JOINING COMPOSITES with ADHESIVES
Theory and Applications

Edited by
Prof. dr. ir. Magd Abdel Wahab
Professor of Applied Mechanics, Ghent University

DEStech Publications, Inc.
Joining Composites with Adhesives

DEStech Publications, Inc.
439 North Duke Street
Lancaster, Pennsylvania 17602 U.S.A.

Copyright © 2016 by DEStech Publications, Inc.
All rights reserved

No part of this publication may be reproduced, stored in a
retention system, or transmitted, in any form or by any means,
electronic, mechanical, photocopying, recording, or otherwise,
without the prior written permission of the publisher.

Printed in the United States of America
10 9 8 7 6 5 4 3 2 1

Main entry under title:
Joining Composites with Adhesives: Theory and Applications

A DEStech Publications book
Bibliography: p.
Includes index p. 315

Library of Congress Control Number: 2013914647
ISBN No. 978-1-60595-093-8
There is no doubt that nowadays composite material becomes one of the most important structural materials in many industrial applications. In any application where the strength-to-weight ratio plays an important role, composite materials are the best candidate and offer the most efficient solution. Therefore, they are very popular in aerospace industry, race cars, and marine technology. Moreover, they have been used in repairing and manufacturing structural elements of heavy structures such as bridges and buildings. Joining composites components to each other or to other surrounding components such as metal, wood, and plastic is a vital step in the manufacturing of composite structures. Adhesive bonding is one of the powerful joining techniques for composite materials because of its high fatigue resistance and high strength-to-weight ratio. The design of an adhesive joint is much more complicated than the design of a composite laminate, due to the complex geometry of an adhesively bonded joint, which includes different materials having different properties, and the stress singularity at the joint’s edges. Moreover, the quality of bonding is an important issue, requiring significant efforts to produce high-quality bonding. The purpose of this book is to provide an up-to-date account of how composite materials are joined using adhesives.

This volume contains 14 chapters by internationally recognized scientists in the field of adhesive bonding used for joining composite materials. After an introductory chapter covering the history of adhesive composite joints, the book contains two parts: Part I examines theoretical aspects and Part II applications. Part I consists of seven
chapters and covers the topics of material properties and general aspects related to the strength of adhesive composite joints. Furthermore, Part I focuses on the theoretical aspects of joining composite to composite and other types of materials, including metal, concrete, and timber. Part I concludes with a chapter on composite repair. Part II concentrates on industrial applications of adhesive bonding to composite materials. Its six chapters cover the applications to aerospace, automotive, public transport services, civil engineering, marine technology, and dentistry.

MAGD ABDEL WAHAB

Editor
1.1. INTRODUCTION

The use of lightweight, high-strength composite structures for applications in industries such as aeronautics, aerospace, electronics, automotive, construction, sports, and packaging has recently increased. Consequently, the application of adhesive bonding to composite joints has grown significantly in recent decades.

Adhesives are used for bonding a wide range of similar and dissimilar metallic as well as non-metallic materials, composite materials and components with different shapes, sizes and thicknesses. The advantages of adhesive bonding over traditional joining techniques (mechanical fastening) are now well accepted. In particular, adhesives provide greater design flexibility, distribute load over a much wider area, reduce stress concentrations, and increase fatigue as well as corrosion resistance of bonded joints. In addition, they provide weight savings to the whole structure, improving the appearance of the bond while joining different materials. High-performance structural adhesives have thus become common in the aerospace, automotive, marine, medical science, and construction sectors. Advanced structural adhesives are not only being applied as a joining method but also in manufacturing of composite materials such as Glare, a specific type of fiber-metal laminate made from aluminium and fiberglass composite. Glare is now
poised to be only the third new material used in aircraft primary structures. Although adhesive composite joints have several advantages, understanding and quantifying the long-term durability of adhesively bonded composite joints under service conditions is a key area of interest and receiving reasonably good research attention.

Most of the early work on adhesive joining of composites was done in the 1970s and early 1980s for the aerospace industry. There have been many analytical, finite element analysis, and experimental studies performed over the years. Matthews et al. (1982) and, more recently, Baneal and da Silva (2009) presented a comprehensive review on the strength of adhesive joints in composite structures. This chapter focuses on published works concerned with the historical development of adhesive composite joints. We explore the literature dealing with adhesives and composites in ancient times and their continuous development in modern times. We conclude with a brief section highlighting some of the limitations that hindered the widespread of this technology.

In its broadest sense, an adhesive is a substance that joins or bonds the surfaces of items together and resists their separation. According to this categorization, mortar and solder also come under the banner of adhesives. Conversely, although they show some phenomena of adhesion, substances like paint and printing inks are not considered as adhesives.

The process of joining two or more structures using adhesive is commonly known as adhesive bonding. The parts being joined are called adherends or substrates, depending on the context. Substrate, for example, refers to the material before bonding and adherend after bonding. In this chapter, we will use adherend throughout.

Structural adhesives are of primary interest in the field of engineering because they form strong permanent joints between adherends. The bonding undergoes physical and chemical hardening reaction causing parts to be joined together through internal strength (cohesion) and surface adherence (adhesion).

Composite materials have some unique advantages over monolithic materials. The advantage of composites is that a range of technical characteristics are possible because so many different matrix and reinforcement materials can be selected. This characteristic of composites provides high strength, long fatigue life, high stiffness, low thermal expansion, low density, and low weight. The basis for the superior structural performance of composite materials is in the high specific strength, high specific stiffness, and in the anisotropic and heterogeneous property of the material. Furthermore, within a particular choice
of matrix and reinforcement, the orientation of the reinforcements, manufacturing method, processing conditions, and combinations made with other materials all give additional variety in the mechanical properties (Strong, 2008).

The following sections present a brief history of adhesive bonding technology. Then we briefly review the history of composite materials, followed by a discussion of types of adhesives used to join composite structures. We look at typical configurations of adhesive joints and their modes of failure, and then we summarize the limitations of adhesive composite joints.

1.2. A BRIEF HISTORY OF ADHESIVE BONDING

Adhesive bonding has a long history, but determining a date for its first use is nearly impossible. It has even been difficult to trace the origin of the names of adhesives. It is clear that adhesives in their present forms arrived after a long, gradual process starting from naturally “sticky” products used in many civilizations, including the Egyptians, Greeks, Romans, and by medieval artists, all of whom contributed their own advances and developments (Fay, 2005). It would, however, be worth noting that by around 1700, adhesives were produced on a very small scale. By then, glue was being manufactured for individual and industrial uses. The first mention of glue in patent literature comes from a 1754 British patent for “a kind of glue called fish glue” (British patent (1754) number 691). Later the need for the standard of the glue was pointed out, as in the beginning the experience of the glue maker was sufficient. To overcome this technical deficiency, two important steps were taken: first, by documenting and publishing the available knowledge of glue manufacturing; and secondly, by implementing quality control on raw materials and manufacturing processes. Through the implementation of these steps, comprehensive testing of the adhesive products became standard practice (Fay, 2005).

