. Epoxies offer high strength, low shrinkage, excellent adhesion to various substrates, effective electrical insulation, chemical and solvent resistance, low cost, and low toxicity. They are easily cured without evolution of volatiles or by-products by a broad range of chemical specie. Epoxy resins are also chemically compatible with most substrates and tend to wet surfaces easily, making them especially well suited to composites applications.
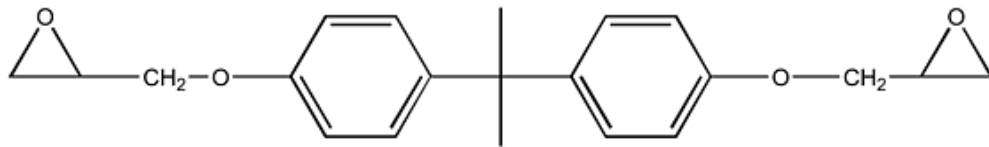
Fig. 2.2.2.3.1. - Chemical structure of diglycidyl ether of bisphenol-A.

Epoxy is a very versatile resin system, allowing for a broad range of properties and processing capabilities. It exhibits low shrinkage as well as excellent adhesion to a variety of substrate materials. Epoxies are the most widely used resin materials and are used in many applications, from aerospace to sporting goods. There are varying grades of epoxies with varying levels of performance to meet different application needs. They can be formulated with other materials or can be mixed with other epoxies to meet a specific performance need. By changing the formulation, properties of epoxies can be changed; the cure rate can be modified, the processing temperature requirement can be changed, the cycle time can be changed, the drape and tack can be varied, the toughness can be changed, the temperature resistance can be improved, etc. Epoxies are cured by chemical reaction with amines, anhydrides, phenols, carboxylic acids, and alcohols. An epoxy is a

liquid resin containing several epoxide groups, such as diglycidyl ether of bisphenol A (DGEBA), which has two epoxide groups as in Fig. 2.2.2.3.1. - Chemical structure of diglycidyl ether of bisphenol-A. In an epoxide group, there is a three-membered ring of two carbon atoms and one oxygen atom. In addition to this starting material, other liquids such as diluents to reduce its viscosity and flexibilizers to increase toughness are mixed. The curing (crosslinking) reaction takes place by adding a hardener or curing agent (e.g., diethylenetriamine [DETA]). During curing, DGEBA molecules form crosslinks with each other. These cross-links grow in a three-dimensional network and finally form a solid epoxy resin. Cure rates can be controlled through proper selection of hardeners and/or catalysts. Each hardener provides different cure characteristics and different properties to the final product. The higher the cure rate, the lower the process cycle time and thus higher production volume rates. Different chemical classes of epoxy resins are available in the market, as it is shown in Table 2.2.2.3.1. Epoxy Resins.

Table 2.2.2.3.1. - Epoxy resins.

Chemical class	Form	Functionality [a]	Equivalent weight [b]	Viscosity at 25 °C (77 °F)		Trade name (supplier)
				Pa · s	cP	
Diglycidyl ether of bisphenol-A	Liquid	2	174–200	5–20	5,000–20,000	Epon 825, 828 (Shell) GY 2600, 6004, 6005, 6008, 6010, 6020 (Vantico) DER 330, 331, 332 (Dow) Epiclon 840, 850 (DIC)
	Solid	2	>500	...	...	Epon 1001, 1002,

						1004, 1007, 1009 (Shell) GT 6063, 6084, 6097 (Vantico) DER 661, 662 (Dow) Epiclon 1050, 2050, 3050, 4050, 7050 (DIC)
Diglycidyl ether of bisphenol-F	Liquid	2	165–190	2–7	2,000–7,000	Epon 862 (Shell) GY 281, 282, 285 (Vantico) DER 354, 354LV (Dow) Epiclon 830, 835 (DIC)
Phenol novolac	Semisolid	2.2–3.6	170–210	varies	varies	EPN 1138, 1139, 1179, 1180 (Vantico) DEN 431, 438 (DOW) N-738, 740, 770 (DIC)
Cresol novolac	Semisolid	2.7–5.4	200–245	varies	varies	ECN 1273, 1280, 1285, 1299, 9511 (Vantico) N-660, 665, 667, 670, 673, 680, 690, 695 (DIC)
Bisphenol-A novolac	Semisolid-solid	…	…	…	…	SU 2.5, 3, 8 (Shell)
Dicyclopentadiene novolac	Solid	…	210–280	…	…	Tactix 556 (Vantico) HP-7200 (DIC)
Triglycidyl ether of trisphenol-methane	Solid	3	150–170	…	…	Tactix 742 (Vantico)
Triglycidyl p-aminophenol	Liquid	3	95–115	0.55–5	550–5,000	MY 0500, 0510 (Vantico) ELM-100 (Sumitomo)
Tetraglycidyl methylene dianiline	Liquid-semisolid	4	109–134	…	…	MY 720, 721, 9512, 9612, 9634, 9655, 9663 (Vantico) Epiclon 430 (DIC) ELM-434 (Sumitomo)
3,4 epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate	Liquid	2	131–143	0.25–0.45	250–450	CY 179 MA (Vantico) UVR-6105, 6110 (Union Carbide)

Epoxy-based composites provide good performance at room and elevated temperatures. Epoxies can operate well up to temperatures of 200 to 250°F, and there are epoxies that can perform well up to 400°F. For high-temperature and high-performance

epoxies, the cost increases, but they offer good chemical and corrosion resistance. Epoxies come in liquid, solid, and semi-solid forms. Liquid epoxies are used in RTM, filament winding, pultrusion, hand lay-up, and other processes with various reinforcing fibers such as glass, carbon, aramid, boron, etc. Semi-solid epoxies are used in prepreg for vacuum bagging and autoclave processes. Solid epoxy capsules are used for bonding purposes. Epoxies are more costly than polyester and vinylesters and are therefore not used in cost-sensitive markets (e.g., automotive and marine) unless specific performance is needed. Epoxies are generally brittle, but to meet various application needs, toughened epoxies have been developed that combine the excellent thermal properties of a thermoset with the toughness of a thermoplastic. Toughened epoxies are made by adding thermoplastics to the epoxy resin by various patented processes.

2.2.2.4.   Polyester Resins

Polyesters are low-cost resin systems and offer excellent corrosion resistance. The operating service temperatures for polyesters are lower than for epoxies. Polyesters are widely used for pultrusion, filament winding, SMC, and RTM operations. Polyesters can be a thermosetting resin or a thermoplastic resin. Unsaturated polyesters are obtained by the reaction of unsaturated difunctional organic acids with a difunctional alcohol. Fig. 2.2.2.4.1. shows the chemical structure of polyester resin. The acids used include maleic, fumaric, phthalic, and terephthalic. The alcohols include ethylene glycol, propylene glycol, and halogenated glycol. For the curing or crosslinking process, a reactive monomer such

as styrene is added in the 30 to 50 wt% range. The carbon-carbon double bonds in unsaturated polyester molecules and styrene molecules function as the cross-linking site. With the growing health concerns over styrene emissions, the use of styrene is being reduced for polyester-based composite productions. In recent methods, catalysts are used for curing polyesters with reduced styrene.

$$-(CH_2)_n-C-O-$$
$$\overset{\displaystyle O}{\overset{\displaystyle \|}{}}$$
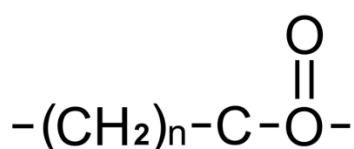
Fig. 2.2.2.4.1. - Chemical structure of polyester polymer.

Mechanical properties are often the critical factor in selecting a polyester resin for a specific application. Table 2.2.2.4.1. lists the common test methods of the American Society for Testing and Materials (ASTM) that are used to characterize the mechanical properties of polyester resin composites.

Table 2.2.2.4.1. - ASTM test methods for characterizing mechanical properties of polyester resins.

Properties	ASTM Test Method
Tensile strength, modulus, and % elongation	D 638
Flexural strength and modulus	D 790
Compressive strength, modulus, and % compression on break	D695
Izod impact	D256
Heat distortion	D 648
Barcol hardness	D 2583

While the physical properties of polyester composites are predominately controlled by reinforcement, the physical properties of the polyester resin do affect the durability and thermal performance. Representative examples of clear- cast polyester resin data are shown in Table 2.2.2.4.2. It should be noted that within each class of resins, modifications are made to the polymer. These modifications effectively trade off thermal performance for increased toughness (Table 2.2.2.4.2). Table 2.2.2.4.2. highlights the differences among the classes of polyesters.

Table 2.2.2.4.2 Mechanical properties of clear-cast (unreinforced) polyester resins.

Material	Barcol hardness	Tensile strength		Tensile modulus		Elongation, %	Flexural strength		Flexural modulus		Compressive strength		Heat-deflection temperature	
		MPa	ksi	GPa	10^6 psi		MPa	ksi	GPa	10^6 psi	MPa	ksi	°C	°F
Orthophthalic	...	55	8	3.45	0.50	2.1	80	12	3.45	0.50	...	...	80	175
Isophthalic	40	75	11	3.38	0.49	3.3	130	19	3.59	0.52	120	17	90	195
BPA fumarate	34	40	6	2.83	0.41	1.4	110	16	3.38	0.49	100	15	130	265
Chlorendic	40	20	3	3.38	0.49	...	120	17	3.93	0.57	100	15	140	285
Vinyl ester	35	80	12	3.59	0.52	4.0	140	20	3.72	0.54	...	...	100	212

Isophthalic resins tend to show higher tensile and flexural properties than orthophthalic resins. This may be because isophthalics usually form more linear, higher-molecular-weight polymers than orthophthalics. In contrast, the BPA fumarate and chlorendic resins are formulated for service in aggressive corrosive conditions and consequently are much more rigid. This results in clear castings that are brittle and have low tensile elongation and strength. The vinyl ester, because of its bisphenol diepoxide content, exhibits excellent tensile and flexural properties as well as high elongation.

2.2.2.5. Vinylester Resins

Vinyl ester resin is the common name for a series of unsaturated resins that are prepared by the reaction of a monofunctional unsaturated acid, typically methacrylic acid, with an epoxy resin. The epoxy resin is "endcapped" with an unsaturated ester to form the vinyl ester resin. The resulting polymer, which contains unsaturated sites only in the terminal positions, as shown in Fig. 2.2.2.5.1., is mixed with an unsaturated monomer, generally styrene. At this point, the appearance, handling properties, and curing characteristics of vinyl ester resins are the same as conventional polyester resins. However, the corrosion resistance and mechanical properties of vinyl ester composites are much improved over standard polyester resin composites. These improved properties have enabled vinyl ester resins to become the workhorse of the polyester custom corrosion industry. However, the properties of vinyl ester resins are not as easily tailored to a specific application as are standard unsaturated polyester resins. This combined with the use of higher-cost raw materials has somewhat limited the ability of vinyl ester resins to penetrate the unsaturated polyester resin market.
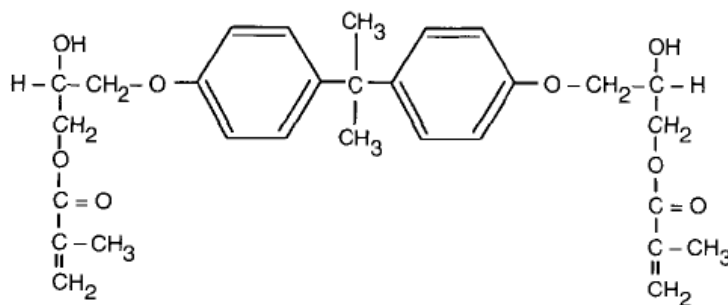
Fig. 2.2.2.5.1. - Chemical structure of vinylester resin polymer.

Vinylesters are widely used for pultrusion, filament winding, SMC, and RTM processes. They offer good chemical and corrosion resistance and are used for FRP pipes and tanks in the chemical industry. They are cheaper than epoxies and are used in the automotive and other high-volume applications where cost is critical in making material selection. Vinylesters are formed by the chemical reaction of an unsaturated organic acid with an epoxide-terminated molecule. In vinylester molecules, there are fewer unsaturated sites for cross-linking than in polyesters or epoxies and, therefore, a cured vinylester provides increased ductility and toughness.

2.3. Composite Materials Properties

The mechanical properties of composite materials can vary widely depending on the matrix-reinforcement fiber combination, reinforcement architecture, fillers and chosen manufacturing process. Consequently a table of outline material properties must have a large variation in quoted values. Such a table is still of use as it allows initial comparison of material properties as well as providing a benchmark against which to measure the success of the recycling process in achieving acceptable material properties. Table 2.3.1. presents average mechanical properties for some of the more commonly encountered composite material types, indicating the chosen fiber type and fiber volume fraction (v.f.). The mechanical performance of the selected composites varies from being only slightly above that expected of unfilled polymer for the low (~20%) volume fraction, randomly

oriented, short fiber reinforced flow forming materials, towards metal-like properties for

high v.f. continuous aligned fiber reinforced laminates.

Table 2.3.1. - Mechanical properties of production composites.

Processing	Material	Fibre	v.f. (%)	Modulus (GPa)	Strength (MPa)	Specific gravity
Flow (injection)	BMC	Glass	20	13	31	1.8
	PP-LFT	Glass	30	6.5	100	1.12
Flow (compression)	SMC	Glass	30	11	80	1.9
	PP-GMT	Glass	40	5.3	100	1.2
Hand lay	Polyester	Glass	40	20	320	1.25
	PP	Glass	35	15	310	1.2
RTM	Polyester	Glass	55	22	360	1.9
VARTM	Epoxy	Glass	55	24	550	1.9
VARTM (UD)	Epoxy	Carbon	55	130	1200	1.6
Prepreg	Epoxy	Carbon	50	60	890	1.5

The advantages of high performance composites are many, including lighter weight;

the ability to tailor lay-ups for optimum strength and stiffness; improved fatigue strength;

corrosion resistance; and with good design practice, reduced assembly costs due to fewer

detail parts and fasteners. The specific strength (strength/density) and specific modulus

(modulus/density) of high strength fiber composites, especially carbon, are higher than

other comparable aerospace metallic alloys. This translates into greater weight savings

resulting in improved performance, greater payloads, longer range, and fuel savings. A

comparison of the overall structural efficiency of carbon/epoxy, Ti-6Al-4V, and 7075-T6

aluminum is given in Fig. 2.3.1.
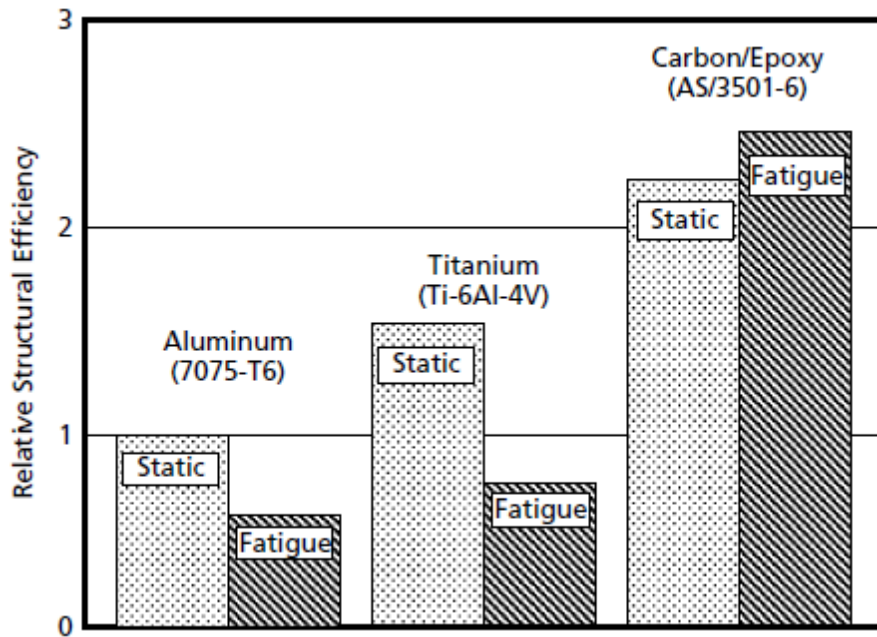
Fig. 2.3.1. - Relative structural efficiency of aircraft materials.

Composites do not corrode and their fatigue resistance is outstanding. Corrosion of aluminum alloys is a major cost, and a constant maintenance problem, for both commercial and military aircraft. The corrosion resistance of composites can result in major savings in supportability costs. The superior fatigue resistance of composites, compared to high strength metals, is shown in Fig. 2.3.2.
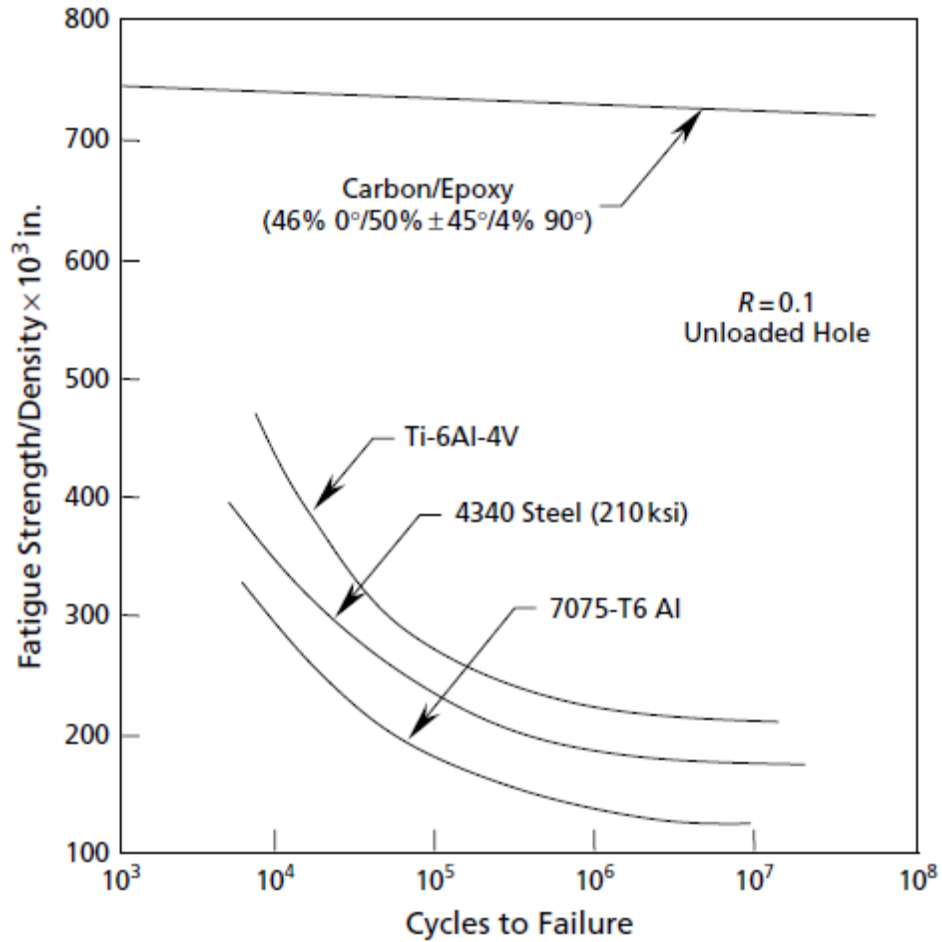
Fig. 2.3.2. - Fatigue properties of aerospace materials.

As long as reasonable design strain levels are used, fatigue of carbon fiber composites should not be a problem.

2.4. Composite Materials Manufacturing Processes

Continuous fiber composites are laminated materials Fig. 2.4.1., in which the individual layers, plies, or lamina are oriented in directions that will enhance the strength in the primary load direction. Unidirectional 0° laminates are extremely strong and stiff in the 0°

direction but are also very weak in the 90° direction because the load must be carried by the much weaker polymeric matrix.

Fibers appear as ovals because they were cut at an angle to the 0° direction.

0.0003 in. Diameter Carbon Fiber

0.005 in. Thick Ply
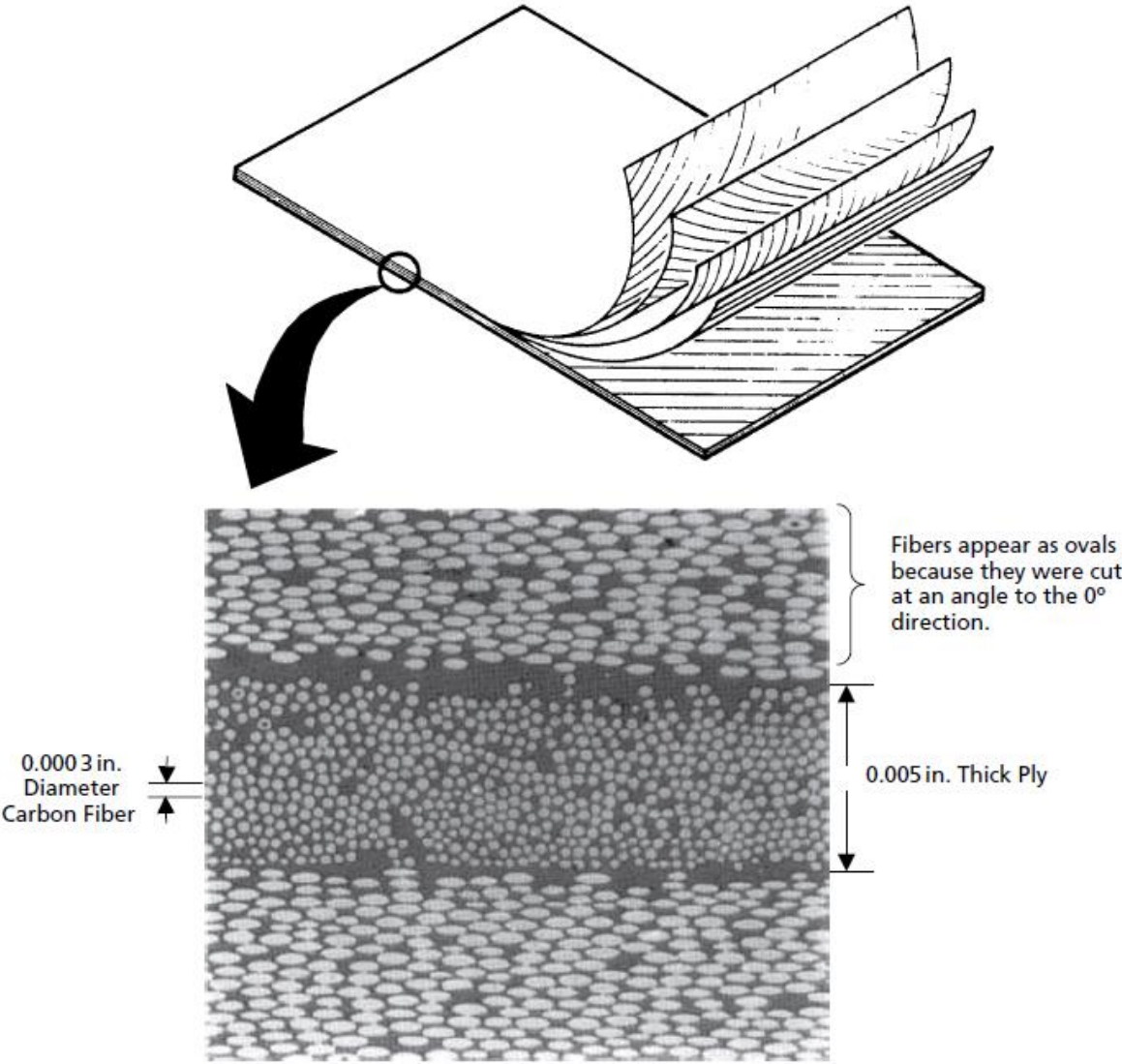
Fig. 2.4.1. - Laminate construction.

There are a multitude of material product forms used in composite structures. The fibers can be continuous or discontinuous. They can be oriented or disoriented (random). They can be furnished as dry fibers or preimpregnated with resin (prepreg). Since the

market drives availability, not all fiber or matrix combinations are available in all product forms. In general, the more operations required by the supplier, the higher the cost. For example, prepreg cloth is more expensive than dry woven cloth. While complex dry preforms may be expensive, they can translate into lower fabrication costs by reducing or eliminating hand lay-up costs. If structural efficiency and weight are important design parameters, then continuous reinforced product forms are normally used because discontinuous fibers yield lower mechanical properties. Rovings, tows, and yarns are collections of continuous fiber. This is the basic material form that can be chopped, woven, stitched, or prepregged into other product forms. It is the least expensive product form and available in all fiber types. Rovings and tows are supplied with no twist, while yarns have a slight twist to improve their handleability. Some processes, such as wet filament winding and pultrusion, use rovings as their primary product form. Continuous thermoset prepreg materials are available in many fiber and matrix combinations. A prepreg is a fiber form that has a predetermined amount of uncured resin impregnated on the fiber by the material supplier. Prepreg rovings and tapes are usually used in automated processes, such as filament winding and automated tape laying, while unidirectional tape and prepreg fabrics are used for hand-lay up. Unidirectional prepreg tapes, Fig. 2.4.2. offer better structural performance than woven prepregs, due to absence of fiber crimp and the ability to more easily tailor the designs. However, woven prepregs offer increased drapeablility.

Fig. 2.4.2. - Unidirectional prepreg tape.

Woven fabric, shown in Fig. 2.4.3., consisting of interlaced warp and fill yarns, is the most common continuous dry material form. The warp is the 0° direction as the fabric comes off the roll and the fill, or weft, is the 90° fiber. Typically, woven fabrics are more drapeable than stitched materials; however, the specific weave pattern will affect their drapeablility characteristics. The weave pattern will also affect the handleability and structural properties of the woven fabric. Many weave patterns are available. All weaves have their advantages and disadvantages, and consideration of the part configuration is necessary during fabric selection. Two of the more widely used weave patterns are shown in Fig. 2.4.4. The plain weave has the advantage that it has good stability and resists distortion, while the satin weaves have higher mechanical properties, due to less fiber crimp, and are more drapeable. Most fibers are available in woven fabric form; however, it can be very difficult to weave some high modulus fibers due to their inherent brittleness. Advantages of woven fabric include drapeablility, ability to achieve high fiber

volumes, structural efficiency, and market availability. A disadvantage of woven fabric is the crimp that is introduced to the warp or fill fiber during weaving. Finishes or sizings are typically put on the fibers to aid in the weaving process and minimize fiber damage.
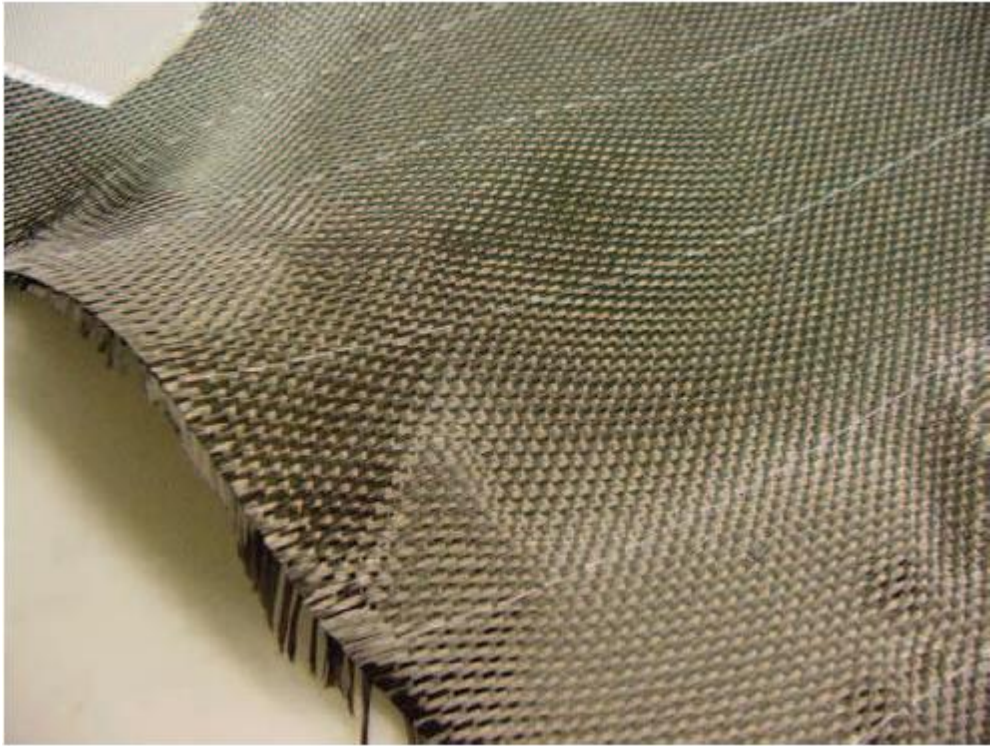
Fig. 2.4.3. - Dry woven carbon cloth.
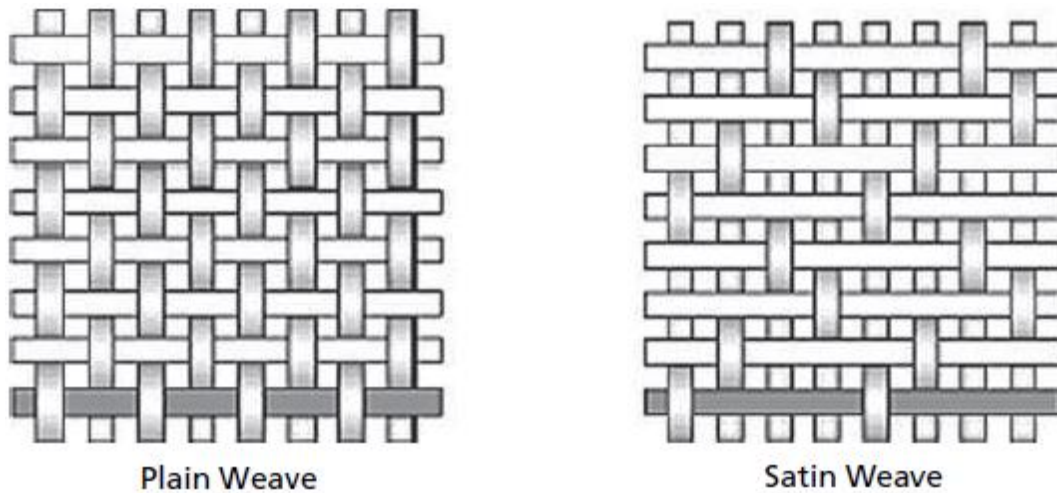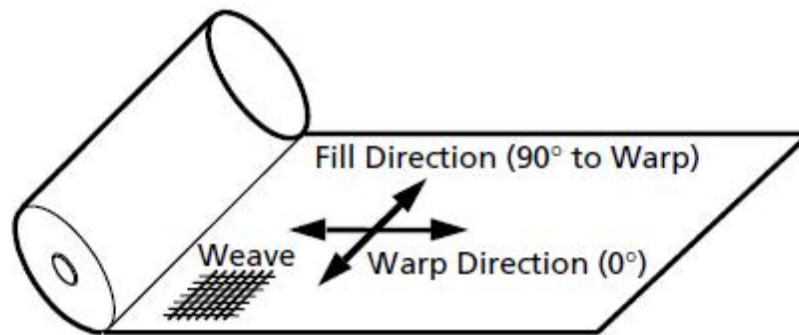
Fig. 2.4.4. - Plain and satin wave cloth.

