Study Of Durability of Epoxy Bonded Joints In Aqueous Environments

by

Michelle K. Lian

Thesis submitted to the Faculty of the
Virginia Polytechnic Institute and State University
In partial fulfillment of the requirements for the degree of
Master of Science
In Materials Science and Engineering

Dr. Brian Love, Chair
Dr. Wallace Grant
Dr. Ronald Kander
Dr. James Keiser

August 4, 1998
Blacksburg, Virginia

Keywords: underwater repair, epoxy, steel, three-point flexure

Study Of Durability Of Epoxy Bonded Joints In Aqueous Environments

by

Michelle K. Lian

Dr. B. J. Love, Chairman

Department Of Materials Science and Engineering

ABSTRACT

There are instances where efficiency and safety may be compromised as a result of wear and tear of fluid transporting pipe systems. Consequently, it is sometimes necessary to shut down the entire operation to fix the problem. Thus, it is worth evaluating other methods that can repair the damage for a temporary period without shutting down the operation while a new pipe is being constructed. The objective was to evaluate the durability of the epoxy bonded steel in aqueous environments that might be the conditions of such a repair. EPON® 828 was chosen as the epoxy resin, and dicyandiamide and polyamidoamine were two types of curing agent evaluated in this study. The epoxy bonded steels were exposed in either distilled water or 3.4% NaCl solution for various time periods. The mechanical strengths of the bonded joints were evaluated using a three-point flexure test. The neat epoxy samples were also aged under the same conditions, and three-point flexure test and dynamic mechanical analysis (DMA) were performed to evaluate their mechanical properties. The moisture uptake of the neat epoxy increased with exposure time, and the bending modulus of the neat epoxy decreased with aging time and moisture uptake. It was found that the interfacial shear strength decreased with aging time for both epoxy bonded systems. Scanning Electron Microscopy (SEM), optical microscopy, and X-ray Photoelectron Spectroscopy (XPS) were used to determine the locus of failure of the bonded joints. It was concluded that failure occurred cohesively within the oxide layer if oxides were present on the substrate surface prior to the bonding procedure.

Acknowledgements

Many people have helped me in completing my research and writing this thesis. They have made this process an enjoyable and educational experience for me. I especially would like to thank the following people for their assistance:

Dr. Brian Love for serving as the chairman on my committee and for his guidance and encouragement. His support during my pursuit of the masters degree will always be appreciated.

Dr. Ronald Kander and Dr. Wallace Grant for editing this thesis and for serving on my committee. Dr. James Keiser from the Oak Ridge National Laboratory for editing this document and serving on my committee and for his help during my summer internship at the Oak Ridge National Laboratory. Their assistance has been valuable in my research and writing process.

Corrosion Science and Technology Group of the Oak Ridge National Laboratory for their technical assistance and for making my internship experience educational and delightful. Advanced Industrial Materials Fellowship Program of the Oak Ridge Institute for Science and Education for funding.

Dr. Love's and Dr. Kander's research groups for being great friends and labmates.

My parents, Jeng and Jua Lian, for their support. Their encouragement has made my goal of pursuing a masters degree possible.

Rob Jensen for his love and support. His patience and help has made my research and thesis writing successful.

Table of Contents

List of Figures

List of Tables

Chapter 1 : INTRODUCTION

Metals are often the materials of choice because of their excellent mechanical properties and durability. However, performance of metals is greatly compromised by corrosion. Corrosion is defined as the deterioration of the metals by environmental factors.[1,2] Many metals commonly used in structural applications tend to corrode in environments containing oxygen, and the rate of corrosion is increased significantly by higher temperatures. The rate of corrosion is also expedited by the presence of water because water provides a convenient medium for electrochemical reactions that are the primary processes in corrosion. The service lifetime of most structures, from bicycles to bridges, from buckets to battleships, is limited by wet corrosion.[3] It has been documented that heat exchangers tubed with nickel alloys and low-carbon steel have been seriously damaged as a result of corrosion.[4] When a pipe is corroded in a fluid transporting system, the plant is shut down to inspect and repair the damage. If the damage is not severe, welding is usually the repair method of choice, and the defective part will eventually have to be replaced. If the damage is beyond repair, the defective part will have to be replaced. While the plant is shut down, there is a loss of production time and labor and materials costs associated with the repair.[2] In addition to the expenses, there is a certain level of danger involved with welding. The pipe might contain reactive fluid that might escape the pipe through the damage site and result in explosive reactions. The complexity and difficulty of welding increase dramatically when the defective pipe is part of an underwater fluid transporting network. Underwater welding requires special technicians who are trained in welding in challenging environments, such as in a marine environment. The costs of materials and labor involved in repairing the damage increases

---

[1] A. D. Mercer, Corrosion in Seawater Systems, First Edition, Ellis Horwood Limited, 1990

[2] G. Butler, M.A., Ph.D., H. C. K. Ison, A.I.M., Corrosion and its Prevention in Waters, First Edition, The Gresham Press, 1966

[3] M. F. Ashby, D. R. H. Jones, Engineering Materials 1, An Introduction to Their Properties and Applications, First Edition, Pergamon Press, 1980

[4] A. M. Brennenstuhl, T.S. Gendron, and R. Cleland, Corrosion Science, Vol. 35, pp. 699, 1993

rapidly as the welding has to be performed underwater as well as the level of danger associated with this repair method. As more and more fluid transporting piping systems are being constructed offshore, there is an urgent need for an alternative method to repair defective pipes.

An alternative repair method using adhesives seems to be a logical choice because of many advantages of adhesive applications. As advantages, an adhesive:

(1) can connect different materials, such as metals and polymers,
(2) can couple thin pieces of metals effectively,
(3) can provide excellent dynamic-fatigue resistance to the bonded joints,
(4) can be a cost effective and convenient technique,
(5) can be automated,
(6) can be applied to wide variety of geometry in the bonding structure,
(7) can give a smoother finished surface than repair welding, and
(8) can improve corrosion resistance.

However, there are certain disadvantages associated with using adhesives. Some of the disadvantages are listed as follows:

(1) some surface pretreatment may be required to obtain long service life time of the bonded joint in severe and challenging environments,
(2) the upper service temperature of the adhesives is limited, and
(3) the strength and toughness in tension or shear is relatively low.[5]

Although adhesive bonded joints may not be as durable as welded ones, the use of an adhesive is an excellent repair method for a temporary period of time without shutting down the plant while a new part is being constructed. There is a considerably less risk connected with using adhesives than with welding. There is also no need for special training in using adhesives because of the convenience in bonding procedures. Some research has been performed by the Admiralty Research Establishment in the UK in

---

[5] A. J. Kinloch, Adhesion and Adhesives Science and Technology, First Edition, Chapman and Hall, 1987

using adhesives to repair steel structures offshore in the North Sea.[6] Before adhesives can be applied in such a repair, the effects of environments on the mechanical properties of the neat adhesives and the bonded joints need to be studied extensively in order to understand how adhesive bonded joints behave in underwater environments. In the following sections, several aspects of adhesive bonded joints will be discussed.

Adhesives are a class of materials with the ability to couple the components when applied to their surfaces and allowed to solidify. Several classifications are used to describe adhesives. Liquid adhesives, liquid two-part adhesives, and film adhesives are used to specify the physical state of an adhesive. Metal-to-metal adhesives, paper adhesives, and wood adhesives are just a few of the terms used to indicate the types of materials bonded. Epoxy adhesives, cyanoacrylate adhesives, polychloroprene adhesives are several chemical forms of adhesives. The terms that are used to describe the conditions of applications include solvent-based adhesives, cold-hardening adhesives, and hot-melt adhesives.[5]

At the beginning of a bonding procedure, the adhesive must be in a liquid form in order to achieve intimate contact with the bonding surface. This intimate contact between the adhesive and the substrate is termed wetting or spreading and is a very important factor in the formation of a strong bonded joint. After the adhesive has completely wet the substrate surface, the adhesive then transforms into a solid state. The transformation of an adhesive from the liquid to the solid state can be accomplished by solvent removal, by cooling or by chemical reaction.[5]

In the solvent removal process, the viscosity of the adhesive is sufficiently low to wet the substrate because the adhesive is dissolved or dispersed in solvents or water. After the adhesive has made intimate contact with the substrate, it is hardened by the removal of water or other solvents. The major disadvantage with this hardening process is that the

---

[6] M. R. Bowditch, J. D. Clarke, and K. J. Stannard, Adhesion, Vol. 11, pp. 1, Elsevier Applied Science, 1986

solvent removal process slows down the bonding procedure. In the cooling process, the viscosity of a thermoplastic adhesive is lowered by melting the material with heat. The thermoplastic adhesive is then spread over the substrate and is solidified upon cooling. This hardening mechanism occurs in a matter of few seconds. If the substrate has high thermal conductivity, the adhesive might harden prematurely before it has a chance to wet the substrate. This can result in a weakly bonded joint; therefore, this type of adhesive is not recommended for metal substrates.[5]

In the chemical hardening process, the adhesive is applied to the substrate as an agglomeration of monomers or oligomers which is referred to as a resin and polymerized *in situ* in the region between the substrates. The physical forms of this type of adhesives consist of thixotropic pastes, powders, rods, tacky or tack-free films, and low-viscosity liquids which can be either solvent-based or as 100% solids. Two types of polymerization reactions are step-growth polymerization and addition polymerization. A step-growth polymerization involves multifunctional monomer molecules. This reaction often yields small molecules, such as water or acetic acid, as by-products. Room temperature vulcanizing silicone rubbers and thermosetting phenolic and amino resins are resins that polymerize by step growth. An addition polymerization takes place by adding monomer molecules onto the growing polymer chain one at a time, and it does not produce small molecules as by-products. Cyanoacrylates, anaerobics and radiation-curable polymers are classified in this group. Some chemical reactions proceed by the addition of a hardener, such as a crosslinking agent. Two-part adhesives are classified in this category. The hardener is added just before the bonding procedure, and the adhesive is spread over the substrate and hardened. The chemical reaction can also be catalyzed by moisture, ultraviolet light, release of an enclosed hardener, and absence of oxygen. Elevated temperature is sometimes used to assist some chemical reactions. There are many advantages with hardening by chemical reactions. There is no water or solvent to eliminate, and many adhesives can be hardened at room temperature without the use of heating equipment. These adhesives are excellent choices for bonding to high thermal conductivity substrates, such as metals. The temperature resistance of the adhesives that are hardened by chemical reactions is exceptional compared to the other hardening mechanisms. However, there may be some disadvantages associated with this class of adhesives. The rate of hardening might be slower compared to other hardening mechanisms, but there are some adhesives that can achieve sufficient strength for handling within a short period of time. Two-part adhesives have to be mixed together; however, automatic mixers have become a popular choice to ensure an exact mixing ratio.[5]

The advantages of using adhesives that are hardened by chemical reactions surpass their disadvantages. It would be impractical to use adhesives for underwater applications that require the removal of solvents or water. The part that needs to be repaired is underwater, and difficulty would be encountered if solvents or water need to be eliminated from the adhesive. If there is a sufficient amount of solvent or water present in the adhesive, the bond strength may be greatly reduced. Problems can also arise from the need for underwater heating equipment to melt the adhesives that are hardened by cooling prior to the bonding procedure. The adhesives that are hardened by cooling are also not recommended for applying to metals underwater because the adhesives might harden too quickly for satisfactory wetting on the substrate. Since most fluid transporting pipe systems are made of metals, this type of adhesive is not useful. Therefore, the use of adhesives that are hardened by chemical reactions is thought to be superior to other hardening mechanisms for pipe repair underwater.

The adhesives that are hardened by chemical reactions are also termed structural adhesives because relatively high modulus and high strength may be obtained by using this class of adhesives. The most common structural adhesive is formed from epoxy resins. Epoxy resins are usually based on the diglycidyl ether of bisphenol A (DGEBA) and are hardened to produce a thermosetting polymer. The epoxy resin can be step-growth polymerized by a curing agent that has reactive groups, such as amines or amides. A typical reaction is shown in Figure 1.[5]

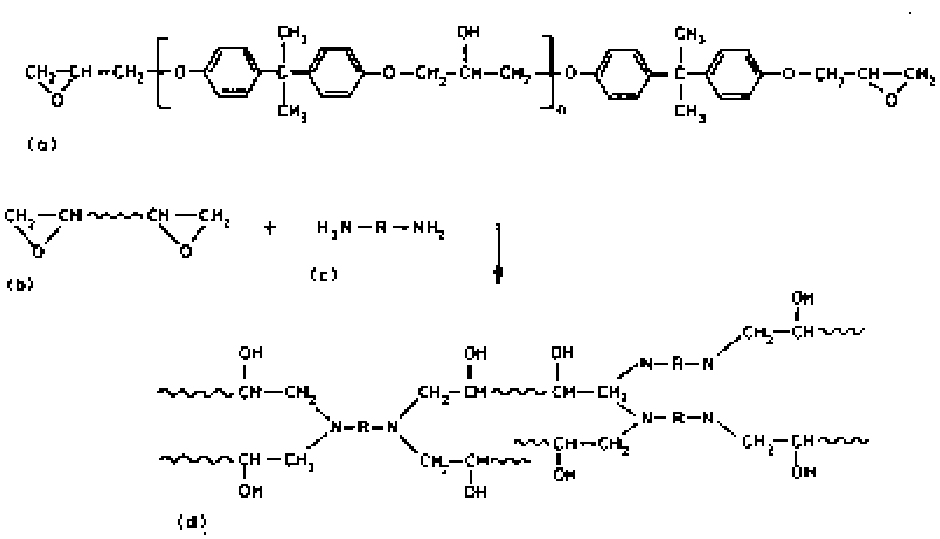


Figure 1: Typical epoxy hardening reaction using a primary diamine hardening agent. (a) A bisphenol A-epichlorohydrin based epoxy resin. (b) n=0.2, the liquid resin is a simple DGEBA. (c) A primary diamine hardener, (d) a crosslinked thermosetting epoxy adhesive.

This chemical reaction does not yield small molecule by-products and can proceed at room or elevated temperature. The common curing agents used include polysulphides, aliphatic polyamines, and polyamine-amides. Epoxy resins can also be polymerized by addition polymerization. This reaction is prompted by catalysts that are capable of initiating ionic intermolecular reactions between epoxy groups. Dicyandiamide, some aromatic amines, and imidazole complexes are typical catalysts. This polymerization usually proceeds at elevated temperature. There are many epoxy resins and hardeners commercially available that are able to produce strong bonds and are temperature resistant. Numerous grades of epoxy resins and curing agents are formulated for a wide variety of applications.[5] Epoxy resin was chosen as the adhesive to be studied for underwater pipe repair because of the variety of epoxy resins and curing agents available and of the ability to produce strong bonds.

The mechanical properties of epoxy are greatly affected by the presence of water, and it is critical to understand the effects of water on the epoxy in order to predict their behavior in aqueous environments where they may be applied.[7,8,9,10,11,12,13,14,15,16,17,18,19] Numerous research efforts have been done in recent years to study the epoxy-water interactions. The most common and most convenient technique to measure the moisture uptake of epoxy is to measure the mass before and after moisture exposure and to calculate the mass difference.[14,20,21] The amount of water absorbed by the epoxy is

---

[7] Sang-Baek Lee, and T. J. Rockett, Polymer, Vol. 33, No. 17, pp.3691-3697, 1992

[8] D. R. Lefebvre, K. M. Takahashi, A. J. Muller, and V. R. Raju, J. Adhesion Sci. Thehnol., Vol. 5, No. 3, pp.201-227, 1991

[9] I. Ghorbel and D. Valentin, Polymer Composites, Vol. 14, No. 4, pp.324, August 1993

[10] A. Apicella, L. Nicolais, G. Mensitieri, and M. Del Nobile, Composite Materials, pp. 11, Elsevier science Publishers, 1992

[11] E. Lee McKague, Jr., J. D. Reynolds, and J. E. Halkias, Journal of Applied Polymer Science, Vol. 22, pp. 1643-1654, 1978

[12] L. C. Bank and T. R. Gentry, Journal of Reinforced Plastics and Composites, Vol. 14 pp. 559-587, June 1995

[13] L. V. Smith, and Y. J. Weitsman, International Journal of Fracture, 82, pp. 31-42, 1996

[14] B. G. Min, D. K. Shin, Z. H. Stachurski, and J. H. Hodgkin, Polymer Bulletin, 33, pp. 465-470, 1994

[15] J. K. Gillham, Torsional braid analysis of Polymers, Applied Science Publishers, London, pp.159-227, 1982

[16] J. B. Enns and J. K. Gillham, Journal of Applied Polymer Science, Vol. 28, pp.2831, 1983

[17] M. J. Adamson, Journal of Mater. Sci., Vol. 115, pp.2831, 1983

[18] J. T. Lindsay, M. Matsubayashi, and M. N. Islam, Deutshe Gesellschaft fur Zerstorundsfreie Prufung E. V., pp. 644-649, 1997

[19] P. Pissis, C. Maggana, G. Spathis, and E. Kontou, Netherlands Society for Materials Science, Polymers and Ceramics, Vol. 2, pp. 159-162, 1997

[20] L. Barral, J. Cano, A, J, Lopez, J. Lopez, P. Nogueira, and C. Ramirez, Journal of Thermal Analysis, Vol. 47, pp. 791-797, 1996

determined by the chemical structure, morphology, and degree of cure.[9,22] The amount of water absorbed in epoxy resins also has been found to increase with temperature.[23,24] Chateauminois et al have successfully described the moisture uptake in epoxy in distilled water using Fick's law.[25] It has been observed that the fatique strength of the epoxy can become significantly lower after exposure to water at elevated temperature.[26] Techniques, such as X-ray Photoelectron Spectroscopy (XPS) and Fourier Transform Infrared (FTIR), have been used to study the degradation products produced during moisture exposure at elevated temperature, and it was concluded that irreversible interactions between the resin and water took place. Shanahan et al. stated that the water might cause chain scission of the epoxy backbone.[27] Ploehn et al. have used dynamic mechanical analysis (DMA) to study the effects of water on the material properties of the epoxy.[28] The effect of water on the glass transition temperature of the resin has been studied using DMA.[19] The glass transition temperature of an epoxy has been observed to decrease with water content suggesting that water acts as a plasticizer or diluent in the system.[29,30,31]

---

[21] D. Jiao, K. Pourrezaei, S. Li, and J. L. Rose, British Journal of Non-Destructive Testing, Vol. 34, No. 10, pp. 494-498, October 1992

[22] J. Verdu, Vieillissement des plastiques, Afnor Techniques, 1984

[23] C. Maggana, G. Spathis, and P. Pissis, Institute of Materials (UK), pp. 147-150, 1994

[24] Q. Zheng and R. J. Morgan, Journal of Composite Materials, Vol. 27, No. 15, pp. 1465-1478, 1993

[25] A. Chateauminois, L. Vincent, B. Chabert, and JP Soulier, Polymer, Vol. 35, No. 22, pp. 4766-4774, 1994

[26] K. Komai and S. Shiroshita, Journal of the Society of Materials Science, Japan, vol. 41, No. 469, pp. 1539-1544, October, 1992

[27] M. Shanahan, G. Z. Xiao, and M. Delamar, Journal of Applied Polymer Science (UK), Vol. 65, No. 3, pp.449-458, July 18 1997

[28] H. J. Ploehn, J-Y Wang, Journal of Applied Polymer Science, Vol. 59, No. 2, pp. 345-357, 1996

[29] M. C. Lee and N. A. Peppas, Progress in Polymer Science (UK), Vol. 18, No. 5, pp. 947-961, 1993

Research has been performed to study the effects of environments on the mechanical strength and durability of adhesive bonded joints. Tai et al. observed that epoxy delaminated from steel substrate exposed to distilled water and NaCl solutions using a three-point bending device.[32] They measured the area of epoxy delaminated from a steel substrate as functions of exposure time and environments. It was found that the percentage of area delaminated increased up to 90% after five weeks of exposure and that the delaminated area was greater in the NaCl solutions than in the distilled water. They have also concluded that the delamination area increased with the concentration of the NaCl solutions and with exposure time.[32] Gledhill and Kinloch studied the effect of moisture on the tensile strength of the epoxy bonded mild steel butt joints. They found that the joint tensile strength decreased with exposure time and relative humidity and that the tensile strength decreased up to 80% after 2500 hours of exposure.[33]

The mechanisms of how adhesives bond to the metal substrate and how failure occurs have also been extensively studied. Venables stated that surface characteristics, such as porosity and roughness, played a critical role in the strength of the bonded joints. He studied the oxide morphology of aluminum and titanium using extended resolution scanning electron microscopy (XSEM). He found that stronger bonds resulted from the adhesives bonded to substrates that were higher in porosity and roughness by mechanical interlocking.[34] Gledhill, Kinloch, and Shaw developed a model to predict the durability of tensile butt joints. They proposed that three stages were involved in the environmental failure of adhesive joints. The first stage was thought to be water collecting in the interfacial region and was controlled by the water diffusion rate through the adhesive. It

---

[30] K. Tanaka, M. Yamaguchi and Y. Tanaka, Advanced Composite Materials (Netherlands), Vol. 6, No. 3, pp. 197-213, 1997

[31] J. M. Hale, A, G. Gibson, Journal of Composite Materials, Vol. 32, No. 6, pp. 526-543, 1998

[32] R. C. L. Tai and Z. Szklarska-Smialowska, Journal of Materials Science, Vol. 31, pp. 1925-195, 1996

[33] R. A. Gledhill and A. J. Kinloch, Journal of Adhesion, Vol. 6, pp. 315-330, 1974

[34] J. D. Venables, Journal of Materials Science, Vol. 19, pp. 2431-2453, 1984

has been documented that the kinetics of the environmental failure are influenced by the water ingression rate. The second stage resulted from damage in the interfacial region. Two common mechanisms that can lead to damage in the interfacial region were suggested and include: (1) the adhesive is being displaced from the metal oxide by water, and the interfacial bonds are broken and (2) the oxide layer is weakened by hydration of the oxide particles. The third stage is the ultimate failure of the adhesive joint.[35] They have also calculated the work of adhesion for the epoxy-ferric oxide interface in dry and humid environments and found that the work of adhesion is 291 mJ/m^2 and –255 mJ/m^2 for dry and humid conditions respectively. They concluded that this change in the work of adhesion provided a driving force for the water to displace the adhesive from the oxide layer and that the bonding strength was reduced as the result.[35] Gontcharova-Benard et al. also suggested that the lifetime of a bonded joint was controlled by the diffusion of water through the adhesive.[36]

Many mechanical tests have been used to determine the strength of adhesive bonded joints and include single lap shear tests, peel tests, cleavage tests, and three point bending tests. However, no single test can describe a bonded joint thoroughly. A single lap shear test gives an apparent average stress, but it does not detail the actual stress distribution along the joint.[37] Studies have shown that maximum stress actually takes place at the joint extremities.[38] Peel tests and cleavage tests do not consider the actual area under stress in the analytical calculations. A three-point bending test gives some information on the interfacial characteristics; however, the testing parameters have to be selected carefully.[37] It has been shown that a three-point flexure test is sensitive to the substrate surface characteristics and can yield properties of the adhesive bonded joint interphase. It has also been observed that the stresses are distributed uniformly along the specimen

---

[35] R. A. Gledhill, A. J. Kinloch, and S. J. Shaw, Journal of Adhesion, Vol.11, pp. 3-15, 1980

[36] E. Gontcharova, A. Roy, J. L. Gacougnolle, and P. Davis, Editions Pluralis (France), pp. 295-300, 1997

[37] E. Ziane, G. Beranger, and C. Coddet, Journal of Adhesion, Vol. 19, pp. 197-205, 1986

[38] O. Volkersen, Construction metallique, Vol. 4, pp. 3-13, 1965

length and are parallel to the interfacial region and that this testing geometry leads to failure along the interface between the substrate and the adhesive.[39]

The surface characteristics of the substrates have been studied to understand the bonding mechanisms of adhesive bonded joints. Bowditch et al. conducted studies on the strength and durability of bonded joints fabricated underwater. They concluded that the steel surface needed to be grit blasted underwater and the sacrificial pretreatment technology was applied to produce a hydrophobic film that was compatible with the adhesive in order to form a strong and durable bond between the adhesive and the steel.[6] Levingstone presented information on showing that a stronger bond formed between the hot-dip galvanized steel surface and the paint when there was an oxide protective layer on the steel surface.[40] Leidheiser reported that the air-formed oxide on most metals is usually not uniform in thickness and not stable for structural bonding and that it is necessary to remove the oxide layer for long service lifetime.[41] However, the freshly formed oxide has high surface roughness and chemical reactivity and can contribute to excellent durability of bonded joints in corrosive environments.[42]

It is also important to determine the locus of failure when a bonded joint fails in order to improve its strength. Several techniques, such as Ion Scattering Spectrometry (ISS), Secondary Ion Mass Spectrometry (SIMS), Auger Electron Spectrometry (AES), and X-Ray Photoelectron Spectroscopy (XPS), are often used to study the failure surfaces. It is shown that many materials and interfacial regions exist between the adhesive and the

---

[39] A. A. Roche, M. J. Romand, and F. Sidoroff, Adhesive Joints, Formation, Characteristics, and Testing, pp.19-30, Plenum Press, New York and London, 1984

[40] J. J. Levingstone, Paint Varnish Prod., Vol. 69, No. 7, 1979

[41] H. Leidheiser, Jr., Corrosion, Vol. 39, pp. 189, 1983

[42] J. D. Minford, Adhesive Bonding, Plenum Press, New York and London, Ch. 9, pp. 239, 1991

substrate. These interfaces do not have sharp boundaries between each other.[43] An interphase can sometimes better describe these areas.[44] ISS analyzes the first atomic layer at the surface by measuring the energy lost by the incoming ion beam to determine the atomic masses. SIMS makes use of mass spectrometry to analyze the surface atoms ionized by the probing ion beam.[43] AES uses a small diameter electron beam to excite Auger electrons from the atoms at the uppermost surface region.[5] In XPS, a sample is irradiated with a X-ray beam to produce excited electrons that are analyzed for their energy. XPS is able to determine the chemical states of elements on a surface because the peak shape, position or intensity of the photoelectron spectrum changes with the chemical environment.[43] Gettings et al. used AES and XPS to study the failure surface of epoxy steel joints after aging in water at 60°C followed by impact testing and found that the failure occurred adhesively.[45]

The objective of this work is to study the effects of environments on the mechanical properties of neat epoxy and of epoxy bonded joints for possible applications in underwater pipe repair. In the following chapters, the experiments performed and the results obtained will be discussed in details.