Peter Cooper (Mack, 1949) classified jelly strength and grouped the variety of glues into relatively few classes or grades. The gradual development of the methodologies laid down the foundations for test methods such as viscosity assessments, and strength and durability of the adhesive joints, still in use today.

In 1665, Hooke said, “I have often thought that probably there might be a way found out, to make an artificial glutinous composition,” leading researchers to think about artificial polymers. In 1862, Alexander
Parkes earned the credit to prepare first man-made glutinous composition: celluloid (Kaufman, 1963).

It is a fact that most adhesives used for structural applications were still of natural origin until the 1920s. Judge (1921) listed the adhesives available at that time for aircraft and automobile manufacture as animal glues (hide, bone, or hoof), fish glues, liquid glues (animal glues in liquid, ready-to-use state), marine glues (made from Indian rubber, naphtha, and shellac), casein glues, waterproof glues (modified “ordinary” glue), vegetable glues, flexible glues (modified animal glue), and albumen glues (Fay, 2005). Over the next twenty years, they were rapidly replaced by modern adhesives based on synthetic polymers. Probably the single-most important landmark in the history of structural adhesives is the emergence of epoxy (or epoxide as sometimes called) resins in late 1930s. Epoxy adhesives gained rapid success in aerospace, automotive, construction, electronic, and woodworking applications, largely because of their ease of use, versatility, and mechanical properties. Typically they possessed high shear strengths but relatively low toughness and peel strength. Attempts were made to improve these properties. Various different approaches were tried, using additives and developing epoxy hybrids, but the major breakthrough came in the early 1970s with the introduction of butadiene-based rubber modifiers from Goodrich. These advances transformed the performance of epoxy and acrylic adhesives, adding peel, and impact and fatigue resistance without compressing the existing performance characteristics. Since then, the use of adhesives in ever-increasing technical applications has led many engineers and scientists to develop new and improved materials and identify the need for studies for more fundamental aspects of the underlying sciences. This variety of synthetics polymers and products has enabled adhesive specialists to develop specific combinations to meet the production, manufacturing, and performance requirements of diverse applications for industrial and domestic usage (Fay, 2005).

The structural adhesives industry is considered mature and sophisticated. At present, the analytical tools, surface analysis methods, stress analysis, fracture mechanics, and inspection techniques necessary to exploit the potential of structural adhesives have been developed (Ali, 2011).

1.3. A BRIEF HISTORY OF COMPOSITE MATERIALS

The underlying concept of composite materials goes back to antiq-
uity. Human development and civilization are closely related to the use of different materials. In the Stone Age, humans relied primarily on stones (ceramics) for tools and weapons and on wood (natural polymers and composites). Early in history, it was found that combinations of materials could produce properties superior to those of the individual components. Mongols made composite bows by using glue made from animal hoofs and bones to bond together five pieces of wood to form the core of a bow—center grip, two arms, and two tips. Cattle tendons were bonded on the tension side and strips of cattle horns on the compression side. There are biblical references to the Egyptians using straw-reinforced clay bricks in ancient times (Exodus 5:7). Homer’s Iliad (verses 468–480) has described Achilles’ shield, which is a good example of composite design laminate in old ages. The usage of metals started with gold and proceeded with iron, copper, and bronze. Steel and aluminum became dominant starting in the last century and are still gaining attention. Presently composites, polymers, and ceramics are regaining their relative importance. Humans have used the natural forms of these materials, though recent developments emphasize man-made materials (Astrom, 1992; Isaac and Ori, 2006).

Although composites have a long history, the technology was essentially developed and improved in the last century. This development accompanied a proliferation of literature in the form of technical reports, journals, books, and conference proceedings. The history of modern engineering composites probably began in 1937 when salesmen from the Owens Corning company began to sell fiberglass and realized that it can be a good source of reinforcement. Fiberglass had been made in 1930 when an engineer became intrigued by a fiber formed during the process of applying lettering to a glass milk bottle. Although the initial product made of this finely drawn molten glass was insulation, structural products soon followed. Fiberglass companies realized that the aircraft industry was a likely customer for this new type of material, as many of the tools in the industry for forming and holding aircraft sections and assemblies needed to be strong, thin, and highly shaped, often with compound curves. Metal did not easily meet these criteria, therefore fiberglass-reinforced production tooling became the preferred material for many engineering applications (Strong, 2008).

The modern era of composites, starting with World War II, can be grouped into four main categories:

- 1940s: Glass fiber reinforced composites
• 1960s: High-performance composites
• 1970–1980s: New markets and the synergies of properties
• 1990s–to present: Hybrid materials, nanocomposites, biomimetic strategies

The fast pace of composites development accelerated in 1940s. Some of the underlying reasons and motivations may have been significant progress in materials science and technology in the area of fibers, polymers, and ceramics, and the continuous demand for high-performance materials in aircraft and aerospace structures. The development of powerful and sophisticated numerical methods for structural analysis using modern computer technology and the availability of powerful desktop computers for the engineering community has also played a vital role in the fast pace of composites development.

The rapid development and use of composite materials had three main driving forces:

1. Military vehicles placed a premium on high-strength, low-weight materials. The heavy weight of metallic components was prohibitive.
2. The emergence of new lightweight polymers increased the uses provided by the mechanical properties of plastics.
3. The high theoretical strength of certain materials, such as glass fibers, was being explored.

The question was how to use these potentially high-strength materials to overcome the issue posed by the military vehicles. Therefore, the use of composites for structural and semistructural parts of engineering applications was being explored and adopted. Phenolic resin reinforced with asbestos fibers was introduced in the beginning of 1900s. The first fiberglass boat was made in 1942, accompanied by the use of reinforced plastics in aircraft and electrical components. It was a great concern in 1942 that the supplies of metals for aircraft might not be available during the World War II. Therefore a major effort was initiated to develop the design rules and manufacturing processes for composites as possible replacements for aircraft metals. Critical parts including filament winding and spray-up, sandwich structures, fire-resistant composites, and prepreg materials were developed to prove out the design concepts and manufacturing methods. Filament winding was invented in 1946, followed by missile applications in the 1950s. In 1945, the first automobile developed with a fiberglass composite body was made and tested.
The body was reasonably successful and led to the development of the Chevrolet Corvette fiberglass body in 1953. Composites have evolved since the 1950s in architectural applications, starting with semipermanent structures and continuing with restoration of historic buildings and structural applications. Typical products developed were domes, shrouds, translucent sheet panels, and exterior building panels. Some of the products made after the 1940s now represent the major markets for composite materials. In addition to aircraft, these include boats, automobiles, tube and shower assemblies, noncorrosive pipes, appliance parts, storage containers, and furniture. The initial driving force in the technology development, dominated by the aerospace industry, was performance through weight savings. Later, cost competitiveness with more conventional materials became equally important. In addition to these two requirements, today there is a need for quality assurance, reproducibility and predictability of behavior over the lifetime of the structure (Strong, 2008; Isaac and Ori, 2006).