A preform is a pre-shaped fibrous reinforcement that has been formed into shape, on a mandrel or in a tool, before being placed into a mold. As shown in Fig. 2.4.5., the shape of the preform closely resembles the final part configuration. A simple multi-ply stitched fabric is not a preform unless it is shaped to near its final configuration. The preform is the most expensive dry, continuous, oriented fiber form; however, using preforms can significantly reduce fabrication labor.

Fig. 2.4.5. - Fiberglass preform.

2.4.1. Manual Lay-up

Manual hand collation is conducted using either prepreg tape or broadgoods. Prior to actual lay-up, the plies are usually precut and kitted into ply packs for the part. The cutting operations are normally automated unless the number of parts to be built does not justify the cost of programming an automated ply cutter. However, if hand cutting is selected, templates to facilitate the cutting operation may have to be fabricated. If the lay-up has any contour of the plies, the contour will also have to be factored into the templates. Automated ply cutting of broadgoods, usually 48–60 in. wide material, is the most prevalent method used today. Both reciprocating knives and ultrasonically driven ply-cutting methods are currently used in the composites industry. The ultrasonic ply cutter

operates in a similar manner; however, the mechanism is a chopping rather than a cutting action. Instead of a bristle bed that allows the cutter to penetrate, a hard plastic bed is used with the ultrasonic method. A typical ultrasonic ply cutter, shown in Fig. 2.4.1.1., can cut at speeds approaching 2400 fpm, while holding accuracies of ±0.003 in.

Fig. 2.4.1.1. - Large ultrasonic ply cutter.

One of the primary advantages of any of the automated methods is that they can be programmed off-line and nesting routines are used to maximize material utilization.

2.4.2. Flat Ply Collation and Vacuum Forming

To lower the cost of ply-by-ply hand collation directly to the contour of the tool, a method called flat ply collation was developed in the early 1980s. This method, shown

schematically in Fig. 2.4.2.1., consists of manually collating the laminate in the flat condition, and then using a vacuum bag to form it to the contour of the tool. If the laminate is thick, this process may have to be done in several steps to prevent wrinkling and buckling of the ply packs.

Collate

Shape to Tool
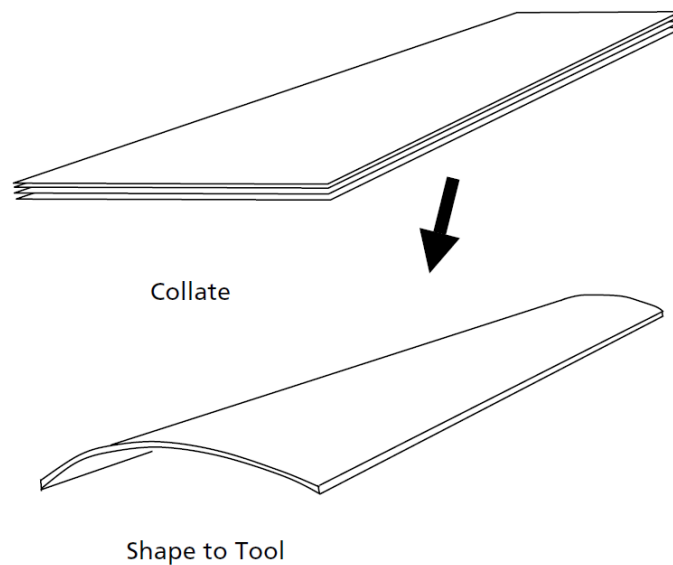
Fig. 2.4.2.1 - Flat ply collation.

Heat (<150° F) can be used to soften the resin to aid in forming if the contour is severe. This process has also been used to successfully make substructure parts, such as C-channels. Normally woven cloth is used and the parts are again flat ply collated, placed on a form block tool, covered with a release film, and then vacuum formed to shape using a silicone rubber vacuum bag. Note that it is important to keep the fibers in tension during the forming process. If compression occurs, the fibers will wrinkle and buckle. To maintain uniform tension during the forming operation, a double diaphragm forming technique can be used, in which the plies are sandwiched between two thin flexible diaphragms pulled

together with a vacuum. Again, the application of low heat to soften the resin and aid in forming is quite prevalent. After cure, these long parts can be trimmed into shorter lengths, thus saving the cost of laying-up each individual part on its individual tool.

2.4.3. Automated Tape Laying

Automated tape laying (ATL) is a process that is very amenable to large flat parts, such as wing skins. Tape layers usually lay-down either 3, 6, or 12 in. wide unidirectional tape, depending on whether the application is for flat structure or mildly contoured structure. Automated tape layers are normally gantry style machines, Fig. 2.4.3.1., which can contain up to 10 axes of movement. Normally, 5 axes of movement are associated with the gantry itself and the other 5 axes with the delivery head movement. A typical tape layer consists of a large floor-mounted gantry with parallel rails, a cross-feed bar that moves on precision ground ways, a ram bar that raises and lowers the delivery head, and the delivery head that is attached to the lower end of the ram bar. Commercial tape layers can be configured to lay either flat or mildly contoured parts.
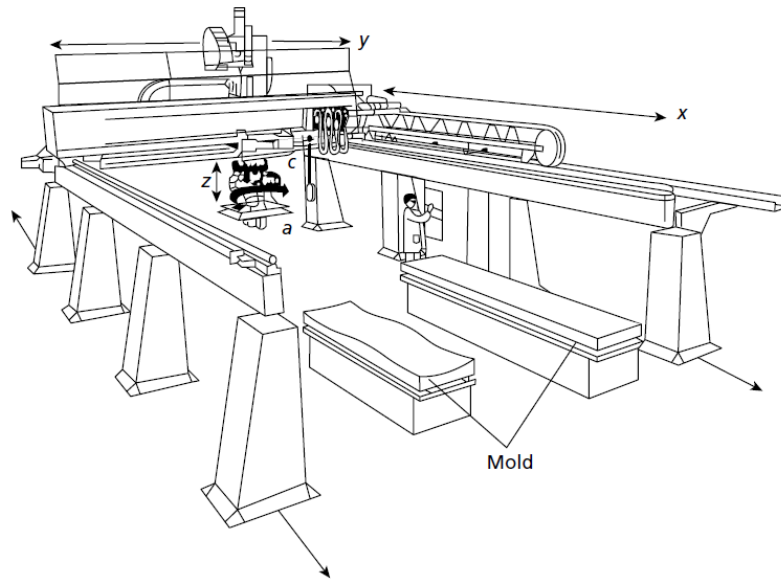
Fig. 2.4.3.1. - Typical gantry style tape laying machine.

Flat tape laying machines (FTLM) are either fixed bed machines or open bay gantries, while contour tape laying machines (CTLM) are normally open bay gantries. The tool is rolled into the working envelope of the gantry, secured to the floor, and the delivery head is initialized onto the working surface.

2.4.4. Filament Winding

Filament winding is a high rate process in which a continuous fiber band is placed on a rotating mandrel. Lay-down rates as high as 100–400 lb/h are not uncommon. It is also a highly repeatable process that can fabricate large and thick-walled structure. Filament winding is a mature process, having been in continuous use since the mid-1940s. It can be used to fabricate almost any body of revolution, such as cylinders, shafts, spheres, and

cones. Filament winding can also fabricate a large range of part sizes; parts smaller than 1 in. in diameter (e.g., golf club shafts) and as large as 20 ft in diameter have been wound. The major restriction on geometry is that concave contours cannot be wound, because the fibers are under tension and will bridge across the cavity.
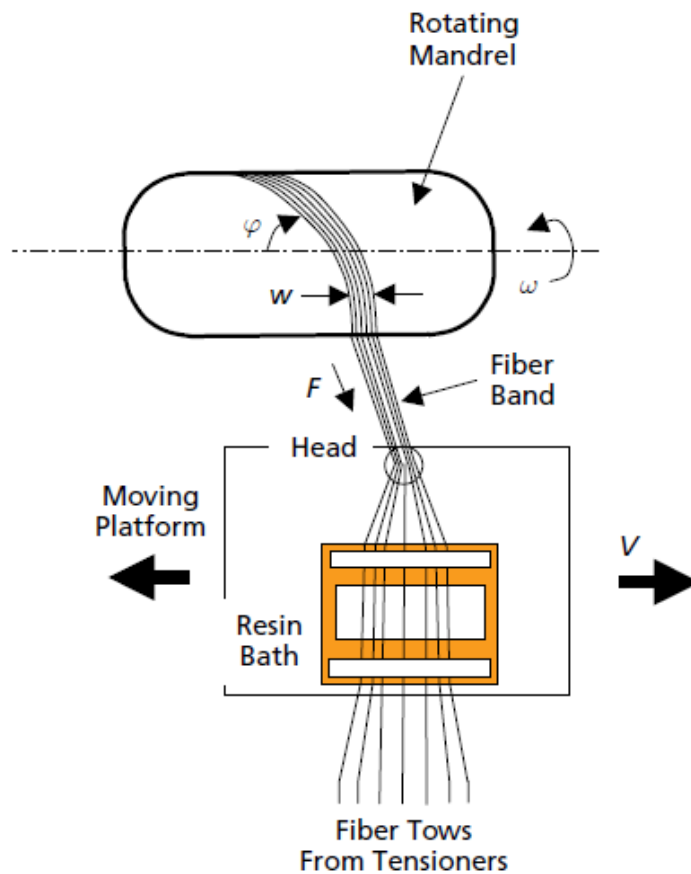
Fig. 2.4.4.1. - Filament winding process.

Typical applications for filament winding are cylinders, pressure vessels, rocket motor cases, and engine cowlings. End fittings are often wound into the structure producing strong and efficient joints. A typical filament winding process is shown in Fig. 2.4.4.1. Dry

tows are drawn through a bath containing liquid resin, collimated into a band, and then wound on a rotating mandrel.

2.4.5. Vacuum Bagging

After ply collation, the laminate is sealed in a vacuum bag for curing. A typical bagging schematic is shown in Fig. 2.4.5.1. To prevent resin from escaping from the edges of the laminate, dams are placed around the periphery of the lay-up. Typically, cork, silicone rubber, or metal dams are used. The dams should be butted up against the edge of the lay-up to prevent resin pools from forming between the laminate and dams. The dams are held in place with either double-sided tape or Teflon pins.
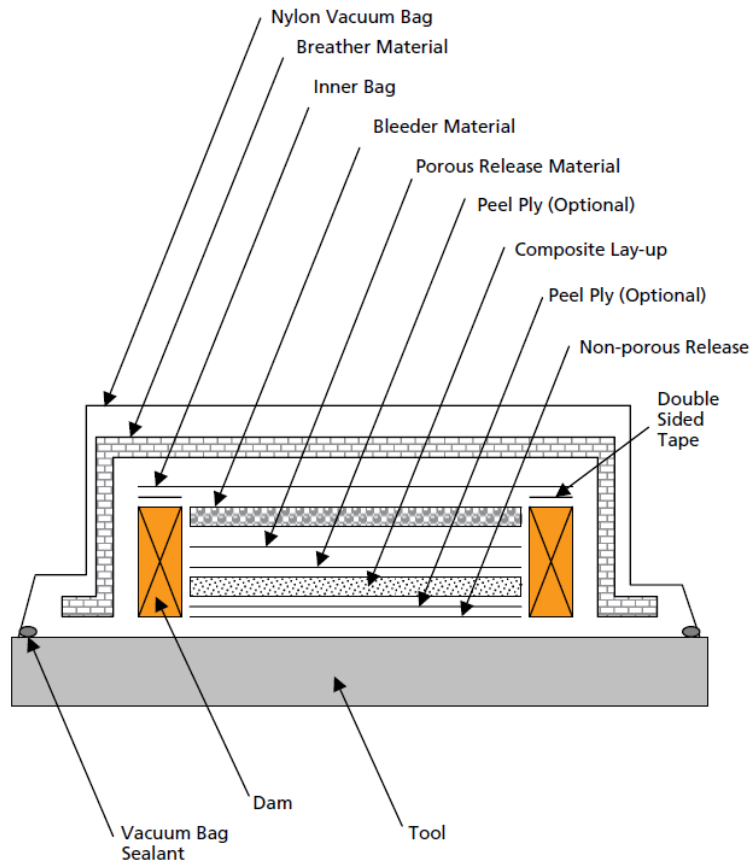
Fig. 2.4.5.1. - Typical vacuum bagging schematic.

A peel ply may be applied directly to the laminate surface if the surface is going to be subsequently bonded or painted. Then, a layer of porous release material, usually a layer of porous glass cloth coated with Teflon, is placed over the lay-up. This layer allows resin and air to pass through the layer without having the bleeder material bond to the laminate surface. The bleeder material can be a synthetic material (e.g., polyester mat) or dry fiberglass cloth, such as 120 or 7781 style glass. The amount of bleeder material depends on the laminate thickness and the desired amount of resin to be removed. For the newer net resin content prepregs, bleeder cloth is not required since it is not necessary to remove any excess resin. After the bleeder is placed on the lay-up, an inner

bag made of Mylar (polyester), Tedlar (PVF), or Teflon (TFE) is placed over the lay-up. The purpose of the inner bag is to let air escape while containing the resin within the bleeder pack. The inner bag is sealed to the edge dams with double-sided tape and then perforated with a few small holes to allow air to escape into the breather system. The breather material is similar to the bleeder material, either a synthetic mat material or a dry glass cloth can be used. If dry glass cloth is used, the last layer next to the vacuum bag should be no coarser than 7781 glass. Heavy glass fabrics, such as style 1000, have been known to cause vacuum bag ruptures during cure. The nylon bagging material can be pushed down into the coarse weave of the fabric and rupture. The purpose of the breather is to allow air and volatiles to evacuate out of the lay-up during cure. It is important to place the breather over the entire lay-up and extend it pass the vacuum ports. The vacuum bag, which provides the membrane pressure to the laminate during autoclave cure, is normally a 3–5 mil thick layer of nylon-6 or nylon-66. It is sealed to the periphery of the tool with a butyl rubber or chromate rubber sealing compound.

2.4.6. Autoclave Curing

Autoclave curing is the most widely used method of producing high quality laminates in the aerospace industry. An autoclave works on the principle of differential gas pressure, as illustrated in Fig. 2.4.6.1. The vacuum bag is evacuated to remove the air, and the autoclave supplies gas pressure to the part. Autoclaves are extremely versatile pieces of equipment. Since the gas pressure is applied isostatically to the part, almost any shape can

be cured in an autoclave. The only limitation is the size of the autoclave, and the large

initial capital investment to purchase and install an autoclave.
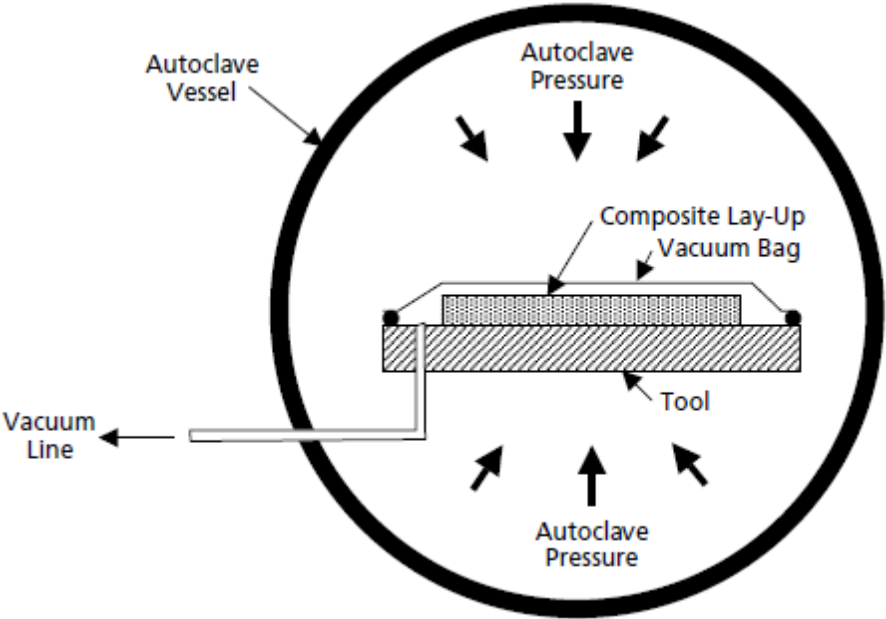
Fig. 2.4.6.1. - Principle of autoclave curing.

A typical autoclave system, shown in Fig. 2.4.6.2., consists of a pressure vessel, a

control system, an electrical system, a gas generation system, and a vacuum system.

Autoclaves lend considerable versatility to the manufacturing process. They can

accommodate a single large composite part, such as a large wing skin, or numerous

smaller parts loaded onto racks and cured as a batch.
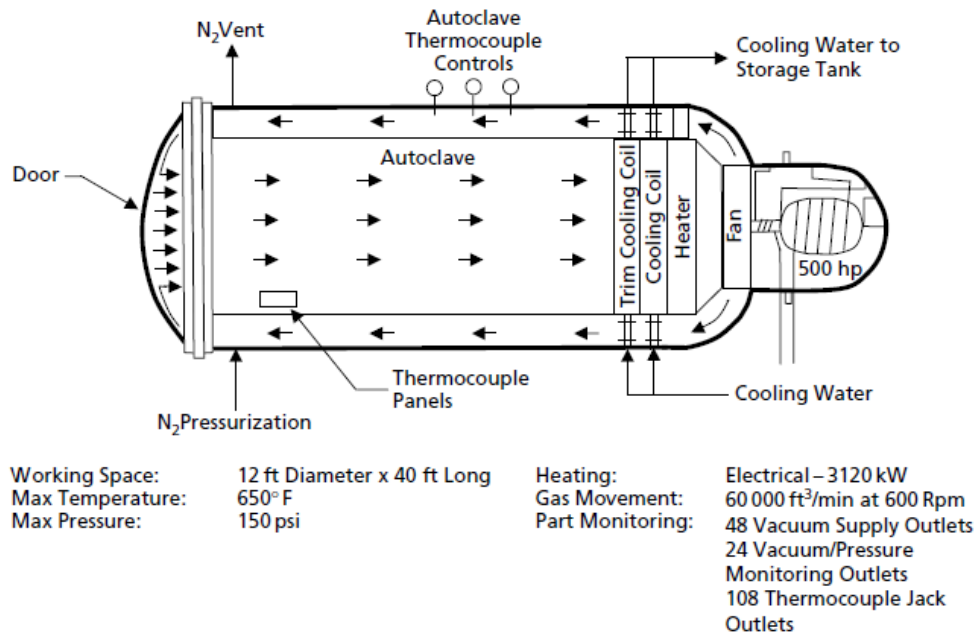
Fig. 2.4.6.2. - Typical autoclave schematic.

While autoclave processing is not the most significant cost driver in total part cost, it does represent a culmination of all the previously performed manufacturing operations, because final part quality (per ply thickness, degree of crosslinking, and void and porosity content) is often determined during this operation.

2.4.7. Curing of Epoxy Composites

A typical cure cycle for a 350F curing thermoset epoxy part is shown schematically in Fig. 2.4.7.1. It contains two ramps and two isothermal holds. The first ramp and isothermal hold, usually in the range of 240–280° F, is used to allow the resin to flow (bleed) and volatiles to escape. The imposed viscosity curve on the figure shows that the semi-solid resin matrix melts on heating and experiences a dramatic drop in viscosity.
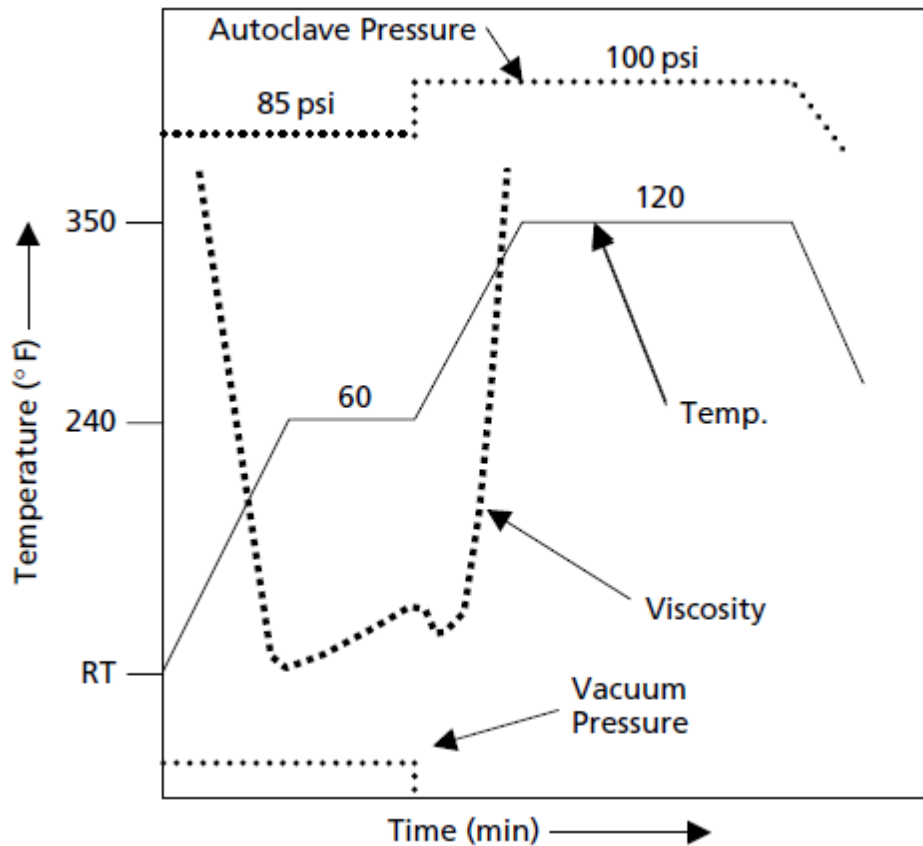
Fig. 2.4.7.1. - Typical autoclave curing cycle for epoxy resin composites.

The second ramp and hold is the polymerization portion of the cure cycle. During this portion, the resin viscosity initially drops slightly due to the application of additional heat, and then rises dramatically, as the kinetics of the resin start the crosslinking process. The resin gels into a solid and the crosslinking process continues during the second isothermal hold, usually at 340–370° F for epoxy resin systems. The resin is held at this cure temperature for normally 4–6 h, allowing time for the crosslinking process to be completed. It should be noted that as the industry has moved toward net resin content systems, the use of the first isothermal hold, which allows time for resin bleeding, has

been eliminated by many manufacturers, resulting in a straight ramp-up to the cure temperature.

2.4.8. Resin Transfer Molding

Liquid molding is a composite fabrication process that is capable of fabricating extremely complex and accurate dimensionally parts. One of the main advantages of liquid molding is part count reductions, in which a number of parts that would normally be made individually, and either fastened or bonded together, are integrated into a single molded part. Another advantage is the ability to incorporate molded-in features, such as a sandwich core section in the interior of a liquid molded part. Resin transfer molding (RTM), the most widely used of the liquid molding processes, is a matched mold process that is well suited to fabricating three-dimensional structures requiring tight dimensional tolerances on several surfaces. Excellent surface finishes are possible, mirroring the surface finish of the tool. The major limitation of the RTM process is the relatively high initial investment in the matched-die tooling. Sufficient part quantities, usually in the 100-5000 range, are necessary to justify the high non-recurring cost of the tooling. A summary of the advantages and disadvantages of the RTM process are given in Table 7.5. The RTM process consists of fabricating a dry fiber preform which is placed in a closed mold, impregnated with a resin, and then cured in the mold.

Table 2.4.8.1. - RTM Process advantages and disadvantages

Advantages	Disadvantages
• Best tolerance control-tooling controls dimensions • Class A surface finish possible • Surfaces may be gel coated for better surface finish • Cycle times can be very short • Molded-in inserts, fittings, ribs, bosses, and reinforcements possible • Low pressure operation (usually less than 100 psi) • Prototype tooling costs relatively low • Volatile emissions (e.g., styrene) controlled by close mold process • Lower labor intensity and skill levels • Considerable design flexibility: reinforcements, lay-up sequence, core materials, and mixed materials • Mechanical properties comparable to autoclave parts (void content < 1%) • Part size range and complexity makes RTM appealing • Smooth finish on both surfaces • Near net molded parts.	• Mold and tool design critical to part quality • Tooling costs can be high for large production runs • Mold filling permeability based on limited permeability data base • Mold filling software still in development stages • Preform and reinforcement alignment in mold is critical • Production quantities typically range from 100–5000 parts • Requires matched, leakproof molds.

The basic resin transfer molding process, shown in Fig. 2.4.8.1., consists of the following steps:

- Fabricate a dry composite preform.

- Place the preform in a closed mold.

- Inject the preform with a low viscosity liquid resin under pressure.

- Cure the part at elevated temperature in the closed mold under pressure.