---

[43] W. L. Baun, Adhesive Joints Formation, Characteristics, and Testing, pp.3-17,Plenum Press, New York and London, 1984

[44] L. Sharpe, Recent Advances in Adhesion, L. H. Lee, Ed., pp.437-453, Gordon and Breach, New York, 1973

[45] M. Gettings, F. S. Baker, and A. J. Kinloch, Journal of Applied Polymer Science, Vol. 21, pp. 2375-2392, 1977

Chapter 2 : EXPERIMENTAL

2.1 Materials

EPON® resin 828 is an undiluted difunctional bisphenol A/epichlorohydrin derived liquid epoxy resin manufactured by Shell Chemical Company, and its chemical structure is illustrated in Figure 2. This resin has good mechanical, adhesive, dielectric, and chemical resistance properties when cross-linked with an appropriate curing agent.[46] EPON® resin 828 has become a standard epoxy resin formulation, fabrication, and fusion technology because of its versatility.[46] Typical properties for the resin include: epoxide equivalent weight of 185-192 g/mole, a viscosity of 110-150 poise at 25°C, a density of 1.16g/ml at 25°C, no flash point as high as 249°C, a vapor pressure of 0.03 mm Hg at 77°C, a refractive index of 1.573 at 25°C, and a specific heat of 2.10J/g.°C.[46]

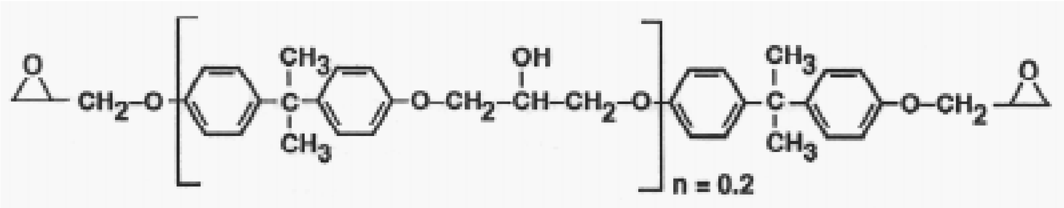
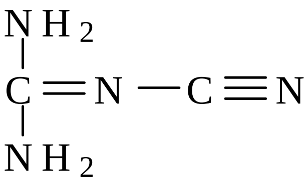


Figure 2: Chemical structure of EPON® resin 828

Dicyandiamide and EPI-CURE® 3090 were the two types of curing agents used in this study. Dicyandiamide was used in conjunction with N, N- Dimethyl formamide and 2-methylimidazole, and its chemical structure is given in Figure 3. The chemical structure of 2-methylimidazole is also illustrated in Figure 4.



$$(NH_2)_2C{=}N{-}C{\equiv}N$$

Figure 3: Chemical structure of dicyandiamide

---

[46] Shell Resin Literature, SC:235-95.828

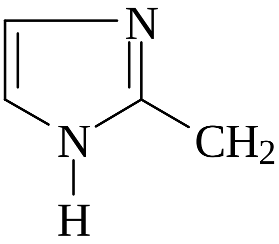
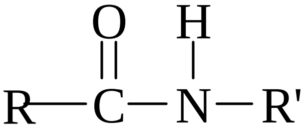


Figure 4: Chemical structure of 2-methylimdizole

EPI-CURE® 3090 is a modified polyamidoamine adduct and blush-resistant epoxy curing agent, and its structure is illustrated in Figure 5. It has a viscosity of 45 poise at 25°C.[47] EPI-CURE® 3090 consists of 90% solids in ethanol, and its flash point is at 35°C.[47] It is capable of curing the epoxy resin at and below room temperature on damp or underwater substrates, including concrete and steel, and it is corrosion resistant.[47]



$R-C(=O)-N(H)-R'$

Figure 5: Functional groups of EPI-CURE® 3090

Two types of low-carbon alloy steel were studied. Their chemical compositions are listed in Table 2.1 and Table 2.2. The steel used with the EPON® resin 828/dicyandiamide system was supplied by U. S. Navy Coastal Systems Command, Panama City, Florida, and the steel used with the EPON® resin 828/EPI-CURE® 3090 system was supplied by McMaster-Carr supply company.

---

[47] Shell Resin Literature, SC: 1706-93

Table 2.1: Chemical Composition of Steel used with EPON® resin 828/dicyandiamide

Element	Concentration (%)	Element	Concentration (%)
C	0.043	Co	0.003
Mn	0.25	Cu	0.03
P	0.011	Al	0.05
S	0.006	B	0.001
Si	0.02	W	0.001
Ni	0.02	As	0.007
Cr	0.04	Sn	0.004
Mo	0.01	Zr	0.001
V	0.001	N	0.005
Nb	0.002	O	0.002
Ti	0.001		

Table 2.2: Chemical Composition of Steel used with EPON® resin 828/EPI-CURE® 3090

Element	Concentration (%)	Element	Concentration (%)
C	0.17	Co	0.014
Mn	0.79	Cu	0.17
P	0.022	Al	0.035
S	0.030	B	0.01
Si	0.15	W	< 0.01
Ni	0.17	As	0.023
Cr	0.20	Sn	0.014
Mo	0.05	Zr	0.002
V	0.002	N	0.013
Ti	0.002	O	0.001

2.2 Sample Preparation

2.2.1 EPON® resin 828 / Dicyandiamide system

Four weight percent of dicyandiamide was dissolved in N, N-Dimethyl formamide in a beaker on a hot plate with the solvent slightly heated above room temperature. The solution was mixed until it was free of any visible solid dicyandiamide particles. After the curing agent was completely dissolved in the solvent, 0.5 % of 2-methylimidazole, that served as a catalyst, was added to the solution. EPON® resin 828 was then poured into the mixture of curing agent, solvent, and catalyst. The resin system was transferred into a silicone mold in which the bulk epoxy bars would be cast. The mold was placed in an oven at 50°C for 12 hours to evaporate the N, N-Dimethyl formamide. Teflon films and aluminum weights were placed on top of the mold to insure uniform thickness of the samples. The oven temperature was increased to 180°C at a heating rate of 1°C per minute, and the temperature was held at 180°C for one hour to cure the epoxy resin. The oven temperature was then lowered to room temperature at a cooling rate of 1°C per minute to avoid thermal shock of the samples.

2.2.2 Steel Surface Pretreatment For Bonding With EPON® resin 828 / Dicyandiamide

Steel bars were machined from a large sheet of steel into strips of 96mm in length, 3 mm in thickness, and 15 mm in width. The steel bars had visible corrosion products on the surface prior to any surface pretreatment, and three surface pretreatment methods were performed before the bonding procedure with the EPON® resin 828 / Dicyandiamide system. Method I was to scrub the surface with soap and water, method II was to sand the surface with 220 grit sandpaper, and method III was to sandblast the surface with glass beads to remove the visible corrosion products.

2.2.3 EPON® resin 828 / Dicyandiamide Bonded Steel

A silicone mold that has cutouts for adhesive was used to fabricate the epoxy bonded joints. Figure 6 illustrates the top view of the mold with the shaded area representing the cutouts of the mold. The surface pretreated steel bars were sealed onto the bottom of the mold with a silicone sealant to prevent the epoxy resin from leaking. The mold was then placed in the oven for one hour at 180°C to cure the sealant in order to prevent the sealant from releasing volatiles into the epoxy. The epoxy resin and catalyst system was prepared and poured into the cutouts of the mold. The curing schedule of the EPON® resin 828 / Dicyandiamide system was followed. After the epoxy had completed the curing process, the mold was removed to produce epoxy bonded steel specimens. The epoxy on the steel had average dimensions of 77mm in length, 5mm in thickness, and 5mm in width. The side view of an epoxy bonded sample is illustrated in Figure 7.

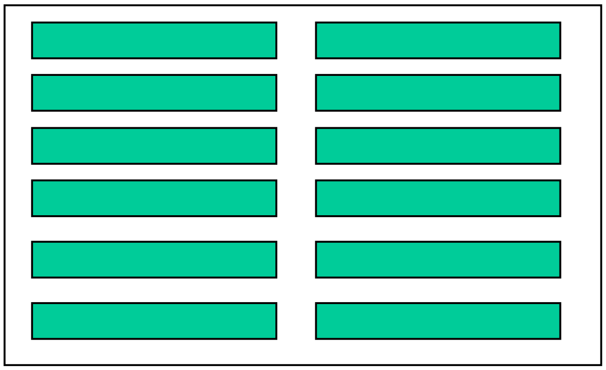


Figure 6: Top view of the silicone mold

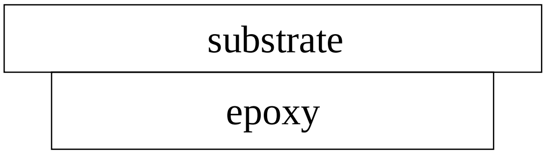


Figure 7: Side view of an epoxy bonded steel

2.2.4 EPON® resin 828 / EPI-CURE® 3090 system

EPON® resin 828 and EPI-CURE® 3090 were mixed in a 1:1 weight-mix-ratio using a mechanical stirrer to insure the complete mixing of the two components. The mixture was then degassed using a centrifuge. The adhesive system reached its gel point at ambient temperature in one hour. A vacuum oven was undesirable for degassing the adhesive system because of the time constraint. The temperature of the adhesive system was raised to reduce the resin viscosity and void content; however, the higher temperature only shortened the gel time of the adhesive. It was found that the centrifuge worked best in removing the voids from the adhesive system.

The adhesive was poured into the silicone mold to be cast into bulk epoxy bars. Teflon films and aluminum weights were placed on top of the mold to insure uniform thickness of the epoxy bars. The mold was then placed in a water bath, and the adhesive was cured at 65°C for 24 hours.

2.2.5 Steel Surface Pretreatment For Bonding With EPON® resin 828/EPI-CURE® 3090

A large sheet of steel was machined into steel bars with dimensions of 96 mm in length, 3 mm in thickness, and 15 mm in width. There was no visible corrosion product on the steel surfaces. Two surface pretreatment methods were performed. Method I was to wipe the steel surface with acetone to remove contamination off the surface. Method II was to submerge the steel bars in a 3.4% NaCl solution bath at 50°C for one month to yield corrosion products on the surface. SEM was used to study the surface characteristics of the surface pretreated steels. The SEM micrographs for the acetone wiped substrate with different magnifications are shown in Figures 8-10 and for the corroded substrate are included in Figures 11-13.

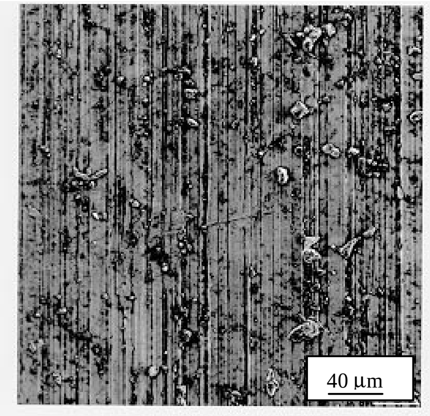


Figure 8: SEM of acetone wiped steel

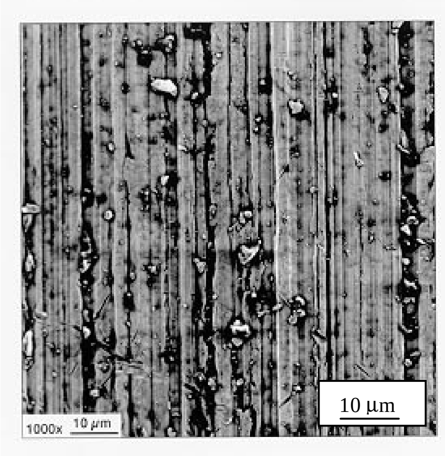


Figure 9: SEM of acetone wiped steel

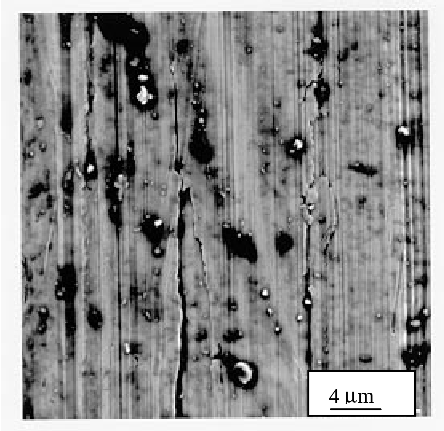


Figure 10: SEM of acetone wiped steel

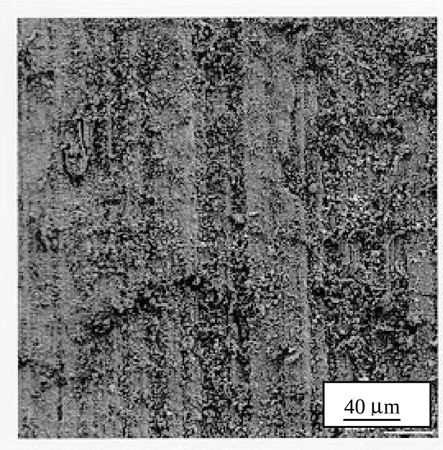


Figure 11: SEM of corroded steel

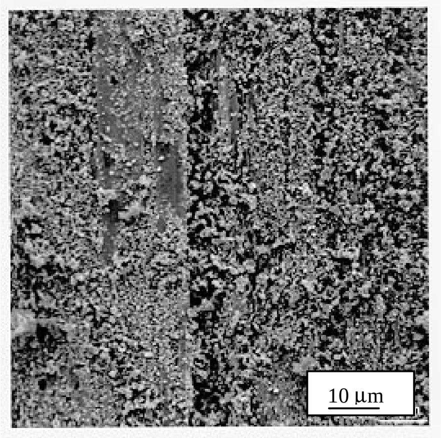


Figure 12: SEM of corroded steel

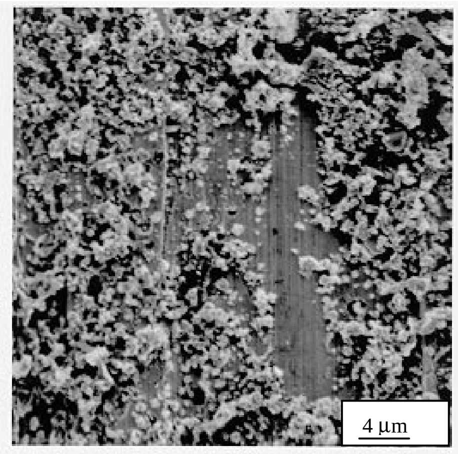


Figure 13: SEM of corroded steel

2.2.6 EPON® resin 828 / EPI-CURE® 3090 Bonded Steel

A silicone mold that has cutouts for the adhesive deposition process was used to fabricate the epoxy bonded joints. Figure 6 shows the top view of the mold. The surface pretreated steel bars were sealed onto the mold with a silicone sealant and were placed in the oven at 65°C to cure the sealant. This step was necessary to prevent the sealant from releasing volatiles into the epoxy. The adhesive system was prepared and poured into the cutouts of the mold. Teflon films and aluminum weights were placed on top of the mold to make sure that uniform thickness of epoxy was obtained. The mold was then immersed in a water bath, and the adhesive was cured at 65°C for 24 hours. The silicone mold was released from the steel bars to produce epoxy bonded samples. The epoxy on the steel had average dimensions of 70mm in length, 8mm in thickness, and 4mm in width.

2.3 Aging Experiments

2.3.1 EPON® resin 828 / Dicyandiamide System

The testing program consisted of four sample types: neat epoxy bars and epoxy bonded steel with three different surface treatments. Five samples from each type were exposed in air as controls. The rest of the samples were divided into 16 groups for exposure in two aqueous environments for two time periods, and each group consisted of five samples. The sample groups were placed in separate plastic bottles filled with the aging solution, and they were positioned in a distilled water bath at 50°C. The aging environments were distilled water and 3.4% NaCl solution, and the aging time ranged from one to two weeks. Sea water contains approximately 3.4% salt, predominately sodium chloride.[48] A 3.4% NaCl solution was chosen as one of the aging solutions to simulate the sea water which may be the actual service environment.

---

[48] W. D. Callister, Jr., Materials Science and Engineering, An Introduction, Third Edition, John Wiley & Sons, INC., New York, 1994, pp. 573

2.3.2 EPON® resin 828 / EPI-CURE® 3090 System

Two aging experiments were designed for this adhesive system: (1) constant aging temperature of 50°C, and (2) cycling temperature from 25°C to 50°C.

2.3.2.1 Constant Aging Temperature

Three sample types made up this aging program: neat epoxy bars, and epoxy bonded steels with two different surface treatments. Five samples from each sample type were exposed in air as controls, and the rest of the samples were divided into 19 sample groups. The sample groups were to be exposed in two aging environments for three different time periods, and each sample group consisted of five samples. The sample groups were placed in different plastic bottles filled with the designated aging solution, and they were submerged in a water bath at 50°C. The aging environments were distilled water and 3.4 % NaCl solution, and the aging time ranged from one to four weeks.

2.3.2.2 Cycling Aging Temperature

This aging experiment was designed to study the effects of environments and temperature cycling on the durability of the epoxy bonded joints.

Three sample types including neat epoxy bars and epoxy bonded steels with two different surface treatments were studied in this experiment. Five samples from each sample type were exposed in air as the control groups. The rest of the samples were divided into ten sample groups for exposure in two environments and two different time periods, and each sample group contained five samples. The sample groups were placed in separate plastic bottles filled with a selected aging solution, and they were immersed in a water bath. The aging temperature was cycled between 25°C and 50°C. The aging time ranged from one to two weeks, and the aging environments were distilled water and 3.4% NaCl solution.

2.4 Three-Point Flexure

2.4.1 Neat epoxy bars

Three-point flexure testing was used to evaluate the elastic bending modulus of the neat epoxy bars. A Universal Testing Machine L-200 was utilized to test the neat EPON® resin 828 / dicyandiamide bars, and a Texture Analyzer TA-XT-2i was used to test the neat EPON® resin 828 / EPI-CURE® 3090 samples. These mechanical tests were performed at room temperature. The testing geometry of a three-point flexure experiment for the neat epoxy is illustrated in Figure 14.

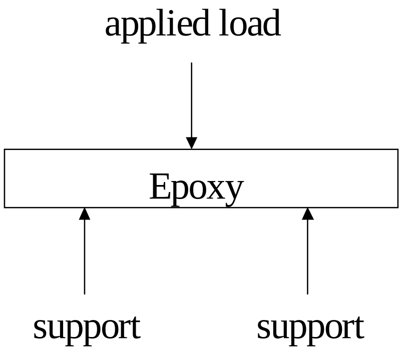


Figure 14: Three-point flexure geometry

The epoxy sample rests on two supports, while the load is applied at midpoint between the supports. The distance between the supports is denoted as the span length. The test was performed until the samples were fractured. A force-deflection curve was obtained for each specimen and used for analysis. A typical force-deflection curve is illustrated in Figure 15.

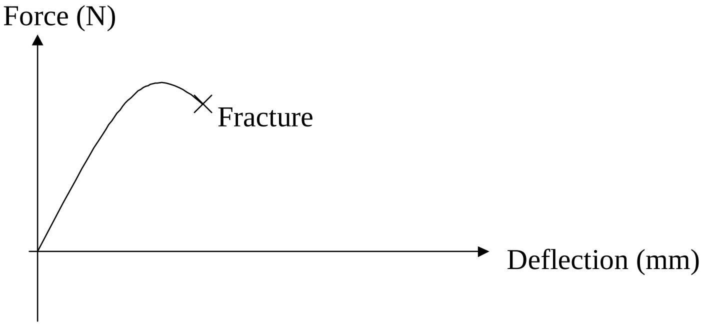


Figure 15: A typical force-deflection curve from a three-point flexure testing of a neat epoxy specimen

The span length was 20 mm for the EPON® resin 828 / dicyandiamide bars and 25 mm for the EPON® resin 828 / EPI-CURE® 3090 samples. The cross-head speed was set at 2.5 mm/min for the EPON® resin 828 / dicyandiamide bars and 0.5 mm/min for the EPON® resin 828 / EPI-CURE® 3090 samples.

2.4.2 Epoxy Bonded Joint

The mechanical properties of the epoxy bonded joints were evaluated using the three-point flexure configuration. These mechanical tests were also performed at room temperature. The testing geometry is shown in Figure 16.

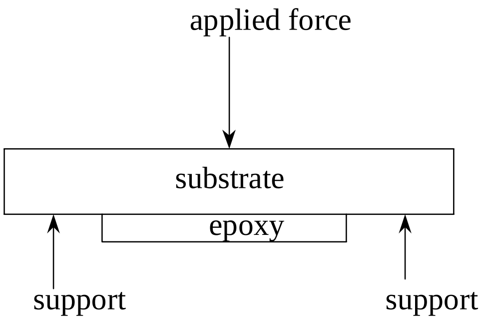


Figure 16: Three-point flexure geometry for epoxy bonded steel

An epoxy bonded specimen was set on the two supports with the adhesive facing down, and a load was applied at a midpoint between the supports. The distance between the supports was the span length. The span length was 90 mm for the EPON® resin 828 / dicyandiamide bonded steels and 88.9 mm for the EPON® resin 828 / EPI-CURE® 3090 bonded samples. The cross-head speed was set at 2.5 mm/min for the EPON® resin 828 / dicyandiamide bonded steels and 4.5 mm/min for the EPON® resin 828 / EPI-CURE® 3090 bonded samples. It was the purpose of this test to obtain the interfacial strength of a bonded joint; therefore, the test was performed until the epoxy delaminated from the substrate, and the force at delamination was recorded. A force-deflection curve was obtained for each specimen and is illustrated in Figure 17. The force at delamination and sample geometry would be used for analysis.

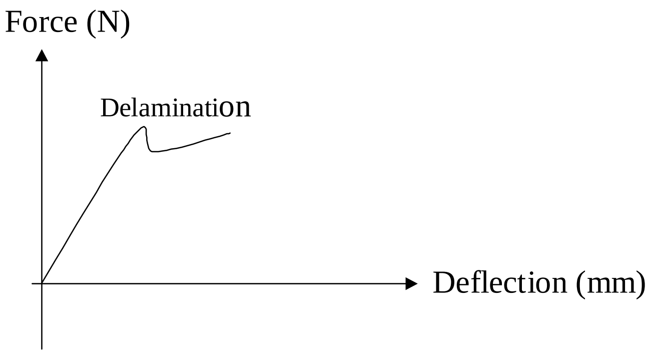


Figure 17: A typical force-deflection curve from a three-point flexure testing of a epoxy bonded joint

2.5 Dynamic Mechanical Analysis

Dynamic Mechanical Analysis (DMA) was performed on the neat EPON® resin 828 / EPI-CURE® 3090 samples to determine the effect of environmental factors on the glass transition temperature (T_g) of the adhesive. A Perkin Elmer DMA 7 was used to analyze the EPON® resin 828 / EPI-CURE® 3090 samples. A three-point bend mode was chosen for this test, and each sample had dimensions of 37mm in length, 6 mm in width, and 3 mm in thickness. The span length was set at 10 mm by installing the appropriate three-point bend platform. The set-up of this test mode is illustrated in Figure 18. The sample was held at 25°C for one minute and was heated to 100°C at a heating rate of 2°C per minute. The frequency was set at 1 Hz. Two DMA measurements were performed on each sample to evaluate whether curing had advanced due to the first heating.