The marine market was the largest consumer of composite materials in the 1960s. The first boron and high-strength carbon fibers were introduced in the early 1960s, followed by the applications of advanced composites to aircraft components in 1968. Metal matrix composites such as boron/aluminum were introduced in 1970. DuPont developed Kevlar (or aramid) fibers in 1973. Starting in the late 1970s, applications of composites expanded widely to the aircraft, marine, automotive, sporting goods, and biomedical industries. The 1980s marked a significant increase in high-modulus fiber use. The use of new and conventional composite materials is intimately related to the development of fabrication methods. The manufacturing process is one of the most important stages in controlling the properties and assuring the quality of the finished product. A great deal of activity is devoted to intelligent processing of composites aimed at the development of comprehensive and commercially viable approaches for fabrication of affordable, functional, and reliable composites. This includes the development and use of advanced hardware, software, and online sensing and controls (Astrom, 1992).

In 1989, the National Academy of Engineering issued its list of top 10 engineering achievements of its lifetime. It ranked the development of advanced composite materials as sixth and cited advanced composite materials such as graphite-epoxy materials, used to make lighter and stronger products. The technology of composite materials has reached a stage of greater maturity. The cost of basic constituents is decreasing
due to market expansion. The fabrication process is becoming less cost-
ly as more experience is accumulated, techniques are improved, and
innovative methods are introduced. The need for energy conservation
motivates more uses of lightweight materials and products. The need for
multifunctionality is presenting new challenges and opportunities for
the development of new material systems such as nanocomposites with
enhanced mechanical, electrical, and thermal properties. The availabil-
ity of many good interactive computer programs and simulation meth-
ods makes structural design and analysis simpler and more manageable.
Some composite product applications are very new, such as stealth air-
craft, space structures, wrapping of concrete structures with composites
for improvement of earthquake performance, composite bridges, and
other construction edifices. It is interesting that construction is still a
major market for composites, just as it was in 1500 B.C. when the Egyp-
tians used straw to reinforce mud bricks (Strong, 2008). The 1990s
marked a further expansion to infrastructure. Presently a new frontier is
opening, that of nanocomposites. The full potential of nanocomposites,
having phases of dimensions on the order of nanometers, remains to be
explored (Isaac and Ori, 2006).

1.4. TYPES OF ADHESIVES USED IN COMPOSITE JOINTS

The selection of an adhesive for a given situation is necessary. There
is a need for selecting the appropriate adhesive because adhesives are
versatile and there is frequent overlap of their usage. It requires detailed
knowledge of the properties of a particular adhesive and the application
in which it is being used. The adhesive selection process is difficult
because there is no universal adhesive that works in every application,
and the selection of the proper adhesive is often complicated by the va-
riety of available options. However, adhesive selection includes many
factors, such as type and nature of substrates to be bonded, cure and ad-
hesive application method, and the expected environments and stresses
that the joint will face in service. Also, the cost of the adhesive may
sometimes be an important factor of adhesive selection in a particular
production situation. Mechanical actions like impact loads, quasistatic
loads, and low and high cycle fatigue loads need to be identified. The
mechanical characteristics of an adhesive vary with factors such as high
and low strength, brittle and flexible behavior, as shown in Figure 1.1.
To meet the requirement of a particular application, an adhesive may
need one or more of the following properties:
• Strength (shear and peel)
• Resistance to various fluids and chemicals
• Ability to wet the surfaces to be bonded
• Toughness
• Resistance to environmental degradation (including heat and moisture)
• Creep
• Fatigue

The increased use of high-temperature resin-matrix systems for composite materials has necessitated the development of compatible and equally heat-stable adhesive systems. Epoxy adhesives that are frequently used for the composite matrixes, are commonly used to bond composites based on epoxy matrix because of the compatibility between resin and adhesive. Apart from epoxy adhesives, there are several other types of adhesive, as mentioned in Table 1.1, that are frequently used in various structural applications.

1.5. ADHESIVE BONDED JOINT CONFIGURATIONS AND FAILURE MODES

Special equipment like fixtures, presses, tooling, autoclaves, and ovens for curing are usually required to manufacture any joint so that
TABLE 1.1. Typical Properties of Adhesives (Baneal and da Silva, 2009).

<table>
<thead>
<tr>
<th>Adhesive Type</th>
<th>Typical Adhesive Properties/Applications</th>
<th>Service Temp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy</td>
<td>High strength and temperature resistance, relatively low cure temperatures, easy to use, low cost.</td>
<td>–40 to +100 (180&lt;sup&gt;a&lt;/sup&gt;)</td>
</tr>
<tr>
<td>Cyanoacrylates</td>
<td>Fast bonding capability to plastic and rubber but poor resistance to moisture and temperature.</td>
<td>–30 to +80</td>
</tr>
<tr>
<td>Anaerobics</td>
<td>Designed for fastening and sealing applications in which a tight seal is formed without light, heat, or oxygen; suitable for bonding cylindrical shapes.</td>
<td>–55 to +150</td>
</tr>
<tr>
<td>Acrylics</td>
<td>Versatile adhesives with capabilities of fast curing; tolerates dirtier and less prepared surfaces.</td>
<td>–40 to +120</td>
</tr>
<tr>
<td>Polyurethanes</td>
<td>Good flexibility at low temperatures and resistant to fatigue, impact resistance, and durability.</td>
<td>–200 to +80</td>
</tr>
<tr>
<td>Silicones</td>
<td>Excellent sealant for low stress applications; high degree of flexibility and very high temperature resistance; capability to seal or bond materials of various natures, long cure times, and low strength.</td>
<td>–60 to +300 (350&lt;sup&gt;b&lt;/sup&gt;)</td>
</tr>
<tr>
<td>Phenolics</td>
<td>Good strength retention for short periods of time; limited resistance to thermal shocks.</td>
<td>–40 to +175 (260&lt;sup&gt;b&lt;/sup&gt;)</td>
</tr>
<tr>
<td>Polyimides</td>
<td>Thermal stability, dependent on a number of factors, difficult process ability.</td>
<td>–40 to +250 (300&lt;sup&gt;b&lt;/sup&gt;)</td>
</tr>
<tr>
<td>Bismaleimides</td>
<td>Very rigid, low peel properties.</td>
<td>–50 to +200 (230&lt;sup&gt;b&lt;/sup&gt;)</td>
</tr>
</tbody>
</table>

<sup>a</sup>With different filler materials.