- Demold and clean up the cured part.
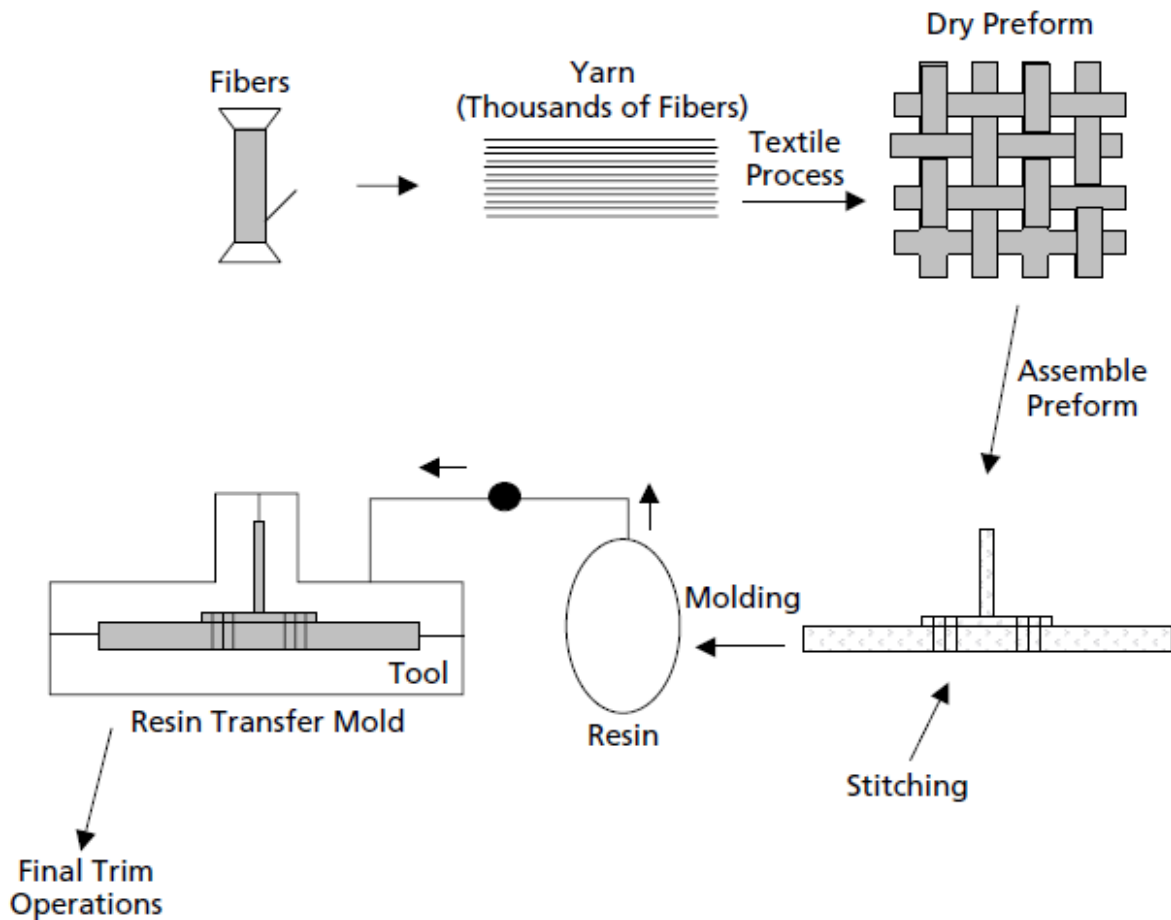
Fig. 2.4.8.1. - Process flow for resin transfer molding.

Over the past several years, there have been many variations developed for this process, including RFI (Resin Film Infusion), VARTM (Vacuum Assisted Resin Transfer Molding) and SCRIMP (Seeman's Composite Resin Infusion Molding Process), to name a few. The objective of all of these processes is to fabricate near net molded composite parts at low cost.

Resin injection follows Darcy's law of flow through a porous media, that predicts that the flow rate per unit area (Q/A) is proportional to the preform permeability (k) and the

pressure gradient (ΔP), and inversely proportional to the viscosity (η) of the resin and the

flow length (L):

$$\underline{Q} = \underline{k\Delta P}$$
$$A \quad \eta\,L$$

Using this equation can provide useful guidelines for RTM: (1) use resins with low

viscosity; (2) use higher pressures for faster injections; and (3) use multiple injection ports

and vents for faster injections. The ideal resin for RTM will have (1) a low viscosity to allow

flow through the mold and complete impregnation of the fiber preform; (2) a sufficient

pot life where the viscosity is low enough to allow complete injection at reasonable

pressures; (3) a low volatile content to minimize the occurrence of voids and porosity; and

(4) a reasonable cure time and temperature to produce a fully cured part.

Resin viscosity is a major consideration when selecting a resin system for RTM. Low

viscosity resins are desirable with an ideal range being in the 100–300 cP range with about

500 cP being the upper limit. Although resins with higher viscosities have been

successfully injected, high injection pressures or temperature are required, which results

in more massive tools to prevent tool deflection. Normally, the resin is mixed and

catalyzed before it is injected into the mold, or if the resin is a solid at room temperature

with a latent curing agent, it must melted by heating. Vacuum degassing in the injection

pot, Fig. 2.4.8.2., is a good practice to remove entrained air from mixing and low boiling point volatiles.
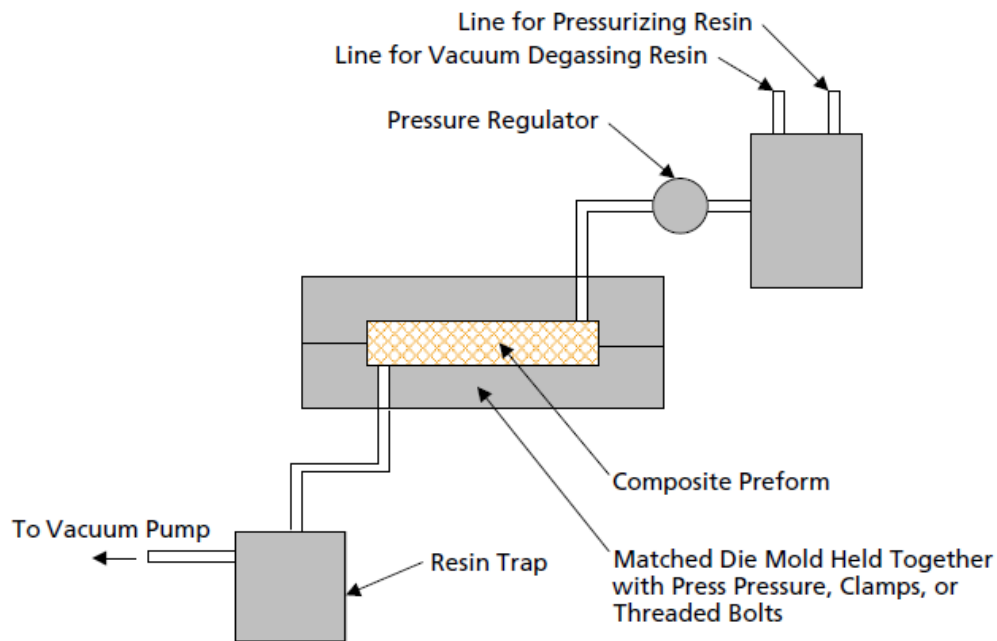
Fig. 2.4.8.2. - Schematic of a typical RTM process.

Both epoxies and bismaleimides are amenable to RTM, with preformulated resins available from a large number of suppliers. Similar to prepreg resins, it is important to understand the resin viscosity and cure kinetics of any resin used for RTM. Vacuum assistance during injection will usually help to reduce the void content significantly. However, it is important that the mold be vacuum tight (sealed) if vacuum assistance is going to be used. If the mold leaks, air will actually be sucked into the mold, causing a potentially higher void content. During the injection process, when the mold is almost full, resin will start flowing out through the porting system. If there is evidence of bubbles in the exiting resin, the resin should be allowed to continue to bleed out until the bubbles

disappear. To further reduce the possibility of voids and porosity, once the injection is complete, the ports can be sealed, while the pumping system is allowed to build-up hydrostatic resin pressure within the mold.

Since vacuum assisted resin transfer molding (VARTM) processes use only vacuum pressure for both injection and cure, the single biggest advantage of VARTM is that the tooling cost is much less, and simpler to design, than for conventional RTM. In addition, since an autoclave is not required for curing, the potential exists to make very large structures using the VARTM process. Also, since much lower pressures are used in VARTM processes, lightweight foam cores can easily be incorporated into the lay-ups. VARTM type processes have been used for many years to build fiber-glass boat hulls, but have only recently attracted the attention of the aerospace industry.
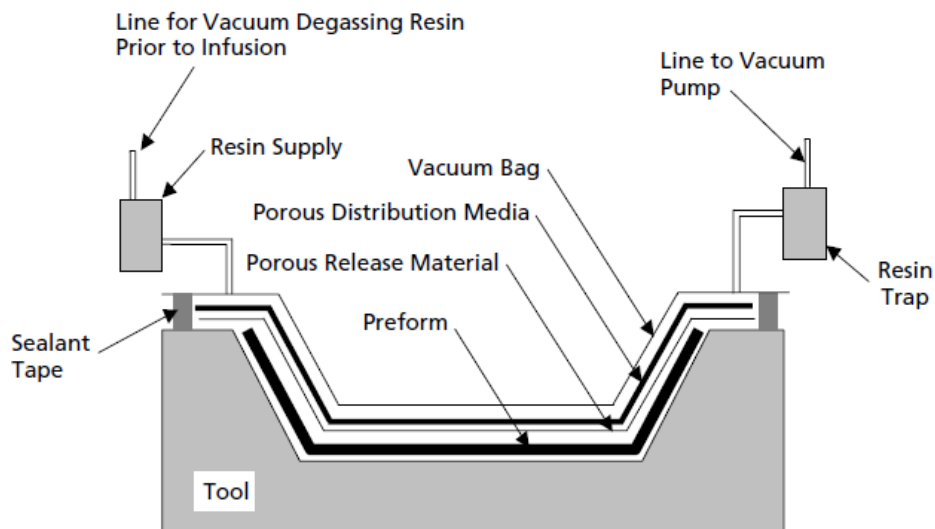
Fig. 2.4.8.3. - Typical VARTM process setup.

A typical VARTM process, shown in Fig. 2.4.8.3., consists of single-sided tooling with a vacuum bag. VARTM processes normally use some type of porous media on top of the preform to facilitate resin distribution. The porous distribution media should be a highly permeable material that allows resin to flow through the material with ease. When a porous distribution media is used, the resin typically flows through the distribution media and then migrates down into the preform. Typical distribution media include nylon screens and knitted polypropylene. Since resin infiltration is in the through-the-thickness direction, race tracking and resin leakage around the preform are largely eliminated.

2.4.9. Pultrusion

Pultrusion is a rather mature process that has been used in commercial applications since the 1950s. In the pultrusion process, a continuous fibrous reinforcement is impregnated with a matrix that is continuously consolidated into a solid composite. While there are several different variations of the pultrusion process, the basic process for thermoset composites is shown in Fig. 2.4.9.1. The reinforcement, usually glass rovings, is pulled from packages on a creel stand and gradually brought together and pulled into an open resin bath, where the reinforcement is impregnated with liquid resin. After emerging from the resin bath, the reinforcement is first directed through a preform die that aligns the rovings to the part shape and then guides it into a heated constant cross-section die, where the part cures as it progresses through the die. Curing takes place from the outside of the part toward the interior. Although the die initially heats the resin, the exotherm

resulting from the curing resin can also provide a significant amount of the heat required for cure. The temperature peak caused by the exotherm should occur within the confines of the die and allow the composite to shrink away from the die at the exit. The composite part emerges from the die as a fully cured part that cools as it is being pulled by the puller mechanism. Finally, the part is cut to the required length by a cut-off saw.
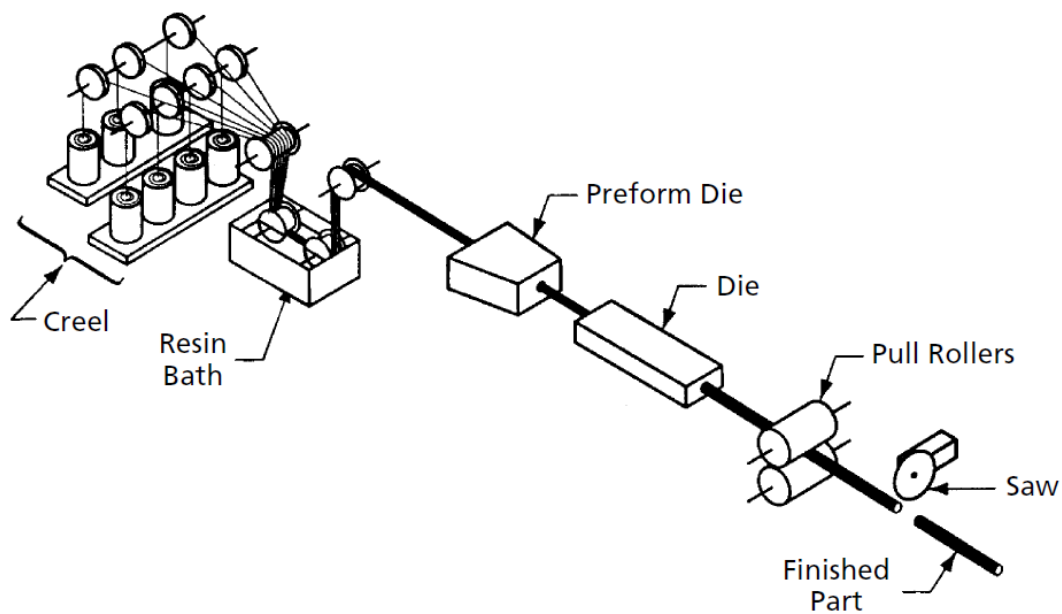
Fig. 2.4.9.1. - Pultrusion process.

While pultrusion has the advantage of being an extremely cost-effective process for making long constant cross-section composite parts, it is definitely a high volume process, as the set-up time for a production run can be rather costly. In addition, there are limitations in that the part must be of constant cross-section, and the flexibility in defining reinforcement orientation is some-what limited. While glass fiber/polyester materials

dominate the market, a considerable amount of work has been done to develop the process for the aerospace industry with higher performance carbon/epoxy materials.

2.5. Composite Materials Industry and Market

The composites industry has increased globally; in 2000, the European consumption of thermoset composites reached 10^6 tons per year; in 2005, plastics production in Japan was over 6.1 million tons and more than 210 million tons worldwide, and in 2008, the global demand of carbon fibers reached 20,000 tons per year. The advantages of composite materials are many, including monolithic construction of components, lower density, high resistance, and relatively good behavior in fatigue compared with metals in structural applications such as aerospace and automotive. Consequently, manufacturers are increasing the percentage of composite materials used in aircraft and automobiles, such that, the latest designs of commercial aircraft are being constructed with more than 50 % in weight of composites, namely, carbon fiber and epoxy resin systems.

The most recent figures for glass reinforced plastic (GRP) production in Europe show an overall production volume of ~1,200,000 t in 2007 (Witten, 2008). This represents a yearly growth of over 5% since 2005 (1,060,000 t). Europe produces 31% of the worldwide supply of GRP, and GRP comprises 90% of the world composites market (Bunsell and Renard, 2005). We could therefore estimate that the worldwide production of GRP in 2007 would be approximately 3,600,000 t, and that the global production volume for all

polymer matrix composites is nearer to 4,000,000 t. Figure 1.4 shows European GRP production by processing method. It can be seen from this breakdown that the primary thermosetting composite production methods account for more than 70% of total GRP output: compression/injection molding (SMC/BMC), 26%; open mould methods (hand-lay, spray-up), 30%, RTM and continuous processing methods, ~20%.
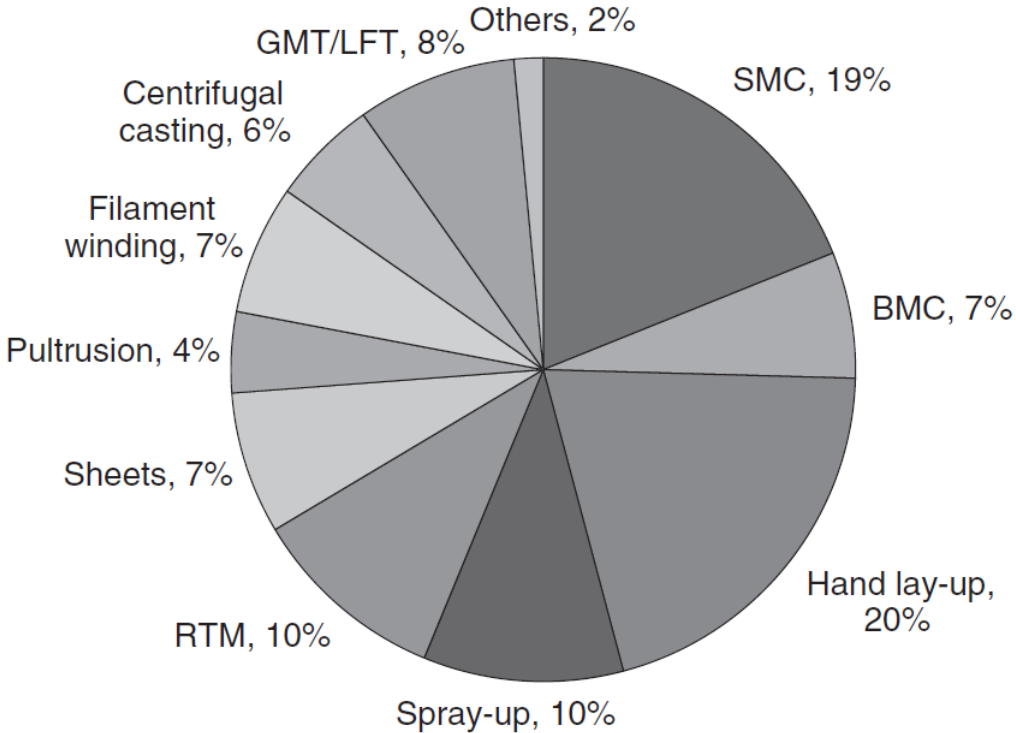
Fig. 2.5.1. - European GRP production by process route, 2005-2007 (Witten, 2008)

Recent figures for the total annual biomaterials usage in Europe amount to approximately 350,000 t, with ~200,000 t of this total representing natural fiber (NF) reinforced composites (Carus and Gahle, 2008). Over two-thirds of this NF composite

usage is composed of wood reinforced plastic compression and extrusion/injection molding for the automotive, construction and furniture industries.

3. Waste Management

Composites are generally considered high value, high performance materials that are employed in producing high net worth end products. When considering a typical end-of-life product made using composite materials, if the cost of raw material, the production tooling and the associated manufacturing equipment (including both molding and finishing processes) are taken into account, it is obvious that such a component represents significant prior investment and embodied energy. Products made using materials of such high intrinsic value can be a wise target for the recycling industry when compared with lower net value materials as the corresponding recyclate material could have a similar high value, depending on the effort required to retrieve and reprocess the material.

3.1. Legislation

Legislation programs in the European Union (EU) are leading the environmental policies that can shape the international legislation framework for composite materials recycling. EU environmental policy and legislation have been developed and shaped by six

environment action programs for over 30 years. The first batch of environmental legislation put in place the framework for dealing with specific problems such as waste oil. This was built upon by legislation that developed standards for landfills and incinerators for example whilst the third batch of legislations introduced recycling directives which put in place the necessary organization and finances to assist the recycling of key waste flows such as end-of-life vehicles. Some lack of clarity in the wording of the directives meant that implementation among member states was variable and the current legislation seeks to harmonize and streamline environmental law making it simpler and more enforceable.

The origins of environmental law and policy in Europe lie in the European Community dating back to 1972. The European Community founding treaty, the Treaty of Rome, does not contain any reference to environmental legislation and a number of further amendments, including the Maastricht Treaty (1992) and the Amsterdam Treaty (1999), have been necessary to bring forth the legislation: more than 80% of the UK's environmental legislation today is drawn from the EU. However, it was in 1972 that the European Community determined that a community environmental policy was needed. The framework which developed and shaped environmental legislation was provided by the Environment Action Programs (EAPs), of which there are six to date (EAP1 1973, EAP2 1977, EAP3 1983, EAP4 1987, EAP5 1993, EAP6 2002). Each program is specific to a particular environmental issue and spans a 5–10 year time frame. The EAPs are the main driving force behind today's and tomorrow's future environmental policy in the EU and

the UK as well as the global agenda. Whilst the environment action programs are not legally binding, they do clearly set out the aspirations of the community.

The fifth EAP (EAP 5 1993), began to set longer-term environmental objectives and introduced the concept of sustainable development as well as managing waste not just on a community level but on a global level. The program stated that the attitude to waste management needed to change and suggested two strategies, one of avoiding waste by improving product design in the first instance but, where waste arises, a second strategy of recycling and reusing the waste. This European Community strategy led almost seamlessly into new legislation on managing of waste streams and from this flowed the End-of-Life Vehicle (ELV) Directive (Directive 2000/53/EC). The regulations were subsequently amended in 2005 by the End-of-Life Vehicles (Producer Responsibility) Regulations 2005 with further minor revisions in 2008 (Environmental Permitting Regulations 2007, SI 3538). The first focus of the ELV legislation is to prevent waste in the first place and then to consider reuse and recycling as well as other forms of energy recovery. The scope of the legislation is not just contained to the vehicle itself but extends to their components and materials, irrespective of whether or not they were factory fitted to the vehicle. One of the first obligations placed on manufacturers was to stop the use of hazardous waste such as lead and mercury in vehicles made after July 2003. For the first time, the regulations place a requirement on vehicle manufacturers to take back vehicles at the end of their life via authorized treatment facilities (ATF), which would be charged with its environmentally sound recovery. The cost of treatment by the ATFs is to be borne

for the large part by the producers rather than by the last keeper or owner and since the regulations were amended in 2005 there is a requirement that authorized treatment facilities are required to provide the service free of charge, effective from 1 January 2007 (where vehicles are largely complete and have not had extra waste added). The original regulations (End-of-Life Vehicle Regulations 2003) set out national targets for reuse and recycling as follows:

- No later than 1 January 2006 the reuse and recovery rate for all ELVs will be at least 85% (average weight per vehicle and year). However, the rate for vehicles produced before 1 January 1980 was set at 75%.
- By no later than 1 January 2015, all ELVs will need to have a reuse and recovery rate of no less than 95%.

3.2. Waste Management

There are many factors which can affect suitability for recycling, but the driving arguments must be "is there a market for the recyclate?" and "is the market economically viable?" Without these drivers in place a recycling plan is almost certain to fail and a material must be considered unsuitable for recycling. Many technical factors affecting the recyclate such as collection, separation and reprocessing, can be overcome, but lack of market demand will stop any further development.
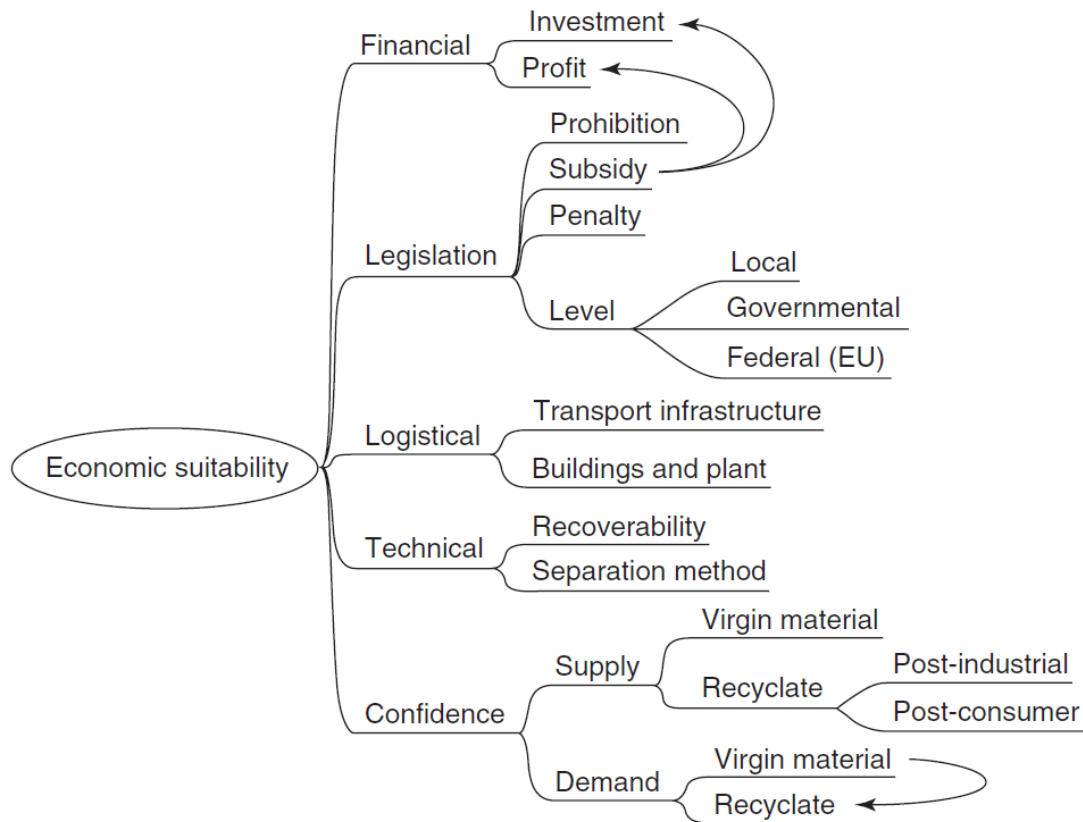
Fig. 3.2.1. - Schematic showing economic drivers for recycling suitability.

The basic economic model must consider a number of factors. Many of these factors are closely interlinked, as shown in Fig. 3.2.1. When embarking upon a recycling plan all of the factors need to be considered and some given action whilst others may be ignored. These factors are: technical, logistic, financial, confidence, supply and demand, and legislative.

In many cases it is often down to the simple practicality of the process that can drive the suitability for recycling. This practicality is affected by: waste stream type, recoverability, contamination and reliability of feedstock. Legislative and financial

instruments: subsidies/penalties. Governments are able to stimulate markets by legislative means (e.g. Council Directive 1999/31/EC). They can legislate to influence the final recyclate cost and likely demand in two ways: subsidies and penalties (commonly phrased "carrot versus stick"). Subsidies are regularly used to stimulate demand, but will often be short-lived, and their subsequent removal can easily destroy demand that has come to rely on the effect of subsidies too much. These subsidies can take two forms, either assistance with plant investment or payments upon recyclate produced. Penalties take the form of financial disincentives such as increased landfill taxes that actively encourage reuse and recycling thus ultimately making disposal economically unviable. Within the economic argument, legislation can have a large effect, as it is used to drive the existence of a market until the infrastructure is in place to create usable volumes at a competitive market price. Additionally, penalties are likely to be much longer lived (indeed indefinite) and so have a more permanent effect on the market than the more transient subsidies. End user confidence plays a vital part in a recycling program, particularly with respect to the supply side. This can be seen in the need to guarantee volume of supply to large users, who cannot afford to stop production, and a lack of confidence in ability to supply sufficient reprocessed material can provide problems, particularly for small recyclers. Demand and confidence are closely interlinked, as one will tend to create the other. It is still important that a need is developed as this demand will create a market and obviously dictates the prices. The market demand for resultant recyclate is of huge importance. Unlike the initial cost, it is often the lower value materials with a high usage volume where the greatest demand exists. Typically here glass reinforced PP has a

relatively low initial value but the volumes used make it easy to feed recycled material into the virgin feedstock with no problems. Governmental legislation can be employed, not just to provide financial incentives/penalties, but to prohibit current practices (e.g. disposal) thus making reuse and recycling the only option (Waste Electrical and Electronic Equipment, Council Directive 2002/96/EC; End-of-Life Vehicles, Council Directive 2000/53/EC). This direct action approach can create supply without necessarily stimulating demand and presents a significant challenge to the recycling industry.

3.3. Disposal and Landfill

Landfill is defined as waste disposal site for the deposit of waste onto or into land and the overall objective of the regulations is to prevent or reduce the negative effects of landfilling on the environment as well as any risk to human health posed as a result. The 1999 EU Landfill Directive (Directive 1999/31/EC) was transposed into English law through the Landfill (England and Wales) Regulations 2002. It was subsequently amended in 2004 and 2005, which incorporated the council decision in 2003 (Council Decision 2003/33/EC). It is now implemented in the UK through the Environmental Permitting Regulations (SI 3538). The overall objective of the regulations is to supplement the requirements of the Waste Framework Directive (Directive 2006/12/EC) discussed in the preceding section and prevent, or reduce, the negative effects of landfilling on the environment as well as any risk to human health as a result. The regulations attempt to achieve this through specifying technical standards of landfill sites and operations and setting out requirements

for the location, conditioning, management, control, closure and preventative and protective measures. A strategy on biodegradable waste must also be implemented as part of the regulations that provides for the progressive diversion of biodegradable municipal waste from landfill in order for the UK to meet challenging targets:

- By 2010 to reduce biodegradable municipal waste landfilled to 75% of that produced in 1995.