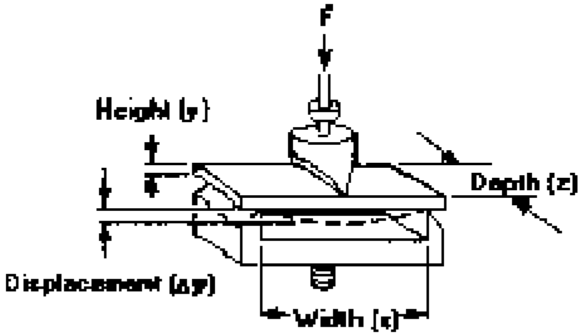


Figure 18: Three-Point Bending Measuring System[49]

2.6 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was also performed to monitor the degree of cure for the neat EPON® resin 828 / EPI-CURE® 3090 system, and a DuPont 2100 was utilized for this measurement. The sample was heated from 30°C to 175°C at a heating rate of 15°C per minute. DSC was performed one day after the resin was cured by the heating schedule.

2.7 Moisture Uptake of Neat Epoxy Bars

The moisture uptake of the neat epoxy bars during the aging experiments was monitored in this study. The moisture uptake equilibrium might not be established because the exposure time might not be long enough to reach the equilibrium state. The mass of epoxy bars was measured using a precision balance before the environmental exposure and again ten minutes after the completion of the aging experiment. The moisture uptake during curing for the neat EPON® resin 828 / EPI-CURE® 3090 system was also measured. The mass of the samples was measured after curing, and the samples were placed in the oven at 100°C for two days. The mass of the samples was measured again after the drying process.

---

[49] DMA Operator Manual

2.8 Bulk Density and Apparent Porosity Measurements for the Neat Epoxy Bars

Bulk density and apparent porosity of the neat EPON® resin 828 / EPI-CURE® 3090 samples were measured using a density kit. The sample holder consisted of a pan and a wire loop. The sample holder was attached onto the balance, and the balance was tared. The dry mass of a sample was measured by placing it in the pan of the sample holder. The wire loop portion of the sample holder was then submerged in ethanol, and the balance was tared again. The suspension mass of a sample was determined by placing it in the wire loop of the sample holder. The sample was removed from the wire loop, and it was lightly dabbed with paper towels. The saturated mass was measured by placing it on the pan of the sample holder. The bulk density and apparent porosity of each sample were measured before and after the aging experiment.

2.9 Failure Mode Analysis

The three-point flexure testing resulted in delamination of the resin from the substrate, and it was important to determine the locus of failure. The failure surface was defined to be the new surfaces on both the resin and steel sides of the interface formed by the debonding procedure.

2.9.1 EPON® resin 828/ dicyandiamide bonded joints

The failure mode of the EPON® 828/ dicyandiamide bonded steels was determined by inspecting the failure surface of the epoxy side using optical microscopy. The failed epoxy strip was placed on the microscope sample stage with the failure side facing up, and appropriate magnification was chosen for each specimen. Polaroid pictures were taken to show the failure surface.

The failed steel surface as well as the surface before the bonding procedure were examined using SEM. The specimen was cut to a suitable size to be fit onto a sample holder and was attached to the sample holder using a double sided tape. The SEM micrographs of the pre-bonding and post-failure surfaces will be compared to see if any epoxy was left on the substrate surface after failure.

2.9.2 EPON® resin 828 / EPI-CURE® 3090 bonded joints

The failure surfaces of the epoxy and the steel were examined using electron spectroscopy for chemical analysis (ESCA or XPS). The samples were attached to the sample mount using double stick tape and degassed in vacuum at 115°C overnight prior to the analysis. The spot size analyzed was 1mm x 1mm. The XPS spectra were obtained using a Perkin-Elmer PHI model 5400 photoelectron spectrometer. Mg Kα radiation was utilized to initiate photionization. All spectra were measured with the sample surface at an angle of 45^{o} with respect to the entrance to the electron analyzer. Areas under the peaks were used to determine the atomic percent concentrations.

Chapter 3 : RESULTS

3.1 Three-Point Bend Results For The Neat Epoxy Systems

The bending moduli of the neat epoxy bars were calculated using Equation 1.[3,50]

$$E_b = \frac{F * L^3}{4 * \delta * w * d^3}$$

Equation 1

E_b = bending modulus (GPa)
F = loading force (N)
L = span length (mm)
δ = deflection of the sample (mm)
w = width of the sample (mm)
d = thickness of the sample (mm)

The force (F) and the deflection (δ) were obtained from the force-deflection curve as the slope of the initial straight line for each sample. The slope and the sample dimensions were entered into the equation to determine the bending modulus for each epoxy sample.

3.1.1 EPON® resin 828/ dicyandiamide system

The bending moduli of the neat epoxy bars are shown in Figure 19. Each error bar shown in the figure represents the standard deviation of its corresponding data group. The bending modulus of the control group was calculated to be 1.45 GPa. The bending modulus decreased slightly and was evaluated to be 1.39 GPa and 1.45 GPa after one week of exposure in distilled water and in 3.4% NaCl solution respectively. After two weeks, the bending modulus decreased significantly to 0.99 GPa and 0.70 GPa after exposure in distilled water and in 3.4% NaCl solution respectively. There was an average of 4% decrease and no loss in the bending modulus after one week of exposure in

---

[50] F. P. Beer, E. R. Johnston, Jr., Mechanics of Materials, Second Edition, McGraw-Hill, Inc.,1992

distilled water and in 3.4% NaCl solution respectively; however, the bending modulus loss increased significantly to 32% and 52% after two weeks of exposure in distilled water and in 3.4% NaCl solution respectively. It was observed that the loss in modulus was not significant after one week and decreased more dramatically after two weeks. It was also observed that the effect of 3.4% NaCl solution was more detrimental to the loss in modulus than distilled water after two weeks of aging.

3.1.2 EPON® resin 828/EPI-CURE® 3090 system

The bending moduli of the EPON® resin 828/EPI-CURE® 3090 samples that were aged at constant temperature were analyzed using Equation 1, and the results are shown in Figure 20. Each error bar shown in the figure is the standard deviation of its corresponding data group. The bending modulus of the control group was 1.0 GPa. It decreased significantly to 0.43 GPa and 0.53 GPa after one week of aging in distilled water and in 3.4% NaCl solution respectively. After four weeks of aging time, it was determined to be 0.40 GPa and 0.35 GPa in distilled water and in 3.4% NaCl solution respectively. The modulus loss was 57% in distilled water and 47% in 3.4% NaCl solution after one week of exposure and was 60% and 65% after four weeks of exposure in distilled water and in 3.4% NaCl solution respectively. The modulus loss was significant after just one week of exposure time and remained steady after four weeks of exposure time. The effect of 3.4% NaCl solution on the modulus loss was more deleterious at longer exposure time.

The bending moduli of the EPON® resin 828/EPI-CURE® 3090 samples that were aged under the temperature cycling condition were calculated using Equation 1, and the results are shown in Figure 21. Each error bar in the figure is the standard deviation of its corresponding data group. The bending modulus was calculated to be 0.36 GPa and 0.38 GPa after one week of exposure in distilled water and in 3.4% NaCl solution respectively. After two weeks of aging, it was evaluated to be 0.44 GPa and 0.40 GPa in distilled water and in 3.4% NaCl solution respectively. The average modulus loss was calculated to be 64% and 62% after one week of exposure in distilled water and in 3.4% NaCl solution respectively. It was determined to be 56% and 60% after two weeks of aging in distilled water and in 3.4% NaCl solution respectively. The loss in modulus was dramatic after just one week of aging and remained approximately the same after two weeks. There was no significant difference in the loss of modulus with the environments and the exposure time.

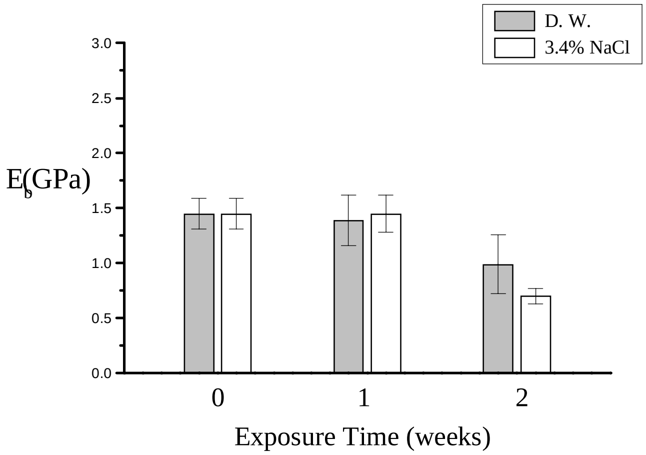


Figure 19: Bending Modulus of Neat EPON® 828 /Dicyandiamide system

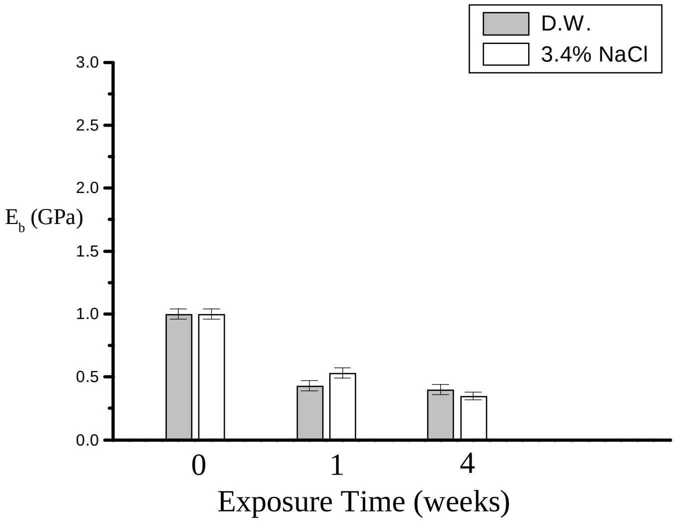


Figure 20: Bending Modulus of Neat EPON® 828 / EPI-CURE® 3090 system (constant aging temperature)

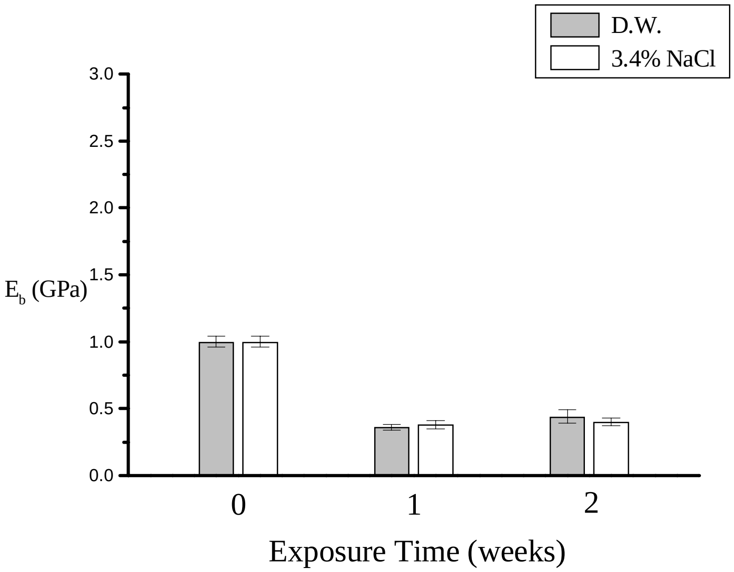
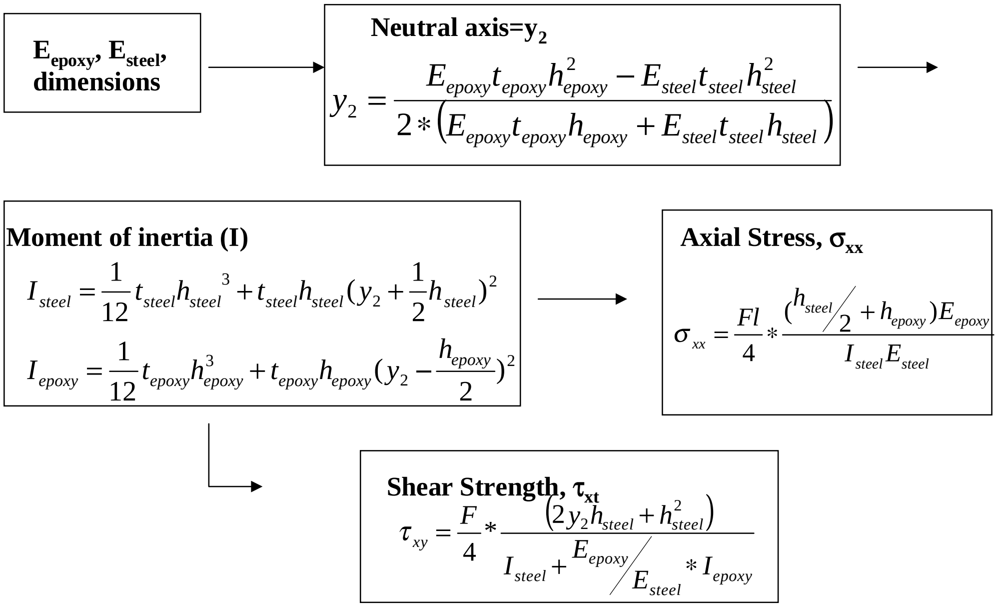


Figure 21: Bending Modulus of Neat EPON® 828 / EPI-CURE® 3090 system (cycling aging temperature)

3.2 Three-Point Bend Results For The Epoxy Bonded Joints

The analytical method that were used to evaluate the mechanical properties of the bonded joints is outlined in Figure 22. The equations that were used to calculate the mechanical properties of the epoxy bonded joints were derived in Appendix 1. The locations of the mechanical properties that were analyzed are illustrated in Figure 23.


E_{epoxy}, E_{steel}, dimensions

Neutral axis=y_2

$$y_2 = \frac{E_{epoxy} t_{epoxy} h_{epoxy}^2 - E_{steel} t_{steel} h_{steel}^2}{2 * \left(E_{epoxy} t_{epoxy} h_{epoxy} + E_{steel} t_{steel} h_{steel}\right)}$$

Moment of inertia (I)

$$I_{steel} = \frac{1}{12} t_{steel} h_{steel}{}^3 + t_{steel} h_{steel} (y_2 + \frac{1}{2} h_{steel})^2$$

$$I_{epoxy} = \frac{1}{12} t_{epoxy} h_{epoxy}^3 + t_{epoxy} h_{epoxy} (y_2 - \frac{h_{epoxy}}{2})^2$$

Axial Stress, σ_{xx}

$$\sigma_{xx} = \frac{Fl}{4} * \frac{(h_{steel}/2 + h_{epoxy}) E_{epoxy}}{I_{steel} E_{steel}}$$

Shear Strength, τ_{xt}

$$\tau_{xy} = \frac{F}{4} * \frac{\left(2 y_2 h_{steel} + h_{steel}^2\right)}{I_{steel} + E_{epoxy}/E_{steel} * I_{epoxy}}$$

Figure 22: Analytical Model for Mechanical Property Evaluation

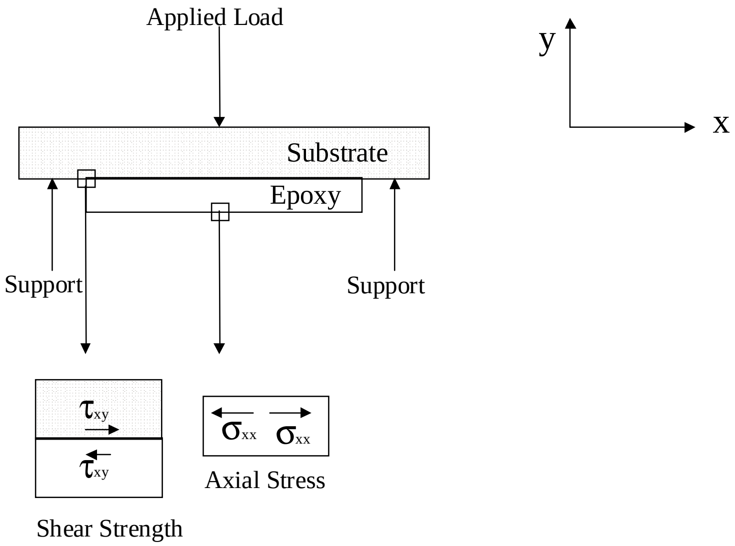


Figure 23: Locations of Mechanical Properties Analyzed

It was observed that all bonded samples failed when epoxy delaminated from the substrate; therefore, the shear strength between the substrate and the epoxy is the limiting failure mechanism.

3.2.1 EPON® 828 / Dicyandiamide Bonded Joints

The average shear strength and the average axial stress for the EPON® 828 / dicyandiamide bonded joints were calculated using the equations provided in Appendix 1. The shear strength results for the bonded joints that were aged in distilled water and in 3.4% NaCl solution are shown in Figure 24 and Figure 25 respectively. Each error bar shown in the figures represents the standard deviation of its corresponding data group. The maximum calculated axial stress of epoxy at failure was 34 MPa. The tensile strength of epoxy is 70 MPa. Thus, the axial stress in the resin when the interface failed was less than its tensile strength, and this confirmed the observation that the failure mechanism of the epoxy bonded joints resulted from epoxy delaminating from its substrate. If the axial stress had exceeded the tensile strength, the failure would have resulted from the epoxy failing in tension.

The average shear strength of the control group whose substrate was the soap and water scrubbed steel was calculated to be 0.93 MPa and decreased to 0.46 MPa and 0.05 MPa after one and two weeks of exposure in distilled water respectively. After one and two weeks of aging in 3.4% NaCl solution, the average shear strength decreased significantly to 0.08 MPa and 0.03 MPa. The loss in shear strength was 51% and 91% after one week of exposure in distilled water and in 3.4% NaCl solution respectively and was calculated to be 95% and 97% after two weeks of aging in distilled water and in 3.4% NaCl solution respectively. After just one week of aging in either environment, the bonded joints had lost most of their initial shear strength. It was observed that the bonded joints performed better in distilled water than in 3.4% NaCl solution.

The average shear strength of the control group whose substrate was the 220 grit sandpaper sanded steel was 0.37 MPa. The average shear strength decreased to 0.14 MPa and 0.06 MPa after one and two weeks of exposure in distilled water and reduced to 0.11

MPa and 0.03 MPa after one and two weeks of exposure in 3.4% NaCl solution. The average loss in shear strength was 62% and 70% after one week of aging in distilled water an in 3.4% NaCl solution respectively. It increased to 84% and 92% after two weeks in distilled water and in 3.4% NaCl solution respectively. The bonded joints had lost most of their original strength after two weeks of aging. It was again observed that the performance of the bonded joints was better in distilled water.

The average shear strength of the control group with the sandblasted substrate was 0.32 MPa. The average shear strength decreased to 0.12 MPa and 0.08 MPa after one and two weeks of aging in distilled water and reduced to 0.12 MPa and 0.03 MPa after one and two weeks of aging in 3.4% NaCl solution. There was a 63% decrease in shear strength after one week of exposure in distilled water or in 3.4% NaCl solution. The loss in shear strength increased to 75% and 91% after two weeks of exposure in distilled water and in 3.4% NaCl solution respectively. It was again observed that the bonded joints lost most of their initial shear strength after two weeks of aging. The 3.4% NaCl solution was more detrimental to the shear strength of the bonded joints.

3.2.2 EPON® 828 / EPI-CURE® 3090 Bonded Joints

The average shear strength and axial stress of the EPON® 828 / EPI-CURE® 3090 bonded joints were calculated using the equations outlined in Appendix 1. The shear strength results for the bonded joints that were aged in distilled water and in 3.4% NaCl solution are shown in Figure 26 and Figure 27 respectively. Each error bar in the figures is the standard deviation of its corresponding data group. The maximum axial stress in the resin when the interface failed was 14 MPa which was less than its tensile strength of 70 MPa. This further confirmed the observation that the failure resulted from epoxy delaminating from the substrate. If the axial stress exceeded the tensile strength, the epoxy would have failed in tension instead of delaminating from the substrate.

The average shear strength of the control group whose substrate was acetone wiped was 0.43 MPa. The average shear strength decreased to 0.14 MPa, 0.11 MPa, and 0.09 MPa after one, two, and four weeks of exposure in distilled water. They were calculated to be 0.15 MPa, 0.14 MPa, and 0.07 MPa after one, two, and four weeks of aging in 3.4% NaCl solution. After one week of exposure in distilled water, there was a 67% loss in the shear strength. The loss in shear strength, between 74% and 79%, was gradual after two and four weeks of exposure in distilled water. The decrease in shear strength was 65% after one week of exposure in 3.4% NaCl solution. The decrease in shear strength was 67% and 84% after two and four weeks of aging in 3.4% NaCl solution. There is no significant difference in the shear strength of bonded joints between the two environments.

The average shear strength of the control group whose substrate was corroded was calculated to be 0.47 MPa. The average shear strength decreased to 0.19MPa, 0.15 MPa, and 0.12 MPa after one, two, and four weeks of aging in distilled water and declined to 0.20 MPa, 0.18 MPa, and 0.10 MPa after one, two, and four weeks of exposure in 3.4% NaCl solution. The loss in shear strength was 60% and 57% after one week of exposure in distilled water and in 3.4% NaCl solution respectively. It increased gradually to 68% and 74% after two and four weeks of aging in distilled water respectively, and it augmented slightly to 62% and 79% after two and four weeks of exposure in 3.4% NaCl solution. The difference in shear strength loss was not significant between the environments.

The shear strength results for the bonded joints that were aged in distilled water and in 3.4% NaCl solution under the cycling temperature condition are shown in Figure 28 and Figure 29 respectively. Each error bar in the figures is the standard deviation of its corresponding data group. The maximum axial stress in the epoxy at failure of the interface failed was 14 MPa and was less than the tensile strength of 70 MPa. This suggested that the epoxy did not fracture in tension and that failure resulted from the epoxy delamination.

The average shear strength of the sample groups whose substrate was acetone wiped were 0.17 MPa and 0.17 MPa after one and two weeks of exposure in distilled water and was 0.18 MPa and 0.15 MPa after one and two weeks of aging in 3.4% NaCl solution. There was a 60% decrease in shear strength after one week of exposure in distilled water, and there was no further shear strength loss after two weeks. The loss in shear strength was 58% and 65% after one and two weeks of aging in 3.4% NaCl solution respectively. The difference in shear strength loss was not significant between environments.

The average shear strength of the sample groups whose substrate was corroded was 0.19 MPa and 0.15 MPa after one and two weeks of exposure in distilled water and was 0.17 MPa and 0.12 MPa after one and two weeks of aging in 3.4% NaCl solution. The loss in shear strength was 60% and 68% after one and two weeks of exposure in distilled water and was 64% and 74% after one and two weeks of aging in 3.4% NaCl solution respectively. It was again observed that the difference in shear strength loss was not significant between environments.