<sup>b</sup>Intermittent.

considerable care can be taken in assembly. Figure 1.2 summarizes the main types of joint used in engineering structures for either metallic or composite adhesively bonded joints. From a mechanical viewpoint, the combination of shear and peel loading, which in turn influences the strength, varies from one geometry to another. This is important in understanding the conditions that lead to failure of a joint.

Failure modes are determined by the quality of the bond at each interface, specimen geometry, and loading. They must be characterized to gain a full understanding of the properties of the adhesive and the joint being investigated. In composite adhesive joints, according to the standard ASTM D5573 (Baneal and da Silva, 2009), there are seven typical characterized modes of failure: adhesive failure, cohesive failure, thin-layer cohesive failure, fiber-tear failure, light-fiber-tear failure, stock-break failure, or mixed failure.

In many situations adhesive failure is the limiting factor, although
in some applications, for instance in the bonding of thin metal sheet or with composite adherends, adherend failure may be a concern. Interface failure is generally a result of poor surface preparation or incomplete cure. With a true interface failure, the adherend is exposed at the fracture surface. It is sometimes difficult to distinguish between an interface failure and an adhesive failure close to interface (Ali, 2010). Many researchers (e.g., Kim et al., 2006; Tsai and Morton, 1995) experimentally investigated the influences of various parameters on the failure behaviors on composite bonded joints.

1.6. LIMITATION OF ADHESIVE COMPOSITE JOINTS

Adhesives composite joints are currently used in many areas, and there is a continuous rapid increase in their applications. Although the use of adhesive bonding is increasing rapidly, there are still important issues that need to be addressed in joint analysis, design, and durability considerations. The study of joints usually involves consideration of (1) a variety of joint geometries, (2) materials (i.e., adhesives, composites), (3) loading conditions, (4) failure modes and (5) environmental effects.

FIGURE 1.2. Typical engineering adhesive joints.
(Molitor et al., 2001). The analysis of adhesively bonded joints requires a reliable and efficient tool to obtain stresses, strains, and fracture parameters. Adhesive bonding of aircraft structures has been used and is still in use on current aircraft projects as a direct alternative to riveting (Baldan, 2004). In the manufacture of automobiles the adhesives joints are almost always used as basic sealant materials or in noncritical secondary structures. In the manufacture of aircraft the use of adhesively bonded joints has also largely been limited to secondary noncritical structures such as aerodynamic fairings and wing panels. Therefore, the use of adhesives in truly structural applications has been quite limited. The reasons for these limitations are twofold: (1) a concern about the fatigue and durability behavior of bonded structural components over the expected lifetime of the vehicle and (2) the fracture behavior of adhesive bonded joints, particularly those with dissimilar adherends (i.e., composite to metal), is still not well understood, since the adhesive joints must perform satisfactorily under service conditions, which include static and dynamic loadings and exposure to hostile environments such as water, petrol, other organic solvents, in many instances, combinations of these conditions may be experienced (Baldan, 2004).

There is a growing trend to optimize the strength, weight, and durability of aircraft and spacecraft structures by combining traditional metals with polymeric composites. Composites are more structurally efficient than metals and do not experience galvanic corrosion. Metals, however, have better damage tolerance and failure predictability than composites and are unaffected by solvents and temperatures, which tend to degrade polymers. In order to optimize the benefits offered by both types of materials, hybrid composite-to-metal structures are increasingly being developed. An example of these structures is an aircraft engine strut containing a lightweight, high-strength carbon fiber-epoxy fairing joined to damage tolerant aluminum ribs. Although these structures provide an excellent blend of material properties, their success depends on the integrity of the joints that connect them together (Owens and Lee-Sullivan, 2000).

Despite the many advantages of adhesive bonding, its use is still limited. Abdel Wahab et al. (2002) pointed out that this is mainly due to low durability of the joint when the structure is exposed to hostile environmental conditions. The effect of moisture on the strength of adhesively bonded joints is significant due to the deterioration of the adhesive layer and the interface. The strength of a joint decreases dramatically when aged in hot/wet environments, as has been demonstrated in composite bonded joints (Abdel-Wahab et al., 2001; Hart-Smith, 1999).
The major limitations of adhesive bonding are summarized as follows:

- There is no universal adhesive. Selection of the proper adhesive is often complicated by the wide variety of available options.
- The joint cannot be disassembled readily. Assembly times may be greater than for alternative methods, depending on the curing mechanism. Elevated temperatures may be required, as well as specialized fixtures.
- Some adhesives contain objectionable chemicals or solvents, or produce them on curing.
- Surface preparation and cleanliness, adhesive preparation, and curing can be critical if good and consistent results are to be obtained.
- Some adhesives are quite sensitive to the presence of grease, oil, or moisture on the adherend surfaces to be joined. Surface roughness and wetting characteristics must be controlled.
- The thermal residual stresses can be induced.
- High-strength adhesives have poor impact characteristics (often brittle). The toughness of an adhesive joint may decrease considerably under impact loading conditions.
- Most industrial adhesives are not stable above 180°C. Oxidation reactions are accelerated, thermoplastics can soften and melt, and thermosets decompose. While some adhesives can be used up to 260°C, elevated temperatures are usually a cause for concern.
- Many structural adhesives deteriorate under certain operating conditions. The adhesive can be subjected to environmental effects. Therefore, the durability and reliability of a joint over an extended service lifetime may be questioned. Long-term durability and life expectancy are difficult to predict.
- The joint design is thickness-limited and only shear loading is acceptable.
- It is difficult to determine the quality of an adhesive bonded joint by traditional non-destructive techniques, although some inspection methods have been developed that give good results for certain types of joints. (Abdel Wahab et al., 2002; Knox and Cowling, 2000; Loh et al., 2002).

1.7. REFERENCES

6.1. INTRODUCTION

This chapter focuses on the repair of civil engineering structures undergoing mechanical origin disorders (fatigue, shock, earthquake) or physico-chemical damage (alkali-silica reaction, carbonation). These repairs require the study of the mechanical behavior of the fiber-reinforced polymer (FRP)-concrete interface bonded with prepreg for FRP applied by the wet lay-up method or pultruded FRP plates bonded to the concrete substrate (Figure 6.1).

The development of composite or multimaterials requires a zone of contact between the materials. The interface is defined as the border area between the composite and its support. The interface has physico-chemical properties and specific mechanical properties.