- By 2013 to reduce biodegradable municipal waste landfilled to 50% of that produced in 1995.

- By 2020 to reduce biodegradable municipal waste landfilled to 35% of that produced in 1995.

References used in Chapter 3: [17]

4. Composite Materials Recycling Methods

The aim of recycling processes is to reduce environmental impact by reusing materials in a more sustainable way. In general, it makes sense to try to recover as much economic value from a material in a recycling operation since the value of a material represents to a large extent the input of resources needed to produce the material or the scarcity of the material. Recycling processes in which a more valuable recyclate is produced are therefore likely to reduce environmental impact the most and they are also more likely to be cost effective. Recycling polymer composites based on thermoset matrices is much more

difficult as the polymer cannot be remolded. Recycling processes have therefore been developed to separate and recover valuable materials from thermoset composites that have the potential to be reused.

A number or recycling technologies have been proposed and developed for thermoset composite materials and these are summarized in Fig. 4.1. Mainly, there are three categories of process: those that involve mechanical comminution techniques to reduce the size of the scrap to produce recyclates; and those that use thermal and/or chemical processes to break the scrap down into materials and energy.
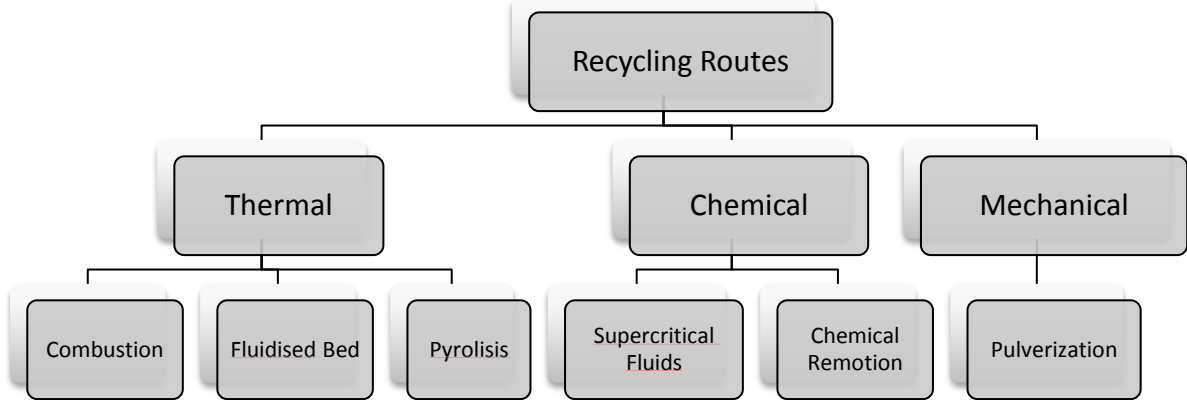
Fig. 4.1. - Potential recycling processes for thermoset composite materials.

Mechanical recycling techniques can recycle all of the composite material, but the recyclate does not usually provide the same function as the original material and so there is a reduction in value. The simplest thermal process is combustion with energy recovery. Whilst this is a robust process capable of dealing with a wide range of different materials,

only the energy value in the scrap composite is recovered. Pyrolysis and other chemical processes have the advantage of being able to recover material from the polymer separated from the inorganic components of the composites, such as glass and carbon fiber and fillers. In some pyrolysis processes the fibers recovered are contaminated with char and in general the processes are less tolerant of mixed and contaminated materials. In a thermoset composite the most valuable constituent within the material is usually the reinforcement fiber, particularly in the case of carbon fiber composites, where the value of the carbon fiber is typically an order of magnitude greater than that of the polymer. In the fluidized bed thermal process the aim is to recover high grade fiber from scrap glass fiber or carbon fiber reinforced thermoset composites. This is done by removing the polymer from the fiber by an oxidative thermal process to yield clean fibers. The process also has the advantage of being very tolerant to mixed and contaminated materials and so it is particularly suitable for recycling waste composites from end-of-life products. This chapter will describe the fluidized bed process, and detail the quality of the fibers that are recovered. Applications for the reuse of the fiber that have been investigated will then be explained and the prospects for commercial scale operation considered.

4.1. Thermal Processing

4.1.1. Combustion - Energy Recovery

Thermosetting polymers, like all organic materials, have a calorific value and can be burned as a source of energy. Measurements of calorific value have been reported for polyester, vinylester, phenolic, urea formaldehyde and epoxy resins. Apart from urea formaldehyde, which has a calorific value of 15,700 kJ/kg, the other resins considered all have calorific values of approximately 30,000 kJ/kg. As the most commonly used fibers and fillers are incombustible, the calorific value of a glass reinforced composite generally depends only on the proportion of polymer as illustrated in Fig. 4.1.1.1.
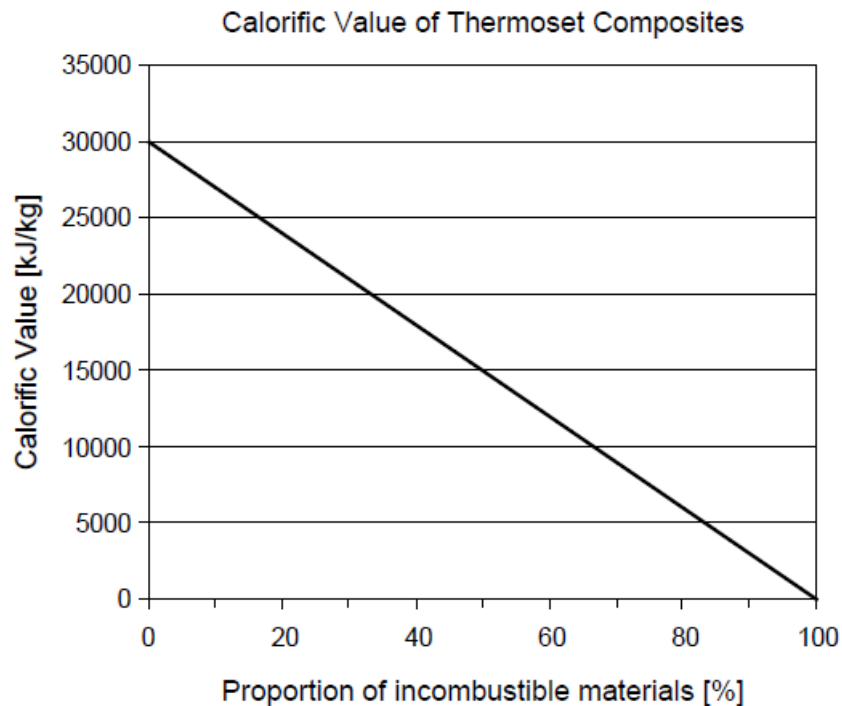
Fig. 4.1.1.1. - Calorific value of thermoset composites.

Some mineral fillers decompose and absorb energy during combustion and fire retardants are used specifically for that purpose. However, although the effect of fire retardants is to reduce the initial ignition and flame spread, the amount of energy

absorbed is small compared with calorific value of the resin. For example, the energy absorbed by alumina trihydrate is 1000 kJ/kg, so, if there is as much alumina trihydrate as there is polymer in a composite, the calorific value will be decreased by 3.3%. Similarly, calcium carbonate another widely used mineral filler decomposes at temperatures between 700 and 900 8 °C and absorbs 1800 kJ/kg. In a composite containing the same weight of calcium carbonate as polymer, the calorific value would thus be decreased by 6%. Combustion trials have shown that composites can successfully be burned for energy recovery. Mixing scrap composites at 10% loading with municipal solid waste has been shown to be a practical way to dispose of scrap if landfill is prohibited. [2]

4.1.2. Fluidized Bed

The basic principle of the fluidized bed recycling process is shown in Fig. 4.1.2.1. The fibers are recovered from the composite by removing the polymer matrix by heat in a bed fluidized with air. Once the polymer has been removed from the fibers and any mineral fillers that may also be present in the composite, they are carried out of the fluidized bed (elutriated) in the gas stream and can be separated from the gas in a cyclone or other gas-solid separation device. At the temperature at which the fluidized bed operates, the polymer does not fully oxidize and so, after separation of the fibers and fillers, the gas stream passes through to a secondary combustion chamber where high temperature combustion achieves full oxidation. Energy in the form of heat can then be recovered from

the high temperature exhaust gases and, if necessary, any pollutants can be scrubbed before being emitted to atmosphere.
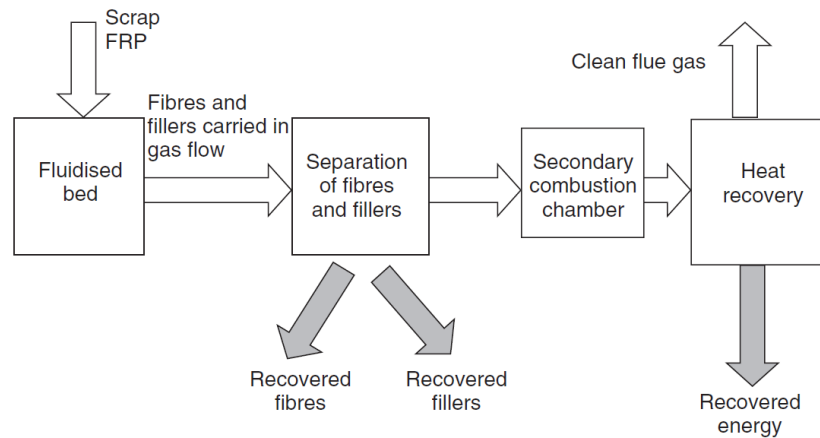
Fig. 4.1.2.1. - Principle of fluidized bed recycling process.

In general, thermoset polymers contain mainly carbon, hydrogen and oxygen and so the products of full oxidation are carbon dioxide and water, which can be emitted directly to the atmosphere. Some composites may contain halogenated resins for fire retardancy and, in this case, the flue gas would require scrubbing to remove the resulting acid gases before being emitted to atmosphere. The process therefore recovers reinforcement fibers and fillers in a clean form for reuse. The polymer is fully oxidized and its energy value is recovered.
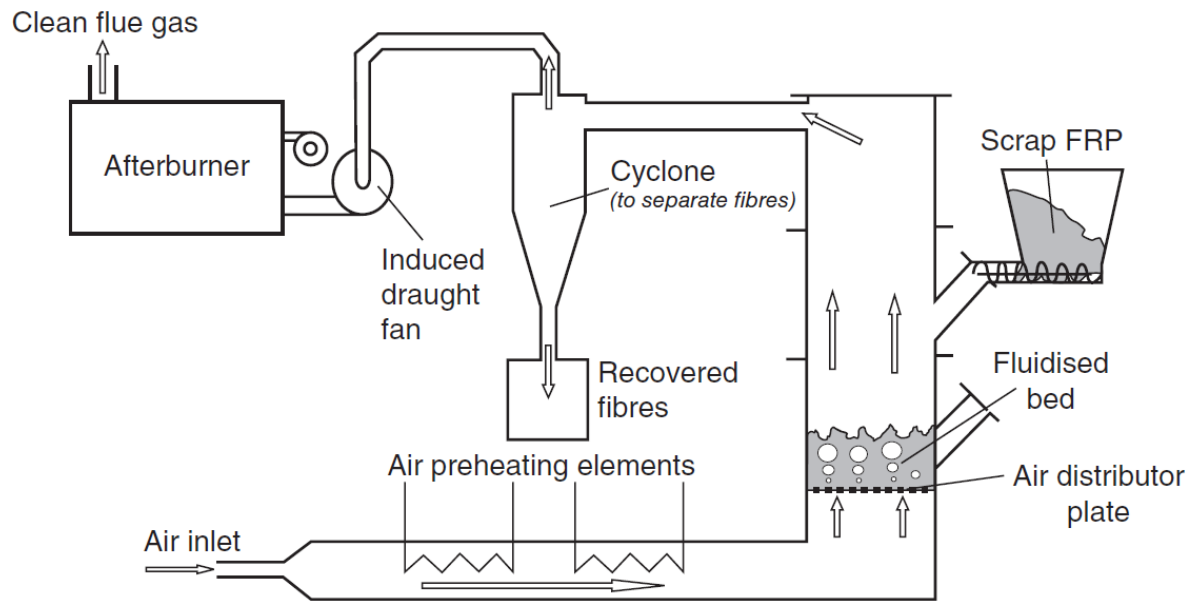
Fig. 4.1.2.2. - Schematics of fluidized bed recycling process.

Figure 4.1.2.2. shows a schematic representation of the fluidized bed recycling process. Fluidizing air, preheated typically to 450–550 °C, is introduced into a bed of silica sand, with particle diameter typically 0.85 mm and with a fluidizing velocity in the region of 1 m/s. At this condition the fluidized bed is in the bubbling regime where there is very good mixing and uniformity of temperature in the bed. The process has been developed on a laboratory pilot scale in which the fluidized bed is 300 mm in diameter. In this test rig, electric heaters are used to preheat the air. However, in a commercial scale process heat could be recovered from the gases downstream of the secondary combustion chamber. The temperature of the fluidized bed is chosen to be high enough to give rapid decomposition of the polymer but not too high that the fibers are degraded significantly. For polyester resins a temperature of 450 °C has been found to be suitable, whereas epoxy resins are more stable thermally and generally require a higher temperature of 550

°C for processing at a practical rate. The process is suitable for the processing of both glass fiber and carbon fiber reinforced composites. Carbon fibers are made of graphite and oxidize at high temperature in air. It has been found that at a fluidized bed temperature of 550 °C epoxy resin decomposes rapidly, but given the residence time of the fibers in the fluidized bed, of about 20 minutes, there is little oxidation of the carbon fiber as indicated by a reduction in fiber diameter. [10]

4.1.3. Pyrolysis

4.1.3.1. Pyrolysis

Pyrolysis is a thermally initiated chemical process that generally decomposes the organic molecules to smaller ones in an inert atmosphere. The term pyrolysis is often misunderstood as meaning a high temperature reaction resulting only in gases and char, but it also means thermolysis of organic macromolecules in the temperature range from 250 to 800 °C resulting in gaseous, liquid and solid products. Above 800 °C carbonization of the organic material occurs, which is applied as a utilization technology mostly for biomass waste.

Pyrolysis of the organic macromolecules is initiated by a primary intramolecular endothermic chemical reaction of the following types:

1. rearrangement of chemical bonds followed by elimination of small molecules, and/or separation of the macromolecule in two parts;

2. scission of chemical bonds followed by the stabilization of the unstable fragments.

The temperature necessary for the initiation reaction depends on the activation energy of the chemical change (reactions of type 1 occur at around 300 °C, and of type 2 at above 500 °C). In network or cross-linked polymers (thermosets) both types of pyrolysis reaction require higher temperatures because of limited flexibility of the macromolecular segments.

The thermal decomposition of a macromolecular network generally occurs at a higher temperature than that of a chain polymer of similar composition for at least two major reasons. The movement of the segments within a three-dimensional network is restricted, so decomposition reactions going through bonding rearrangement of neighboring parts of the macromolecule cannot take place as easily as in a chain polymer. In other cases when the thermal decomposition takes place by radical scission, a much faster initiation reaction is required in a network for the effective formation of fragment molecules by radical chain reaction than in a linear polymer chain because of the high probability of termination of the radical decomposition process by recombination of the radicals that are not able to escape from the cage of the network structure from which they originated.

Polyesters, vinyl esters, phenolic, epoxy, melamine and silicon resins are the standard matrix materials of thermoset composites. These composites are produced by curing the prepolymer mixed with the reinforcement because the thermosetting polymers do not melt after the network structure has been developed. The thermal decomposition of a macromolecular network generally occurs at a higher temperature than that of a chain polymer of similar composition for at least two major reasons. The movement of the segments within a three-dimensional network is restricted, so decomposition reactions going through bonding rearrangement of neighboring parts of the macromolecule cannot take place as easily as in a chain polymer. In other cases when the thermal decomposition takes place by radical scission, a much faster initiation reaction is required in a network for the effective formation of fragment molecules by radical chain reaction than in a linear polymer chain because of the high probability of termination of the radical decomposition process by recombination of the radicals that are not able to escape from the cage of the network structure from which they originated.

In the macromolecule of epoxy resins the ether bonding between aromatic and aliphatic carbons is cleaved at the earliest stage of thermal decomposition, producing volatile compounds between 300 and 400 °C and releasing bisphenol A, irrespective of the nature of the hardener. At above 600 °C the bisphenol segment is also detached at the isopropylidene group, resulting in phenol and methyl-, ethyl- and isopropenylphenol pyrolysis products. Epoxy resins do not leave noteworthy solid residues following pyrolysis. In composites constructed for application in electric and electronic devices

epoxy resins are flame retarded partly replacing bisphenol A by tetrabromobisphenol A. Among the pyrolysis products of such composites are small amounts of bromo-, dibromo-, tribromo- and tetrabromobisphenol A; moreover bromo- and dibromophenols are present. [18]

Comparing the thermal and thermo oxidative decomposition of an epoxy resin/carbon fiber composite using thermogravimetry. The weight loss due to volatilization of thermal decomposition products from the epoxy resin occurred from 300 to 460 °C with a maximum at 420 °C both in argon and in air. A further two additional weight loss steps were observed in air only: the first started at 460 °C and ended at 580 °C, corresponding to a mass loss of 15%, and the last one between 600 and 750 °C agreed with the mass ratio of the carbon fiber (58%). Both related reactions were oxidation as proved by the simultaneous plot of the molecular ion curve of carbon dioxide evolution recorded by mass spectrometry. The first reaction was attributed to the oxidation of the char left on the fiber surface after epoxy pyrolysis.[19]

Table 4.1.3.1.1. - Typical practical characteristics of polymer matrices and of their pyrolysis products.

Polymer	Atomic ratio H/C	Pyrolysis (°C)	Char (%)	Character of liquid
TPU	1.6	300–370	5	Aliphatic ester/aromatic
Polyester	0.9	370–460	26	Aromatic
Epoxy	1.1	370–460	15	Alkylphenol
PBT	1.0	370–430	3	Aromatic acid/aliphatic
PET	0.8	400–460	11	Aromatic ester
PA6	1.8	430–490	0	Aliphatic
PA12	1.9	440–490	0	Aliphatic
PP	2.0	450–500	0	Aliphatic
PC	0.9	480–570	22	Alkylphenol
Phenolics	1.0	450–580	30–50	Methylphenol
PPO	0.7	520–580	54	Phenol
PEEK	0.6	560–620	55	Phenol

Since the thermal decomposition reactions and the nature of their products is strictly related to the polymer chemical composition and structure, the physical characteristics such as melting ability is of marginal importance from the aspect of pyrolytic recyclability. Pyrolysis temperature should be chosen to be high enough for fast decomposition of the given polymer but not too high for avoiding aromatization and carbonization. Char formation is related to the amount of available hydrogen atoms for stabilizing radicals formed by bond scissions in the pyrolysis reactions. Thus the molar ratio of H and C atoms in the macromolecule of polymer matrix is indicative of char-forming ability, namely considerable char formation takes place below H/C value of unity, meaning that the polymer is dominated by aromatic structures. In Table 4.1.3.1.1. the optimal temperature range of pyrolysis for obtaining valuable pyrolysis products from frequent polymer matrix of composites is indicated. The H/C atomic ratio of a given polymer together with the

dominating nature of the pyrolysis products could be a basis of predicting the formation of char, as demonstrated by the char deposition ratios in Table 4.1.3.1.1. [17]

4.1.3.2.   Microwave Assisted Pyrolysis

Carbon fiber composites with an epoxy resin matrix were subjected to microwave-heating experiments in order to volatilize the polymer content and to produce clean fibers for potential reuse in high-grade applications. The composites were processed at 3 kW for 8 s in a multimode microwave applicator. The recovered fibers were characterized by tensile tests and electron microscopy. The results compare favorably with virgin fiber properties.
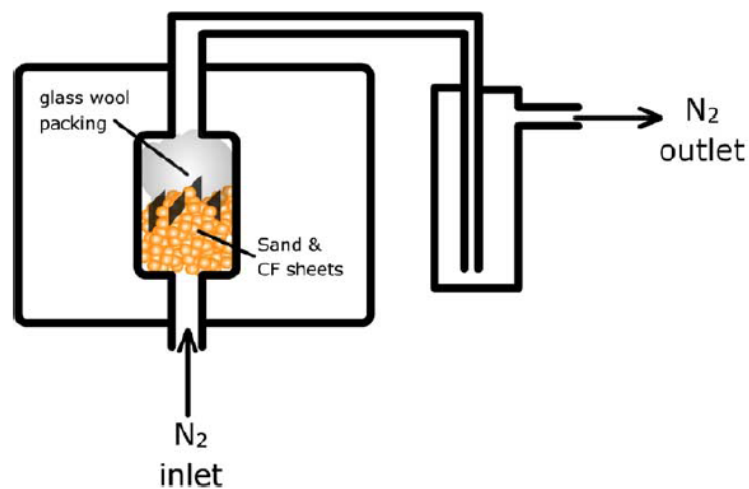
Fig. 4.1.3.2.1. - Schematics of the experimental rig.

A schematic of the experimental rig is shown in Fig. 4.1.3.2.1. The multimode microwave cavity was powered for 8 s at 3 kW. Four 3 g sheets of composite were suspended in a bed of quartz sand, since sand is essentially transparent to microwaves. Glass wool was used to prevent solids leaving the microwave cavity through the glassware. A steady stream of nitrogen gas (5 l/min) was used to create an inert atmosphere and therefore prevent combustion of the fibers during heating. A gas trap was used to reduce the amount of polymer in the exhaust gases reaching the vent. The initial experiments confirmed that the polymer could be separated from the carbon fibers in a multimode microwave cavity. This technique may offer a useful route to recovery of long fibers together with a pyrolyzed polymer vapor. The fibers recovered here were relatively clean, although some small changes in the surface topology were evident after processing. Fiber strength retention was encouraging and superior to that measured in an existing recovery process based on fluidized bed volatilization. Further investigation will also be required into how different polymer coatings respond to microwave heating. However, since it is the carbon fibers themselves that are responding to the microwaves, composites with a higher cure temperature might simply require a higher power setting or longer in the microwave field in order to reach the appropriate pyrolysis temperature. [20]

4.2. Chemical Processing

4.2.1. Supercritical Fluids

A supercritical fluid is a state where matter is compressible and behaves like a gas (i.e. it fills and takes the shape of its container), which is not the case when it is in a liquid state (an incompressible fluid that occupies the bottom of its container). However, a supercritical fluid has the typical density of a liquid and hence its characteristics dissolving power. That is why we cannot define the supercritical fluid as a liquid or as a gas. This is a new state of matter in principle. Supercritical fluids are defined as a substance above its critical temperature (TC) and critical pressure (PC). The critical point represents the highest temperature and pressure at which the substance can exist as a vapor and liquid in equilibrium. The vapor–liquid critical point in a pressure–temperature phase diagram is at the high-temperature extreme of the liquid–gas phase boundary. The dotted green line shows the anomalous behavior of water in Fig. 4.2.1.1.
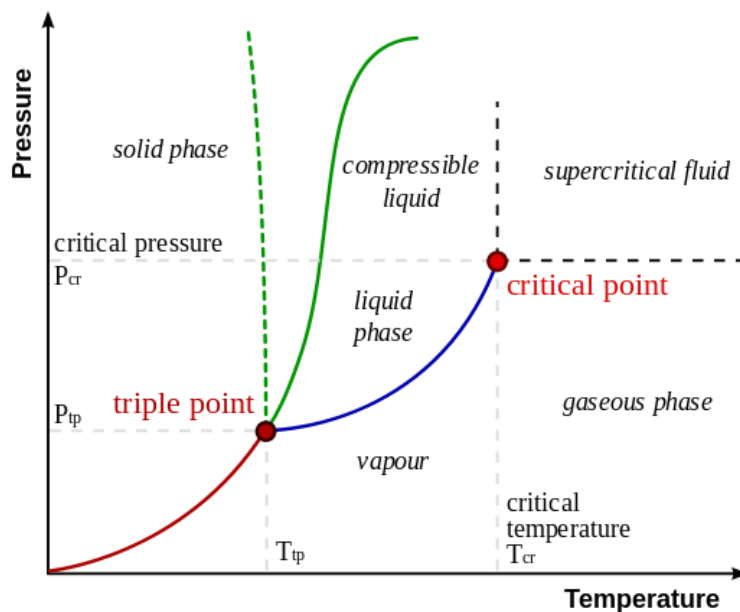
Fig. 4.2.1.1. - Vapor–liquid critical point in a pressure–temperature phase diagram for water.

Sub and supercritical fluids such as water and alcohol are excellent reaction media for depolymerization or decomposition of polymers. By using sub- and supercritical fluids, decomposition of polymers proceeds rapidly and selectively. Composite plastics such as fiber-reinforced plastics are decomposed into smaller molecular components and fiber materials.

Table 4.2.1.1. - Critical parameters of water and alcohols.

	Critical temperature (K)	Critical pressure (MPa)
Water	647.10	22.064
Methanol	512.64	8.097
Ethanol	513.92	6.148
1-Propanol	536.78	5.175
Acetone	508.10	4.700
Benzyl alcohol	715.00	4.300

Water and alcohols were mainly used as sub and supercritical fluids in depolymerization processes of plastics. In most of the case, role of sub and supercritical fluids is both solvent as a reaction medium and reactant. In hydrolysis or alcoholysis reaction of condensation polymerization plastics, water or alcohol is evidently one of the reactants and transformed into the product molecules. In depolymerization of polyethylene, hydrogen was supplied from water, so that, the role of water is not only a solvent but also a reactant. The critical temperature of methanol is much lower than that of water, as shown in Table 4.2.1.1. Properties of water such as dielectric constant and ion product, change drastically around the critical point. Thus, catalytic effect of water can be

expected. When the depolymerized products are not enough stable in high temperature solvent and supercritical condition is required, alcohols may be better solvent than water due to lower critical temperature. During the depolymerization process, plastics phase is often solid or melt state. In that case, dissolution of solvent into solid or melt phase is important to enhance the reaction, especially initial stage of the depolymerization. When we think of whole process of chemical recycling of plastics, separation and purification process of depolymerization products is also important. Thus, we have to select the solvent which can be efficiently used for separation and purification process as well as reaction process. [1]

New recycling methods are being developed using subcritical fluids where unsaturated polyester (UP) resin in FRP can be efficiently depolymerized to separate glass fiber from filler and polymer. Reactions were carried out with or without a catalyst (K_3PO_4) in diethyleneglycol monomethylethter (DGMM) and benzyl alcohol under their subcritical state at temperatures 463–623 K for 1–8 h in a batch reactor. The conversion of UP became fast as the catalyst/solvent molar ratio increased and it was enhanced in the presence of K_3PO_4 catalyst in subcritical benzyl alcohol. The glass fiber recovered after the FRP treatment in subcritical benzyl alcohol was relatively long, while it became short and somewhat damaged at temperature higher than 573 K. The similar trend was observed when DGMM was used as a solvent. In Fig. 4.2.1.2. FRP decomposition process proceeds by removing the filler as well as depolymerization of unsaturated polyester. [3]
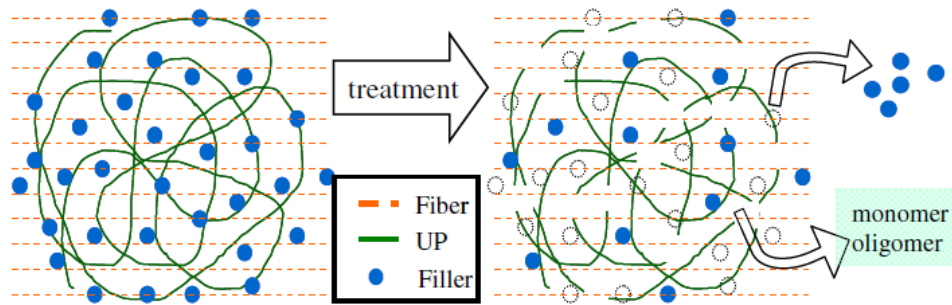
Fig. 4.2.1.2. - Proposed structure of decomposition of unsaturated polyester.