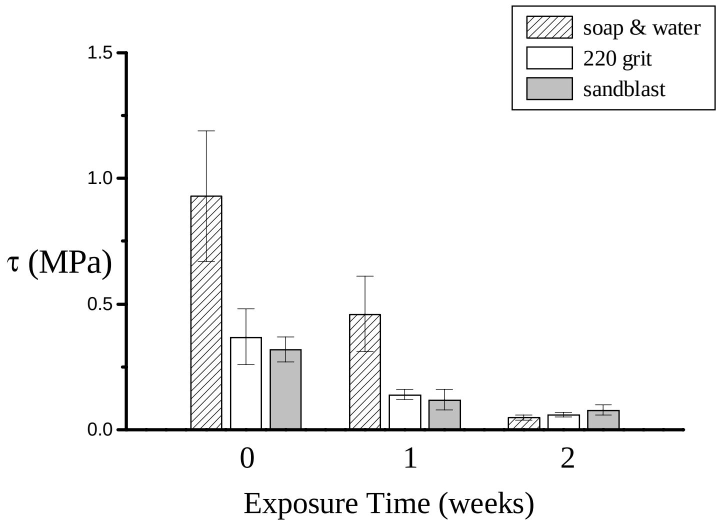


Figure 24: Average shear strengths of EPON® 828/Dicyandiamide bonded joints in distilled water

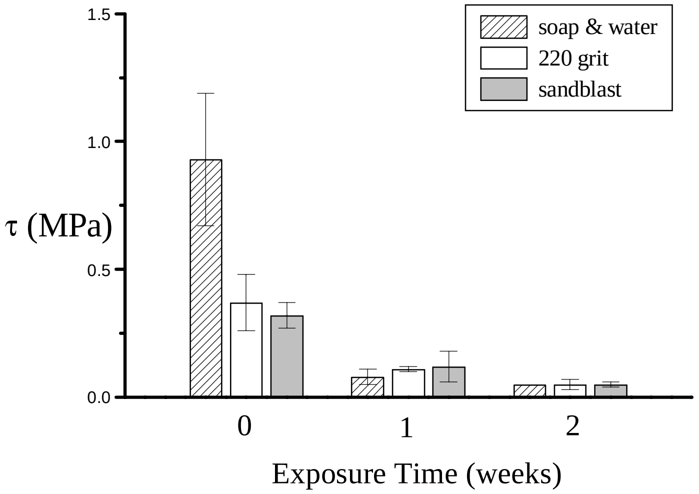


Figure 25: Average shear strengths of EPON® 828/Dicyandiamide bonded joints in 3.4% NaCl solution

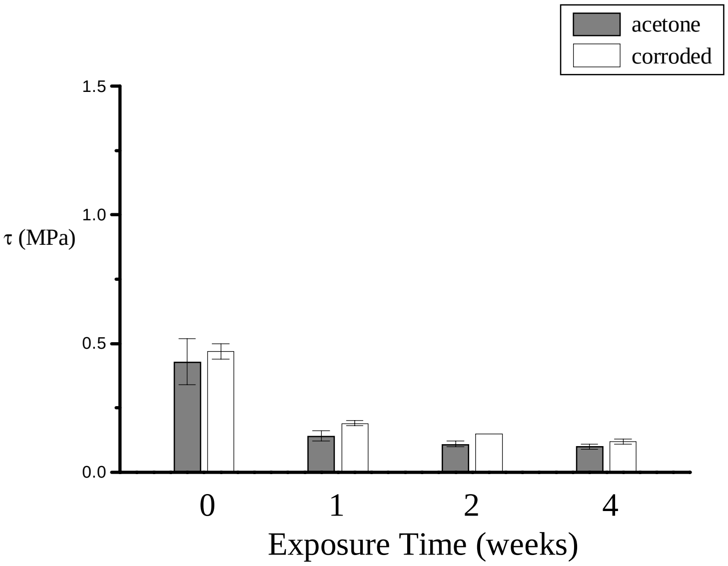


Figure 26: Average Shear Strengths of EPON® 828/ EPI-CURE® 3090 bonded joints in distilled water at 50°C

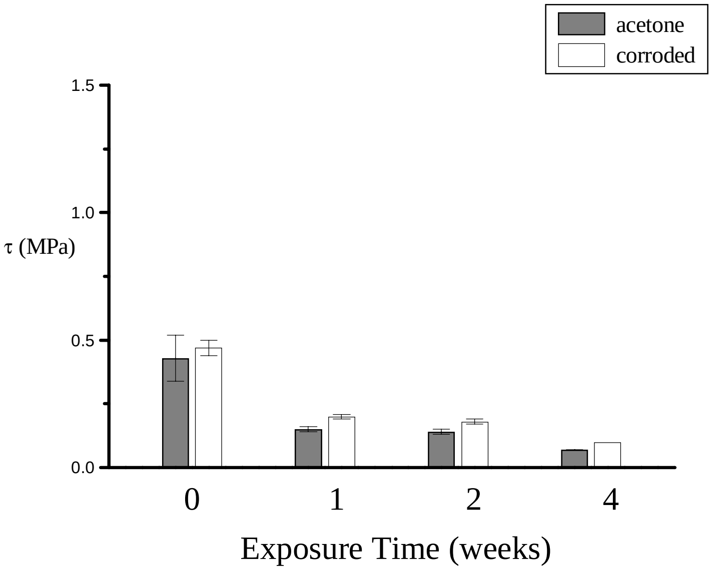


Figure 27: Average shear strengths of EPON® 828/ EPI-CURE® 3090 bonded joints in 3.4% NaCl solution at 50°C

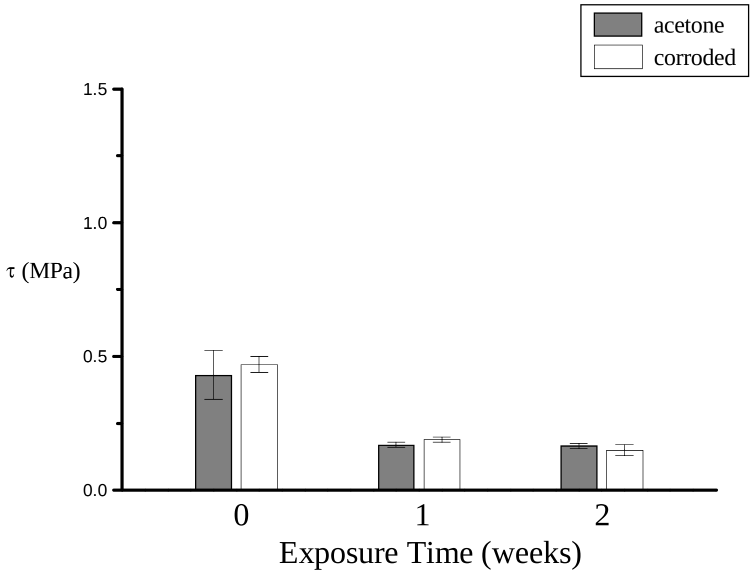


Figure 28: Average shear strengths of EPON® 828/ EPI-CURE® 3090 bonded joints in distilled water, 25°C – 50°C

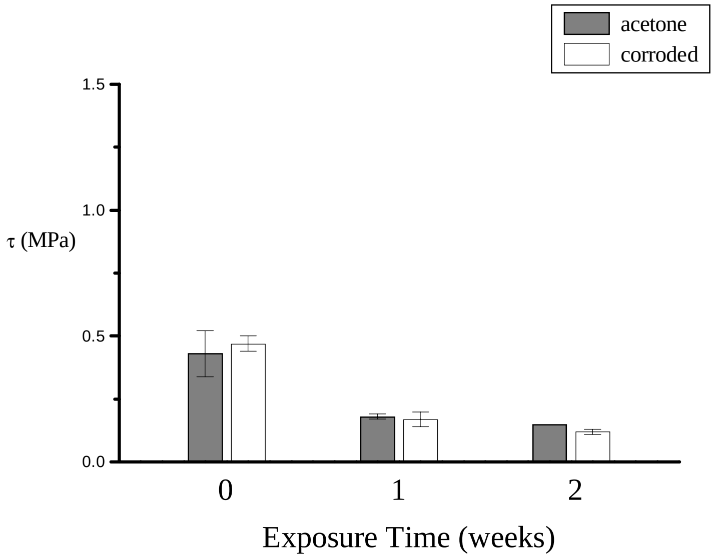


Figure 29: Average shear strengths of EPON® 828/ EPI-CURE® 3090 bonded joints in 3.4% NaCl solution, 25°C – 50°C

3.3 Dynamic Mechanical Analysis

The T_g of the neat EPON® resin 828 / EPI-CURE® 3090 system was defined as the peak of the tanδ curve. The accuracy of the T_g results is estimated to be within 3°C. Figure 30 shows the result for an unaged epoxy sample. The results for the samples that were aged in distilled water and in 3.4% NaCl solution for one week are shown in Figure 31 and Figure 32 respectively. Figure 33 and Figure 34 show the results for the samples that were aged in distilled water and in 3.4% NaCl solution for two week. The DMA results for the samples that were aged in distilled water and in 3.4% NaCl solution for four weeks are shown in Figure 35 and Figure 36. The T_g of a typical unaged sample was 55°C for the first scan and increased 60°C for the second scan. The T_g was 46°C and 55°C for the first and second scans after one week of exposure in distilled water, and it was 46°C and 56°C for the first and second scans after one week of aging in 3.4% NaCl solution. The T_g was 48°C and 58°C for the first and second scans after two weeks of exposure in distilled water, and it was 60°C and 65°C after two weeks of aging in 3.4% NaCl solution. The T_g was 50°C and 60°C for the first and second scans after four weeks of aging in distilled water, and it was 55°C and 60°C for the first and second scans after four weeks of exposure in 3.4% NaCl solution. The differences in the T_g were observed to be approximately within the experimental error.

The tanδ curves were observed to have broad shape. This indicates the presence of wide distribution of relaxation time or distribution of cross-link density in the epoxy resin. After the first heat scan, the epoxy resin might have further cured which resulted in a higher T_g in the second heat scan. The moisture absorbed during the aging experiment might have evaporated from the heat during the first heat scan which could also result in the higher T_g observed from the second heat scan. Figure 34 shows two distinct peaks in the tanδ curve indicating that two T_gs were observed. This suggested that phase separation in the epoxy resin had taken place, which might have resulted from different cross-link density within the resin.

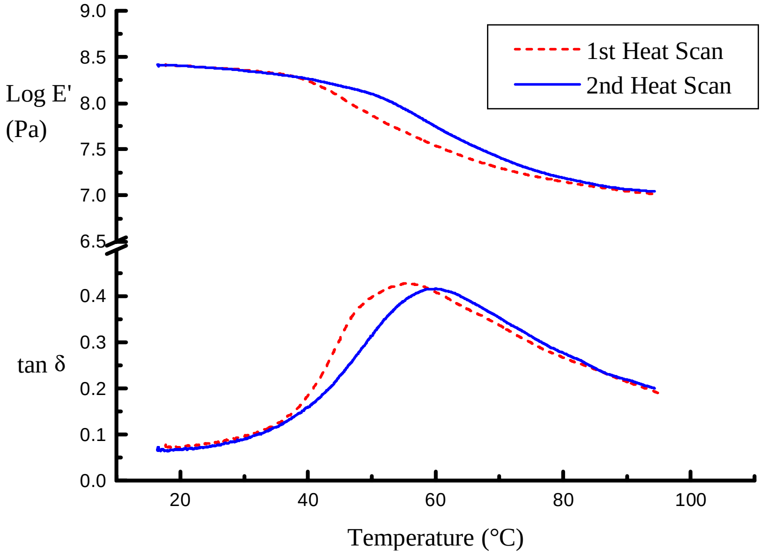


Figure 30: DMA for an unaged sample

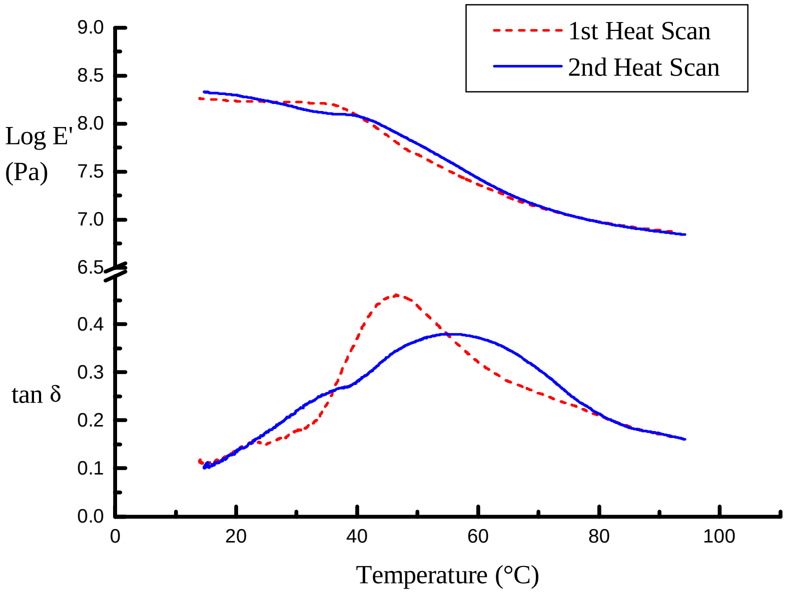


Figure 31: DMA for a sample aged in distilled water for one week

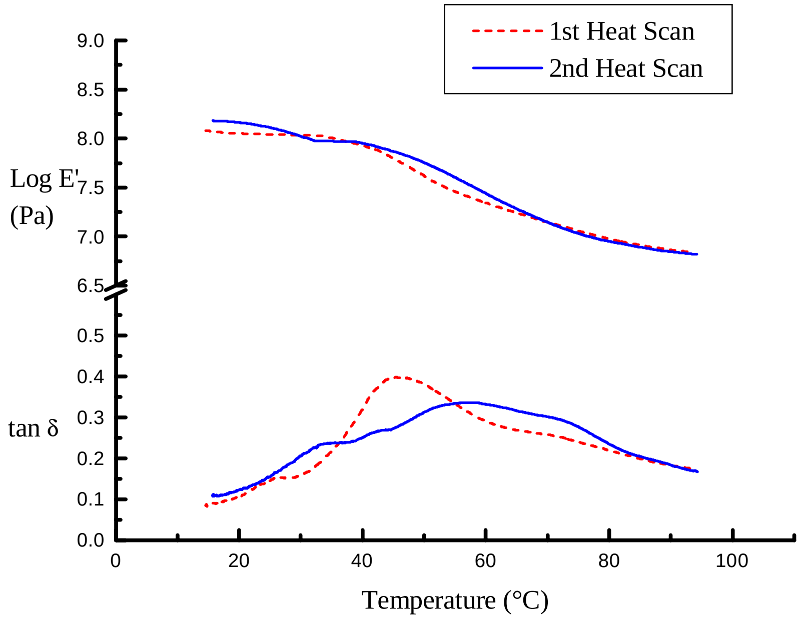


Figure 32: DMA for a sample aged in 3.4% NaCl solution for one week

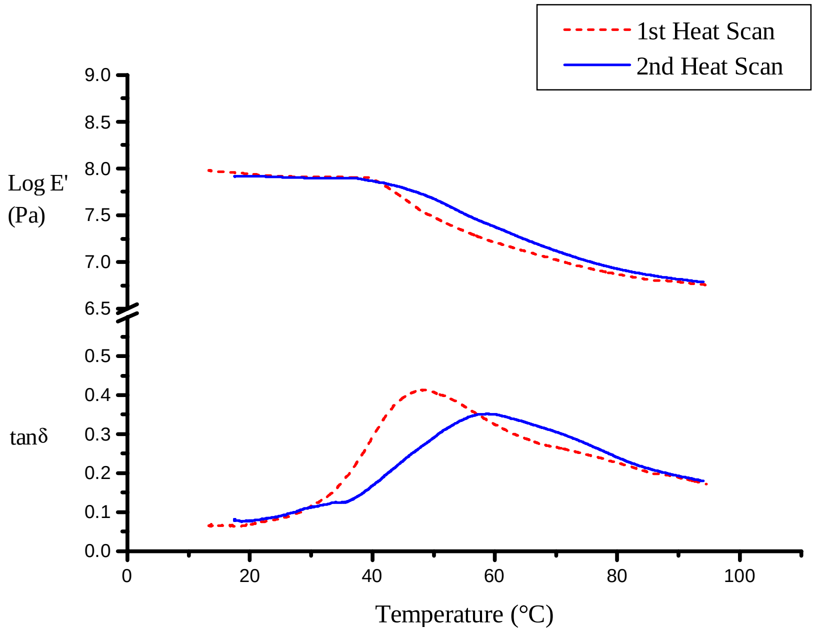


Figure 33: DMA for a sample aged in distilled water for two weeks

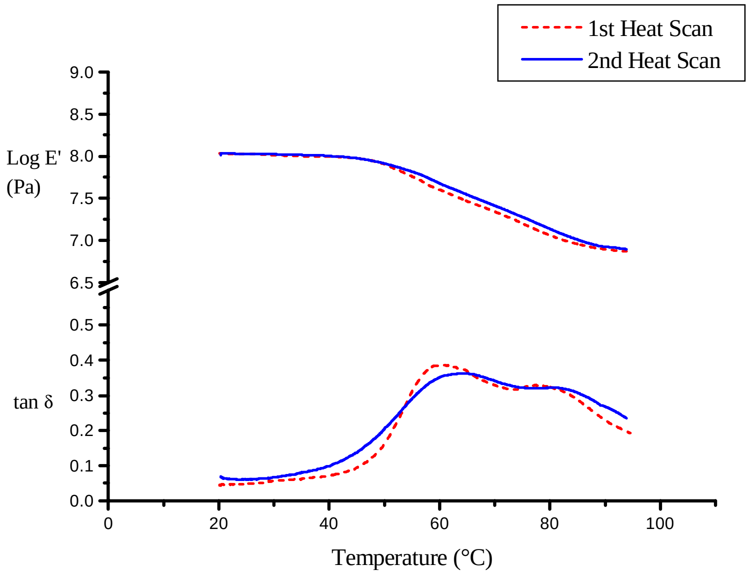


Figure 34: DMA for a sample aged in 3.4% NaCl solution for two weeks

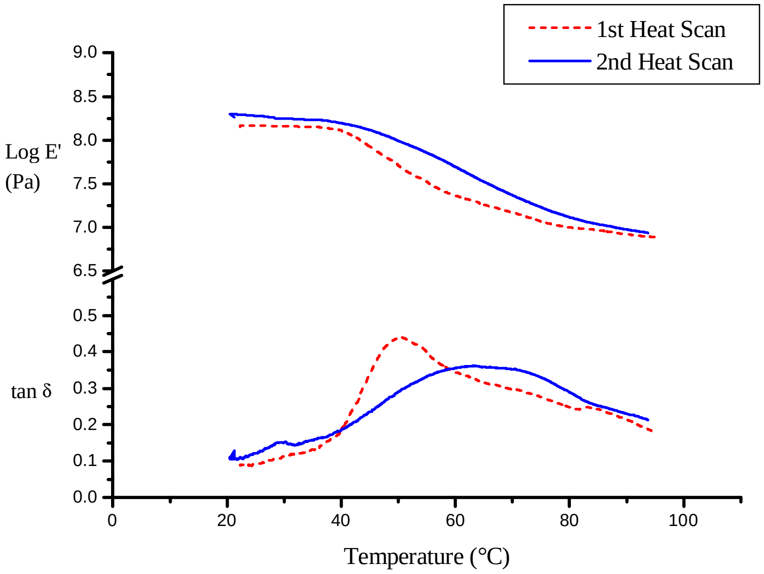


Figure 35: DMA for a sample aged in distilled water for four weeks

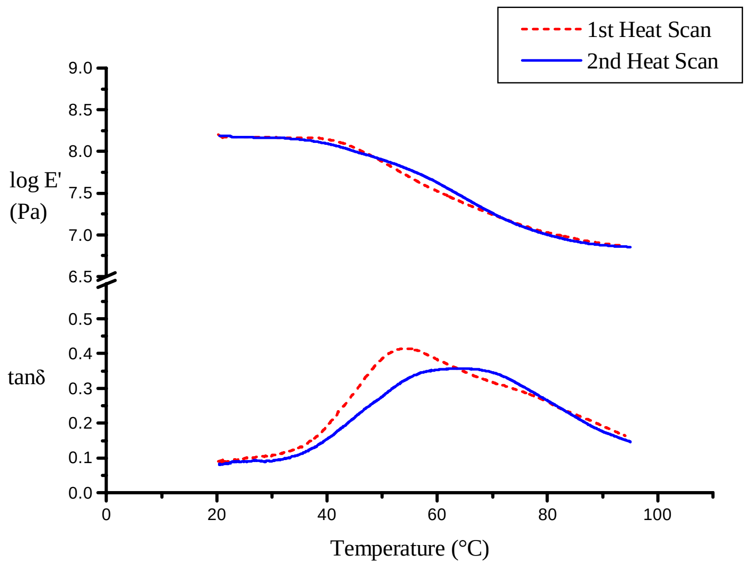


Figure 36: DMA for a sample aged in 3.4% NaCl solution for four weeks

The DMA results for the samples that were aged under the cycling temperature condition are shown in Figure 37 and Figure 38 for the samples that were aged for one week in distilled water and in 3.4% NaCl solution respectively and in Figure 39 and Figure 40 for the samples that were aged in distilled water and in 3.4% NaCl solution for two weeks respectively.

The T_g was 50°C and 60°C for the first and second scans after one week in distilled water, and it was 50°C and 58°C for the first and second scans after one week in 3.4% NaCl solution. The T_g was 55°C and 60°C for the first and second scans after two weeks in distilled water, and it was 60°C and 65°C for the first and second scans after two weeks in 3.4% NaCl solution. The differences in the T_g were approximately within the experimental error. There was no significant change in the T_g with environments and aging time.

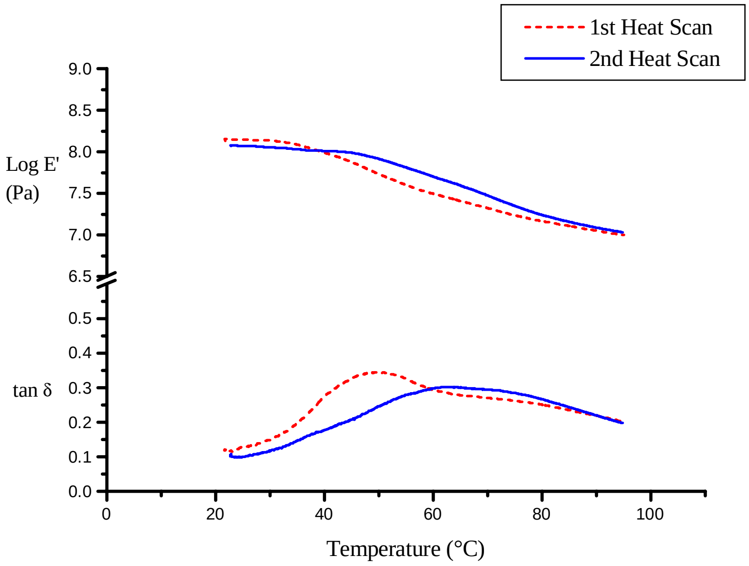


Figure 37: DMA for a sample aged in distilled water for one week

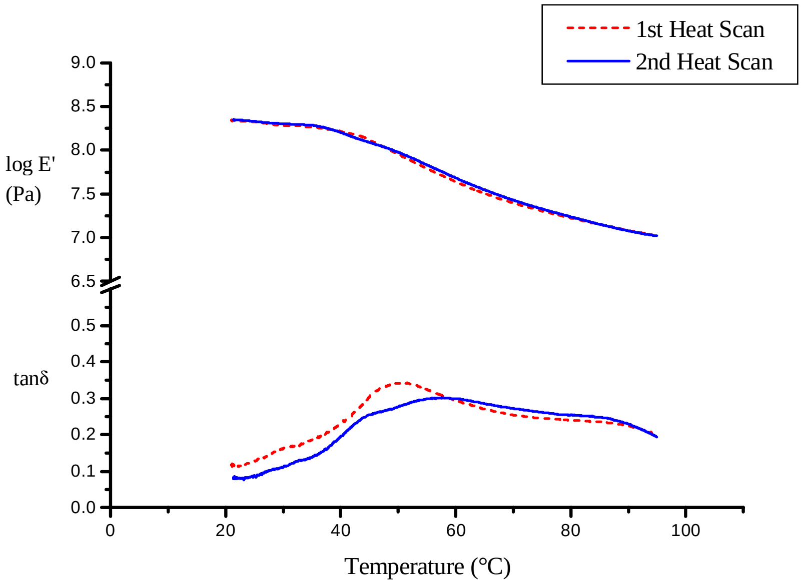


Figure 38: DMA for a sample aged in 3.4% NaCl solution for one week

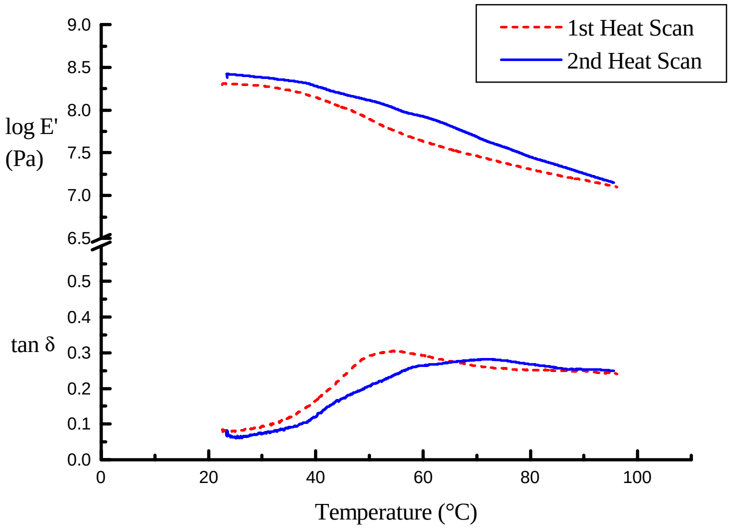


Figure 39: DMA for a sample aged in distilled water for two weeks

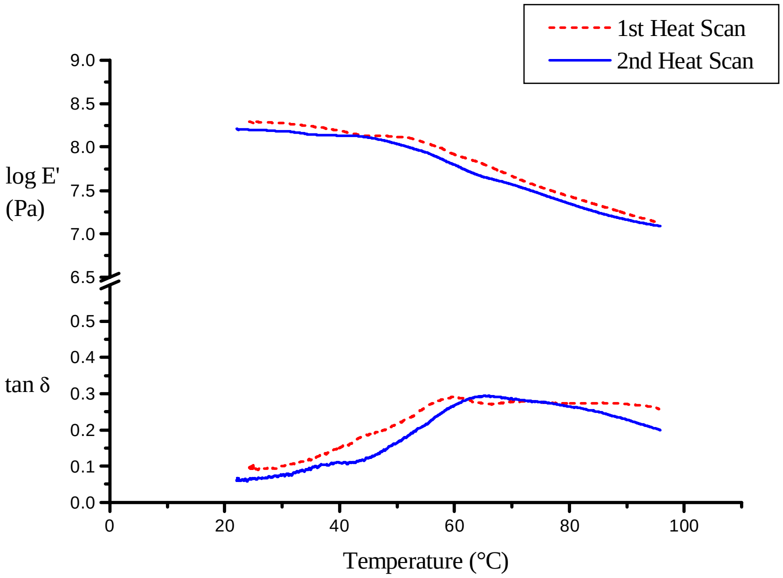


Figure 40: DMA for a sample aged in 3.4% NaCl solution for two weeks

3.4 Differential Scanning Calorimetry (DSC)

The DSC results of the neat EPON® resin 828 / EPI-CURE® 3090 system are illustrated in Figure 41 for first heat scan and in Figure 42 for second heat scan.