The interface provides the load transfer between the involved materials (Courtade and Hamelin, 1997). Several theories have been developed to explain the phenomena of adhesion between a substrate and a polymer: mechanical theory, the theory of chemical bonding, electrical theory, and the theory of thermodynamics absorption.

The mechanical theory focuses on the anchoring or mechanical bonding of the polymer and the pores between the asperities on the surface of the substrate (Figure 6.2). Electrical theory explains the adhesion by electrostatic attractions. According to the theory of chemical...
bonding, adhesion results in the formation of covalent chemical bonds between the polymer and the substrate. Finally, according to the theory of thermodynamic absorption, adhesion is attributed to the establishment of intermolecular hydrogen bonds, or Van der Waals forces. In our case, the adhesion of composite to the concrete support is mechanical, coupled with some chemical contributions. The mechanical connection is provided by a surface treatment that consists of mechanically grinding the concrete. The chemical linkage is provided by the adhesion of the polymer to the interface of the composite polymer.

The above considerations significantly complicate the modelling of the mechanical behavior in terms of geometrical of physical descriptions of the environment.
6.2. TEST METHODS FOR ADHESIVE

A literature review revealed that manufacturers most often repair or strengthen structures as well as reinforce composites with high-strength reinforcement carbon and epoxy matrices, which are cured at room temperature. The development of a shear tensile test is necessary to justify the anchorage lengths for transferring the efforts of composite reinforcement to the support. This test can also judge the specific parameters of materials and technical implementations that influence the adhesion of the FRP to the concrete substrate and establish the mechanical laws of behavior at the interface to be used in calculation or to estimate the durability of the reinforced structure.

The shear behavior of the interface depends on the mechanical properties of the polymer that provide the bond between the composite layers and on the adhesion of the fiber matrix. We aimed to characterize the shear at the composite concrete interface with a test similar to the interlaminar test.

The design of the interface or the adhesive joint as proposed by Hart-Smith, 1994, must consider the short-term behavior and avoid anchorage lengths that would oversize the bonded joint. However, the considered distances should be long enough to prevent premature failures, such as creep, fatigue and aging. The stress in the elastic range is completely reversible. This brief study of the behavior of an adhesive joint highlights the need to study the behavior of composite-concrete joints under static, as well as creep and cyclic loading conditions. The aim of this section is to depict a shear test to define the allowable shear stress rates and justify the reinforced concrete strengthening.

Identifying the shear mechanical behavior of the adhesive joint therefore requires the development of a test to evaluate the shear strain that occurs in the adhesive. A failure that leaves an adhesive layer on both surfaces of the substrate is called a cohesive failure. If the failure occurs at the adhesive-substrate interface, it is an adhesive failure. If a lap joint has a purely cohesive failure, it indicates that the optimal material strength in the bonded joint has been reached. A structural adhesive joint requires knowledge of the change in its mechanical properties.

6.2.1. Shear Test for FRP

The composite was tested as described below:
• **Single lap shear test** (Chiu, 1992): This test allows the characterization of the interlaminar shear (Figure 6.3). Two composite plates are usually bonded to a surface of 2.5 cm × 2.5 cm. A traction force is applied to the composite web. At the break, the average shear stress of the adhesive joint is calculated. For example, Hamada (1990) used this test to characterize the durability of epoxy adhesive. The single lap shear test was used to determine changes in the average shear stress at different levels of aging. According to Edlund and Klarbring (1992), the disadvantage of this test is the creation of a parasite bending moment generated during traction due to the asymmetry of the test that arises from the thickness of the specimen. The use of a symmetric double lap joint test mitigates this problem.

• **Iosipescu test:** This test is subject to the ASTM D5379 standard. Its principle is schematically shown in Figure 6.4. Each end of the spec-

**FIGURE 6.3. Single lap shear test (Chiu, 1992).**

<table>
<thead>
<tr>
<th>Designation</th>
<th>Size [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>L₀</td>
<td>190</td>
</tr>
<tr>
<td>L₁</td>
<td>101.3</td>
</tr>
<tr>
<td>L₂</td>
<td>86.2</td>
</tr>
<tr>
<td>L</td>
<td>12.7</td>
</tr>
<tr>
<td>h</td>
<td>2 × 1.2</td>
</tr>
<tr>
<td>b₁</td>
<td>25</td>
</tr>
<tr>
<td>c</td>
<td>2.5</td>
</tr>
<tr>
<td>b₉</td>
<td>1</td>
</tr>
<tr>
<td>L₉</td>
<td>40</td>
</tr>
</tbody>
</table>

**FIGURE 6.4. Iosipescu test (Pierron and Vautrin, 1997).**
imen is fixed in a specific assembly. The ends move transversely to each other in response to a compressive load, which introduces a pure shear stress to the sample. This test is used on notched or unnotched specimens to characterize materials, such as metals and composites. The use of the test by many authors (Pierron and Grédiac, 2000) allows the definition of modules and the shear strength of the material (Figure 6.4). However, the use of this test is not feasible in our study because the scale factors result in a large test body, which introduces problems when cutting the concrete.

### 6.2.2. Concrete to FRP Adhesive Tests

Several authors have proposed tests to assess the adhesion to concrete necessary to transfer the charge to the composite. In most cases, these tests consist of tensile or compression-type shear tests (Figure 6.5).

![Different FRP to concrete adhesive joint](image)

**FIGURE 6.5.** Different FRP to concrete adhesive joint: (a) Compression shear test; (b) Single lap shear test device 1; (c) Double lap shear test; and (d) Single lap shear test device 2.
Varastehpour et al., 1992, proposed a compression-type shear test [Figure 6.5(a)]: Two concrete blocks are bonded to a surface of 180 mm × 140 mm. The blocks are subsequently subjected to compression, which shears the adhesive joint. This test is a single lap test to determine the mechanical properties and constitutive law of the interface for specific large samples. This test primarily yields a constitutive law of the interface (shear stiffness, ultimate strength), the behavior of which largely depends on the type of glue (polymer).

The test proposed by Karbhari and Navada (2008) is not a pure shear test but a peel test of the composite strip. The author proposed to vary the angle of pull to characterize the adhesion to the substrate.

Chajes et al. (1996) proposed a tensile-type single-lap shear test using 15 cm × 15 cm × 24 cm concrete blocks [Figure 6.5(b)]. This test uses a 2.5 cm wide, 10 cm long FRP strip bonded with an adhesive. The same length is not glued to the tensile force applied. The block is then clamped to a loading frame. A traction force is applied to the composite web, which then transmits a shearing force to the composite-concrete interface. The composite plate consists of six layers of CFRP. The bonding is ensured through several types of epoxy polymer that have previously received several types of surface treatments. The results are given as a measure of the distributions of shear stresses in the adhesive joint. The evaluation of the shear stresses is deduced by measuring the loss of stress in the composite along the glue joint. The shear stress is calculated by measuring the variation in the deformation of the composite between two measuring sections. These deformations are measured by strain gauges bonded along the composite plate.