Experiments have also been devised in order to identify the significant process parameters that affect fiber reinforced composite recovery potential including temperature, time, oxidant and catalyst concentration. Experiments were performed in a batch-type reactor (10 mL) as shown in Fig. 4.2.1.3. without stirring, with temperatures ranging from 523 to 673 K, pressures from 4.0 to 27.0 MPa and reaction times from 1 to 30 min. The efficiency of resin removal reached ca. 79.3 wt.% under supercritical water conditions with further improvement through the use of potassium hydroxide as alkali catalyst (up to 95.3 wt.%). The tensile strength of the reclaimed fibers was between 90% and 98% than that of the virgin fibers. A second-order kinetic equation was implemented to model the reactive extraction process. [4]
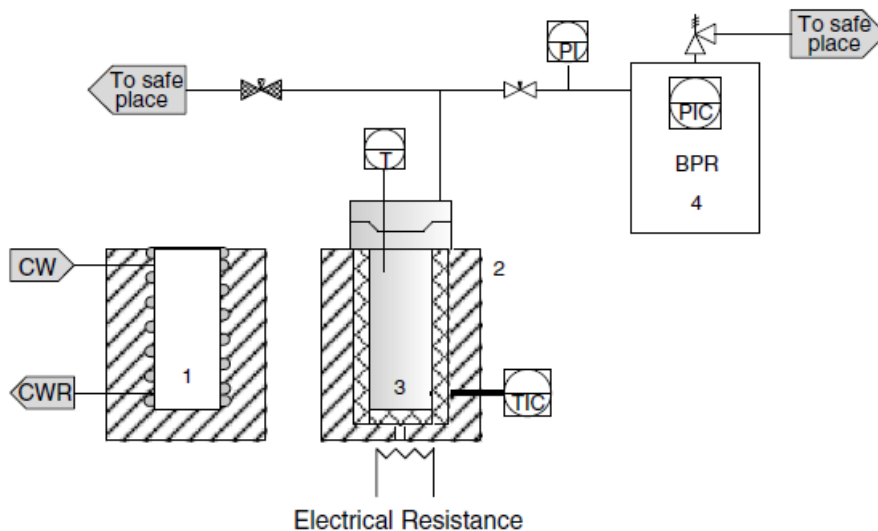
Fig . 4.2.1.3. - Bench-scale plant to perform reactions at high pressure–temperature in batch mode: (1) cooling block, (2) heating block, (3) autoclave reactor, (4) back pressure regulator.

Moreover, chemical recycling of carbon fiber reinforced composites (CFRCs) has been investigated using subcritical and supercritical alcohols as reactive-extraction media. The epoxy resin that joins the fibers is degraded during the process, producing fibers that retain 85–99% of the strength of the virgin fibers. Methanol, ethanol, 1-propanol and acetone were employed as solvent-reagents to conduct experiments in batch and semi-continuous-type reactors at temperatures ranged from 200 to 450 ◦C. The impact of flow rate and the addition of alkali catalysts (i.e. NaOH, KOH and CsOH from 0.016 to 0.50 M), was also investigated. Experiments performed in the semi-continuous flow system, as shown in Fig. 4.2.1.4., which enhanced the mass transfer steps and reduced temperature requirements, thus eliminations of resin of 98 wt. % were achieved using at 350 ◦C and 1.1 kg-alcohol/kg-fiber/min and, at the same solvent flow rate at 275 ◦C using 0.02 mol/L of KOH 96.5 wt.% was obtained. [5]
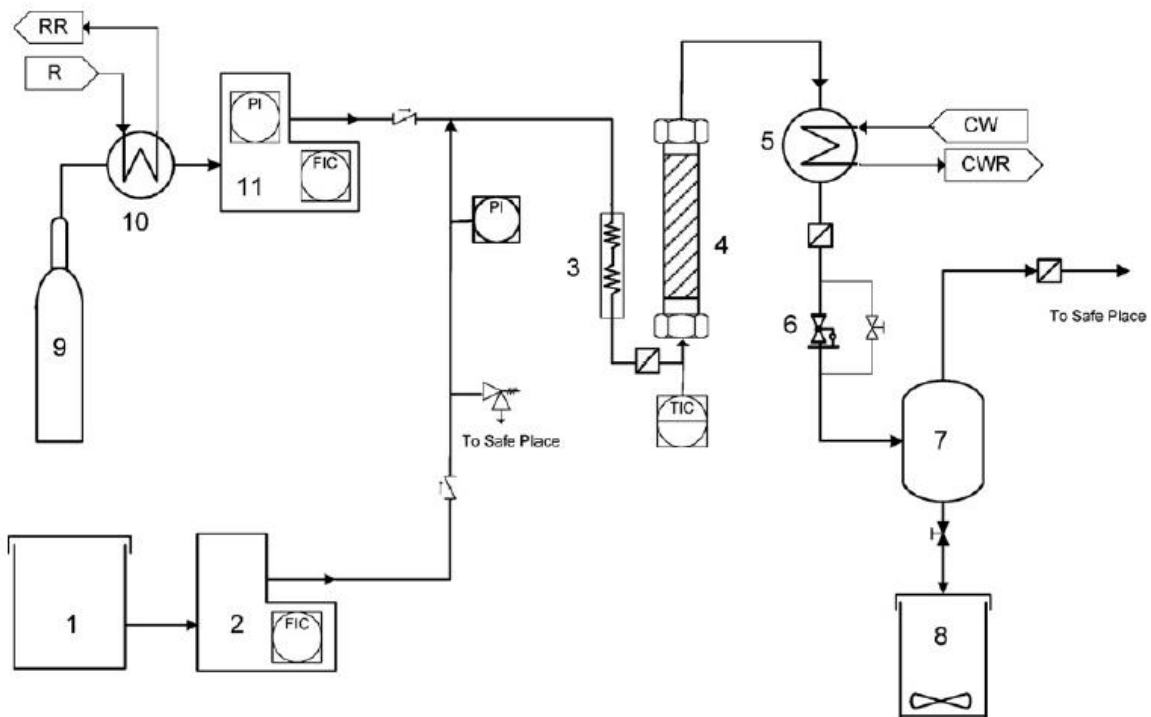
Fig. 4.2.1.4. - Flow diagram of the semi-continuous lab-scale plant: (1) solvent storage tank; (2) high pressure pump; (3) pre-heater (integrated within reactor); (4) reactor; (5) product cooler; (6) back pressure regulator; (7) flash vessel; (8) product storage tank; (9) CO2 cylinder; (10) cooler; (11) high pressure pump.

The reactive dissolution of the resin is a non-steady process in which five main mass transfer steps are found, as shown in Fig. 4.2.1.5.: (1) and (2) diffusion (or dissolution) of the reagent to the surface of the fiber (double-film theory), (3) reaction at the surface of the reinforced fiber, (4) diffusion (or dissolution) of the products to the bulk fluid and (5) external mass transfer by convection in the bulk fluid. Mass transfer steps 1, 2, 4 and 5 can only be enhanced by mixing, but stirring may cause undesired damage to the fibers. [5]
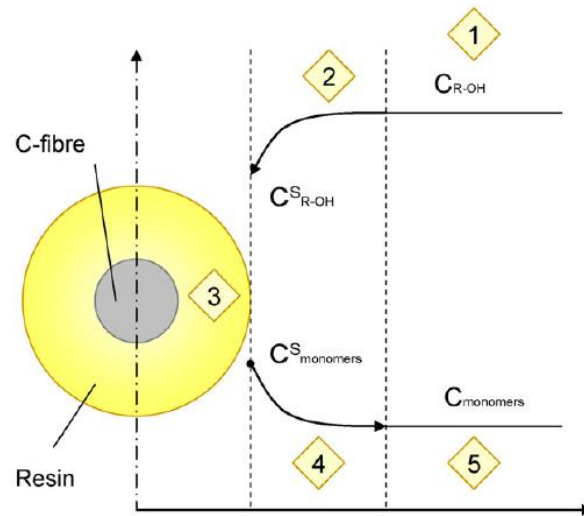
Fig. 4.2.1.5. - Mass transfer steps in the reaction–extraction process of the epoxy resin from CFRCs.

Concentration profile in a single carbon filament.

Supercritical propanol has been used to extract and remove the epoxy resin from the surface of a carbon fiber composite material. The process appeared to be effective when operating above 450 °C and above 50 bar. The recovered fibers were found to be virtually as strong, in terms of tensile strength, as the virgin fibers indicating that little had been done to damage their structural integrity. One advantage of this method is that the polymer, as well as the fiber material, can be recovered. The polymer was analyzed to investigate what chemical transformations had occurred during treatment. It is seems likely that the amide cross-linker is broken in the polymer to release a residue with a relatively high molecular weight. [6]

Several PAN based carbon fibers have also been recycled from epoxy resin/carbon fiber composites using supercritical n-propanol. The recycled carbon fibers were

characterized using single fiber tensile tests, SEM, XPS and micro-droplet test. The tensile strength and modulus of the recycled carbon fiber was very similar to the corresponding as-received carbon fibers. However, the surface oxygen concentration decreased significantly, which caused a reduction of the interfacial shear strength with epoxy resin. [7]

Water has also been used to be reaction medium and the decomposition of carbon fiber reinforced epoxy composites. Experiments have been devised in order to identify the significant process parameters that affect fiber reinforced composite recovery potential including temperature, time, catalyst, feedstock, and pressure. Experiments were performed in a batch-type reactor without stirring. Under the condition that the temperature was 260 ∘C and the ratio of resin and water was 1:5 g/mL, the decomposition rate could reach 100 wt.% and the carbon fibers were obtained. The results from the Scanning Electron Microscopy (SEM) and Atomic Force Microscope (AFM) measurements showed that the fibers were clean and no cracks or defects were found. The average tensile strength of the reclaimed fibers was about 98.2% than that of the virgin fibers. [8]

The carbon fibers have been recovered in oxygen in supercritical water at 30 ± 1 MPa and 440 ± 10 °C. The microstructure of the recovered carbon fibers was observed using scanning electron microscopy and atom force microscopy. The results revealed that the clean carbon fibers were recovered and had higher tensile strength relative to the virgin carbon fibers when the decomposition rate was above 85 wt.%, although the recovered

carbon fibers have clean surface, the epoxy resin on the surface of the recovered carbon fibers was readily observed. As the decomposition rate increased to above 96 wt.%, no epoxy resin was observed on the surface of the carbon fibers and the oxidation of the recovered carbon fibers was readily measured by X-ray photoelectron spectroscopy analysis. The carbon fibers were ideally recovered and have original strength when the decomposition rates were between 94 and 97 wt.%. This study clearly showed the oxygen in supercritical water is a promising way for recycling the carbon fibers in carbon fibers reinforced resin composites. [9]

4.2.2. Chemical Remotion of Matrix

In recent years, the chemical recycling of polymer waste has received a great deal of attention; epoxy resin is of great importance for a number of diverse composite applications, due to its good processability during curing process for forming crosslinking. Research has been carried out with the objective of analyzing the chemical resistance of amine cured epoxy, finding that it had low resistance to acid solution, and was completely decomposed in high concentration acid and at high temperature. This phenomena suggests the possibility of chemical remotion of matrix for composite materials recycling by chemical processing.

The decomposition of epoxy resin cured with amine in acid solution has been studied for chemical recycling due to its poor corrosion resistance. The amine cured epoxy resin

was decomposed in nitric acid solution, and then the decomposed products were repolymerized with bisphenol F and phthalic anhydride (PA) as curing agent to prepare recycled resin. Chemical structures of the mentioned agents are shown in Fig. 4.2.2.1.

Bisphenol F type epoxy resin

MDA (1,8-*p*-menthanediamine)

PA (phthalic anhydride)
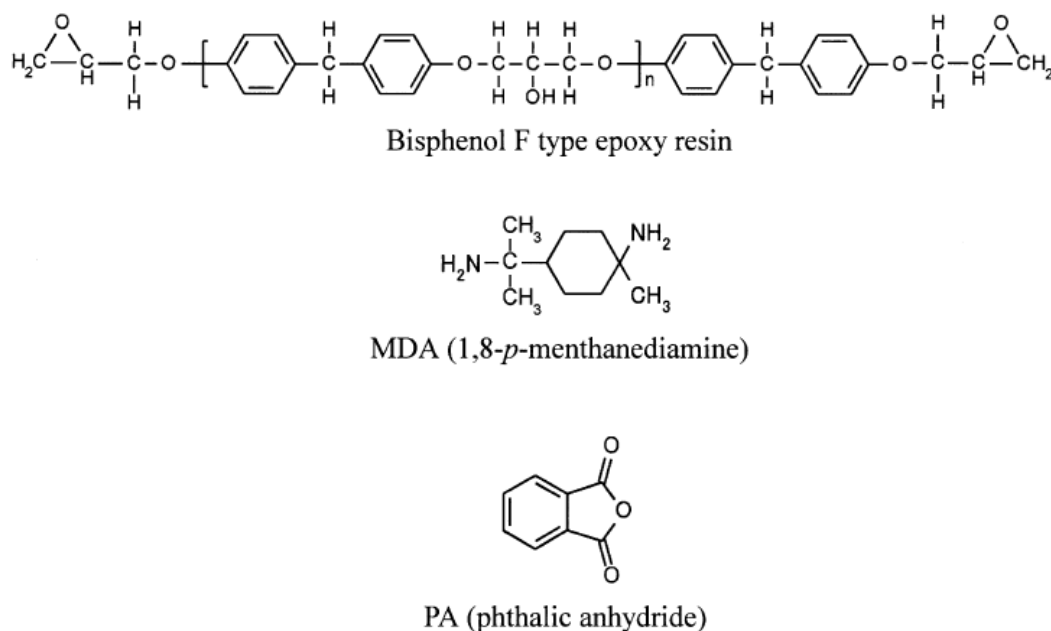
Fig. 4.2.2.1. - Chemical structures of epoxy resin and curing agents.

An example of decomposition reaction can be as follow: Epoxy resin cured with MDA (BPF/MDA) in weight ratio of 100:22 at 80 °C for 2h, and the post curing at 150 °C for 3h, each specimen immersed in 4 M (=mol/l) nitric acid solution at 80 °C. The proposed chemical decomposition reaction is shown in Fig. 4.2.2.2. C-N bond are broken and benzene ring is nitrated under the attack of nitric acid. The decomposed products are similar in structure as bisphenol F.
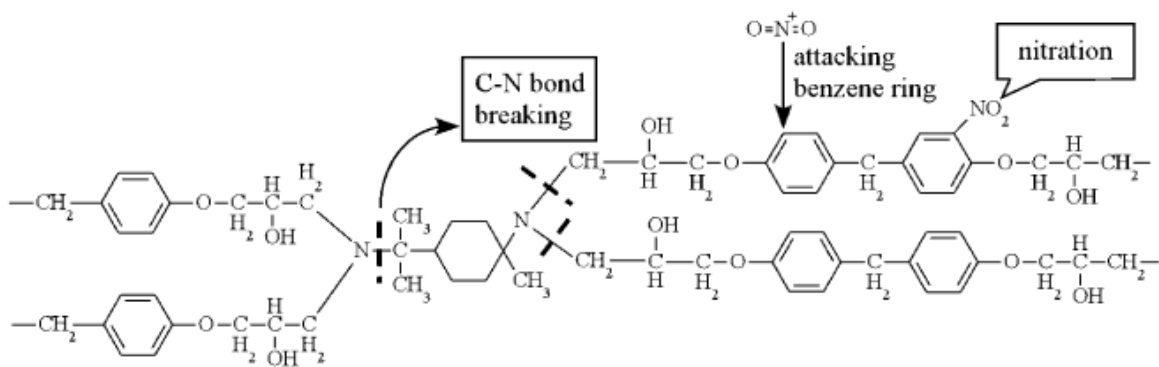
Fig. 4.2.2.2. - Proposed chemical decomposition reaction.

As shown in Fig. 4.2.2.3. With the assistance of tertiary amine catalyst, the reaction is initiated by forming carbonium anion by opening some of the cyclic anhydride (Eq. 1.). The carbonium anion opened the epoxide ring (Eq. 2.), regenerating hydroxyl oxygen anion that further reacted with anhydride (Eq. 3). NE containing hydroxyl group underwent the reaction (Eq. 4) to form polyester chain. After the sequence of these reaction, they were crosslinked to form the network structure of the thermoset. Consequently, the presence of tertiary amine catalyst resulted in the curing reaction of recycled resin faster than the virgin resin, and with a higher density network with the same reaction conditions. [21]
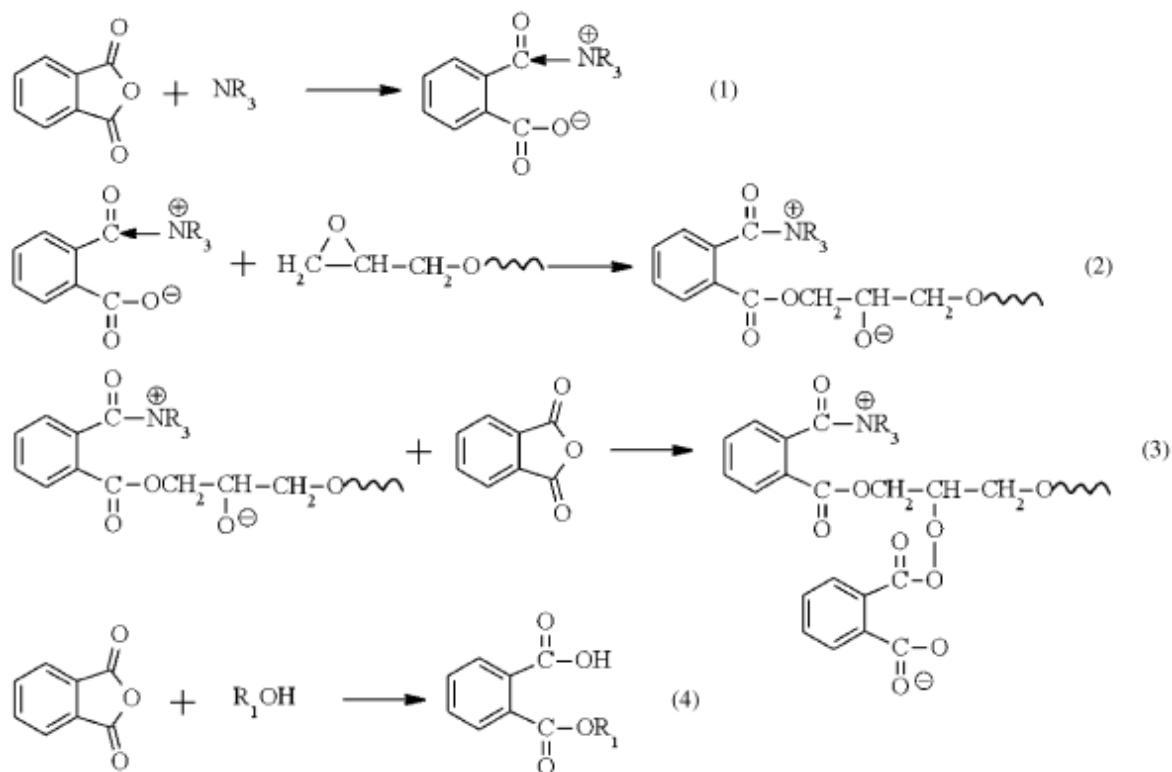
Fig. 4.2.2.3. - Repolymerization reaction.

In order to investigate the practical applicability of the proposed approach, glass fiber reinforced BPF epoxy resin cured with DDM (GFRP) was selected as experimental material for chemical recycling in this study. At first, GFRP was decomposed in nitric acid solution, and the decomposed products and the fiber were recovered. Then, the decomposed product was used to prepare recycled resin, together with original BPF epoxy resin and curing agent of phthalic anhydride (PA). In the experiment, the matrix of the specimen of GFRP was BPF epoxy resin cured with DDM. BPF epoxy resin was cured with DDM in weight ratio of 100:27 at 80 8C for 2 h, and the post curing was conducted at 150 8C for 4 h. In addition, PA, was used as curing agent when the decomposed products were repolymerized to prepare recycled resin. The reinforcement was E-glass fiber, being used

116

in forms of glass cloth. T-glass fiber was employed for comparison with E-glass fiber. The proposed chemical approach to recycling BPF/MDA epoxy resin was successfully applied to recycle glass fiber reinforced BPF/DDM epoxy resin. The GFRP was firstly immersed in nitric acid solution, with the matrix decomposed and glass fiber separated and recovered. And then the decomposed product of extract was collected and neutralized. The neutralized extract was finally repolymerized to prepare recycled resin by substituting a part of BPF epoxy resin using PA as curing agent. [22]

4.3. Mechanical Processing

4.3.1. Grinding and Pulverization - Reuse as Fillers

During the first stages in the process large bales of waste are broken down by shredding them to a size of 25–50 mm. The shredded waste is then granulated to a particle or flake with a size approximately 3.2–9.5 mm. The granulation process also frees up any product labels which are then removed along with any loose debris as the waste passes through an air classifier. An image of a granulator with the blades exposed is shown in Fig. 4.3.1.1. Granulation is based on a rotary cutting system. The equipment needs to have mechanical stability, quick blade change, easy cleaning and high performance. The systems generate heat so they are water cooled or more cost effectively air cooled. The granulators are constructed to have a welded construction and

the installation of external bearings is preferred to prevent grease contamination or the potential of dust fines entering the bearing
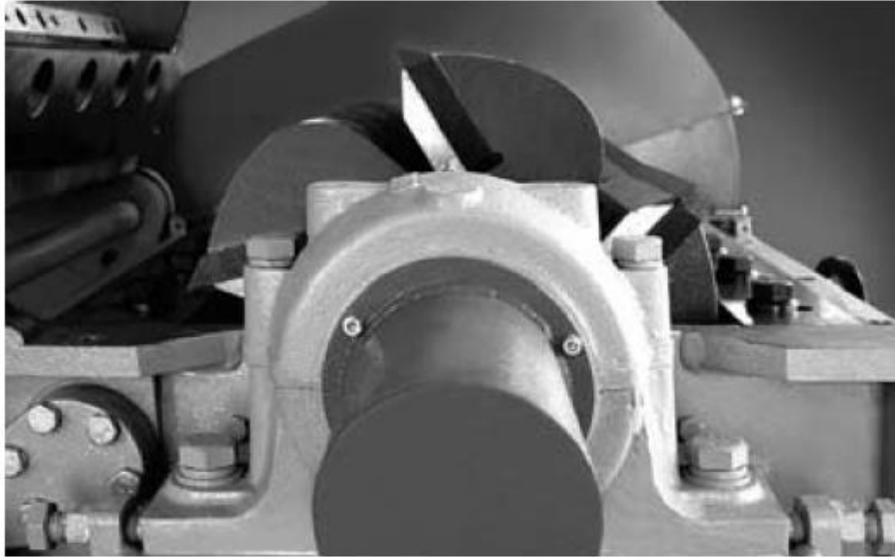
Fig. 4.3.1.1. - Photograph of a granulator with the blades exposed.

The screen must be easily interchangeable, to allow for different flake sizes if required. The blades are double angle cut; they are located diagonally to the rotor in a straight line. The stationary blade is set at the same angle as the rotary blades but is set in the opposite direction. A schematic of the granulator is shown in Fig. 4.3.1.2. The rotary and stationary blades are set apart to a preset gap between each other. The blades are ideally fixed into the machine to allow fast change-over. The processing of components made from composite polymers through the granulator will significantly wear the blades, which will need regular removal and sharpening. The screen enables the granulated waste to fall through using gravity. The size of holes provisioned on the screen dictates the size of the

granulate particle. As the waste is size reduced it becomes sufficiently small to fall through the screen. Other granulation types are profile, rotary, feed, edge trim, large and pipe.
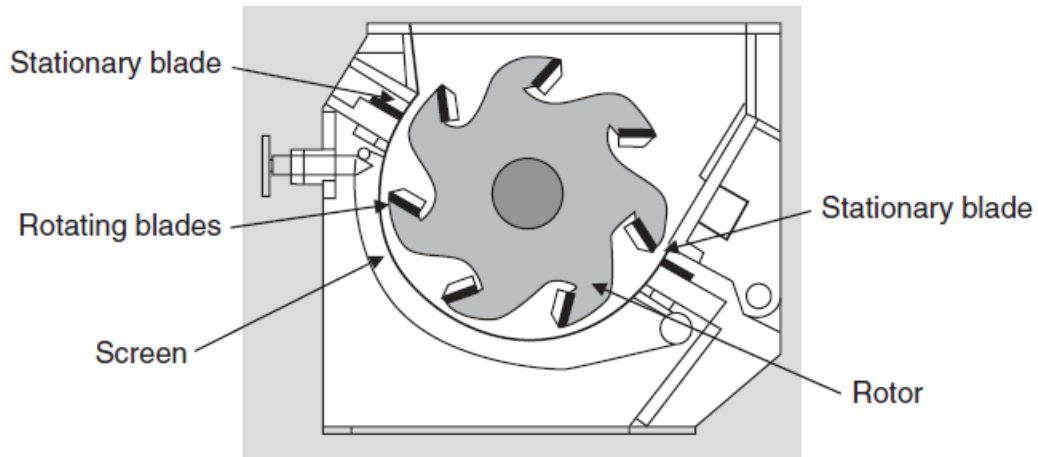
Fig. 4.3.1.2. - Schematic of the internal elements of a granulator.

Granulation of a plastic composite based on fibers will result in mechanical damage to the fibers. The resulting damage will be based on the condition of the granulator blades, the operating speed, screen size and the condition of the fibers entering the granulator. The mechanical damage would result in a fiber length of 2–10 mm. The effect on short fibers entering the granulator will be less than on long fiber-based materials. Figure 4.3.1.3. shows a graph from a study conducted. The graph shows a PA polymer with 35% glass fiber, which has a diameter of 10.5 μm. The average length of the glass fibers has been recorded, following various stages of injection molding processing. The graph shows that the unprocessed pellet has an average length of 338 μm. The effect of injection molding processing reduces the average fiber length to 278 μm, which is an 18% reduction

in length. Subsequent sampling with increased level of the same reprocessed material in the form of a regrind shows an ongoing reduction in fiber length.
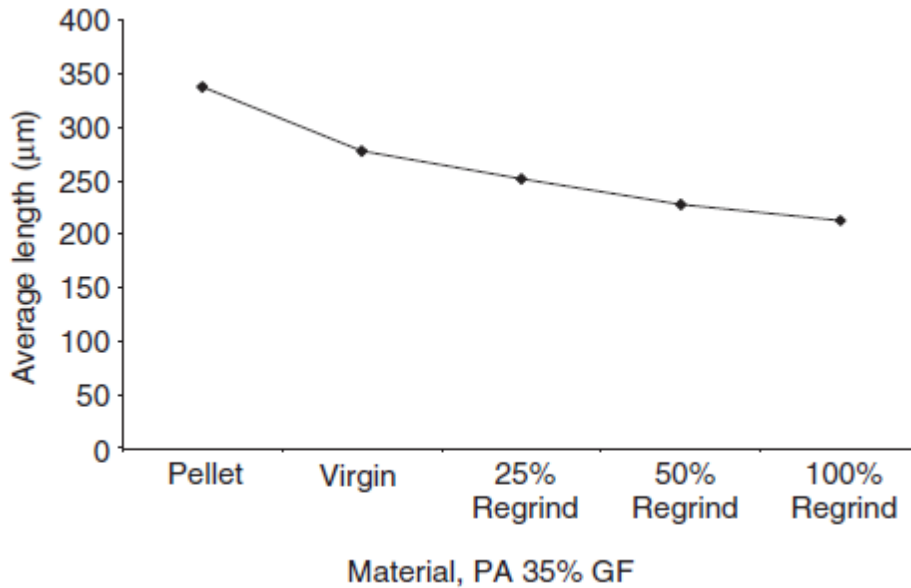
Fig. 4.3.1.3. - Average glass fiber length in reprocessed PA 35% glass fiber.

The 100% regrind version results in an average fiber length of 213 µm, a 37% reduction in average fiber length. The effect of the fiber length reduction results in reduced mechanical properties in tensile test pieces manufactured from the different material types. The modulus values from the experiments are shown in Table 4.3.1.1. and a reduction in modulus is noted as the content of the reground material is increased. [23]

Table 4.3.1.1. - Modulus values based on experiments with reground PA with glass fiber.