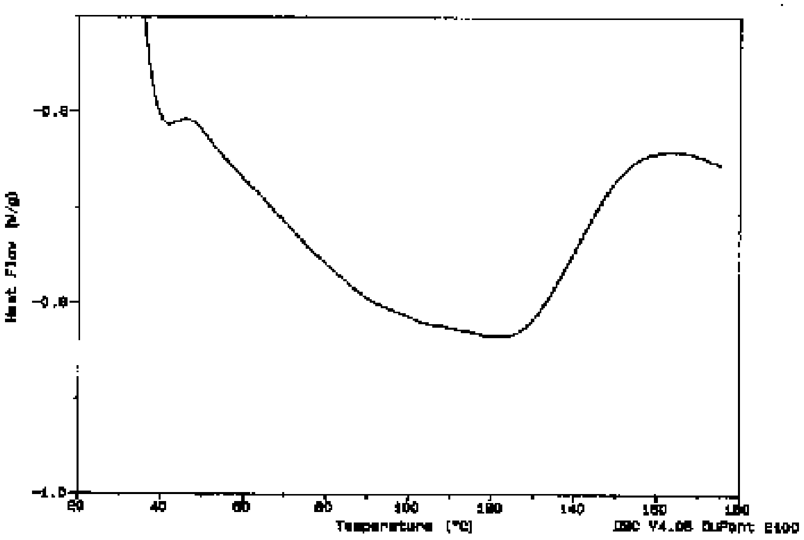


Figure 41: DSC for a neat EPON® resin 828 / EPI-CURE® 3090 sample, first heat

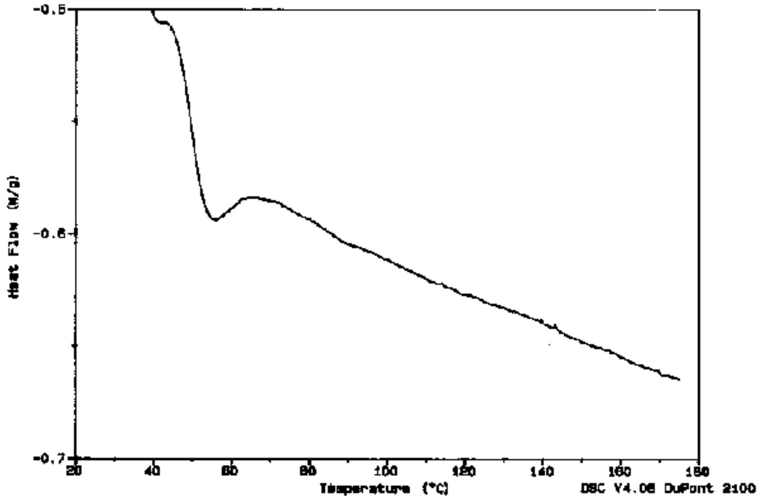


Figure 42: DSC for a neat EPON® resin 828 / EPI-CURE® 3090 sample, second heat

3.5 Bulk Density and Apparent Porosity

The bulk density and the apparent porosity of the neat EPON® resin 828 / EPI-CURE® 3090 samples were calculated using the following equations.[51]

$$V = \frac{M - S}{\rho} \quad \text{Equation 2}$$

V = exterior volume
M = saturated mass
ρ = density of ethanol = 0.785g/cc

$$P = \left[(M - D)/V/\rho\right] * 100 \quad \text{Equation 3}$$

P = apparent porosity
D = dry mass

$$B = \frac{D}{V`} \quad \text{Equation 4}$$

B = bulk density

The results for the bulk density and the apparent porosity of the neat epoxy samples are illustrated in Figure 43 and Figure 44 respectively. Each error bar in the figures is the standard deviation of its corresponding data group.

The initial bulk density of the samples before aging was 1.07 g/cc. The bulk density was 1.09 g/cc and 1.08 g/cc after one week of exposure in distilled water and in 3.4% NaCl solution respectively. It was 1.10 g/cc and 1.09 g/cc after two weeks of aging in distilled water and in 3.4% NaCl solution respectively. After four weeks of exposure in distilled water and in 3.4% NaCl solution, the bulk density was 1.08 g/cc and 1.09 g/cc

---

[51] Standard Test Method for Water Absorption, Bulk Density, Apparent Porosity, and Apparent Specific Gravity, C 373-88

respectively. There was no significant change in bulk density with environments and aging time.

The initial apparent porosity was calculated to be 0.53%. It was 0.51% and 0.41% after one week of aging in distilled water and in 3.4% NaCl solution respectively. The apparent porosity was 0.09% and 0.28% after two weeks of exposure in distilled water and in 3.4% NaCl solution respectively. It was 0.30% and 0.49% after four weeks of aging in distilled water and 3.4% NaCl solution respectively.

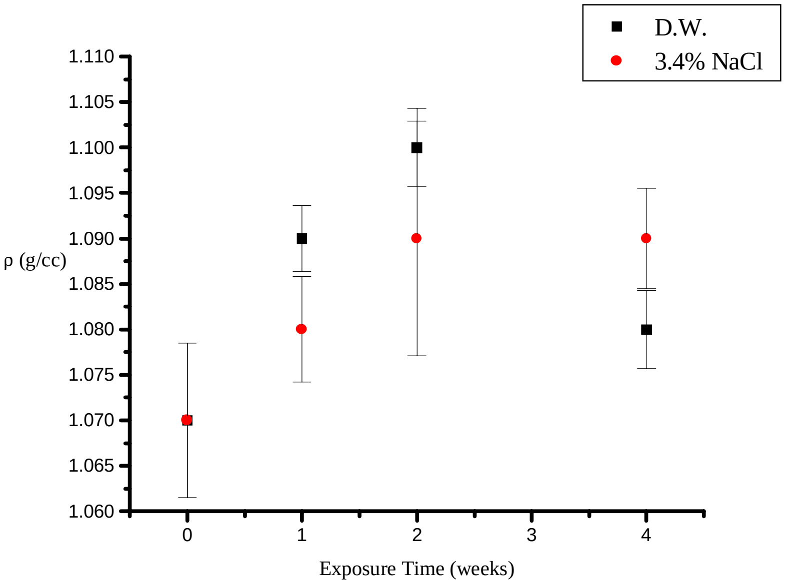


Figure 43: Density of neat EPON® resin 828 / EPI-CURE® 3090 system

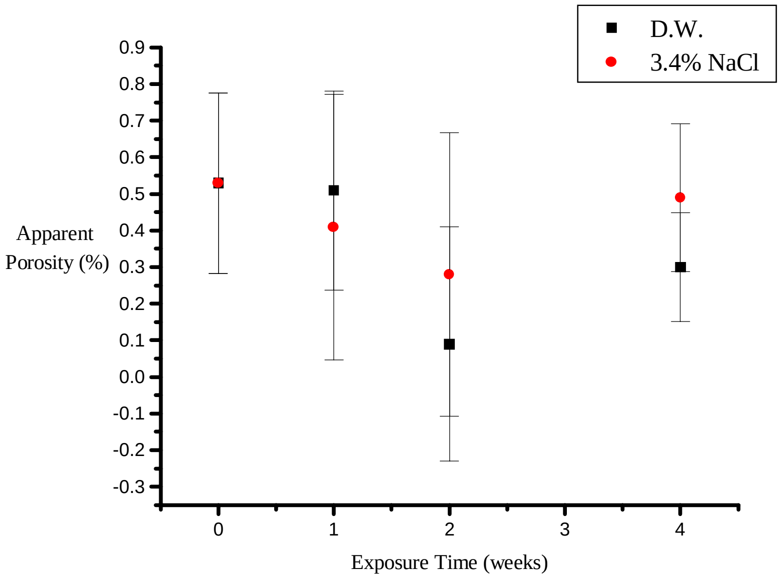


Figure 44: Apparent Porosity of the neat EPON® resin 828 / EPI-CURE® 3090 system

3.6 Moisture Uptake Results For Neat Epoxy Systems

The moisture uptake of the neat epoxy systems was calculated using the following equation.

$$m = \frac{w_f - w_i}{w_i} \times 100 \qquad \text{Equation 5}$$

m = moisture uptake

w_f = mass after aging

w_i = mass before aging

3.6.1 EPON® resin 828/ dicyandiamide system

The moisture uptake for the EPON® resin 828/ dicyandiamide system is illustrated in Figure 45. Each error bar in the figure is the standard deviation of its corresponding data group. The average moisture uptake for the neat epoxy samples was 3.96% in distilled water and 3.21% in 3.4 NaCl solution after one week and 8.51% and

8.70% in distilled water and in 3.4% NaCl solution respectively after two weeks. It was observed that moisture uptake increased with exposure time in both environments.

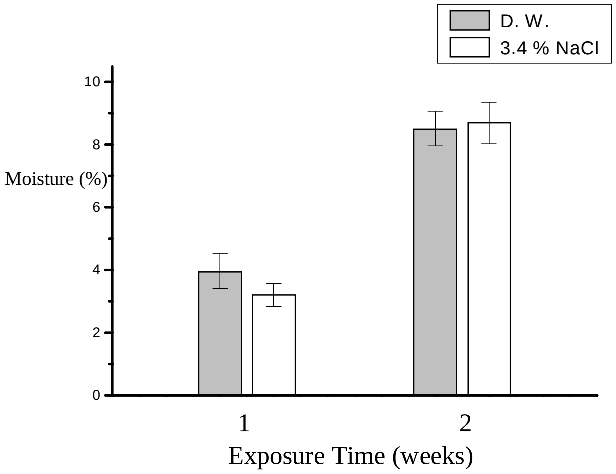


Figure 45: Moisture Uptake for the EPON® resin 828/ dicyandiamide system

3.6.2 EPON® 828 / EPI-CURE® 3090 System

The moisture uptake during curing was measured to be 4.0%. The moisture uptake results for the EPON® 828 / EPI-CURE® 3090 samples that were aged at 50°C are shown in Figure 46, and the results for the samples that were aged under the cycling temperature scheme are illustrated in Figure 47. Each error bar in the figures is the standard deviation of its corresponding data group. The average moisture uptake for the samples that were aged at 50°C was 2.6%, 6.5%, and 5.3% after one, two, and four weeks of aging in the distilled water respectively. The average moisture uptake was 2.2%, 6.1%, and 5.5% after one, two, and four weeks of aging respectively in the 3.4% NaCl solution. It was observed that the moisture uptake increased with exposure time and the change in moisture uptake was not significant after two weeks of exposure in either environment.

The average moisture uptake for the samples that were aged under the cycling temperature condition was 2.3% in distilled water and 2.2% in 3.4% NaCl solution respectively after one week and 2.0% in distilled water and 2.0% in 3.4% NaCl solution respectively after two weeks. It was observed that the change in moisture uptake with exposure time was not significant in either environment.

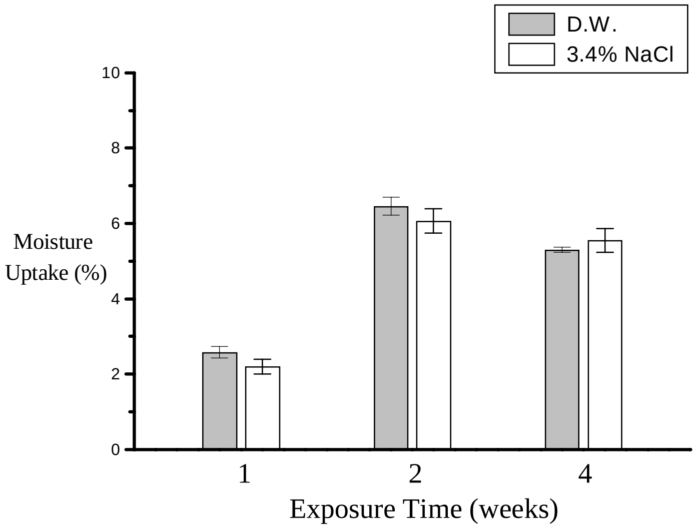


Figure 46: Moisture Uptake for the EPON® 828 / EPI-CURE® 3090 System (50°C)

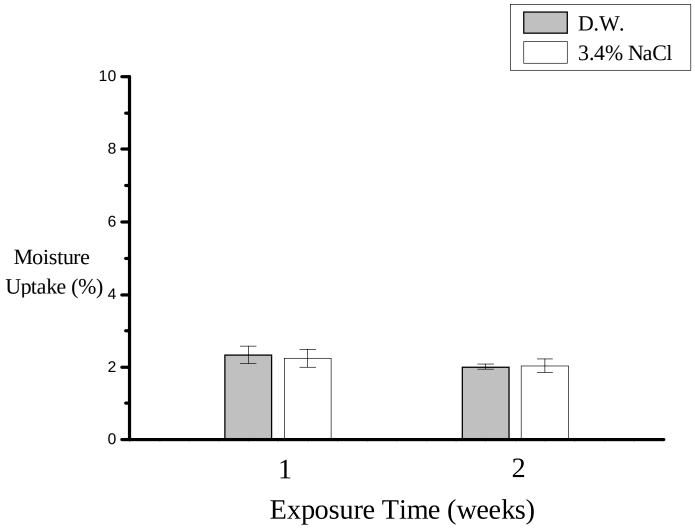


Figure 47: Moisture Uptake for the EPON® 828 / EPI-CURE® 3090 System (25-50°C)

3.7 Failure Mode Analysis Results

3.7.1 EPON® resin 828/ dicyandiamide bonded joints

The failed epoxy surfaces were examined with an optical microscope, and the results are shown in the following figures. Figure 48 and Figure 49 show the epoxy that was bonded to the soap and water scrubbed steel. Figure 50 and Figure 51 show the epoxy that was bonded to the sanded steel. Figure 52 and Figure 53 show the epoxy that was bonded to the sandblasted steel. The dark area represented the corrosion products on the steel surface, and the light area represented the epoxy.

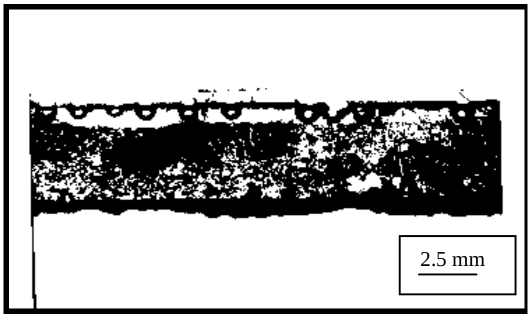


Figure 48: Failed Epoxy Surface, was bonded to the soap and water scrubbed steel

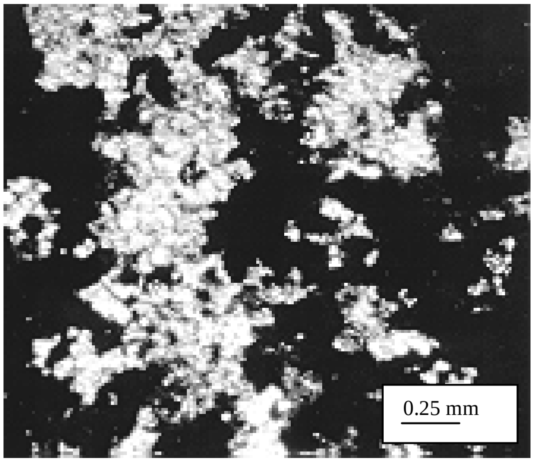


Figure 49: Failed Epoxy Surface, was bonded to the soap and water scrubbed steel

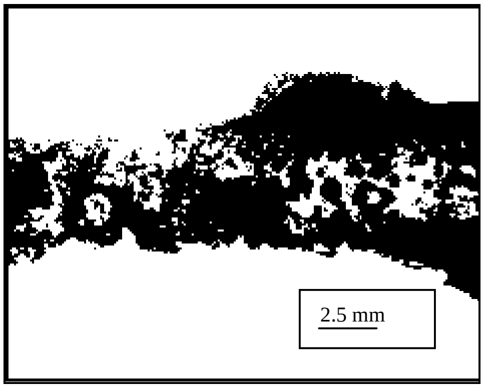


Figure 50: Failed Epoxy Surface, was bonded to the sanded steel

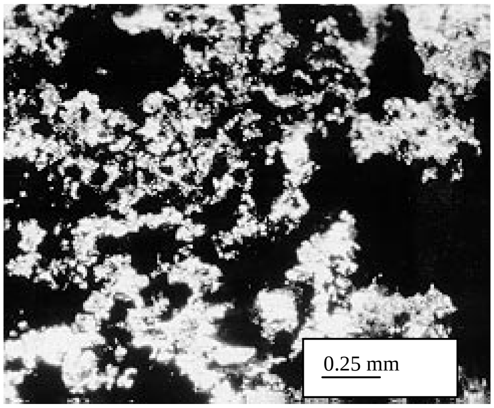


Figure 51: Failed Epoxy Surface, was bonded to the sanded steel

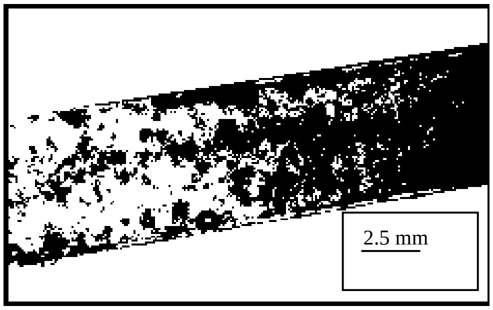


Figure 52: Failed Epoxy Surface, was bonded to the sandblasted steel

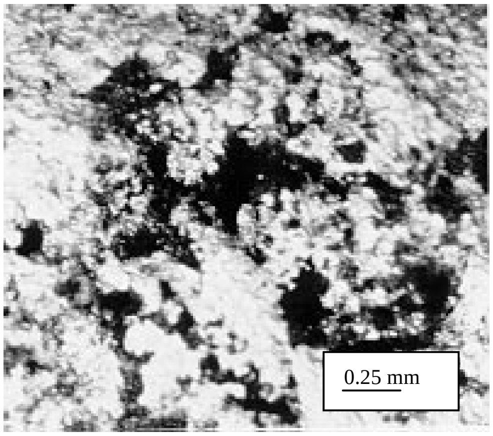


Figure 53: Failed Epoxy Surface, was bonded to the sandblasted steel

SEM was used to investigate the failed steel surfaces, and the results are shown in Figure 54 for the soap and water scrubbed substrate and Figure 55 for the sanded substrate.

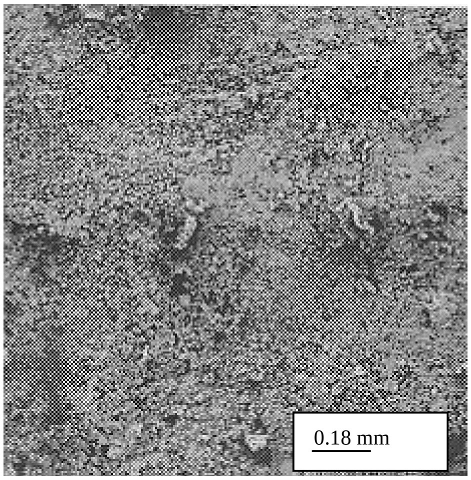


Figure 54: SEM of steel failure surface, soap and water scrubbed

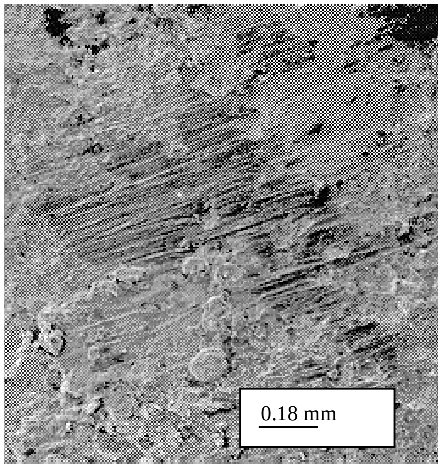


Figure 55: SEM of steel failure surface, 220 grit sandpaper sanded

3.7.2 EPON® 828 / EPI-CURE® 3090 bonded joints

The failure surfaces of the epoxy and the steel were analyzed using XPS. The spectra for the epoxy that was bonded to the acetone wiped steel are shown in Figures 56-62. Figure 56 shows the survey spectrum, and Figures 57-62 show the multiplex spectra for individual elements. The spectra for the acetone wiped steel failure surface are included in Figure 63 for the survey spectrum and in Figures 64-70 for multiplex spectra. The spectra for the epoxy that was bonded to the corroded steel are illustrated in Figure 71 for the survey spectrum and in Figures 72-74 for the multiplex spectra. The spectra for the corroded steel failure surface are shown in Figure 75 for the survey spectrum and in Figures 76-78 for elemental spectra. The concentration of each element was determined from the areas under the peaks. The results for the epoxy that was bonded to the acetone wiped steel are included in Table 3.1 and for the acetone wiped steel are included in Table 3.2. The results for the epoxy that was bonded to the corroded steel are shown in Table 3.3 and for the corroded steel failure surface are shown in Table 3.4.