The main findings of this research show an excess of shear stress the first centimeters, the failure of which depends on the nature of the surface treatment. The best results were obtained when the surface was treated with mechanical grinding. At these conditions, the influence of the resistance of concrete during compression (or shearing) on the mean adhesion constraints was optimized.

Täljsten (1997) characterized the adhesion tests as a tensile single-lap shear adhesive joint [Figure 6.5(d)]. In this test, a steel plate measuring 30 cm × 8 cm is bonded to a 20 cm × 20 cm × 120 cm concrete block. The strength of the steel plate controls the shearing of the adhesive joint. The strain gauges are distributed along the steel plate. The total slip between the steel plate and the concrete substrate as well as that along the glue joint is measured by a displacement sensor. The results are provided as a tensile stress distribution and measurement
of shear stress by means of the evaluation of the loss of force in a steel plate strain gauge device identical to that of Chajes et al. (1996) (Figure 6.5). This study compares the distribution of shear stresses from experimental results and those from an analytical calculation. The key findings highlight the presence of excess shear stress at the beginning of the bonded lap joint.

Hiroyuki and Wu, 1997. This test is a tensile double lap shear adhesive joint test. For this test, two concrete blocks with dimensions of 10 cm $\times$ 10 cm $\times$ 290 cm are assembled using 4 cm wide strips of composite bonded to the concrete substrate with anchoring lengths ranging from 10 to 30 cm [Figure 6.5(c)]. The blocks are loaded with a tensile force, which provides a shear adhesive joint through the composite. The results are given as the mean tensile stress via the ratio of load to failure to the bonding surface. The results of these tests demonstrate that the average failure stress approaches an asymptotic value based on the increase in the anchorage length. The failure mode is cohesive because the shear failure occurred in the concrete anchor for bonded lengths less than 10 cm. When the anchorage length exceeds 10 cm, the failure occurs in the composite strip. This test does not require special instrumentation. Hiroyuki’s work shows that a minimum anchorage length of 10 cm is necessary to absorb the forces in the composite and that the increase in the anchorage length reduces the average strength, which approaches an asymptote for anchor lengths exceeding 10 cm.

Ziraba et al. (1995) proposed a test of a combination of half-girders connected by a steel plate. In this test, a bending force is applied to either side of the half-girders to load the steel plate, which transmits a shearing force to the adhesive joint. This test represents the actual behavior of reinforcements during beam deflection. This type of test is not used to study the pure shear behavior of the adhesive joint. For example, Hart Smith explained the presence of excess stress at the ends of the material. The adhesive bonds reveal excess shear stress, which highlights an important constraint that has also been noted by many authors, including Hart-Smith (1973). According to this author, these excess stresses generate local yielding when the limit of elasticity of the adhesive joint is exceeded. Increasing the length of overlap produced a contradictory phenomenon: the average shear stress is lowered at first and the ultimate strength is increased. However, this phenomenon has a limit, beyond which the stress predominantly concentrates at the ends (with a minimum at near zero at the center), thus determining the maximum strength and optimal length of the joint (Till Vallée et al., 2013).
10.1. INTRODUCTION

In 1953, the Mobile Plastics Division of Carlyle Corporation introduced the first pre-impregnated roving. From 1953 General Motors, working with Molded Fiberglass products Co., launched an exploratory program with its Chevrolet Corvette (Figure 10.1). The Corvette was the first car with a body made from fiberglass, showed the advantages of using glass fiber reinforced plastic (GFRP) in the fabrication of large complex shape parts (Chehroudi, 2007).

Since then, the use of composites in automotive industry has been increasing due to the fact that these materials are easier to process than metal parts as they have excellent mechanical properties and weigh save up to 40%. When some of the metal parts of the vehicle are replaced by composite materials, the total number of components decreases.

Composites are easily molded to shape allowing a greater design freedom; shapes that cannot be made from metal can be made from composite materials. Compared with metals, composites have a good fatigue and corrosion resistance and a noise reduction (Banea, 2009).

However, there are also some disadvantages in the use of composite materials. The processing times are relatively long, resins and fibers are
expensive and achieving surface of high quality can be difficult. Composite materials can suffer UV degradation and the stiffness degradation is higher than metals (Mangino, 2007).

The main interest for the use of composites in the automotive industry is light-weighting. In sports cars, light-weighting translates into increased performance (acceleration and top speed). In mass production vehicles, the most important issue is saving fuel and lowering emissions. A reduction in weight of 100 kg involves reducing the fuel consumption in 0.3 l/100 km and the CO$_2$ emission in 8.5 g CO$_2$/Km.

The main disadvantage of using composite materials is their higher price than most of conventional metals. If carbon fiber is used, the cost increases up to 10 times higher. Therefore, one of the main objectives is to use low-cost fibers in parts that do not require exceptional properties. Aramid and carbon fibers may be used where mechanical behavior is necessary (Ghassemieh, 2011).

Composites parts can be molded from different processes and materials. The most broadly accepted reinforced thermoset composites used by automakers include sheet moulding composite (SMC), bulk molding composite (BMC), reinforced reaction injection moulding (RRIM), and resin transfer moulding (RTM). SMC is a type of composite material formed by a thermosetting resin, a fibrous reinforcement, fillers and additives with a good cost effective for mass production. BMC is a lightweight, heat resistant material that retains excellent modulus properties.
when exposed to cycling temperatures and automotive fluids. Ideal for use in metal replacement applications, BMC enables engineers to design complex components that resist physical creep over the life of a vehicle, even when exposed to temperatures in excess of 200°C with a low cost of the base material. The headlamp reflectors of most cars are made from BMC due to the excellent temperature performance of this material (Sommer, 2002).

Although there are significant benefits in the use of composites there are also some disadvantages: the wear and chemical resistance, a long time of production and the recycling issues (especially thermoset) (Lohse, 2006).

10.2. COMPOSITES IN MASS PRODUCTION CARS

In 1972, Renault Company introduces a SMC bumper in the Renault 5. In the same year, the Audi Quattro had a bonded SMC trunk lid. In 1982 the Citroen BX was the first high volume car with composite exterior parts (SMC front hood and BMC liftgate). The Renault Espace (version 1984–1996) featured polyester SMC body panels and an RTM tailgate (Centro Ricerche Fiat, 2004).