Material	E (GPa)
Virgin	10.84
25% Regrind	10.75
50% Regrind	10.73
100% Regrind	10.27

Further research is required to fully understand the mechanical damage imparted onto fibers as they are granulated in the context of the full cycle of recycling. The waste is granulated into small particles, making it more manageable as it takes less volume, the process also frees up waste which may be assembled or joined locked together. However, the process of granulation mechanically damages fibers in composite materials. The level of damage imparted to fibers or fillers from the original condition is imprecise. It is dependent on factors such as original fiber length, the process used to manufacture the part, damage which may have been experienced during the product life, and finally the damage imparted to the fiber as a result of the waste recycling process. Limited studies have shown that a 37% reduction in fiber length is to be expected, which will reduce the physical properties of the material, when compared to the virgin grade. More research is required into the effects of granulation. Similar studies are needed and will become ever more important as recycling of waste composite materials increases. The studies can ascertain the effect of fibers that have been processed and re-granulated through a number of cycles. This data would provide valuable information on the effect of the re-granulation and aid optimization of the process equipment and parameters. It would also identify how many cycles can be processed before fillers in the composite are rendered

ineffective. Granular or densified materials can then be reformed into an article or a pellet using extrusion equipment. Making an article is the simplest and most cost-effective solution as it reduces processing steps and associated costs. There are numerous process steps and methods for the mechanical recycling of waste composites, which are effective at recovering valuable materials. Quite often these methods are used in conjunction with each other to optimize throughputs and product quality. The characteristics of the final product will vary on the original material, source, type, processing stages and recycling methods; however a high quality reusable end product can be achieved from waste. Industrial waste materials can and should be processed at source; this reduces unnecessary storage, transportation and contamination issues.

5. Experimental

5.1. Materials

Commercially available carbon fiber–epoxy resin prepreg was used for this research. The prepreg was 40 wt% resin. The prepreg curing conditions were 60 min at 180 °C under vacuum. The carbon fiber-epoxy resin composite samples were prepared with 4 layers of prepreg material, of approximately 0.5 g each (1 cm wide, 4 cm long), as shown in Fig. 5.1.1.a.
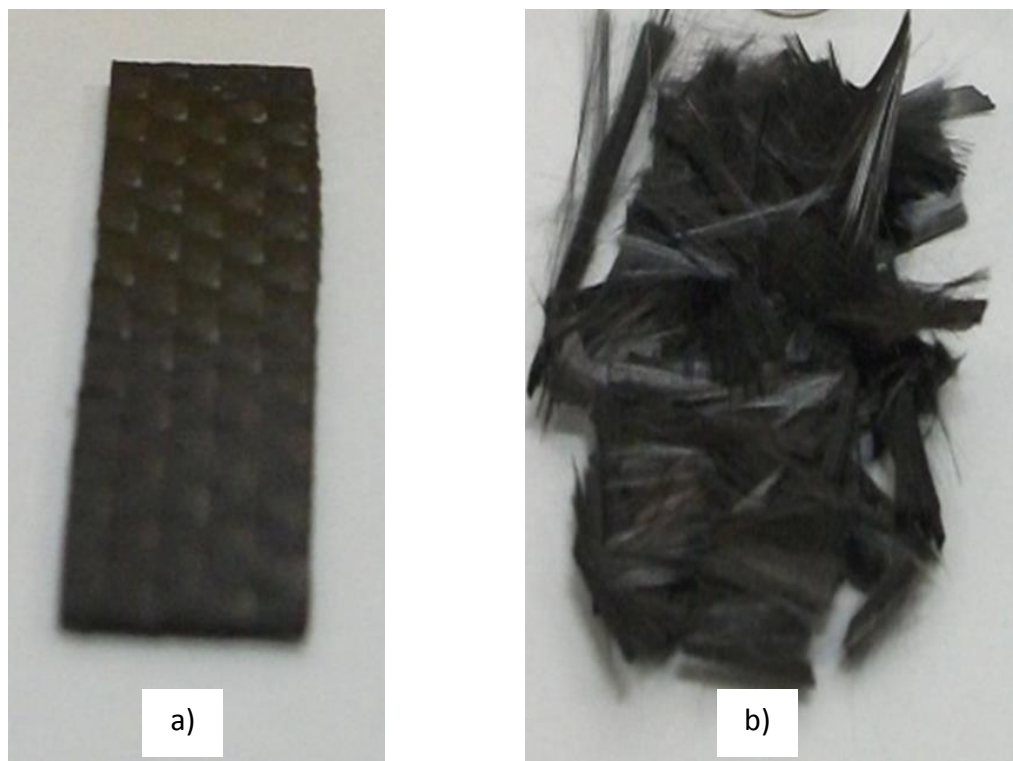
Fig. 5.1.1. a) Composite sample before decomposition reaction. b) Recovered carbon fibers after

decomposition reaction.

Recovered carbon fibers are shown in Fig. 5.1.1.b. after decomposition reaction. Each

sample was weighed before and after the decomposition reaction.

5.2. Subcritical and Supercritical Decomposition Reactions

A schematic diagram of the experimental apparatus (AKICO Co. Japan) is shown in Fig.

5.2.1. The apparatus consists of a batch-type Inconel reactor (about 8.8 cm3 inner

volume) and an electric furnace. Mechanical stirring of the reactor was programmed with

a cyclic horizontal swing span of 2 cm working at a fixed frequency of 60 cycles per minute.
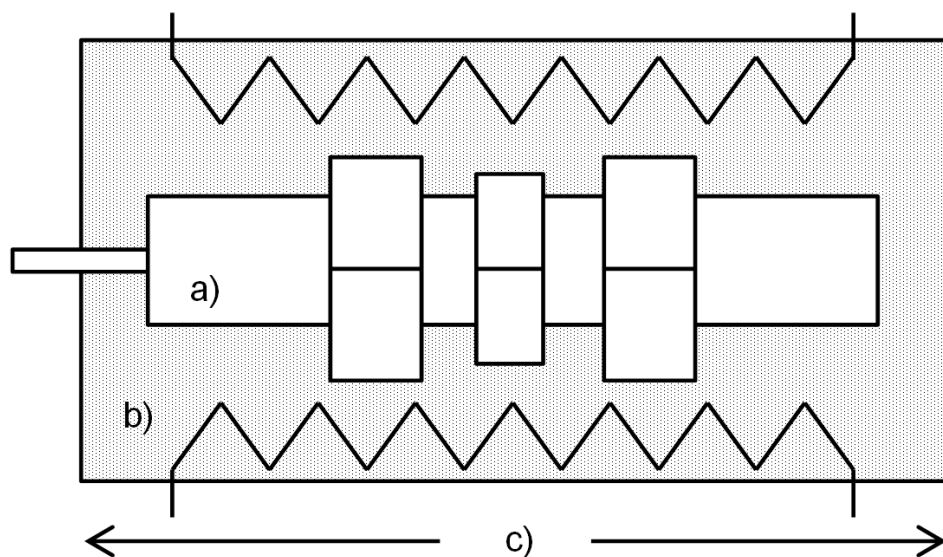
Fig. 5.2.1. Schematic diagram of experimental apparatus. a) Batch reactor, b) Electric furnace, c) Cyclic horizontal mechanical movement.

A fixed volume of 4.4 cm3 of solvent was used in every experiment. Water for hydrothermal decomposition reactions and benzyl alcohol for solvothermal decomposition reactions were used as solvents for the experiments. An optimal and fixed catalyst/solvent ratio of 0.14 w/w was used in experiments with addition of tripotassium phosphate (K_3PO_4) as catalyst [3]. Critical parameters (critical temperature, Tc, and critical pressure, Pc) of water and benzyl alcohol are Tc = 373.95 °C, Pc = 22.06 MPa, Tc = 441.85 °C, Pc = 4.3 MPa, respectively [1]. Time to reach the temperature in the reactor was approximately 15 min. After treatment, the batch reactor was quenched in water.

5.3. Decomposition Rate

The decomposition rate (DR) of the epoxy resin in the composites is defined by equation 5.3.1.:

$$DR = \frac{M_c - M_r}{M_e} \times 100\%$$ (Eq. 5.3.1.)

where DR is the decomposition rate (wt.%), Mc is the mass of composite before decomposition treatment, Mr is the mass of solid composite after decomposition treatment, and Me is the mass of epoxy resin in the composite before decomposition treatment. A 100% decomposition rate indicates that absolutely clean carbon fibers are being recovered.

5.4. Design of Experiments

Hydrothermal experiments were designed according to Table 5.4.1. In experiments 1 to 25, water was used as solvent; in experiments 26 to 50, water and addition of tripotassium phosphate (K_3PO_4) as catalyst was used.

Table 5.4.1. Design of experiments by hydrothermal decomposition reaction using water as solvent.

Experiment	Temperature (°C)	Time	Mass of Composite (g)	Composite/Solvent Ratio (g/mL)

1	250	1 h	0.5201	0.118
2	250	2 h	0.5343	0.121
3	250	4 h	0.5246	0.119
4	250	6 h	0.5244	0.119
5	250	8 h	0.5835	0.133
6	300	1 h	0.559	0.127
7	300	2 h	0.5751	0.131
8	300	4 h	0.5512	0.125
9	300	6 h	0.5683	0.129
10	300	8 h	0.5715	0.130
11	350	1 h	0.5563	0.126
12	350	2 h	0.5216	0.119
13	350	4 h	0.548	0.125
14	350	6 h	0.4973	0.113
15	350	8 h	0.53	0.120
16	375	30 min	0.4956	0.113
17	375	1 h	0.5492	0.125
18	375	2 h	0.5395	0.123
19	375	4 h	0.5288	0.120
20	375	6 h	0.5374	0.122
21	400	15 min	0.5303	0.121
22	400	30 min	0.5618	0.128
23	400	1 h	0.5754	0.131
24	400	2 h	0.556	0.126
25	400	4 h	0.5066	0.115
26	250	1 h	0.5488	0.125
27	250	2 h	0.5559	0.126
28	250	4 h	0.5395	0.123
29	250	6 h	0.5118	0.116
30	250	8 h	0.5511	0.125
31	300	1 h	0.5752	0.131
32	300	2 h	0.5634	0.128
33	300	4 h	0.5081	0.115
34	300	6 h	0.5368	0.122
35	300	8 h	0.5322	0.121
36	350	15 min	0.5707	0.130
37	350	30 min	0.5408	0.123
38	350	1 h	0.5384	0.122
39	350	2 h	0.5569	0.127
40	350	4 h	0.5644	0.128
41	375	15 min	0.5138	0.117

42	375	30 min	0.4968	0.113
43	375	1 h	0.5641	0.128
44	375	2 h	0.4713	0.107
45	375	4 h	0.5292	0.120
46	400	15 min	0.5602	0.127
47	400	30 min	0.5459	0.124
48	400	1 h	0.5313	0.121
49	400	2 h	0.5283	0.120
50	400	4 h	0.5383	0.122

1. Time to reach temperature in reactor: 15 min.
2. Composite/solvent ratio: 4.4 mL volume of solvent was used in every experiment.
3. Catalyst/solvent ratio: 0.14 w/w in experiments 26 to 50.

Solvothermal experiments were designed according to Table 5.4.2. In experiments 51

to 75 benzyl alcohol was used as solvent; in experiments 76 to 100, K_3PO_4 was added as

catalyst to the benzyl alcohol.

Table 5.4.2. Design of experiments by solvothermal decomposition reaction using benzyl alcohol as solvent.

Experiment	Temperature (°C)	Time	Mass of Composite (g)	Composite/Solvent Ratio (g/mL)
51	250	1 h	0.547	0.124
52	250	2 h	0.5365	0.122
53	250	4 h	0.5783	0.131
54	250	6 h	0.5414	0.123
55	250	8 h	0.5627	0.128
56	300	1 h	0.5436	0.124
57	300	2 h	0.5298	0.120
58	300	4 h	0.5541	0.126
59	300	6 h	0.5113	0.116
60	300	8 h	0.5349	0.122
61	350	15 min	0.5196	0.118
62	350	30 min	0.5605	0.127
63	350	1 h	0.5277	0.120
64	350	2 h	0.5606	0.127
65	350	4 h	0.5441	0.124

66	400	15 min	0.5576	0.127
67	400	30 min	0.5586	0.127
68	400	1 h	0.563	0.128
69	400	2 h	0.5261	0.120
70	400	4 h	0.5476	0.124
71	425	15 min	0.549	0.125
72	425	30 min	0.5369	0.122
73	425	1 h	0.5132	0.117
74	425	2 h	0.5517	0.125
75	425	4 h	0.5165	0.117
76	250	1 h	0.5276	0.120
77	250	2 h	0.5167	0.117
78	250	4 h	0.5658	0.129
79	250	6 h	0.5316	0.121
80	250	8 h	0.5493	0.125
81	300	1 h	0.5511	0.125
82	300	2 h	0.5043	0.115
83	300	4 h	0.5398	0.123
84	300	6 h	0.5406	0.123
85	300	8 h	0.5161	0.117
86	350	15 min	0.4812	0.109
87	350	30 min	0.5421	0.123
88	350	1 h	0.5095	0.116
89	350	2 h	0.5431	0.123
90	350	4 h	0.4806	0.109
91	400	15 min	0.5274	0.120
92	400	30 min	0.489	0.111
93	400	1 h	0.4874	0.111
94	400	2 h	0.522	0.119
95	400	4 h	0.4905	0.111
96	425	15 min	0.4984	0.113
97	425	30 min	0.5566	0.127
98	425	1 h	0.4938	0.112
99	425	2 h	0.4834	0.110
100	425	4 h	0.4921	0.112

1. Time to reach temperature in reactor: 15 min.

2. Composite/solvent ratio: 4.4 mL volume of solvent was used in every experiment.

3. Catalyst/solvent ratio: 0.14 w/w in experiments 76 to 100.

Hydrothermal experiments were carried out at 250 °C, 300 °C, 350 °C, 375 °C and 400 °C with an estimated pressure of 3.9 MPa 8.5 MPa 16.5 MPa 24.6 MPa and 37.2 MPa respectively. Solvothermal experiments were carried out at 250 °C, 300 °C, 350 °C, 400 °C and 425 °C, with an estimated pressure of 0.2 MPa, 0.7 MPa, 1.5 MPa, 2.7 MPa, and 3.6 MPa respectively. Only time and temperature were used as main experimental parameters in all experiments. Pressure was not controlled or measured during the experiments. Pressure inside the reactor is estimated according to Antoine equations and extrapolating according to Wagner equations [13].

After the composite material (Mc) was weighed and recorded, the reactor was loaded with the composite sample, solvent and catalyst if applied. The reactor was then placed in the electric furnace, which had been preheated to the desired temperature. After the desired reaction time elapsed, the reactor was quenched in a water bath at room temperature, then the residue was filtered into solid and liquid phases. The carbon fibers were recovered and rinsed with ethanol and distilled water. The carbon fibers were then submerged in an ultrasonic water bath for 10 min and dried in a fume hood for 24 hours at room temperature. The solid phase of the residue after the decomposition reaction (Mr) was then weighed and recorded.

5.5. Thermogravimetric Analysis of Composite Samples

Thermogravimetric analysis was performed on cured samples before treatment at 5 °C/min from room temperature to 900 °C in a N2 atmosphere with a platinum pan to hold the sample and an empty platinum pan as a reference to determine the thermal properties of the carbon fiber-epoxy resin composite material. The equipment used was a TG/DTA SII Nanotechnology EXSTAR 6000.

5.6. Scanning Electron Microscopy

SEM FEI Nova NanoSEM 200 Scanning Electron Microscopy equipment was used to study the recovered carbon fibers.

References used in Chapter 5: [24, 25, 26]

6. Results and Discussion

6.1. Thermogravimetric Analysis of Composite Samples

The thermograms of TGA-DTA analysis of prepreg composite material are shown in Fig. 6.1.1. The results from the TGA-DTA were used as a reference for the temperature needed to recover carbon fibers.
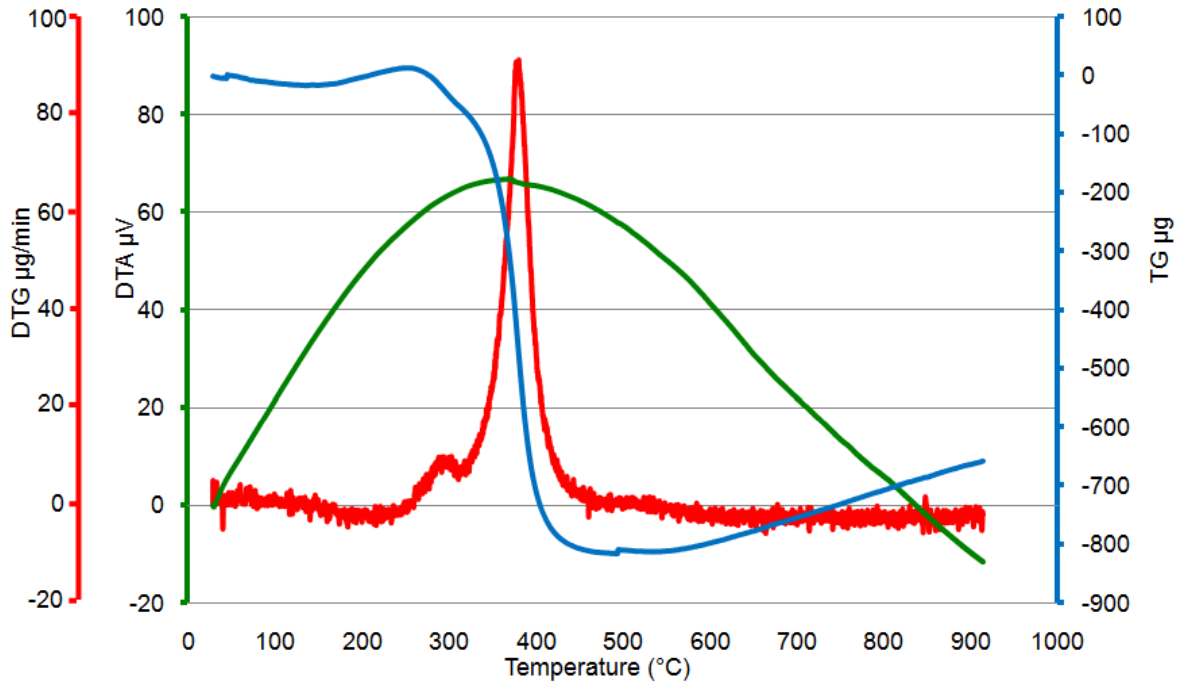
Fig. 6.1.1. TGA-DTA analysis of prepreg composite material.

The derivative weight loss curve profile in Fig. 6.1.1. (red), DTG µg/min, shows only one peak along the temperature interval between 350 °C and 450 °C, indicating that the resin is fully degraded around 450 °C. The TG curve (blue) shows the mass loss of the composite material as a function of increasing temperature having the major slope change around 350 °C. The DTA curve (green) shows the differential energy and the endothermic behavior of the composite versus the increasing temperature, with the higher point of the curve also around 350 °C; it can be deduced from the thermogram that relevant effects of temperature on composite samples start to take place at 350 °C.

6.2. Decomposition Rate of Hydrothermal and Solvothermal Experiments

DR curves of subcritical and supercritical water are shown in Fig. 6.2.1. DR data of hydrothermal decomposition reaction experiments (experiments 1 - 25) is also tabulated in Table 6.2.1. In general, decomposition rates of hydrothermal experiments increased with increasing temperature. Experiments at 250 °C showed relatively poor DR results. After 1 hour the DR was 4%; after 2 hours the DR was 14%; at 4 hours the DR was barely above 21%; at 6 hours the DR was 25% and at 8 hours the DR only reached 24%. The slight decrease in DR from 6 to 8 hours is due to the epoxy residue attached to the composite surface after such a long treatment. This residue cannot be washed away easily from the composite surface. None of the 250 °C experiments yielded any clean, epoxy-free carbon fibers. Composites that endured these treatments remained unaltered, similar to Fig. 1a. Results of experiments at 300 °C show the increasing of DR with time. Delamination of the composite occurred somewhere between 4 and 6 hours. After 8 hours it was possible to recover clean carbon fibers. Experiments at 350 °C are still below the critical point of water; at this point the DR almost reached the maximum value after 2 hours. Delamination of composites occurred after 4 hours and clean carbon fibers could be recovered after 6 hours. Despite the fact that after 8 hours of decomposition the DR was 82%, a high quantity of cleaner carbon fibers could be recovered. For 375 °C, shorter decomposition reaction experiments were carried out since higher DRs were expected near the critical point of water. At this temperature after 30 min, the DR was 34% with no delamination or clean carbon fibers recovered, whereas at 1 hour the DR reached 82% with composite delamination. The DR results were 85%, 84% and 82% for 2, 4 and 6 hours, respectively. The small decrease in DR can be explained by the epoxy residue attached to

the composite surface. The 400 °C experiments showed that after 15 min the DR reached 24%, and at 30 min the DR was 82% with delamination. After this point, clean and loose fibers could be recovered. After 1 hour, the DR reached 89%, but decreased to 80% after 2 hours, then increased again to 87% after 4 hours. The best explanation for the DR decrease in experiments longer than 1 hour is that the mass of the sample (Mr) has increased due to the spherical microparticles attached to the carbon fibers. Therefore, we can infer that a higher yield in resin decomposition was achieved in those experiments. Due to the gravimetric nature of the analysis, and particularly only in these experiments, DR data does not reflect accurately the yield in resin decomposition.
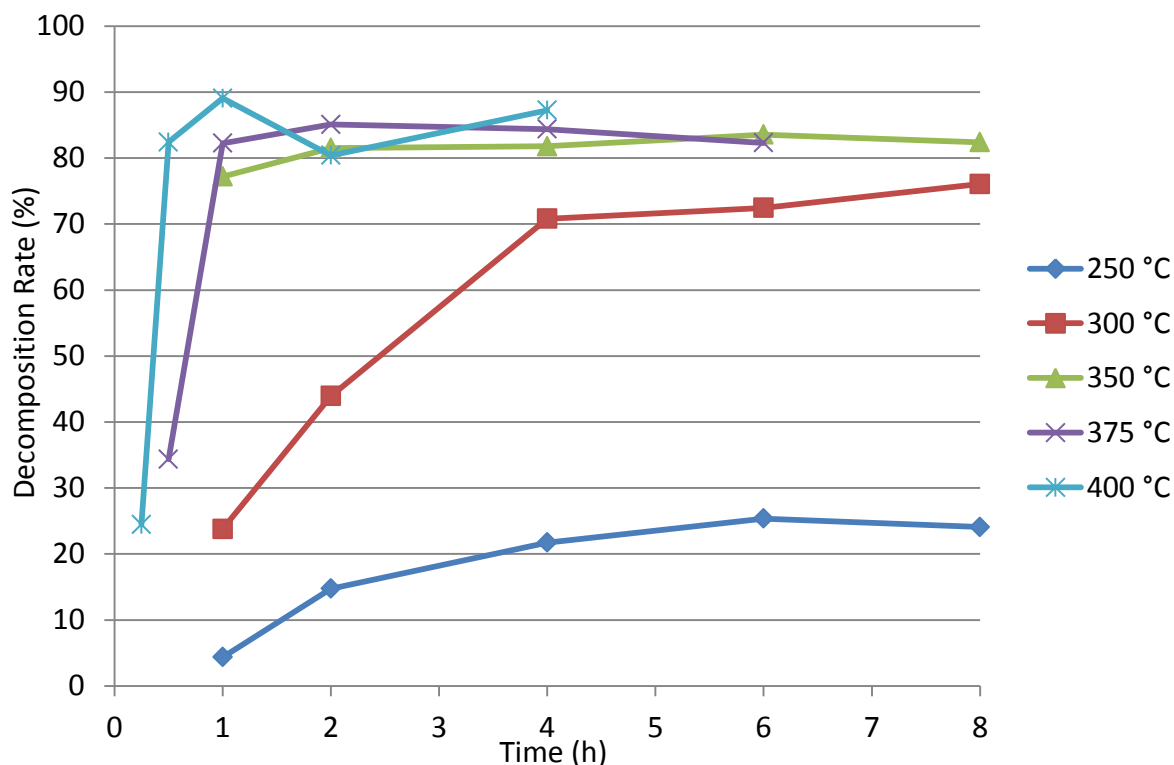
Fig. 6.2.1. Decomposition rate curves of hydrothermal decomposition reaction experiments using water as solvent.

Table 6.2.1. Decomposition rate data of hydrothermal decomposition reaction experiments.

Experiment	Temperature (°C)	Time	Decomposition Rate (%)
1	250	1 h	4.4
2	250	2 h	14.7
3	250	4 h	21.7
4	250	6 h	25.4
5	250	8 h	24.1
6	300	1 h	23.8
7	300	2 h	43.9
8	300	4 h	70.8
9	300	6 h	72.5
10	300	8 h	76.1
11	350	1 h	77.2
12	350	2 h	81.5
13	350	4 h	81.8
14	350	6 h	83.6
15	350	8 h	82.4
16	375	30 min	34.4
17	375	1 h	82.3
18	375	2 h	85.1
19	375	4 h	84.4
20	375	6 h	82.3
21	400	15 min	24.5
22	400	30 min	82.4
23	400	1 h	89.1
24	400	2 h	80.4
25	400	4 h	87.2
26	250	1 h	5.7
27	250	2 h	9.1
28	250	4 h	15.1
29	250	6 h	16.2
30	250	8 h	16.8
31	300	1 h	21.3
32	300	2 h	54.4
33	300	4 h	66.3
34	300	6 h	79.5
35	300	8 h	86.6
36	350	15 min	0.4
37	350	30 min	11.3
38	350	1 h	85.9

39	350	2 h	94.6
40	350	4 h	94.5
41	375	15 min	12.2
42	375	30 min	88.1
43	375	1 h	91.1
44	375	2 h	91.1
45	375	4 h	92.2
46	400	15 min	1.4
47	400	30 min	88.0
48	400	1 h	92.1
49	400	2 h	93.1
50	400	4 h	94.6

DR curves of hydrothermal experiments with tripotassium phosphate (K_3PO_4) as catalyst are shown in Fig. 6.2.2. DR data of hydrothermal decomposition reaction experiments (experiments 26 - 50) is also tabulated in Table 6.2.1. In general, DR of hydrothermal experiments increased with increasing temperature and time. Experiments at 250 °C showed relatively poor DR results, not going over 16.8 % after 8 h, without carbon fiber recovery or delamination of composite samples. Nevertheless, interesting results are obtained with an increase in of 50 °C in temperature, at 300 °C clean carbon fibers were recovered and DR reached 54.4 %, 66.3 %, 79.5 %, and 86.6 % after 2, 4, 6 and 8 h of treatment. At 350 °C, better results were expected, thus, short experiments were proposed, however, after 15 and 30 min, DR resulted in 0.4 % and 11.3 % without carbon fiber recovery; only after 1, 2, and 4 h, relatively good DR values were obtained, 85.9 %, 94.6 % and 94.5 respectively, with clean carbon fibers recovered. Near the critical temperature of water, at 375 °C, interesting results were obtained; clean carbon fibers were recovered and DR reached 88.1 %, 91.1 %, 91.1 %, 92.2 % after 30 min, 1, 2, and 4 h.