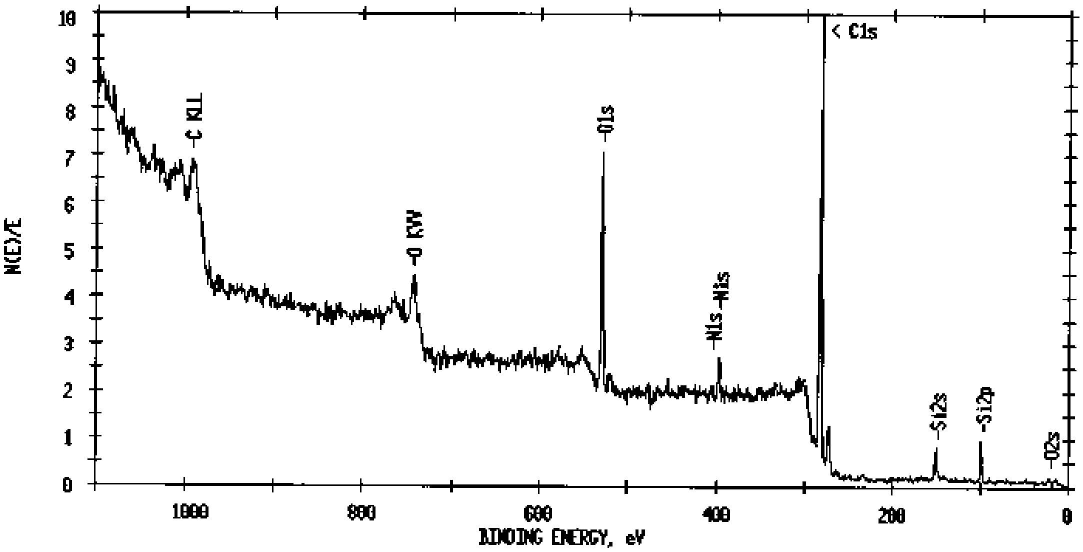


Figure 56: XPS survey spectrum of epoxy failure surface, scale factor= 1.037 k c/s, offset= 0.076 k c/s, pass energy= 44.750 eV

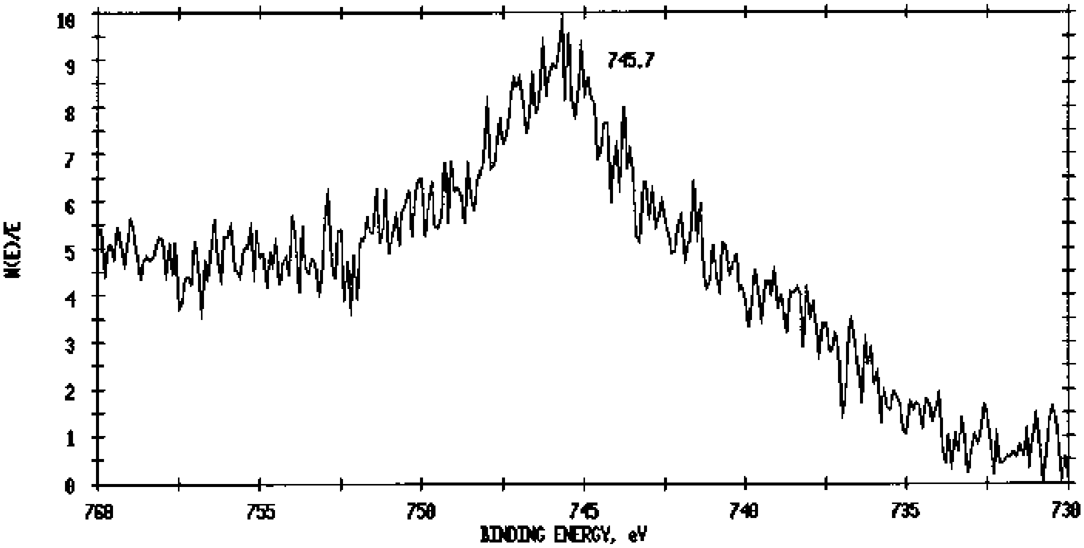


Figure 57: XPS multiplex spectrum for O_{KVV}, scale factor= 0.053 k c/s, offset= 0.800 k c/s, pass energy= 17.900 eV

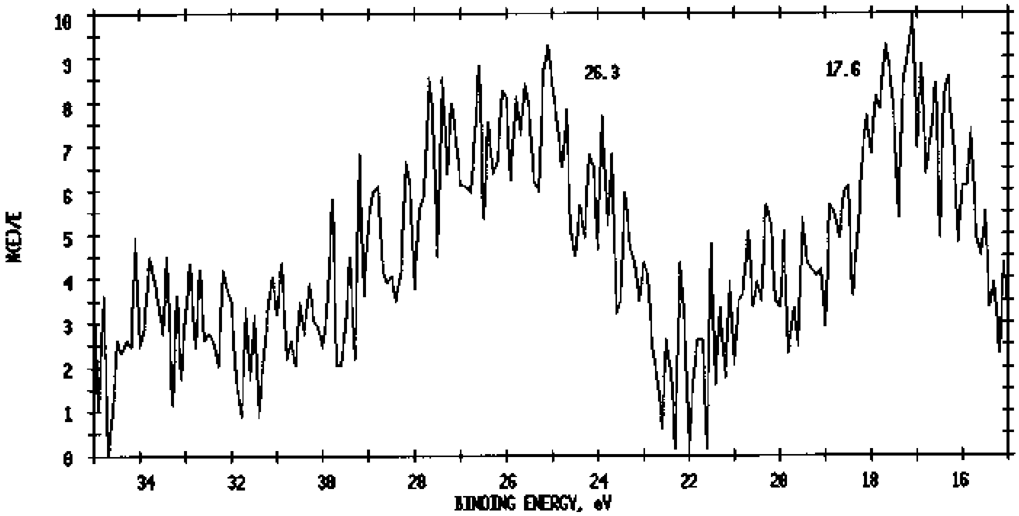


Figure 58: XPS multiplex spectrum for O_{2s}, scale factor= 0.005 k c/s, offset= 0.039 k c/s, pass energy= 17.900eV

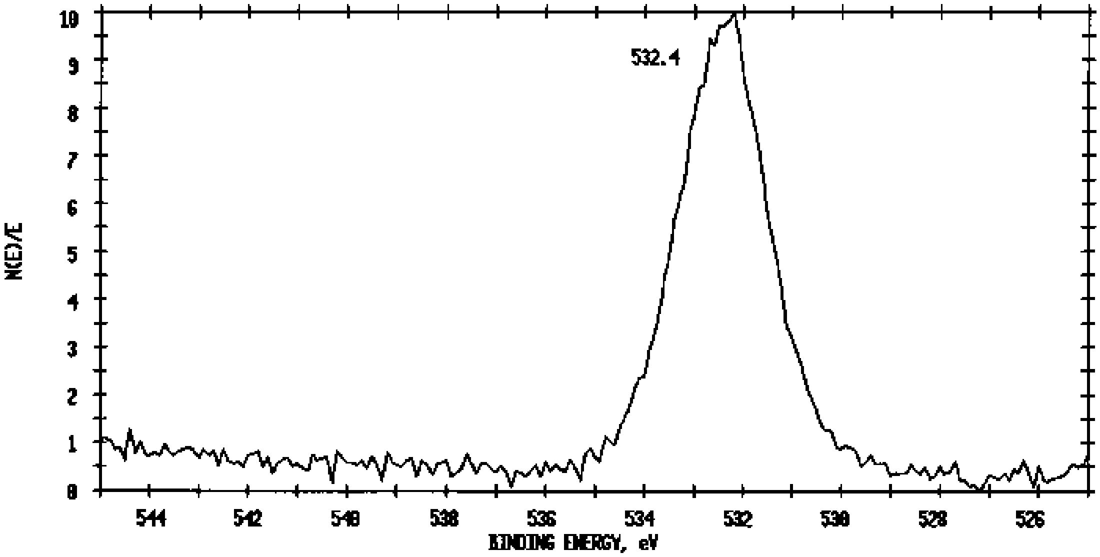


Figure 59: XPS multiplex spectrum for O_{1s}, scale factor= 0.170 k c/s, offset= 0.598 k c/s, pass energy= 17.900 eV

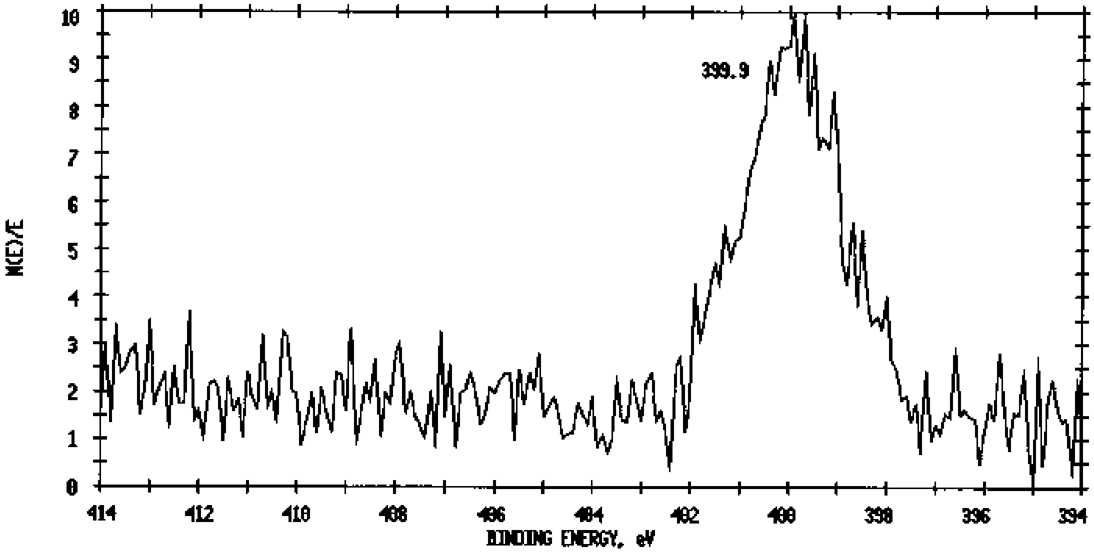


Figure 60: XPS multiplex spectrum for N_{1s}, scale factor= 0.034k c/s, offset= 0.552 k c/s, pass energy= 17.900eV

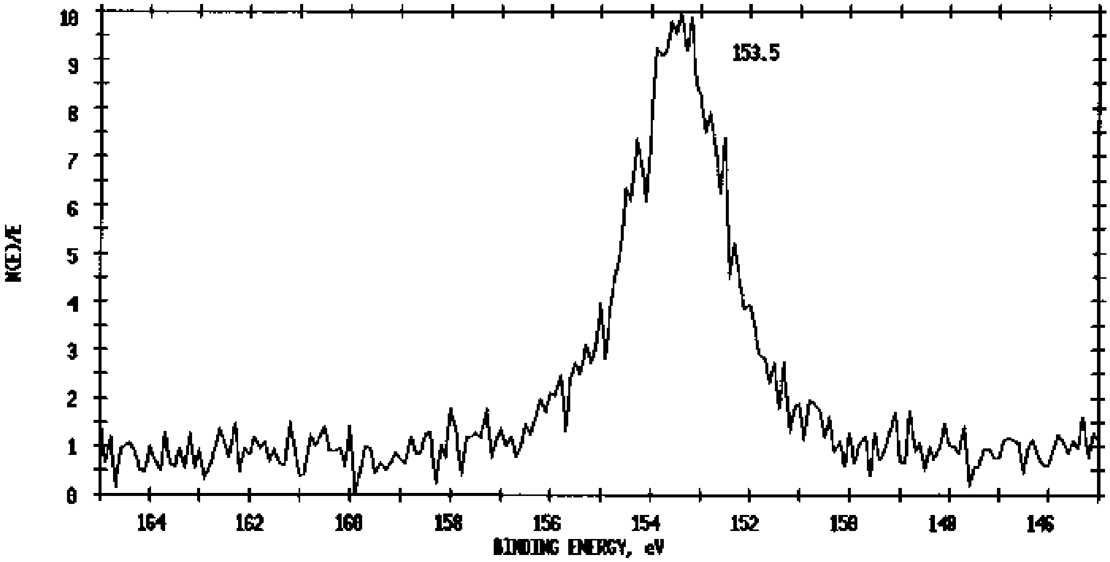


Figure 61: XPS multiplex spectrum for Si_{2s}, scale factor= 0.022 k c/s, offset= 0.058 k c/s, pass energy= 17.900 eV

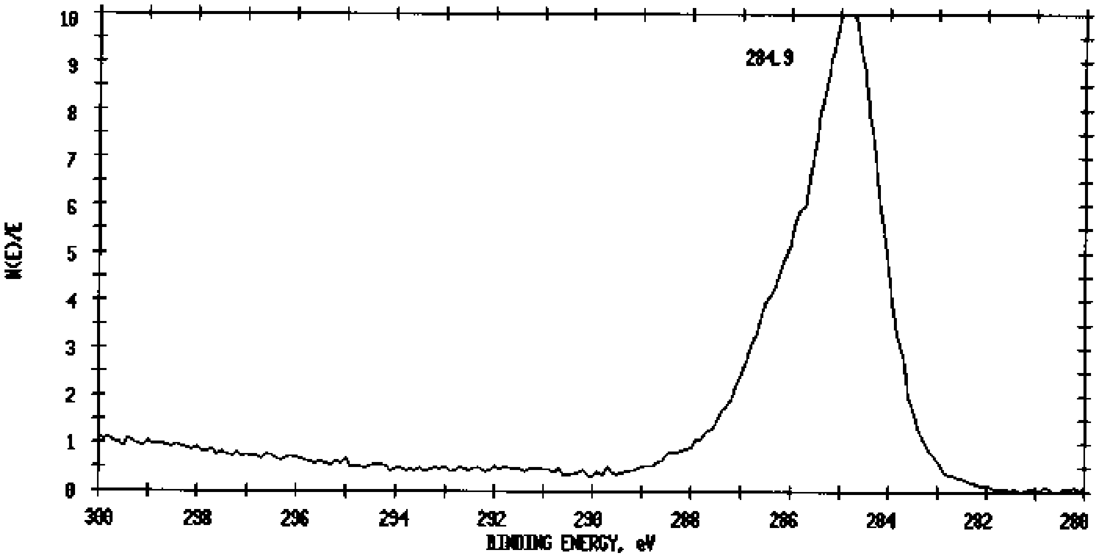


Figure 62: XPS multiplex spectrum for C_{1s}, scale factor= 0.344 k c/s, offset= 0.170 k c/s, pass energy= 17.900 eV

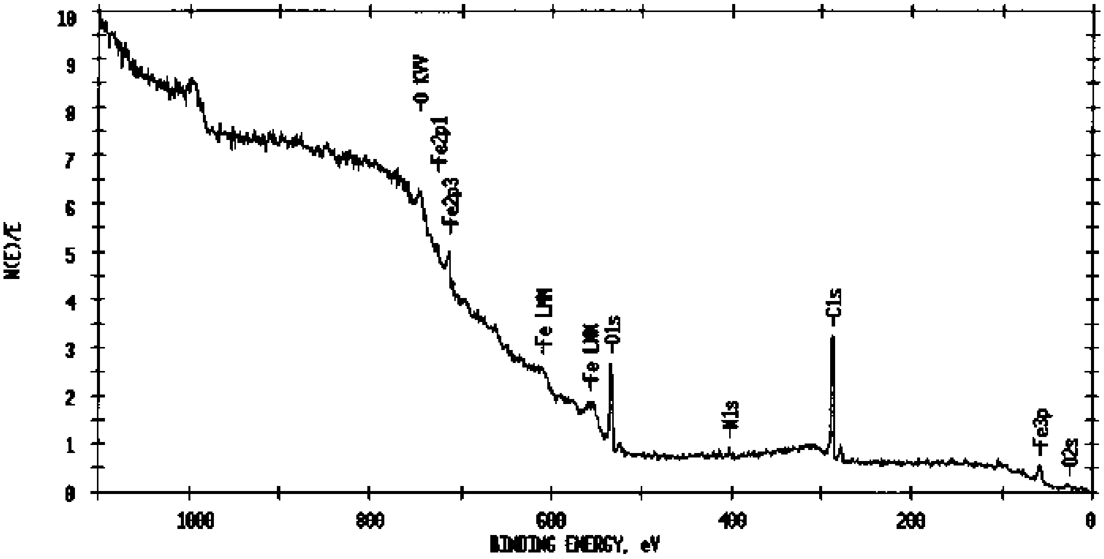


Figure 63: XPS survey spectrum for acetone wiped steel failure surface, scale factor= 3.044 k c/s, offset= 0.248 k c/s, pass energy= 44.750 eV

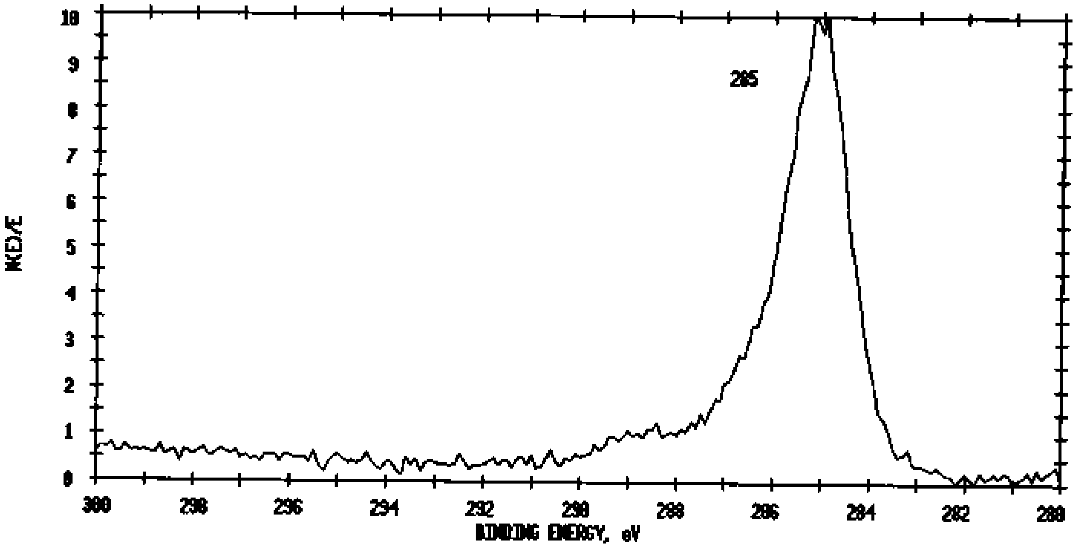


Figure 64: XPS multiplex spectrum for C_{1s}, scale factor= 0.321 k c/s, offset= 0.684 k c/s, pass energy= 17.900 eV

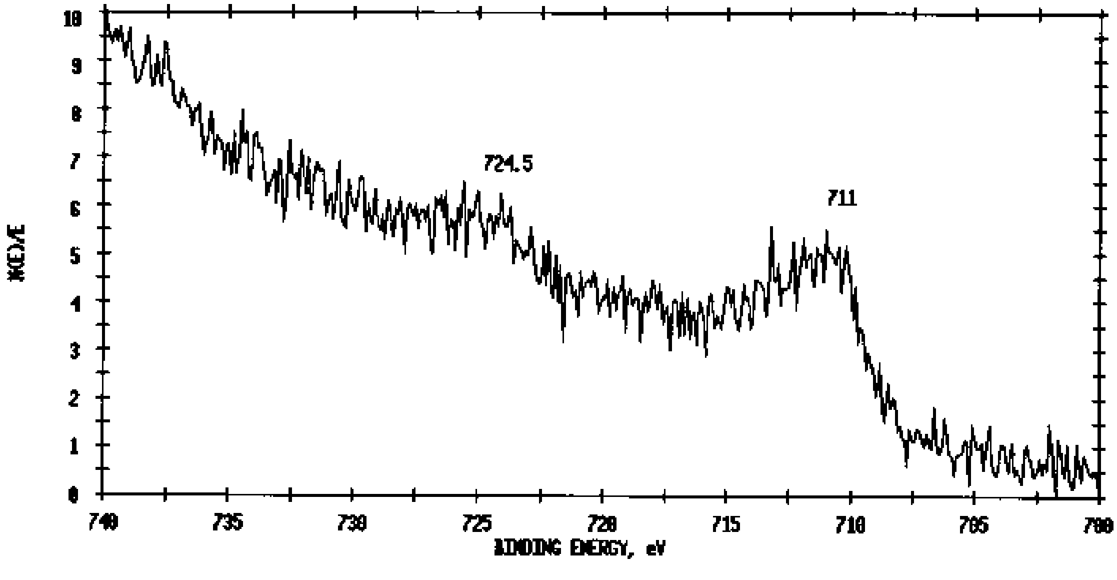


Figure 65: XPS multiplex spectrum for $Fe_{2p1,\,2p3}$, scale factor= 0.180 k c/s, offset= 3.528 k c/s, pass energy= 17.900 eV

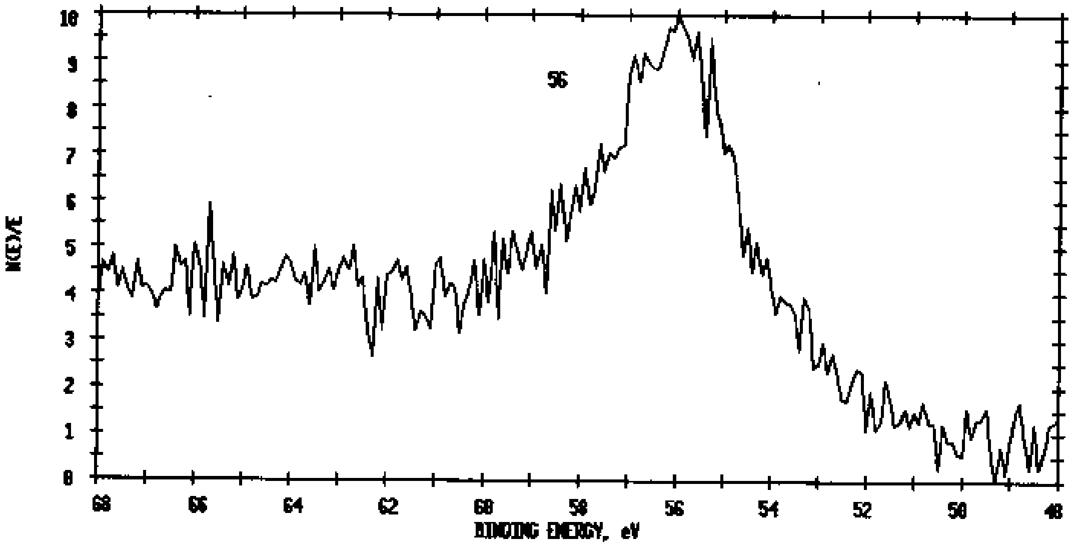


Figure 66: XPS multiplex spectrum for Fe_{3p}, scale factor= 0.041 k c/s, offset= 0.207 k c/s, pass energy= 17.900 eV

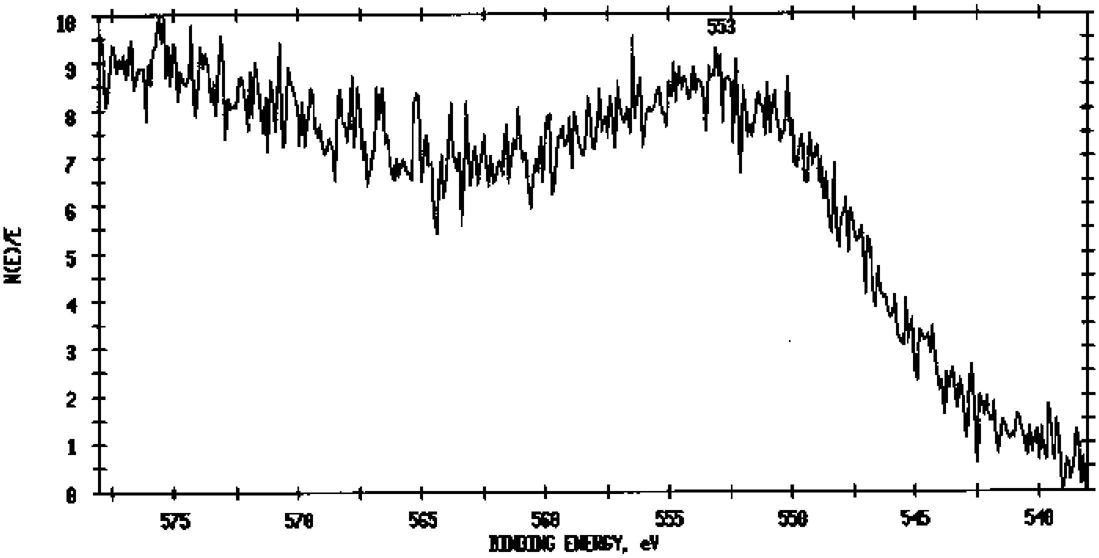


Figure 67: XPS multiplex spectrum for Fe_{LMM}, scale factor= 0.080 k c/s, offset= 1.053 k c/s, pass energy= 17.900 eV

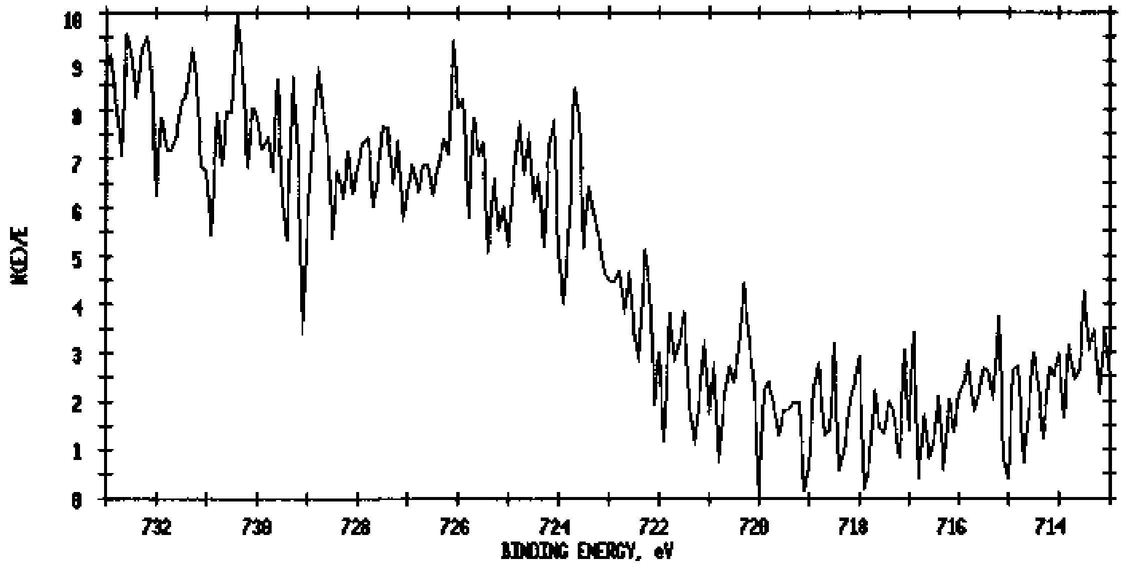


Figure 68: XPS multiplex spectrum for Fe$_{2p3/2,\ 2p1/2}$, scale factor= 0.071 k c/s, offset= 4.098 k c/s, pass energy= 17.900 eV