The front-end of the PEUGEOT 206 is made from SMC due to the higher stiffness of the part opposite to thermoplastic part. In case of accident, the front-end acts like the structural element in the front of the vehicle supporting all attachments even after break.

All body panels of the RENAULT Avantime (2001) are made from SMC. In addition, some structural parts as roof, roof frame, roof extension, side panel rear, side panel door, rocker panel and dashboard are made from SMC too.

Most of the components used at Ford are exterior panels produced using the SMC. The hood and front fender of the Lincoln Navigator, the hood, decklid, front fenders, package tray and removable hard top of the Ford Thunderbird or the pickup box and tonneau cover of the Ford Explorer Sport Trac are some examples. The Ford Explorer Sport Trac has a SMC cargo area with integrated liner and side panels with a great scratch resistant (Kendall, 2005).

In mass vehicles, reinforced thermoplastic are being used increasingly in exterior components for both indoor and exterior applications. For exterior applications, they are used in the manufacture of bumpers, spoilers, tailgate and lift doors. Moreover, these reinforced thermoplastics are used in new applications such as roof modules and front hoods.
in which, with few exceptions, thermoset materials like SMC and BMC have been used traditionally (Lohse, 2006).

The bumper beam of the BMW M3 is a structural thermoplastic component with a high crashworthiness, as well as a significant weight reduction of 60% (Figure 10.2). The bumper is made from TEPEX dynalite Glass/PA6, with a Polyamide matrix that provide a good chemical resistance against oils and light acids, so this material is often applied in the automotive industry (Bond-laminates, 2013).

10.3. CFRP IN CARS

In same sport cars, the chassis is a carbon fiber reinforced plastic (CFRP) monocoque. For example the Lexus LFA is built by a special section of the Toyota Company, which specializes only in composite materials. In other cases the full body is a monocoque CFRP, like in the Lamborghini Aventador (Figure 10.3). The CFRP composite are very light at the same time resistant, even exceed mechanical properties to steel. The entire body structure of the Aventador has a weight of 505 pounds and the monocoque (shell) weighs only 324.5 pounds. The shell is made from a series of individual CFRP parts with specific functions, such as stiffening elements made from Braiding technology, that is one of the best technology to manage energy adsorption in case of crash. After the curing process, however, this structure functions as a single
component including the base section known as the tub and the complete roof. (AUSmotive.com, 2013).

ATR Group is an Italian company, who design and mass produce structural parts and components in CFRP materials. Some samples of CFRP structural components for the automotive market are the Porsche Carrera GT chassis. In the Porsche Carrera GT, the composite parts are made from layers of carbon preimpregnated with an epoxy matrix. The Aston Martin Vanquish V12 utilizes a carbon fiber monocoque bonded to an extruded aluminum substructure, as well as, front and rear glass reinforced polyester crash elements manufactured by RTM (Centro Ricerche Fiat, 2004).

The SLC k200 has a CFRP monocoque produced using structural advanced RTM developing by ATR Group. The K200 is the lightest vehicle on the market. The chassis is a prepare carbon-fiber/epoxy sandwich structure with honeycomb as core material. The body was made completely from composite materials and can be considered as a monolithic structure because the subassemblies are joined by hot bonding techniques in autoclave. This fact increases the stiffness, the shear stress and the wear resistance. Very few structural parts have to be cold-bonded later on.

The BMW Z22 has an occupant cell with the floor panel and side frame made of CFRP, allowing a great reduction in weight. The CFRP roof structure of the BMW M3 CSL manufactured by a RTM process is

![Image](image.png)

**FIGURE 10.3.** Chassis of Lamborghini Aventador. Its monocoque forms a single shell in carbon fiber. (Source: Yolanda Ballesteros).
50% lighter than the conventional roof, so that the car’s center of gravity is lowered. Additionally, the BMW M3 CSL has the front apron, doors and side trim, air intake, central console and diffusers of CFRP. The rear bumper support and front seats are made of GFRP (Kelly, 2004).

CFRP has a number of benefits in vehicle body construction. This composite is strong as steel but around 50% lighter. High stiffness and the ability to absorb an enormous amount of energy, ensures superior occupant protection, similar to that found on F1 cars, in the event of a crash. In fact, in Formula One race cars, after high speed impacts, the driver cell survives intact. However, manufacturing a full CFRP chassis is a long and expensive process that practically prevents the production in series at the rate required in the automotive industry. In fact, any car model produced in large series so far carries a composite structure. BMW has done it with its new electric range. The BMW Megacity is an electrically car with a passenger cell with a life module made from CFRP that improves high strength and lower weight (Markarian, 2011).

The Ferrari Enzo (2003) makes one of the most extensive uses of CFRP. This employs a carbon fiber reinforced chassis and body. The...
good adhesive also should be able to prevent leakage along the restoration’s margin.

The use of composite resins in dental applications is widespread, thanks to numerous advantages. First, it can promote conservation of tooth structure and enable minimally invasive preparation. Furthermore, their use may reinforcement of weakened dental structure and reduction of some possible usual negative effects such as micro-leakage, staining and postoperative sensitivity. But also the aesthetic of these materials has provided an important role in their extensive employment.

Dental adhesive joints may be complex, due essentially to the singular properties of the adherents and environmental conditions. The joint is formed by a dental substrate and a restorative material (such as composite cement or porcelain restoration), the adhesive interface presented two different substrates with different and specific characteristics, and consequently the dental adhesives have to ensure the stable adhesion of both materials. Considered the tooth as substrate involves some special attention due to it involves the use of a living substrate that may show considerable variations.

14.2. ADHESION IN DENTISTRY

Figure 14.1 shows a typical structure of an incisor tooth. In the adhesion process the enamel and the dentin are both the zones that have a more important role. Adhesion to enamel and dentine presents different problems; this is because they have different composition (Table 14.1) and different anatomies.

![FIGURE 14.1. Structure of a typical incisor tooth.](image-url)
The enamel constitutes a relatively thin layer that is smooth and continuous, whereas the dentine is a thicker layer that has numerous tubules running through it. These tubules connect with the pulp, the vital and soft inner section of the tooth. Consequently, dentine is a dynamic substrate in which physiological activity brings about continual changes. In relation to the composition, the dentin is more humid and more organic than enamel (Nicholson, 1997).

The adhesion mechanism of dental adhesives can be explained as the combination of mainly two individual processes: micromechanical and chemical adhesion of the dentin and enamel at the adhesives and chemical bonding through the co-polymerization between the adhesive and the lining composite (Meerbeek et al., 2003).