At 400 °C DR was 88.0 %, 92.1 %, 93.1 %, and 94.6 % after 30 min, 1, 2, and 4 h respectively.
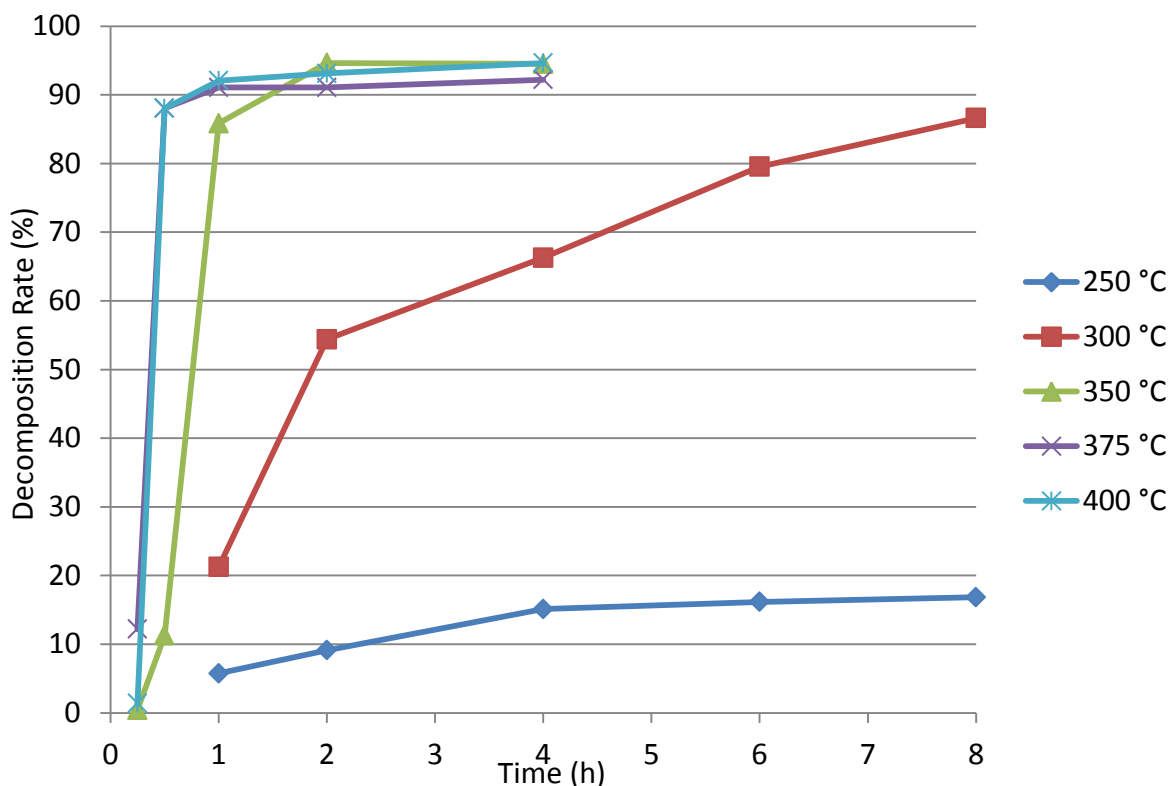
Fig. 6.2.2. Decomposition rate curves of hydrothermal decomposition reaction experiments using water as solvent with tripotassium phosphate (K_3PO_4) as catalyst.

DR curves of subcritical benzyl alcohol are shown in Fig. 6.2.3. DR data of solvothermal decomposition reaction experiments (experiments 51 - 75) is also tabulated in Table 6.2.2. Decomposition reaction experiments with benzyl alcohol yielded relatively higher DR results even at low temperatures and shorter reactions. At 250 °C the DR was -17% and -7% for 1 and 2 hours, respectively. These negative values can be explained by benzyl alcohol swelling into the polymer molecular network due to the decomposition reaction

mechanism. In this scenario, benzyl alcohol is absorbed into the organic matrix and begins solvolysis. At these shorter experiments and relatively low temperatures, not enough energy and time have been provided to complete or even start the decomposition; hence the slight increase of the Mr value. DR was 10%, 36% and 33% for 4, 6, and 8 hours, respectively. Delamination of the composite occurred after 2 hours. Some clean and loose fibers could be recovered after 4 hours. At 300 °C, DR was similar for all five experiments: 92%, 92%, 91%, 92%, and 90% for 1, 2, 4, 6, and 8 hours, respectively. We can infer that most of the carbon fibers could be recovered even after very short reactions. Samples recovered from these experiments showed epoxy-free loose carbon fibers. A similar behavior was observed at 350 °C with DR of -1%, 92%, 92%, 92% and 93% for 15 min, 30 min, 1, 2, and 4 hours, respectively. Clean loose carbon fibers were also recovered from the 350 °C experiments. At 400 °C the DR was 67%, 93%, 93%, 91% and 92% for 15 min, 30 min, 1, 2, and 4 hours, respectively. Delamination, but no loose carbon fibers were noticed in the 15 min experiment, while in the rest of the experiments clean fibers were recovered. At 425 °C, in subcritical benzyl alcohol, the DR was 91%, 93%, 90%, 92% and 90% for 15 min, 30 min, 1, 2, and 4 hours, respectively, and clean fibers could be recovered even at very short decomposition reactions. Most of benzyl alcohol decomposition reaction experiments showed relatively high yields, over 90%, except for experiments at 250 °C or very short reactions, e.g., 15 min at 350 °C.
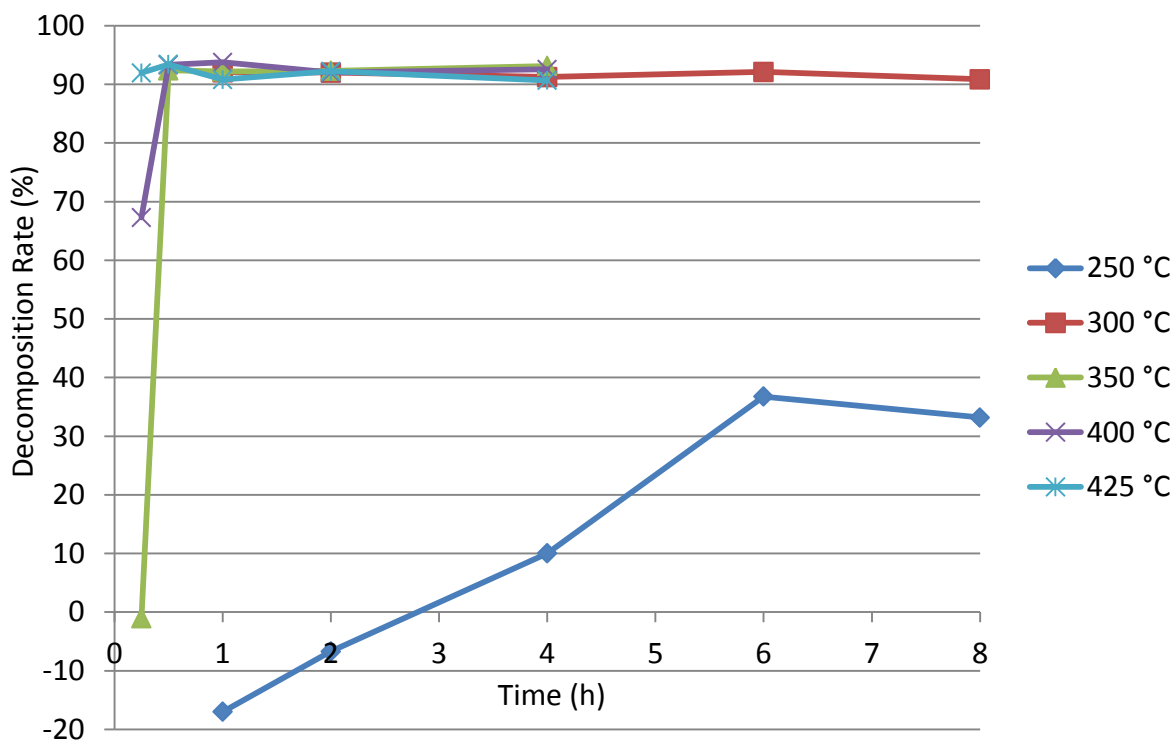
Fig. 6.2.3. Decomposition rate curves of solvothermal decomposition reaction experiments using benzyl alcohol as solvent.

Table 6.2.2. Decomposition rate data of solvothermal decomposition reaction experiments.

Experiment	Temperature (°C)	Time	Decomposition Rate (%)
51	250	1 h	-17.0
52	250	2 h	-6.7
53	250	4 h	10.0
54	250	6 h	36.8
55	250	8 h	33.2
56	300	1 h	92.1
57	300	2 h	92.0
58	300	4 h	91.2
59	300	6 h	92.1
60	300	8 h	90.9
61	350	15 min	-1.1

62	350	30 min	92.4
63	350	1 h	92.2
64	350	2 h	92.3
65	350	4 h	93.1
66	400	15 min	67.3
67	400	30 min	93.3
68	400	1 h	93.7
69	400	2 h	92.0
70	400	4 h	92.5
71	425	15 min	91.9
72	425	30 min	93.4
73	425	1 h	90.8
74	425	2 h	92.2
75	425	4 h	90.7
76	250	1 h	38.1
77	250	2 h	92.9
78	250	4 h	92.7
79	250	6 h	92.4
80	250	8 h	92.2
81	300	1 h	89.9
82	300	2 h	92.5
83	300	4 h	93.3
84	300	6 h	92.8
85	300	8 h	90.3
86	350	15 min	20.5
87	350	30 min	94.3
88	350	1 h	93.3
89	350	2 h	92.2
90	350	4 h	92.3
91	400	15 min	43.5
92	400	30 min	87.1
93	400	1 h	93.7
94	400	2 h	93.1
95	400	4 h	92.7
96	425	15 min	68.2
97	425	30 min	90.0
98	425	1 h	94.8
99	425	2 h	93.3
100	425	4 h	92.0

DR curves of solvothermal experiments with tripotassium phosphate (K_3PO_4) as catalyst are shown in Fig. 6.2.4. DR data of solvothermal decomposition reaction experiments (experiments 76 - 100) is also tabulated in Table 6.2.2. The use of benzyl alcohol as solvent in solvothermal experiments yielded relatively higher DR results even at low temperatures and shorter decomposition reactions. At 250 °C the DR was already 92.9 %, 92.7 %, 92.4 %, 92.2 % after 2, 4, 6, and 8 h, yielding very clean carbon fibers. At 300 °C the DR reached 89.9 %, 92.5 %, 93.3 %, 92.8 %, 90.3 % after 1, 2, 4, 6 and 8 h respectively; it must be noted that after 4 h treatment a slight decrease in DR takes place, this can be explained by the solid residue that is formed after long decomposition reactions which is not easily washed from the recovered carbon fibers surface. This phenomena occurs also in the 350 °C, 400 °C and 425 °C experiments. At 350 °C, relatively high DR results are obtained even with short decomposition reactions, 94.3 %, 93.3 %, 92.2 %, 92.3 % after 30 min, 1, 2, and 4 h. At 400 °C, the DR reached 93.7 %, 93.1 %, and 92.7 % after 1, 2, and 4 h. At 425 °C, the DR reached 90.0 %, 94.8 %, 93.3 % and 92.0 % after 30 min, 1, 2, and 4 h. Apart from very short experiments, i.e. 15 min, most of the solvothermal experiments yielded clean loose carbon fibers.
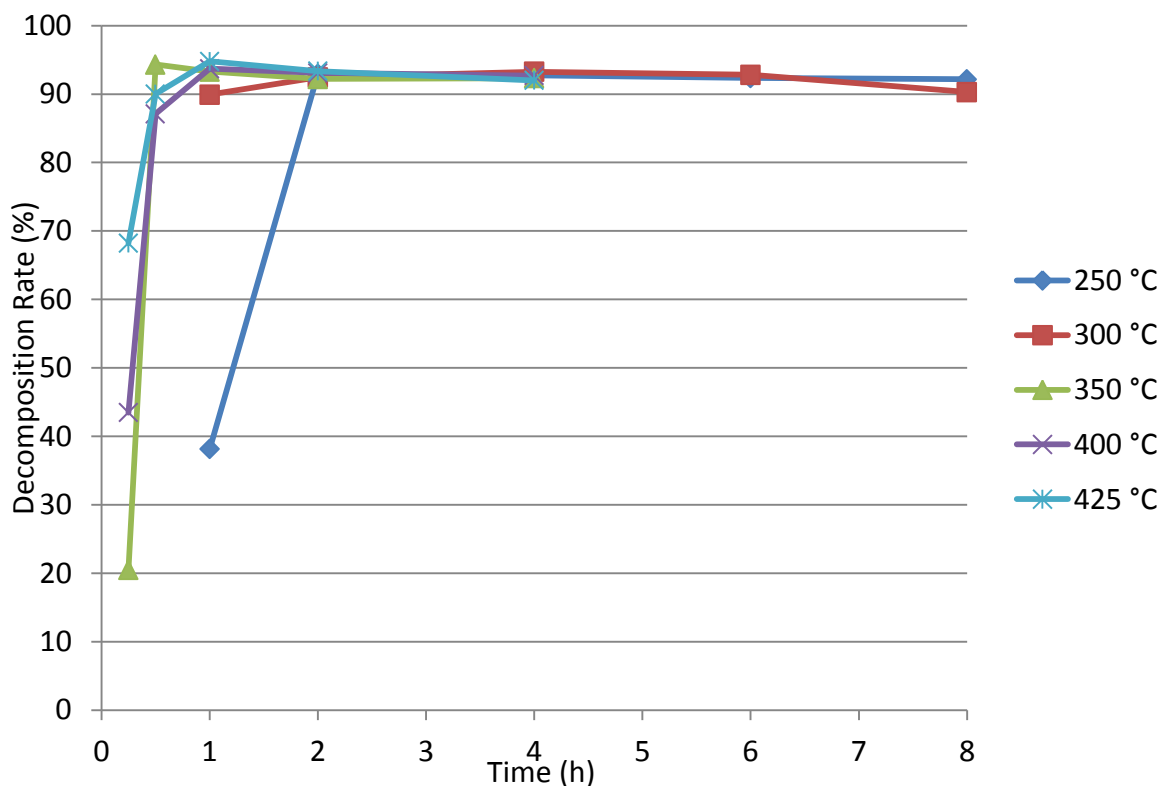
Fig. 6.2.4. Decomposition rate curves of solvothermal decomposition reaction experiments using benzyl alcohol as solvent with tripotassium phosphate (K_3PO_4) as catalyst.

6.3. Scanning Electron Microscopy

SEM micrographs of recovered carbon fibers with supercritical water at 400 °C are shown in Fig. 6.3.1. Fig. 6.3.1.a. shows the recovered sample after 15 min decomposition reaction, which is consistent with a DR of 24%. Cracking of the resin is visible, and solid residue particles are found on the surface of the sample. Based on these results, delamination of the composite samples occurs first, then the resin holding the fibers together in a single layer begins to decompose. Fig. 6.3.1.b. shows clean carbon fibers after 30 min treatment. Fig. 6.3.1.c. shows the recovered carbon fibers after 1 hour. In this

sample some epoxy resin residue is visible on the fiber surfaces. Fig. 6.3.1.d. shows clean recovered carbon fibers after 2 hours. Fig. 6.3.1.e. shows clean recovered carbon fibers after 4 hours. Electron dispersive X-ray spectroscopy (EDS) showed that in supercritical water, the original surface treatment of the carbon fibers (sizing) with sulfur is retained after treatment as presented in Fig. 6.3.1.f.
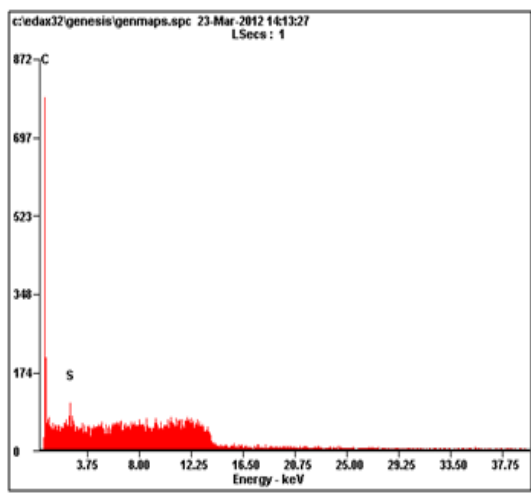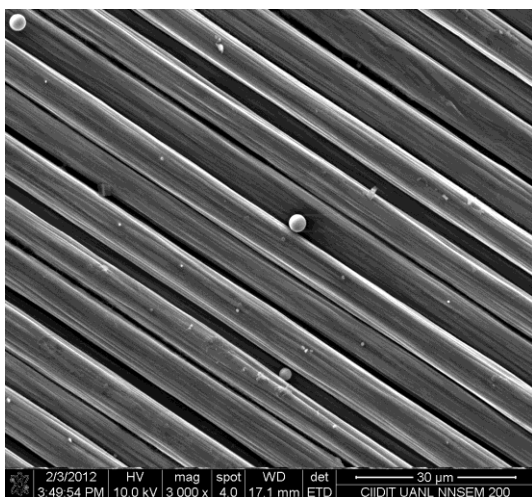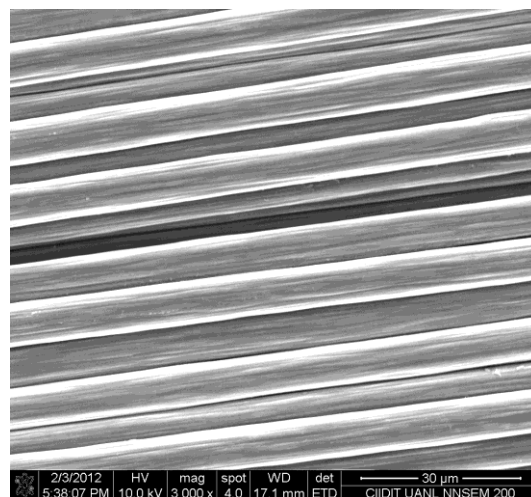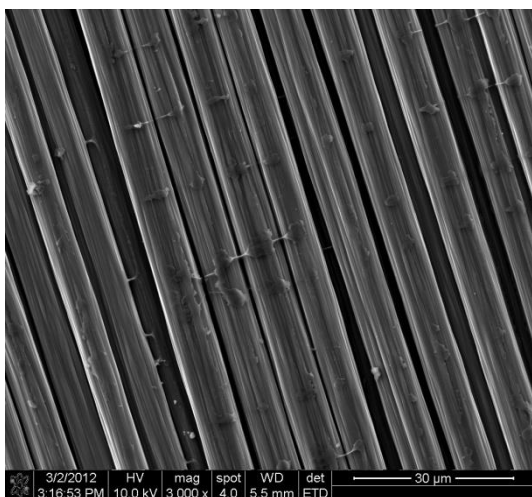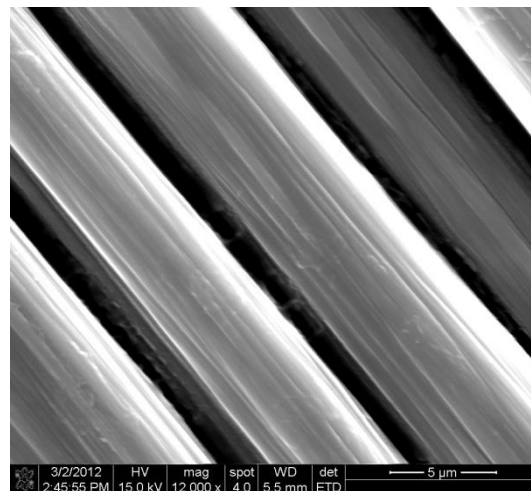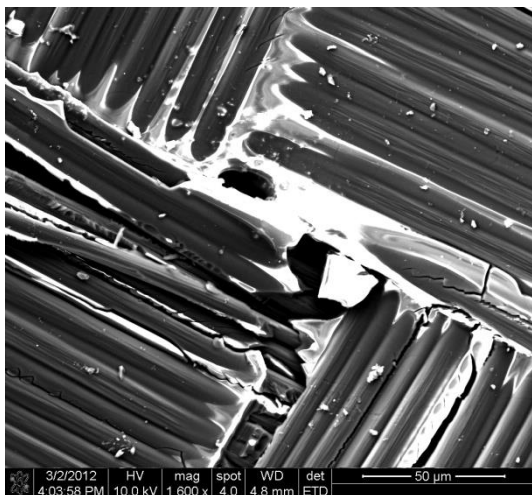
Fig. 6.3.1. SEM micrographs of recovered carbon fibers by supercritical water at 400 °C after: a) 15 min; b) 30 min; c) 1 hour; d) 2 hours; e) 4 hours; f) EDS of recovered carbon fibers with water at 400 °C after 15 min.

SEM micrographs of recovered carbon fibers with supercritical water at 400 °C in presence of K_3PO_4 are shown in Fig. 6.3.2. Fig. 6.3.2.a. shows the composite sample after 15 min of decomposition reaction, which is consistent with a DR of 1.4 % exhibiting the epoxy matrix over the carbon fibers, even that the DR is almost null, the resin shows some degree of surface attack by the supercritical water. Fig. 6.3.2.b. shows the recovered carbon fibers after 30 min decomposition reaction corresponding to a DR of 88.0 %. The resin residues are visible lingering between the carbon fibers, holding still some fiber clusters and in form of micro-residues on the carbon fibers surface. Fig. 6.3.2.c. shows very clean recovered carbon fibers after 1 h treatment, the clean carbon fibers are expected from a DR over 90 %. Fig. 6.3.2.d. shows clean carbon fibers recovered after 2 h decomposition reaction. Fig. 6.3.2.e. shows clean carbon fibers recovered after 4 h treatment. The morphology of the carbon fibers shown in Fig. 6.3.2.c., 6.3.2.d., and 6.3.2.e. is clearly visible showing that no damage occurs to the carbon fibers surface with this treatment. Electron dispersive X-ray spectroscopy (EDS) showed that in supercritical water in the presence of K3PO4, the original surface treatment of the carbon fibers (sizing) with sulfur is removed after treatment as presented in Fig. 6.3.2.f.
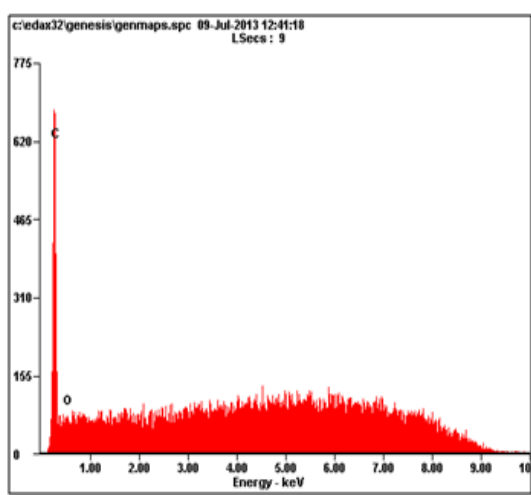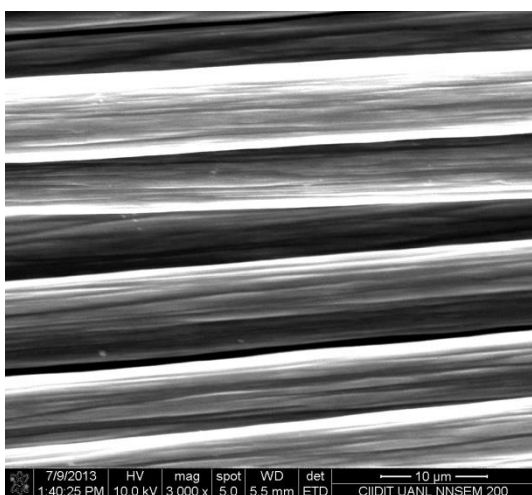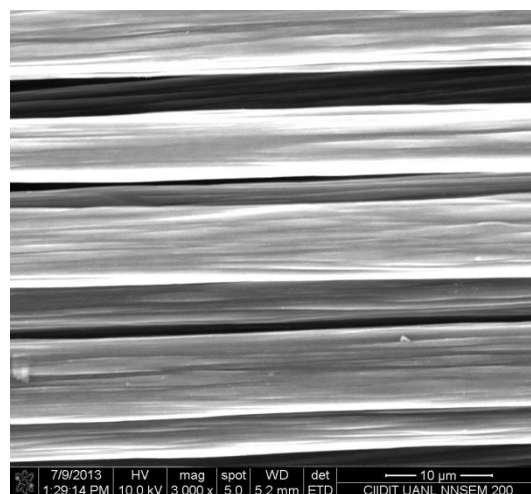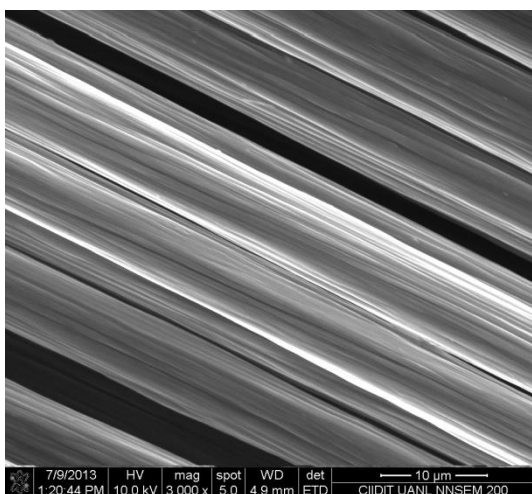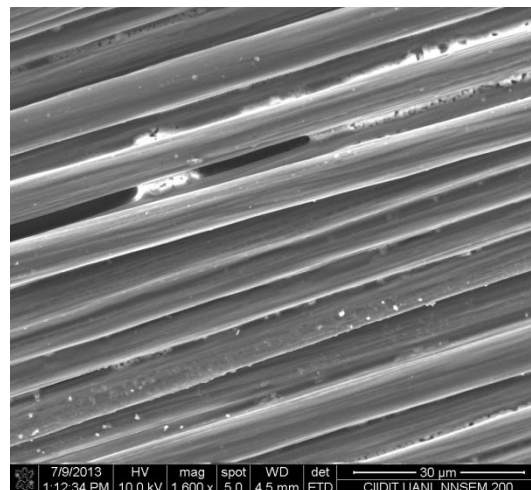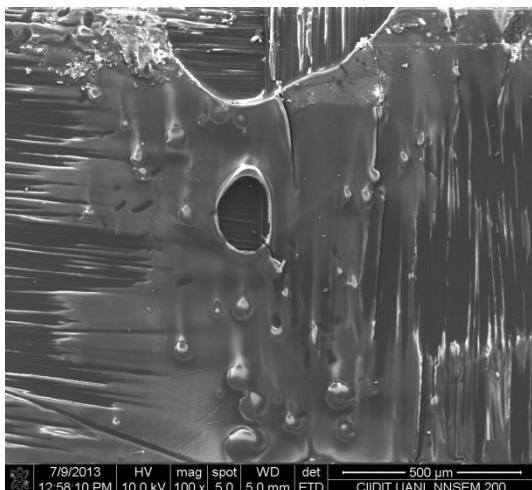
Fig. 6.3.2. SEM of recovered carbon fibers by supercritical water and K_3PO_4 at 400 °C after: a) 15 min; b) 30 min; c) 1 hour; d) 2 hours; e) 4 hours; f) EDS of recovered carbon fibers with water at 400 °C after 4 hours.

Spherical microparticles, 3 - 5 μm in size, were found attached to the recovered carbon fibers surface after 30 min, 1, 2 and 4 hours of decomposition with supercritical water as shown in Fig. 6.3.3. A proposed mechanism of microsphere formation is as follows: epoxy resin is first broken into smaller pieces and microparticles, then the horizontal mechanical stirring leads to turbulence inside the reactor, thus molding the solid residue from the decomposed resin into microspheres. These attached microparticles increase the Mr value, thus decreasing the DR in supercritical water decomposition reaction experiments that are longer than 1 hour. Samples containing these microspheres were washed and rinsed in water, acetone, and tetrahydrofuran, then placed in an ultrasonic bath with the same solvents for 5, 10, 15, and 30 min, and rinsed again. Despite this cleaning procedure, it was observed by SEM that the microspheres remained attached to the carbon fiber surface. Most of the microspheres are attached to small layers of solid resin residue. Fig. 6.3.3.a. shows microspheres of between 2 - 3 μm in size attached to recovered carbon fibers after 30 min. Fig. 6.3.3.b. shows microspheres attached to the solid layer of resin residue after 1 hour. The pattern of these layers of resin residue is due to the waved carbon fabric. In this particular experiment, some of the inner layers of resin were not dissolved by the hydrothermal process. It seems that the microspheres have an affinity for these layers of resin residue. Fig. 6.3.3.c. shows the sample after decomposition reaction of 1 hour. Fig. 6.3.3.d. shows microspheres attached to a solid layer of resin and recovered carbon fibers after 2 hours, with microspheres ranging between 2 - 3 μm. Fig. 6.3.3.e. shows microspheres attached to carbon fibers and a solid layer of resin residue after 4

hours, with relatively smaller microspheres, 1 - 2 µm. Fig. 6.3.3.f. shows the recovered

sample after 4 hours. These smaller microspheres are attached to lose carbon fibers.