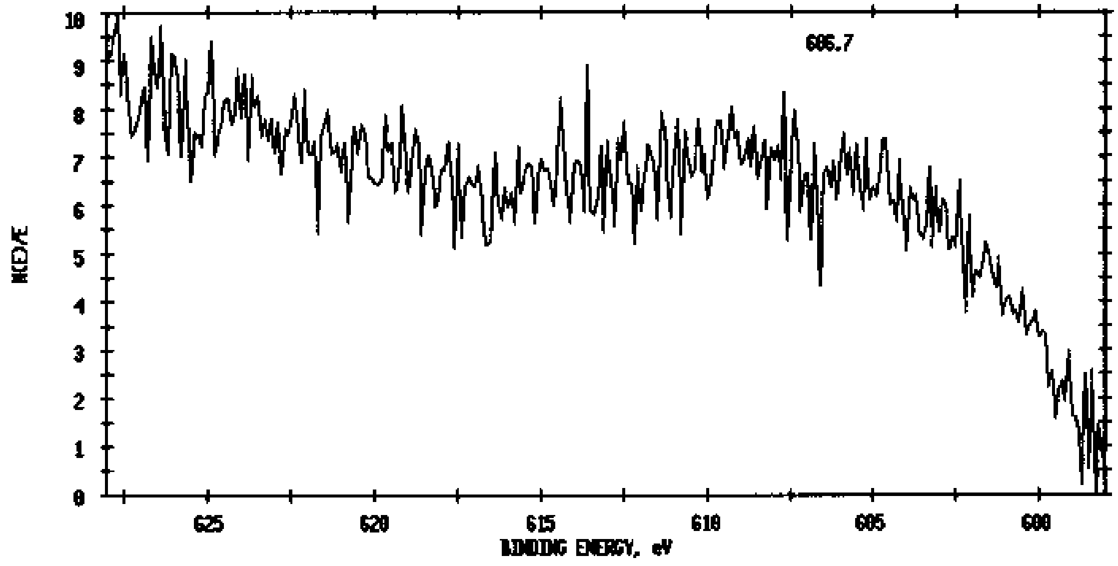


Figure 69: XPS multiplex spectrum for Fe, scale factor= 0.069 k c/s, offset= 1.860 k c/s, pass energy= 17.900 eV

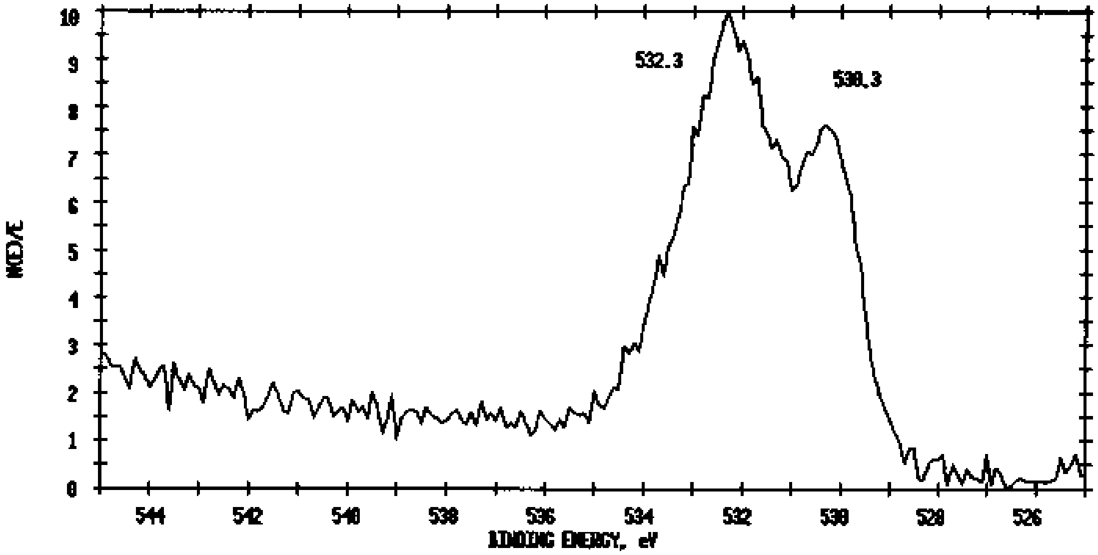


Figure 70: XPS multiplex spectrum for O_{1s}, scale factor= 0.186 k c/s, offset= 0.823 k c/s, pass energy= 17.900 eV

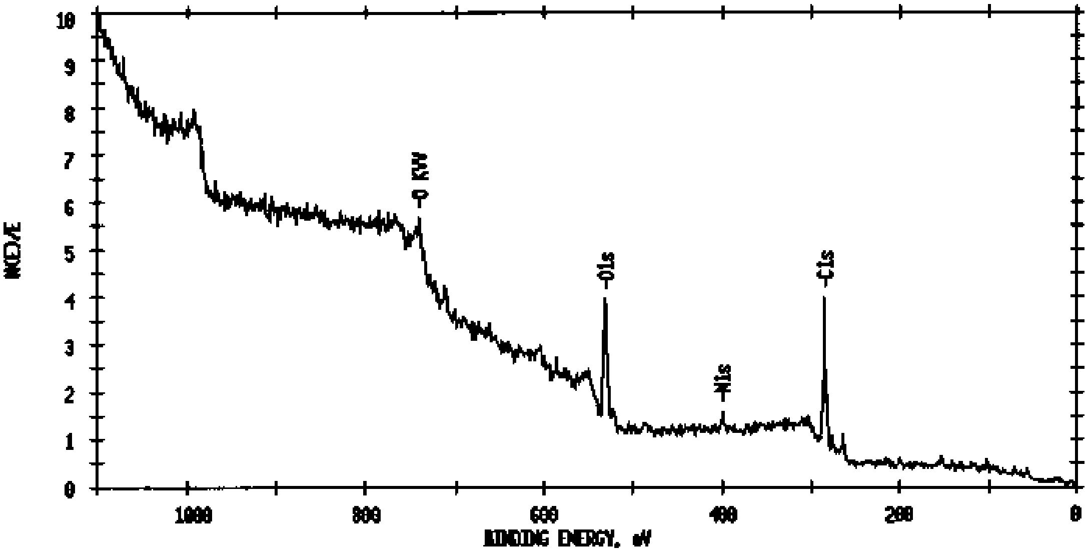


Figure 71: XPS survey spectrum for epoxy failure surface (bonded to corroded steel), scale factor= 1.476 k c/s, offset= 0.144 k c/s, pass energy= 44.750 eV

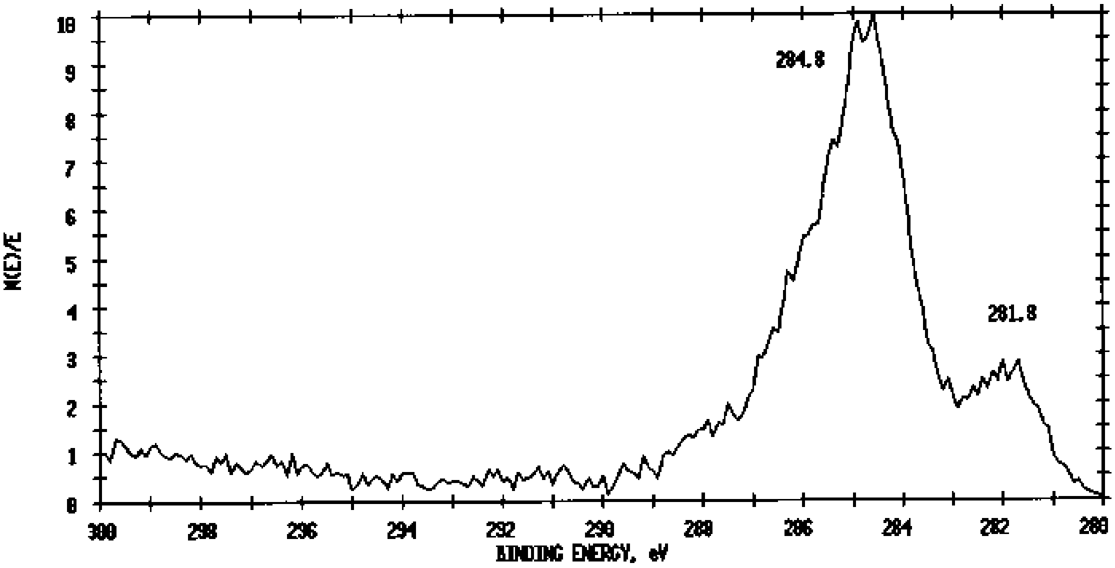


Figure 72: XPS multiplex spectrum for C_{1s}, scale factor= 0.177 k c/s, offset= 0.462 k c/s, pass energy= 17.900 eV

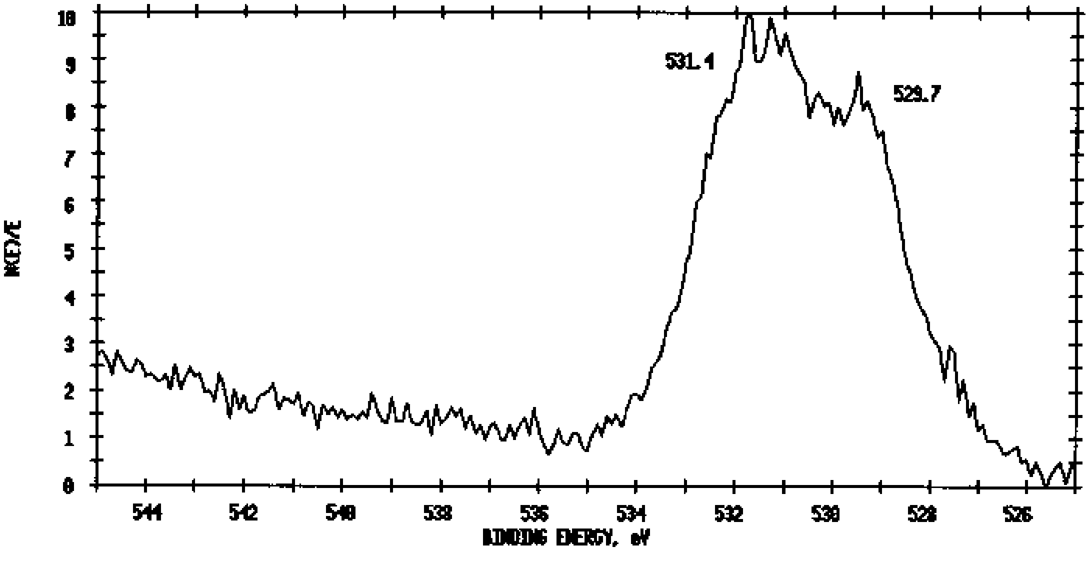


Figure 73: XPS multiplex spectrum for O_{1s}, scale factor= 0.132 k c/s, offset= 0.647 k c/s, pass energy= 17.900 eV

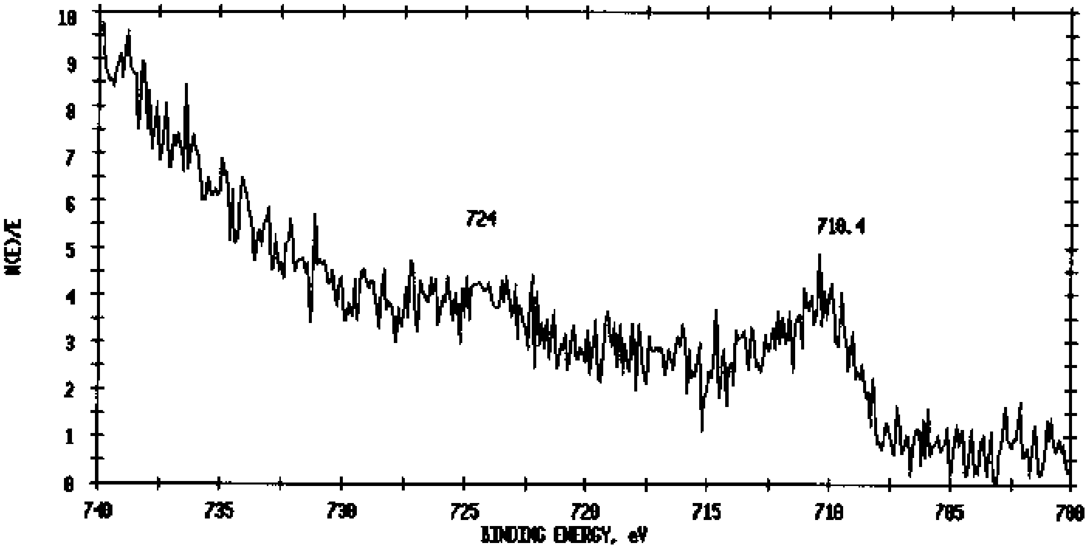


Figure 74: XPS multiplex spectrum for $Fe_{2p1/2,\ 2p3/2}$, scale factor= 0.097 k c/s, offset= 1.582 k c/s, pass energy= 17.900 eV

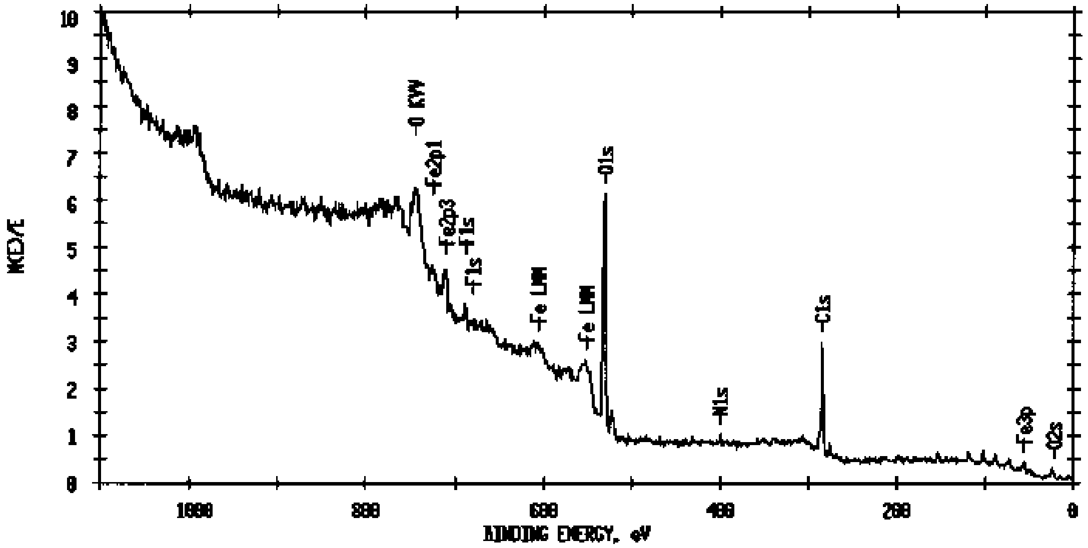


Figure 75: XPS survey spectrum for corroded steel failure surface, scale factor= 2.015 k c/s, offset= 0.152 k c/s, pass energy= 44.750 eV

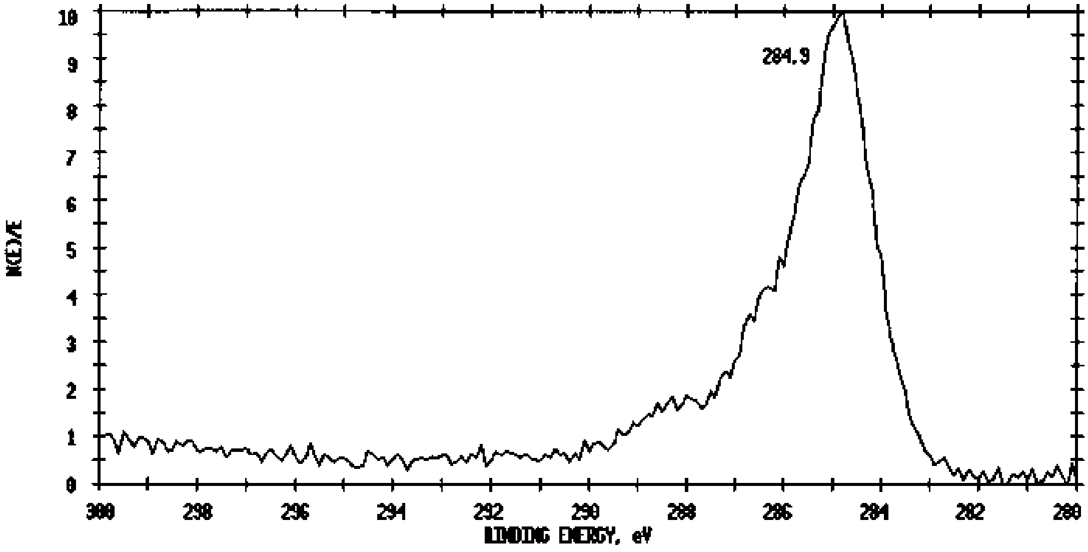


Figure 76: XPS multiplex spectrum for C_{1s}, scale factor= 0.198 k c/s, offset= 0.413 k c/s, pass energy= 17.900 eV

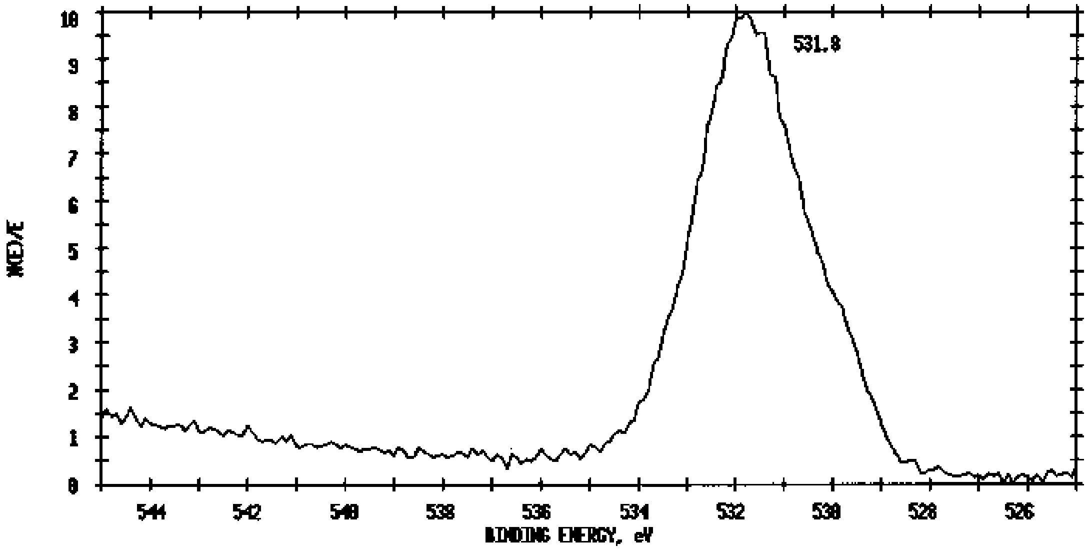


Figure 77: XPS multiplex spectrum for O_{1s}, scale factor= 0.372 k c/s, offset= 0.701 k c/s, pass energy= 17.900 eV

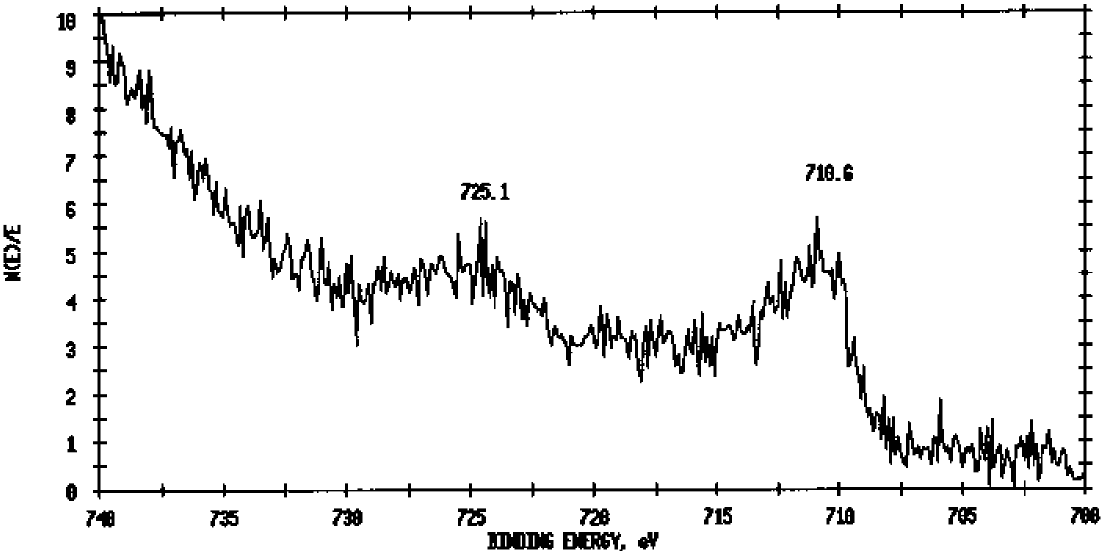


Figure 78: XPS multiplex spectrum for $Fe_{2p1/2,\,2p3/2}$, scale factor= 0.131 k c/s, offset= 2.095 k c/s, pass energy= 17.900 eV

Table 3.1: Atomic Concentration of Epoxy Failure Side (bonded to acetone wiped steel)

Element	Area (cts-eV/s)	Concentration (%)
C 1s	7840	63.30
Si 2s	493	3.66
O 1s	3968	29.17
N 1s	771	3.86

Table 3.2: Atomic Concentration of Acteone Wiped Steel Failure Surface

Element	Area (cts-eV/s)	Concentration (%)
C 1s	6383	69.08
Fe 2p	4328	4.69
O 1s	5821	26.23

Table 3.3: Atomic Concentration of Epoxy Failure Surface (bonded to corroded steel)

Element	Area (cts-eV/s)	Concentration (%)
C 1s	5242	68.35
O 1s	5440	29.53
Fe 2p	1627	2.12

Table 3.4: Atomic Concentration of Corroded Steel Failure Surface

Element	Area (cts-eV/s)	Concentration (%)
C 1s	4545	50.06
O 1s	10015	45.92
Fe 2p	3643	4.02

Chapter 4 : Discussion

4.1 Neat Epoxy Properties

In this section, the effects of the environments on the properties of the neat epoxy samples are discussed.

It can been seen from Figures 45-47 that the moisture uptake of the neat epoxy samples increased with exposure time. No saturation plateau was observed for the neat EPON® resin 828 / dicyandiamide samples, so more time was probably needed for the samples to become saturated. The moisture uptake of the EPON® resin 828 / EPI-CURE® 3090 samples that were aged at constant temperature increased with exposure time and it seemed to have reached a plateau value after four weeks of exposure. The moisture uptake of the EPON® resin 828 / EPI-CURE® 3090 samples that were aged under the cycling temperature condition did not appear to be influenced by exposure time.

More water was absorbed by the neat EPON® resin 828 / dicyandiamide samples than by the EPON® resin 828 / EPI-CURE® 3090 samples. The EPON® resin 828 / EPI-CURE® 3090 samples were cured underwater and had already absorbed 4% of water during the curing cycle. The neat EPON® resin 828 / dicyandiamide samples that were cured in the oven did not take up water during the curing cycle. If the amount of water absorbed during curing was added to the moisture uptake of the EPON® resin 828 / EPI-CURE® 3090 samples, there would be no significant difference in the moisture uptake between the two resin systems. There was no statistical difference in moisture uptake with exposure time for the EPON® resin 828 / EPI-CURE® 3090 samples that were aged between 25°C and 50°C. It has been documented that water sorption increases with temperature.[23,24] The samples that were aged under the cycling condition spent approximately half of their exposure time at a lower temperature of 25°C, and diffusion of water into the samples might have been hindered. Therefore, no significant difference in moisture uptake with time was observed for the samples that were aged under the cycling condition.