The primary mechanisms to obtain micromechanical retention are diffusion and capillarity, retention occurs after consecutive demineralization, resin infiltration and polymer setting. The residual components from the cut of the tooth, well with a bur or other instrument, form a “smear layer” of debris on the surface. This debris forms a uniform coating on enamel and dentin reducing the permeability of dentin. The basic composition of the smear layer is hydroxyapatite and altered collagen. As the smear layer constitutes a true physical barrier, their treatment in the adhesion strategy is different, depending on the type of adhesive employed (Perdigão, 2007). One strategy (etch-and-rinse adhesives) involves removing the smear layer and superficial hydroxyapatite prior to bonding, through etching with a separate acid gel. However, the second strategy (self-etch adhesives) involves making the smear layer permeable without removing it completely.

On the other hand, another concept in this adhesion process is the formation of what is known as “hybrid layer” when the adhesive is applied over the dentin or enamel (with independence of how smear layer has been treated) (Nakabayashi et al., 1982).

The adhesive basically consists in a mixture of resin monomers dissolved in an organic solvent, it applies and infiltrates in etched dentin.
tin or, in the case of self-etch strategy, simultaneously infiltrates and also partially dissolves the smear layer. In both cases, the result is the formation of hybrid tissue composed of collagen, resin, residual hydroxyapatite, and traces of the solvent (and in the case of self-etches also the smear layer). This intimate micromechanical entanglement of resin monomers with dentin may result in a stronger bonding, better seal, decreased postoperative sensitivity, and may even act as an elastic buffer that compensates for the polymerization shrinkage stress during contraction of the restorative composite.

14.2.1. Stability of the Bonded Interface

Since bonding is created by the impregnation of the dentin substrate by blends of resin monomers, the stability of the bonded interface relies on the creation of a compact and homogenous hybrid layer.

Clinical longevity of the hybrid layer seems to involve both physical and chemical factors (Breschi et al., 2008). Physical factors such as the occlusal chewing forces, and the repetitive expansion and contraction stresses due to temperature changes within the oral cavity are supposed to affect the interface stability. Acidic chemical agents in dentinal fluid, saliva, food and beverages, and bacterial products further challenge the tooth/biomaterials interface resulting in various patterns of degradation of unprotected collagen fibrils, elution of resin monomers (probably due to suboptimal polymerization) and degradation of resin components.

As the hybrid layer is created by a mixture of dentin organic matrix, residual hydroxyapatite crystallites, resin monomers and solvents, aging may affect each of the individual components or may be due to synergistic combinations of degradation phenomena occurring within the hybrid layer (De Munk et al., 2005).

14.2.2. Surface Treatments to Improve Adhesion

A strong composite-tooth bond relies on micromechanical interlocking and chemical bonding to the ceramic surface, which requires roughening and cleaning for adequate surface activation. Common composite resin treatment options are: grinding, abrasion with diamond rotary instruments, airborne particle abrasion with aluminum oxide, acid etching, silane coupling agents and combinations of any of these methods (Blatz et al., 2003). Acid etching with solutions of hydrofluoric acid (HF) or ammonium bifluoride can achieve proper surface texture and
roughness, solutions between 2.5% and 10% applied for 2 to 3 minutes seem to be most successful.

The application of a silane coupling agent is currently one of the most-used techniques, the silane agent being applied over pretreated surface provides a chemical covalent and hydrogen bond, and is a major factor for sufficient bond strength. Silanization also increases wettability of the composite surface (Barghi, 2000).

Another technique that is widespread is a combination of airborne particle abrasion (50 μm Al₂O₃), etching with HF acid, and application of a silane coupling agent. Only airborne particle abrasion provides insufficient bond strengths. Excessive airborne particle abrasion induces chipping or a high loss of ceramic material and is therefore not recommended for cementation of silica-based all-ceramic restorations (Este-fan et al., 2000).

14.3. DENTAL ADHESIVES CLASSIFICATION

Commonly the dental adhesives are classified in two different ways: with respect their historical evolution and with respect their application mode or technique.

14.3.1. Historical Evolution

Buonocore (1955) is widely considered to be the first person to propose the application of adhesion technology in dentistry. The technique he introduced consists of etching the enamel with phosphoric acid to bond the resins to the enamel of the tooth. The first dental adhesives presented no dentin adhesions. Since then, many dental adhesives have been developed with the aim of providing higher bond strengths and more substantive bonded interfaces to both enamel and dentin (Swift, 1998).

14.3.1.1. First Generation

Although development of dentin adhesives began in the early 1950s, progress was very slow until recent years. In the early 1960s, the first adhesives products were commercially available, based on a “surface-active-comonomer” (NPG-GMA) that theoretically mediates water-resistant chemical bonds of resins to dentinal calcium. The weak bond strength (2–6 MPa) allowed dentin leakage and demonstrated very poor clinical performance.
Index

Ceramics, 5, 6, 18, 19, 59, 290, 292, 300, 301
Crack
  Growth, 106, 176, 187, 195
  Initiation, 96, 97, 114, 149, 178, 188, 190, 195
  Propagation, 97, 106, 109, 117, 181, 187, 202
Creep
  Behavior, 147
  Effect, 78
  Response, 165
Fatigue
  Behavior, 147–149, 151
  Damage, 151
  Failure, 149
  Life, 2, 203, 232
  Strength, 203
  Resistance, 4, 202, 207, 212, 228, 232, 239, 249
Finite Element, 2, 79, 116–118, 120–123, 126, 144, 146, 151, 165, 175, 176, 179, 184, 188
Glass fiber reinforced plastics GFRP, 93, 113–115, 121, 123, 125, 162–164, 166, 202, 203, 207, 208, 217, 219, 224, 231
Joint
  Double Lap, 40, 126, 127, 136, 140
  Double strap, 40, 92, 111, 113, 122
  Single Lap, 40, 44, 45, 79, 91, 111, 112
  Scarf, 45, 90, 181, 182
  Strength, 39–44, 46, 47, 54
Matrix
  Epoxy, 9, 153, 223
  Metal, 7, 18
  Organic, 159, 300
  Phenolic, 81
  Polymer, 19, 59, 60, 64, 70, 73, 81–83, 147, 156, 167
  Vinylester, 161
Scanning electronic microscope SEM, 21, 26, 27, 34, 78
Strain
  Plastic, 54
  Shear, 135, 141, 147
  Von Mises, 183, 184
Stress
  Axial, 265,
  Bending, 49, 54
  Failure, 40, 44, 139, 180
  Peel, 44, 78, 79, 82, 93, 109, 113, 114, 116, 117, 120
  Residual, 13, 93, 181

Shear, 43, 45, 46, 78, 79, 114, 117, 123–125, 135–141, 143, 144, 146, 147, 149, 151, 180, 223, 293

Yield, 54, 97, 360

Surface treatments, 59, 60, 64, 67, 68, 72, 73, 81–83, 138, 229, 245, 271, 300