Microspheres were found in all samples, in all layers, treated with supercritical water,

except for the sample treated for 15 min.
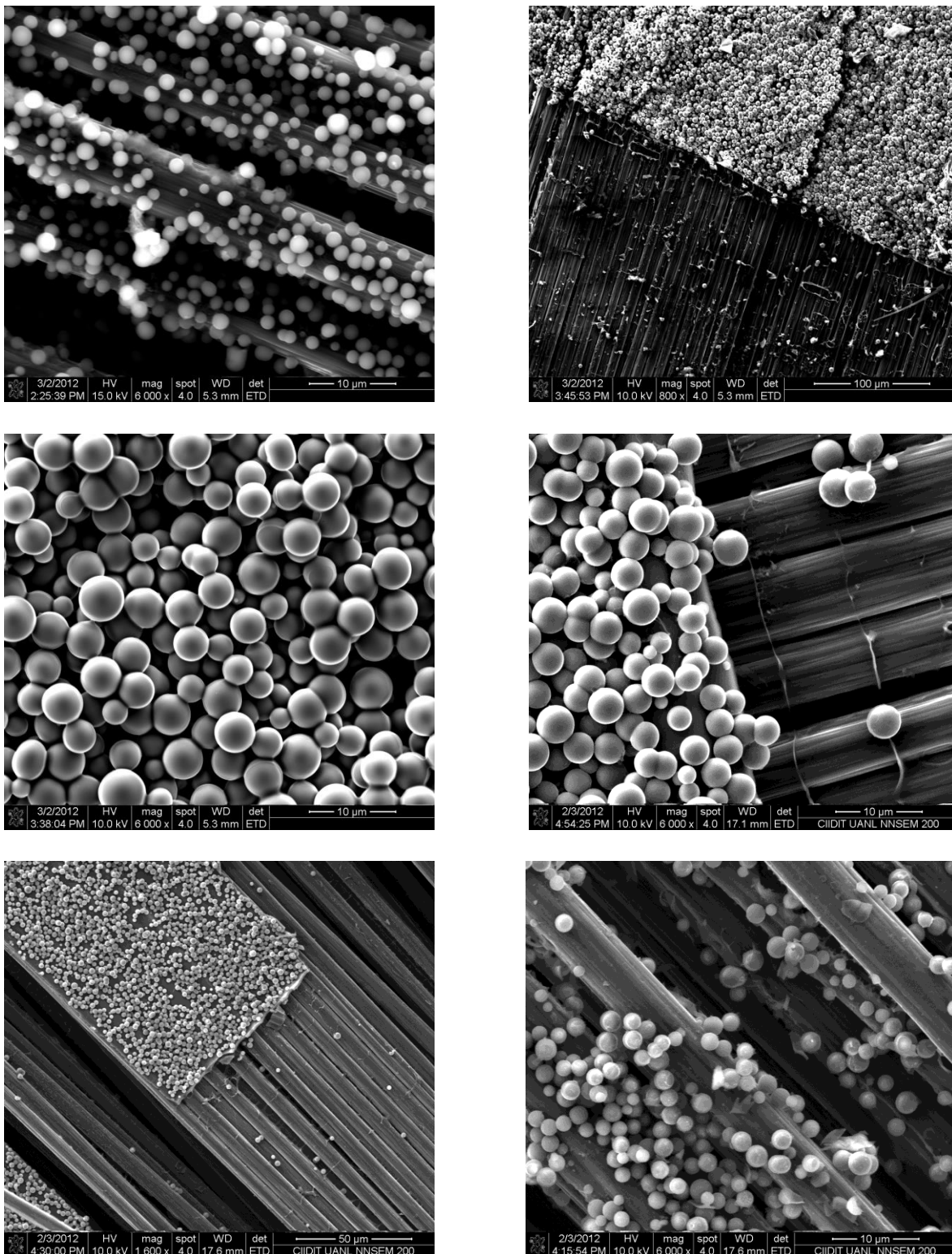
Fig. 6.3.3. SEM micrographs of microspheres on the surface of recovered carbon fibers by supercritical water

at 400 °C after: a) 30 min; b) 1 hour; c) 1 hour; d) 2 hours; e) 4 hours; f) 4 hours.

SEM micrographs of recovered carbon fibers by subcritical benzyl alcohol at 425 °C are shown in Fig. 6.3.4. Fig. 6.3.4.a., 6.3.4.b., 6.3.4.c., 6.3.4.d., 6.3.4.e. show clean carbon fibers recovered by this method at 15 min, 30 min, 1, 2, and 4 hours respectively; loose carbon fibers were found even at very short decomposition reactions, and practically no solid residue was found on the samples by SEM analysis of these recovered fibers. EDS of recovered carbon fibers after 15 min in decomposition reaction with subcritical benzyl alcohol at 425 °C is shown in Fig, 6.3.4.f. no peak for sulfur was detected in EDS; the sizing in carbon fibers seems to be also removed by subcritical benzyl alcohol.
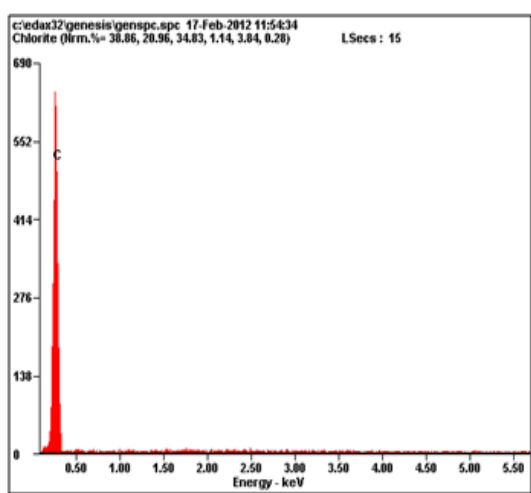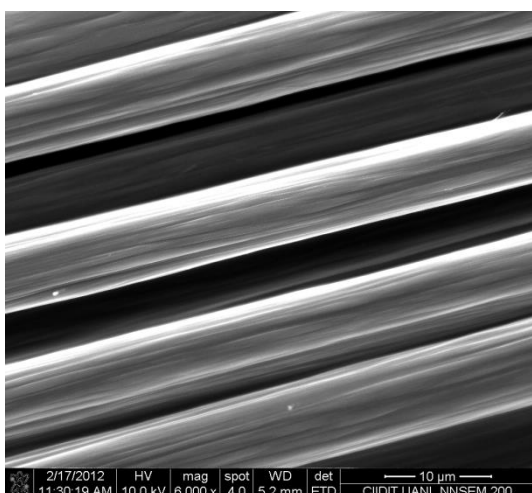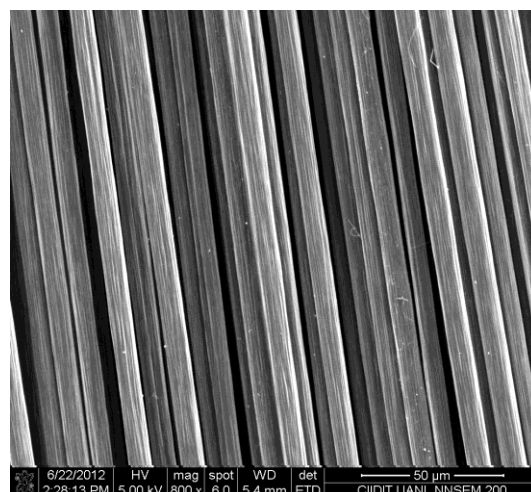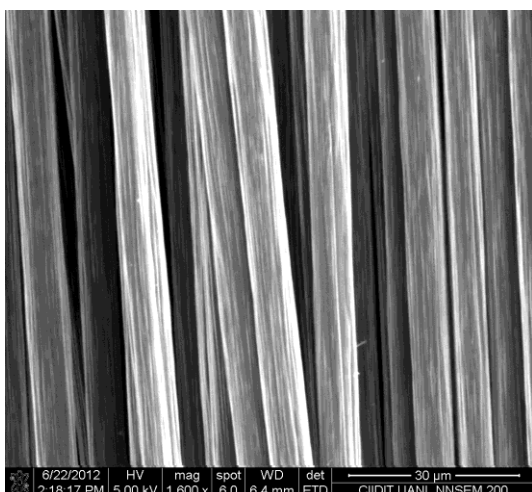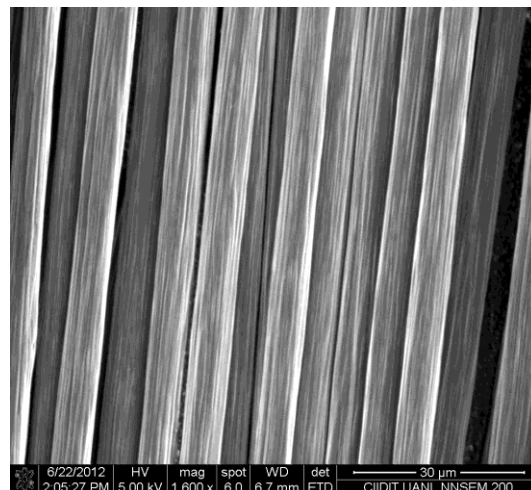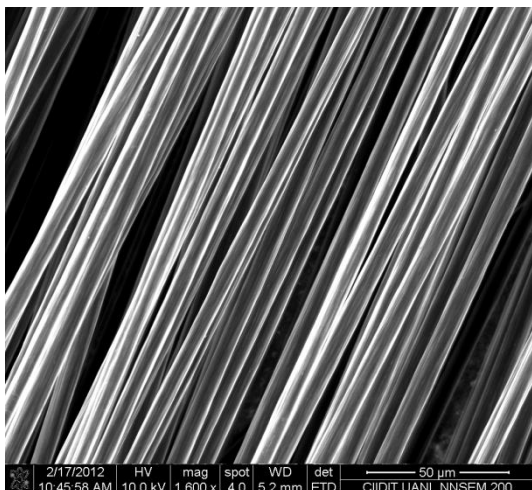
Fig. 6.3.4. SEM of recovered carbon fibers by subcritical benzyl alcohol at 425 °C after: a) 15 min; b) 30 min; c) 1 hour; d) 2 hours; e) 4 hours; f) EDS of carbon fibers recovered with benzyl alcohol at 425 °C after 15 min.

SEM micrographs of recovered carbon fibers by subcritical benzyl alcohol at 425 °C in presence of K_3PO_4 are shown in Fig. 6.3.5. Fig. 6.3.5.a. shows the recovered carbon fibers after 15 min decomposition reaction by this method. This composite sample reached a DR of 68.2 % which is consistent with what is visible in the figure, resin residue is still attached to the carbon fibers holding them still together. Fig. 6.3.5.b., 6.3.5.c. and 6.3.5.d. show the recovered carbon fibers after 30 min, 1, and 2 h of decomposition reaction. In those carbon fibers samples, a little solid residue is visible. The amount of solid residue is clearly increasing with the time duration of the reactions. Fig. 6.3.5.e. shows the recovered carbon fibers after 4 h treatment, with solid residue attached to the carbon fibers surface; given the DR of 92.0 % for this experiment, we can only infer that, a higher decomposition of the epoxy matrix actually occurred, but, only after the extended period of treatment, the epoxy residue has reattached to the carbon fibers; this residue was not washed away during the rinsing process. EDS analysis showed that in subcritical benzyl alcohol in the presence of K_3PO_4, the original sizing is removed after treatment as presented in Fig. 6.3.5.f.
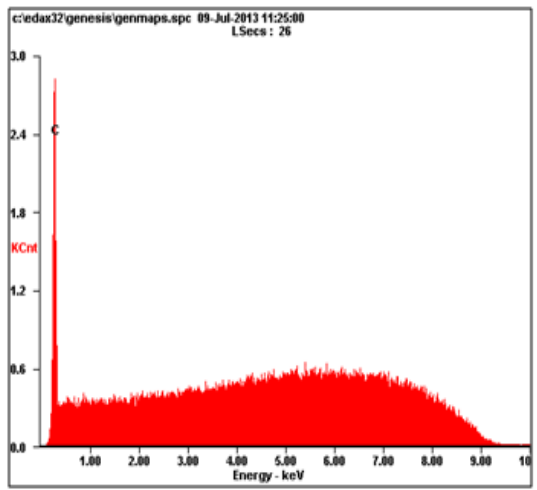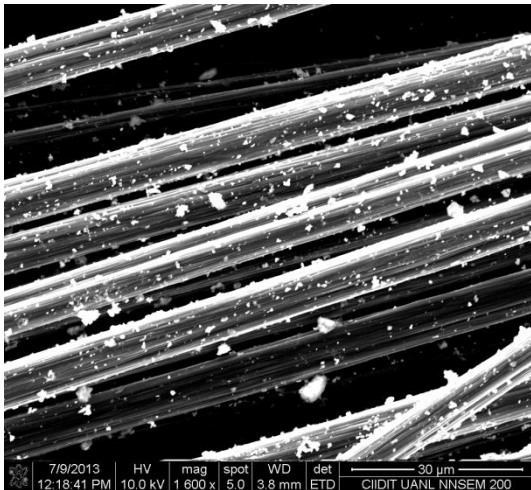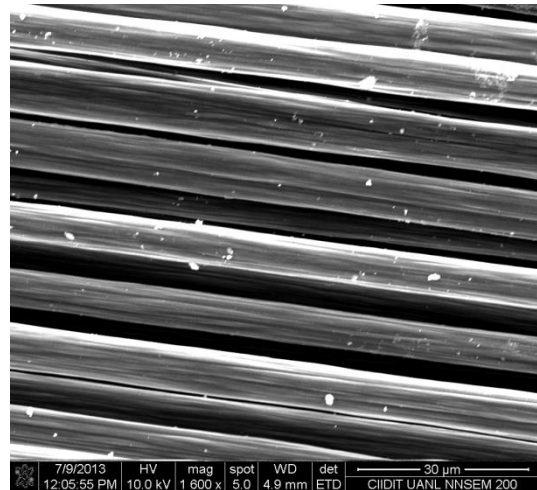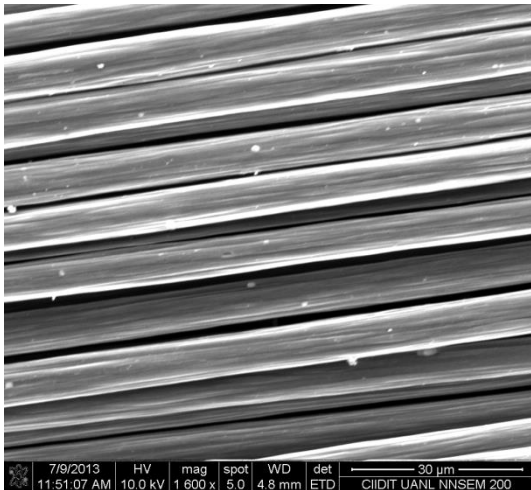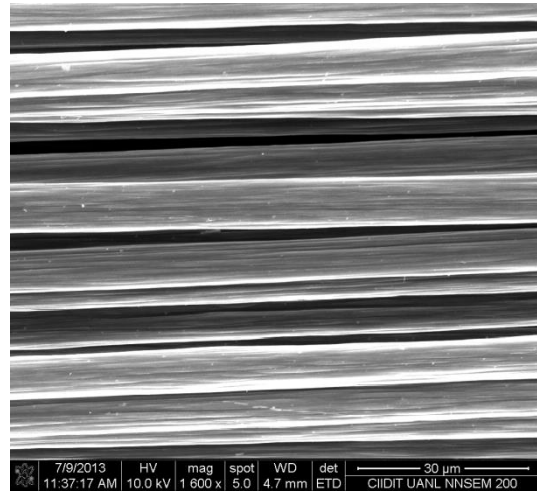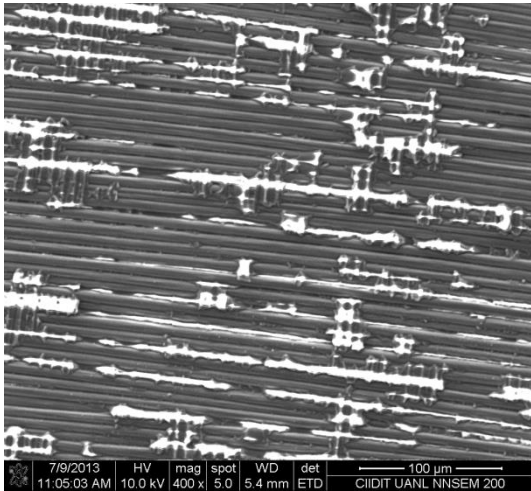
Fig. 6.3.5. SEM of recovered carbon fibers by benzyl alcohol and K_3PO_4 at 425 °C after: a) 15 min; b) 30 min;

c) 1 hour; d) 2 hours; e) 4 hours; f) EDS of carbon fibers recovered by benzyl alcohol at 425 °C after 4 hours.

6.4. Discussion on Gaseous and Liquid Phase Residue

The liquid residue of hydrothermal experiments had always a water-like viscosity; the supercritical water experiments liquid residue had a very pungent hydrogen sulfide odor, which it is expected from the removal of the sulphur sizing from the carbon fibers in a gaseous form released only after opening the batch reactor; the sizing removal was corroborated as explained above by the EDS analysis. Solvothermal experiments presented a viscous blackened liquid residue in every experiment, except in experiments at 425 °C in which, a two phased liquid residue composed of water and the same viscous blackened residue was recovered; a strong hydrogen sulfide odor was also detected in experiments with benzyl alcohol at 425 °C after opening the batch reactor; the removal of the sulphur sizing from the carbon fibers in a gaseous hydrogen sulfide form was also confirmed by the EDS analysis by SEM in these experiments. It is expected that the reaction mechanism for decomposition of epoxy resin differs according to the solvent used. Indeed, the differences are clear in the SEM characterization, since DR was higher using subcritical benzyl alcohol compared with supercritical water. Moreover, carbon fibers recovered by subcritical benzyl alcohol were cleaner and had less solid residue attached to the carbon fiber surfaces compared to samples recovered by supercritical water. Several mechanisms have been described for epoxy resin decomposition in supercritical alcohols and water. It can be considered that the reaction in our experiments is somehow similar to a process of diffusion-decomposition of polymers by scission of C-O-

C and C-N-C bonds, and mass transfer of monomers and compounds. It must be noted that the diffusion of subcritical benzyl alcohol into the matrix is a possible explanation for the negative values obtained by solvothermal decomposition reactions. The mechanism under supercritical water, on the other hand, is different. Water breaks the epoxy matrix first into smaller pieces, followed by dissolution and decomposition, resulting in the presence of resins and solid residues found on the surface of recovered carbon fibers.

References used in Chapter 6: [24, 25, 26]

7. Conclusions

Water and benzyl alcohol under subcritical and supercritical conditions are good solvents for chemical recycling of thermoset composite materials, resulting in very clean carbon fibers after treatment. Benzyl alcohol showed higher DR results, over 90%. Water resulted in a DR of just over 80%. Higher DRs compared to published data could be obtained using this method, e.g., 89.1% after 1 hour treatment with supercritical water. Moreover, a DR of 93.7% after 1 hour of treatment at 400 °C with subcritical benzyl alcohol has been achieved, which is better than results published from experiments conducted in semi-continuous flow systems using organic solvents in the presence of catalysts. Recovery of clean carbon fibers by subcritical benzyl alcohol has been corroborated by SEM analysis. After SEM characterization we can infer that very clean carbon fibers are recovered in supercritical water experiments as well. While these

experiments in fact achieved a higher decomposition, microspheres attached to the carbon fibers surface increased the Mr, thus decreasing the DR result. Solid residue and microspheres were found in all samples treated with supercritical water. EDS analysis show that supercritical water also removes the sizing from the carbon fibers as hydrogen sulfide gas after opening the batch reactor. Water was found in the liquid residue of the benzyl alcohol experiments at 425 °C as a subproduct of the decomposition reaction; water in those experiments create a more complex decomposition, as water at that temperature can increase the pressure above of critical pressure of benzyl alcohol. A hydrogen sulfide odor was also detected in benzyl alcohol experiments at 425 °C due to water generated as a subproduct of the decomposition and the removal of the sulphur sizing from the carbon fibers confirmed by EDS analysis.

Water and benzyl alcohol under subcritical and supercritical conditions with the addition of K_3PO_4 as catalyst, are good solvents for chemical recycling of thermoset composite materials, resulting in very clean carbon fibers after treatment. Benzyl alcohol showed higher DR results constantly over 90.0 % in most experiments, even at low temperatures, while water resulted in DR over 90.0 % only on experiments of temperature of 350 °C and higher temperatures. However, higher DRs compared to published data could be obtained using this method, e.g., 94.6 % after 2 h treatment subcritical water. Moreover, a DR of 94.8 % after 1 hour of treatment at 425 °C with subcritical benzyl alcohol has been achieved, which is also higher than results published from experiments conducted in semi-continuous flow systems using organic solvents in the presence of

catalysts. Recovery of clean carbon fibers by subcritical and supercritical water and benzyl alcohol with addition of K3PO4 as catalyst has been corroborated by SEM analysis. Optimal treatments are reached between 1 and 2 h since the DR has reached the highest value attainable for this method and longer treatments will generate solid residue attached to the carbon fibers surface. EDS analysis show that these methods remove the sizing from the carbon fibers as hydrogen sulfide gas after opening the batch reactor. Water was also found in the liquid residue of the benzyl alcohol and K_3PO_4 experiments at 425 °C as a subproduct of the decomposition reaction. A hydrogen sulfide odor was also detected in benzyl alcohol experiments at 425 °C due to water generated as a subproduct of the decomposition and the removal of the sulphur sizing from the carbon fibers confirmed by EDS analysis.

Hydrothermal and solvothermal processes are feasible for industrial scale given that these methods need to be adjusted for industrial purposes of carbon fiber recovery. Benzyl alcohol decomposition reactions could be safer for possible implementation in industry due to the relatively low critical pressure in the reactor compared with supercritical water. However, these methods have to be adjusted for industrial purposes of carbon fiber recovery, in accordance with other factors such as cost, type of reactors, environmental issues, and properties of recovered fibers. The outlook of these processes seems positive for industrialization from the standpoint of having an increasing lot of waste material confined in disposal with an interesting high intrinsical value and a recycling technology advancing for newer and better results recovering carbon fibers. The

focus of this paper was the Decomposition Rate of composite materials under hydrothermal and solvothermal decomposition reactions and the SEM characterization of residue on recovered carbon fibers; it is acknowledgeable the importance of the possibility of reusing the recovered carbon fibers and the mechanical properties of the fibers, specifically the tensile strength, which will be studied furthermore in the near future in following studies.

8. References

[1] M. Goto, Chemical recycling of plastics using sub- and supercritical fluids, J. of Supercritical Fluids 47 (2009) 500–507.

[2] S.J. Pickering, Recycling technologies for thermoset composite materials—current status, Composites: Part A 37 (2006) 1206–1215.

[3] Tomoko Iwaya, Shinpei Tokuno, Mitsuru Sasaki, Motonobu Goto, Katsuji Shibata, Recycling of fiber reinforced plastics using depolymerization by solvothermal reaction with catalyst, J Mater Sci 43 (2008) 2452–2456.

[4] R. Piñero-Hernanz, C. Dodds, J. Hyde, J. García-Serna, M. Poliakoff, E. Lester, M.J. Cocero, S. Kingman, S. Pickering, K. Hoong Wong, Chemical recycling of carbon fibre reinforced composites in nearcritical and supercritical water, Composites: Part A 39 (2008) 454–461.

[5] Raúl Piñero-Hernanz, Juan García-Serna, Christopher Dodds, Jason Hyde, Martyn Poliakoff, María José Cocero, Sam Kingman, Stephen Pickering, Edward Lester, Chemical

recycling of carbon fibre composites using alcohols under subcritical and supercritical conditions, J. of Supercritical Fluids 46 (2008) 83–92.

[6] J.R. Hyde, E. Lester, S. Kingman, S. Pickering, K. Hoong Wong, Supercritical propanol, a possible route to composite carbon fibre recovery: A viability study, Composites: Part A 37 (2006) 2171–2175.

[7] G. Jiang, S.J. Pickering, E.H. Lester, T.A. Turner, K.H. Wonga, N.A. Warrior, Characterisation of carbon fibres recycled from carbon fibre/epoxy resin composites using supercritical n-propanol, Composites Science and Technology 69 (2009) 192–198.

[8] L. Yuyan, S. Guohua, M. Linghui, Recycling of carbon fibre reinforced composites using water in subcritical conditions, Materials Science and Engineering A 520 (2009) 179–183.

[9] Y. Bai, Z. Wang, L. Feng, Chemical recycling of carbon fibers reinforced epoxy resin composites in oxygen in supercritical water, Materials and Design 31 (2010) 999–1002.

[10] S.J. Pickering, R.M. Kelly, J.R. Kennerley, C.D. Rudd, N.J. Fenwick, A Fluidised-bed process for the recovery of glass fibres from scrap thermoset composites, Composites Science and Technology 60 (2000) 509-523.

[11] The European Parliament and the Council of the European Union: End of Life Vehicles (ELV) Directive; 2000/53/EC, September 2000.

[12] Mitsutoshi Nakagawa, Hiroyuki Kuriya, Katsuji Shibata, Characterization of CFRP using recovered carbon fibers from waste CFRP, The 5th ISFR (October 11-14, 2009, Chengdu, China) 241–244.

[13] D. Ambrose, N.B. Ghiassee, Vapour pressures, critical temperatures, and critical pressures of benzyl alcohol, octan-2-ol, and 2-ethylhexan-1-ol, J. Chem. Thermodynamics 22 (1990) 307–311.

[14] ASM International, ASM Handbook Volume 21 Composites, ASM International, 2001.

[15] Sanjay K. Mazumdar, Composites Manufacturing: Materials, Product and Process Engineering, CRC PRESS, 2002.

[16] F.C. Campbell, Manufacturing Technology for Aerospace Structural Materials, Elsevier, 2006.

[17] Vanessa Goodship, Management, recycling and reuse of waste composites, Woodhead Publishing Limited, 2010.

[18] Blazsó M, Composition of liquid fuels derived from the pyrolysis of plastics, Scheirs J Feedstock Recycling and Pyrolysis of Waste Plastics, (2006) 315–344.

[19] G. Jiang G, S. J. Pickering, G. S. Walker, N. Bowering, K. H. Wong, C. D. Rudd, Soft ionisation analysis of evolved gas for oxidative decomposition of an epoxy resin/carbon fibre composite, Thermochim Acta 454 (2007) 109–115.

[20] E. Lester, S. Kingman, K. H. Wong, C. Rudd, S. J. Pickering, N. Hilal, Microwave heating as a means for carbon fibre recovery from polymer composites: a technical feasibility study, Materials Research Bulletin 39 (2004) 1549–1556.

[21] W. Dang, M. Kubouchi, S. Yamamoto, H. Sembokuya, K. Tsuda, An approach to chemical recycling of epoxy resin cured with amine using nitric acid, Polymer 43 (2002) 2953-2958.

[22] W. Dang, M. Kubouchi, S. Yamamoto, H. Sembokuya, K. Tsuda, Chemical recycling of glass fiber reinforced epoxy resin cured with amine using nitric acid, Polymer 46 (2005) 1905–1912.

[23] A. Bernasconi, D. Rossin, C. Armanni, Analysis of the effect of mechanical recycling upon tensile strength of a short glass fibre reinforced polyamide 6,6, Engineering Fracture Mechanics 74 (2007).

[24] R. Morales Ibarra, M. Sasaki, M. Goto, A. T. Quitain, S. M. García Montes, J. A. Aguilar-Garib, Carbon fiber recovery using water and benzyl alcohol in subcritical and supercritical conditions for chemical recycling of thermoset composite materials, Journal of Materials Cycles and Waste Management (2014 Online), DOI 10.1007_s10163-014-0252-z.

[25] R. Morales Ibarra, M. Sasaki, M. Goto, A. T. Quitain, S. M. García Montes, J. A. Aguilar-Garib, Antonio F. García Loera, Chemical Recycling of Thermoset Composite Materials using Water and Benzyl Alcohol in Subcritical and Supercritical Conditions with Addition of Catalyst, Journal of Materials Cycles and Waste Management (Manuscript Submitted, Jun 2014), JMCW-S-14-00327.

[26] Rodolfo Morales Ibarra, Mitsuru Sasaki, Motonobu Goto, Armando T. Quitain, Saida Mayela García Montes, Recuperación de Fibras de Carbono de Materiales Compuestos Termofijos con Agua y Alcohol Bencílico en Estados Subcríticos y Supercríticos, Ingenierías FIME-UANL (2013) 60 (2013) 41-52.

List of Figures

List of Tables