The moisture uptake of the neat epoxy samples was observed to be slightly higher in the distilled water than in the 3.4% NaCl solution. When NaCl dissolves in water, Na^+ and Cl^- ions form and the water molecules surround the ions to form hydrated ions.[52] The size of these hydrated ions is much larger than the water molecules; therefore, the diffusion rate might be reduced in a NaCl solution. This behavior was also observed by Manrique et al[53] and by Tai et al.[54]

The bending modulus of the neat epoxy samples was plotted as a function of moisture uptake, and the results are shown in Figure 79 for the dicyandiamide cured resin, in Figure 80 for the amidoamine cured resin, and in Figure 81 for the amidoamine cured and aged between 25°C and 50°C. The bending modulus decreased as more moisture had diffused into the epoxy. The water acted as a plasticizer which changed the viscoelastic response of the epoxy network.[55] A plasticizer is usually a small molecule that dissolves in the polymer swelling the network through the polymer-solvent interaction and is capable of lowering the glass transition temperature and the rubber plateau modulus.[56] Lee et al. also observed the plasticizing effect of water on the epoxy.[29] Although moisture diffusion is slower in the 3.4% NaCl solution, the bending modulus of the neat epoxy samples that were exposed in the 3.4% NaCl solution is lower than those exposed in the distilled water after longer exposure time. Manrique et al. stated that the effect of a NaCl solution on the mechanical properties of epoxy is detrimental, despite the fact that moisture diffusion is slower in a NaCl solution.[53]

---

[52] H. F. Holtzclaw, Jr., W. R. Robinson, and J. D. Odom, General Chemistry with Qualitative Analysis, pp. 344-345, Ninth Edition, D. C. Heath and Company, 1991

[53] F. Manrique, J. Bonhomme, and F. J. Belzunce, Woodhead Publishing Limited (UK), pp. 341-347, 1996

[54] R. C. L. Tai, Z. Szklarska-Smialowska, Journal of Materials Science, pp. 6205-6210

[55] J. J. Aklonis, W. J. MacKnight, Introduction to Polymer Viscoelasticity, pp. 43, John Wiley and Sons, New York, 1983

[56] L. H. Sperling, Introduction to Physical Polymer Science, pp. 314, Second Edition, John Wiley & Sons, INC., 1992

Several studies reported that a NaCl solution intensifies the microcavity formation in the adhesives; therefore, the degree of swelling and the adhesive degradation increases.[54,57]

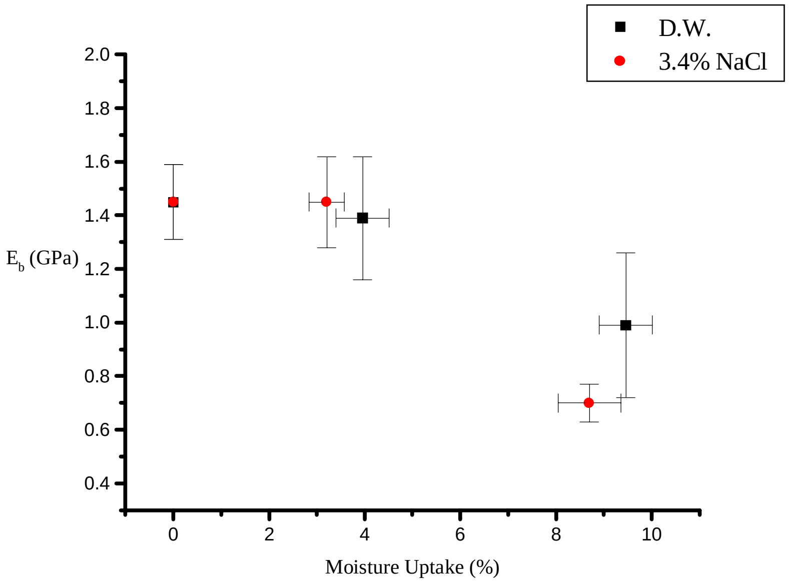


Figure 79: Bending modulus of EPON® resin 828/ dicyandiamide as a function of moisture uptake

---

[57] R. F. Fedors, Polymer, Vol. 21, pp.713, 1980

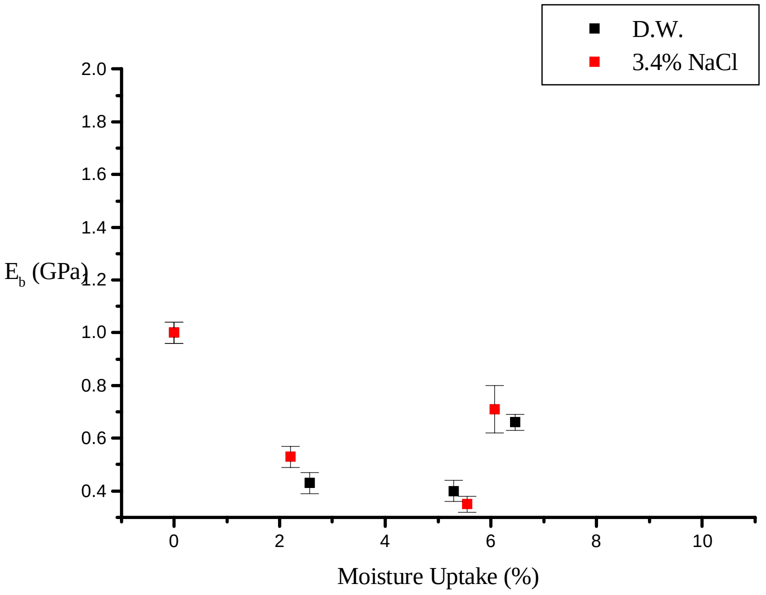


Figure 80: Bending modulus of EPON® resin 828 / EPI-CURE® 3090 (50°C) as a function of moisture uptake

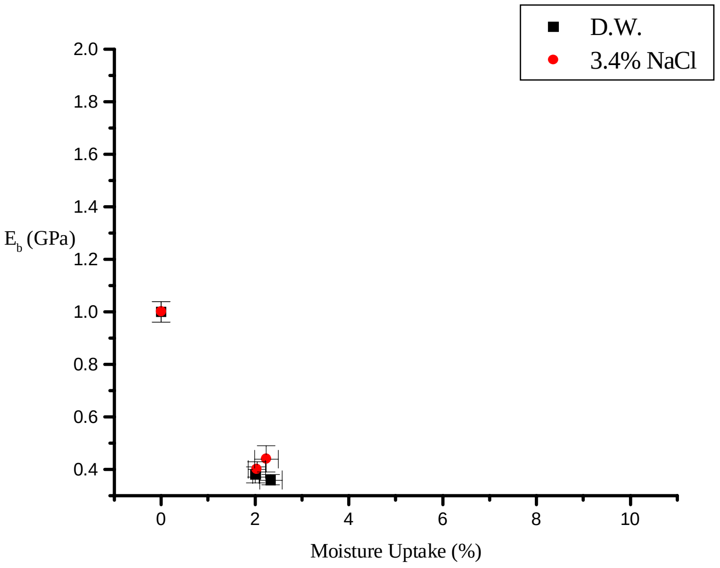


Figure 81: Bending modulus of EPON® resin 828 / EPI-CURE® 3090 (25°C – 50°C) as a function of moisture uptake

It was shown in Figure 41 that there was an endothermic peak at approximately 100°C during the first heat scan of a DSC experiment. The endothermic peak disappeared after the second heat scan as shown in Figure 42. The neat EPON® resin 828 / EPI-CURE® 3090 samples were cured underwater and were shown to absorb 4% moisture during the curing cycle. The endothermic peak could be due to the moisture uptake during curing, and the moisture was removed by the DSC heating cycles.

The effect of moisture on the glass transition temperature of the neat EPON® resin 828 / EPI-CURE® 3090 samples is illustrated in Figure 82 and Figure 83. It can be seen from these figures that the T_g of the neat epoxy is depressed slightly with moisture uptake. This observation confirms that water plasticizes the neat epoxy samples, and the depression of T_g can be affected by the amount of water present in the samples. Lee et al. also observed the decrease in T_g by the plasticizers.[29] The viscoelastic behavior of polymers near the glass transition region can be described using the free-volume theory , and the cooperative motion of polymer chains takes place in the free volume of the polymers.[56] Plasticizer molecules introduce more free volume into the epoxy network through swelling and lower the T_g of the epoxy. The effect of plasticizers on the T_g of polymers can be quantified by using Fox equation and Fox equation is given by:

$$\frac{1}{T_g} = \frac{M_{polymer}}{T_{g,polymer}} + \frac{M_{plasticizer}}{T_{g,plasticizer}}$$

It states that the T_g of a polymer with a plasticizer added is proportional to the amount of each component present in the system and is also a function of the T_g of each component. It is assumed that the plasticizers have to be completely miscible in the polymer in order for the Fox equation relationship to be valid. The T_g of water is documented to be 143K.[58] The Fox equation was used to predict the T_g of the neat epoxy samples that were aged in the distilled water at 50°C, and the results are shown in Figure 84. It can be seen that the experimental T_g deviated from the Fox equation prediction at higher moisture content. At lower moisture content, the water molecules form hydrogen bonds with the

---

[58] Viscoelasticity class notes

hydroxyl groups of the epoxy. The water molecules are completely miscible with the epoxy network; therefore, the experimental T_g agrees with the theoretical value predicted by the Fox equation. At higher moisture content, water molecules agglomerate as a second phase after all the hydroxyl sites of the epoxy network were occupied. The congregated water molecules are not completely miscible in the epoxy network; therefore, the experimental T_g deviates from the theoretical value.

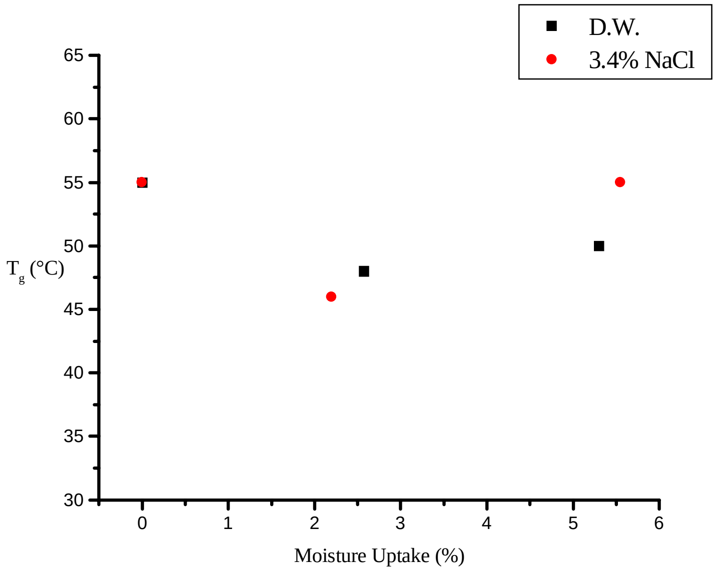


Figure 82: T_g of EPON® resin 828 / EPI-CURE® 3090 (50°C) as a function of moisture uptake

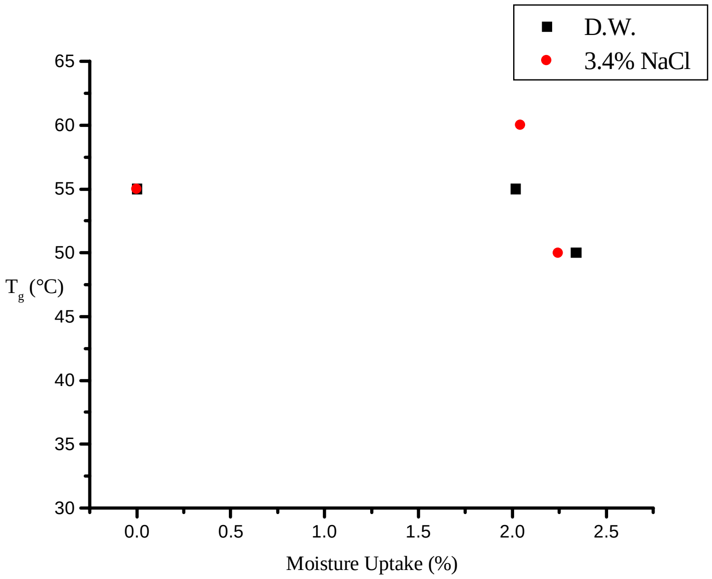


Figure 83: T_g of EPON® resin 828 / EPI-CURE® 3090 (25°C – 50°C) as a function of moisture uptake

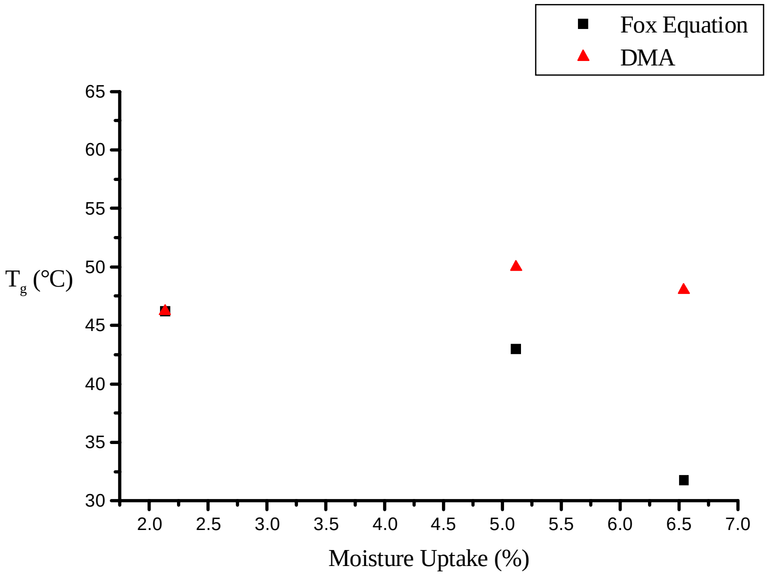


Figure 84: Prediction of T_g by Fox equation for the EPON® resin 828 / EPI-CURE® 3090 (distilled water, 50°C)

It was shown that there is no significant change in the density after aging the samples in the environments. The moisture uptake of the neat EPON® resin 828 / EPI-CURE® 3090 sample was between 3% and 6%. This difference in the epoxy mass may be insignificant for the density kit to measure.

4.2 Bonded Joint Durability

The effects of environmental conditions on the durability of the epoxy bonded joints are discussed in this section.

It was shown in that shear strength decreased with exposure time for all the epoxy bonded joints. There was a corresponding reduction in the axial stress state in the resin at failure, primarily due to the reduction in the interfacial shear strength at the edge with further aging. For the EPON® resin 828/ dicyandiamide bonded joints, the bonded joints with soap and water scrubbed substrate had the highest shear strength initially and after one week of exposure in distilled water. However, the difference in shear strength between the surface pretreatment methods was not significant after two weeks of exposure in distilled water. There was also no significant difference in the shear strength between the surface pretreatment procedures after one and two weeks of exposure in 3.4% NaCl solution. The higher initial shear strength of the bonded joints with soap and water scrubbed substrate resulted from the rougher surface morphology of the oxide layer on the steel substrate. Minford has reported that the loose oxide layers are susceptible to interfacial failure when the bonded joints are under stress, impact or weathering conditions.[42] If the oxide layers were loosely bonded, it would explain why there was no significant difference in the shear strength between the surface pretreatment methods after two weeks of exposure in distilled water and after one and two weeks of aging in 3.4% NaCl solution which is a more severe environment.

For the EPON® resin 828 / EPI-CURE® 3090 bonded joints that were aged at 50°C, the bonded joints with the corroded substrate surface had the higher shear strength initially and throughout the aging experiment in both aging environments. The oxide layer of the corroded surface was formed by immersing the steel with no visible corrosion products in a 3.4% NaCl solution immediately before the bonding procedure. The newly formed oxide layer contributed to the higher strength of the bonded joints because of its high surface roughness and chemical reactivity. Minford also reported this observation.[42] The SEM micrographs of the two steel surfaces showed that the corroded surface appeared to be rougher than the acetone wiped one.

For the EPON® resin 828 / EPI-CURE® 3090 bonded joints that were aged under the cycling temperature condition, there were no significant differences in the shear strength between the surface pretreatment methods. It was shown that the water diffusion was slow in this temperature cycling condition, and water diffusion has been reported to control the failure of bonded joints.[33,35,36] This can be used to explain why there was no significant difference in the strength of the bonded joint that were aged in the temperature cycling condition.

The loss in the shear strength is plotted as a function of exposure time, and the results are shown in the following figures. Figure 85 shows the loss in shear strength for the EPON® resin 828/ dicyandiamide bonded joints. Figure 86 shows the reduction in shear strength for the EPON® resin 828 / EPI-CURE® 3090 bonded joints aged at 50°C. Figure 87 shows the loss in shear strength for the EPON® resin 828 / EPI-CURE® 3090 bonded joints aged under the cycling temperature condition. It is shown in Figure 85 that the bonded joints with the soap and water scrubbed steel substrate experienced the greatest loss in the shear strength in 3.4% NaCl solution. The soap and water scrubbed steel surface had loose oxide layers on the steel surface. Although the oxide layer contributed to the high shear strength initially, the NaCl solution caused the interfacial failure of the bonded joints. Minford suggested that the loose oxide layer on the substrate surface can lead to bonded joint failure under severe weathering conditions.[42] The bonded joints with the sandblasted steel substrate had the least loss in the shear strength in distilled water and in 3.4% NaCl solution. Leidheiser stated that the removal of the oxide layer might be necessary for longer service lifetime of bonded joints.[41] The elimination of the oxide layer by sandblasting stabilized the bonded joints in the aqueous environments to prolong the service lifetime.

It can be seen from Figure 86 that the bonded joints with the corroded steel substrate had the least loss in the shear strength in distilled water and in 3.4% NaCl solution. The oxide layer on the substrate surface was formed immediately before the adhesive bonding and was higher in roughness and chemical reactivity.[42] The oxide layer on the substrate surface lead to the greater durability of the bonded joints. There is no significant difference in the loss of shear strength for the EPON® resin 828 / EPI-CURE® 3090 bonded joints that were aged under the temperature cycling condition. The moisture diffusion rate was low for the cycling temperature conditions, and water diffusion has been reported to cause bonded joint failure.[33,35, 36]

SEM and optical microscopy were used to examine the failure surfaces of the EPON® resin 828/ dicyandiamide bonded joints. Oxide particles were observed from the optical microscopy results of the epoxy failure surface, and no epoxy was found on the steel failure surface from the SEM micrographs. It was also observed that oxide was present uniformly on the epoxy failure surfaces by visual inspection. Thus, it is concluded that the failure occurred cohesively within the metal oxide layer. XPS was used to inspect the failure surfaces of the EPON® resin 828 / EPI-CURE® 3090 bonded joints. It was found that oxide particles, such as Fe_2O_3 and FeO, were found on the epoxy failure surface that was bonded to corroded steel. On the corroded steel failure surface, Fe_2O_3 were present. It can be concluded that the epoxy bonded joints with the corroded steel had failed cohesively within the metal oxide layer because of the oxides present on the epoxy failure surface. Gledhill and Kinloch had also observed adhesive failure of the iron-epoxy system that was exposed under wet conditions.[33] For the bonded joints with the acetone wiped steel, no ferrous oxides were found on the epoxy failure surface and no nitrogen, which is unique in the epoxy system, was found on the steel failure surface. It was concluded that failure also occurred adhesively.

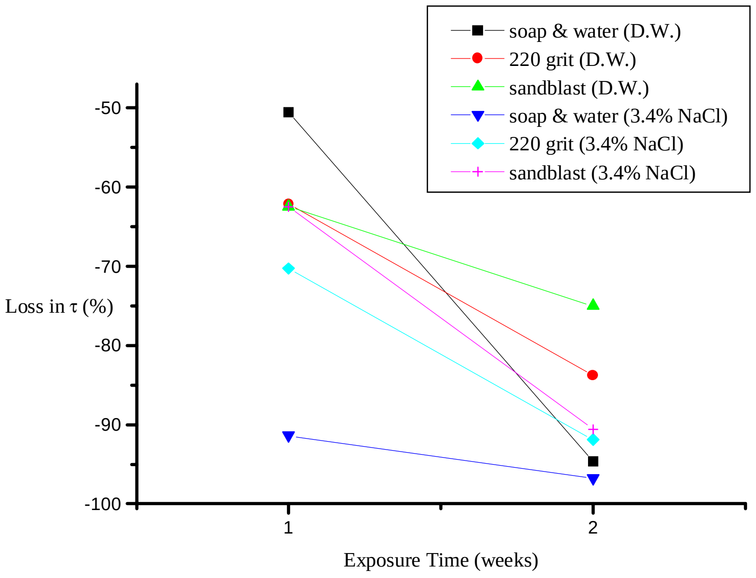


Figure 85: Loss in shear strength for the EPON® resin 828/ dicyandiamide bonded joints

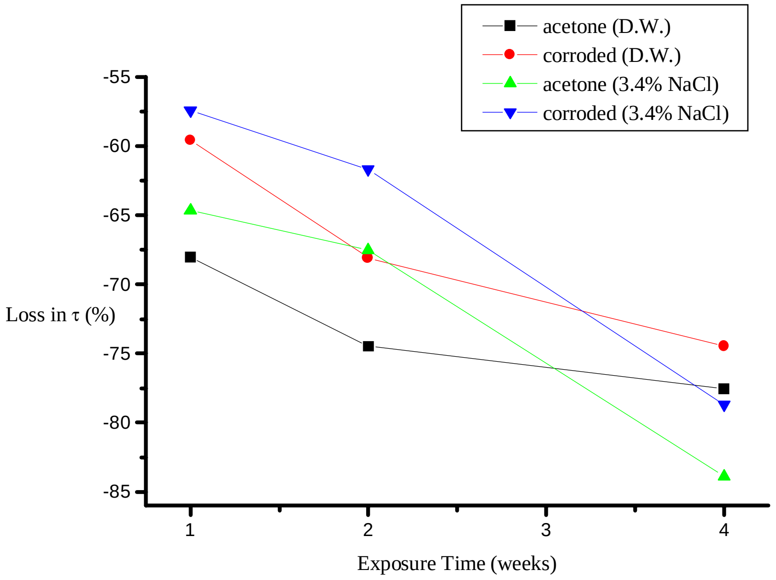


Figure 86: Loss in shear strength of the EPON® resin 828 / EPI-CURE® 3090 bonded joints (50°C)

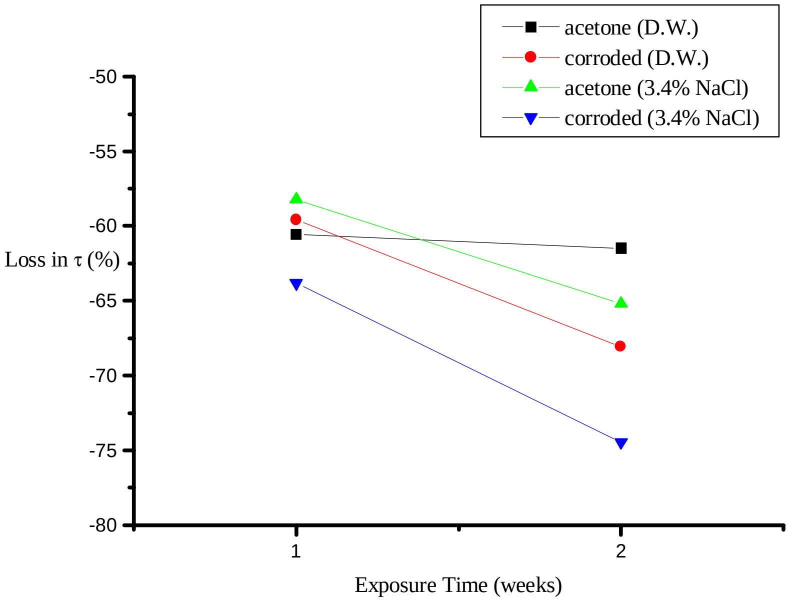


Figure 87: Loss in shear strength for the EPON® resin 828 / EPI-CURE® 3090 bonded joints (25°C – 50°C)

It was observed that failure always occurred cohesively within the metal oxide layers if oxides were present on the substrate prior to the bonding procedure for both resin systems under all experimental variables. The oxide layers are thought to be the weakest component of the bonded joints; therefore, failure should take place within the oxide layers. This suggests that optimum substrate surface morphology is essential in order to extend the service lifetime of the bonded joints. The substrate surface characteristics are the limiting factors in the performance of the bonded joints. Therefore, a proper surface pretreatment procedure is crucial for a bonded joint to maintain the appropriate mechanical strength throughout its service lifetime.

Chapter 5 : Conclusions

The objective of this work was to study the effects of environments on the mechanical properties of the neat epoxy and of the epoxy bonded joints. The interest for applying adhesives in an aqueous environment arises from the need for a temporary pipe repair method to replace welding. It was concluded that two main causes contributed in the failure of the bonded joints in the aqueous environments.

First, water acts as plasticizer through swelling of the epoxy network. This is evident in the reduced bending modulus of the neat resin with exposure time and with moisture content. The loss of bending modulus is greater in a NaCl solution than in distilled water, although the moisture uptake is less in a NaCl solution. This observation agrees with previous work performed.[53,54] The plasticizing effect of water can also be seen in the depression of T_g of the neat epoxy with moisture content. Since the epoxy is an integral part of a bonded joint, the loss in its bending modulus will lead to a decrease in the mechanical strength of a bonded joint.

Second, water diffuses through the interface between the epoxy and the steel substrate resulting in a weaker bond. It would be less resistance for the water to diffuse along the interface than through the bulk of the epoxy because of the thickness of the epoxy strip which ranged from 5mm to 8mm. Since the oxide layers are the weak region in a bonded joint, it would experience the greatest loss in strength in a severe environment. In a bonded joint, the epoxy is bonded to the oxide layer. When the integrity of the oxide layer is compromised by the environment, so is the interfacial strength of a bonded joint. It has been shown that the interfacial shear strength of the bonded joints decreases with exposure time. The loss of shear strength of the EPON® resin 828 / EPI-CURE® 3090 bonded joints that were aged between 25°C and 50°C is less than that of the ones that were aged at 50°C. The diffusion rate increases with temperature; therefore, the diffusion of water into the interface is slower under the temperature cycling condition. The attack on the oxide layers was not as severe under the temperature cycling condition; thus, the loss of shear strength would not be as severe. It was also shown that the NaCl solution was more deleterious to the shear strength of the bonded joints because a NaCl solution is more corrosive than distilled water. When the NaCl solution diffuses into the interface, redox or electrochemical reactions might take place resulting in dissolution of the oxide layers.

It is important to predict approximately the service lifetime of a bonded joint to avoid any catastrophic failure. It was found that for the EPON® resin 828/ dicyandiamide bonded joints with the soap and water scrubbed steel substrate suffered the greatest loss in shear strength, up to 97% after two weeks of exposure in the NaCl solution. This was due to the loosely bonded oxide layers that were susceptible to environmental attacks present prior to the bonding procedure. The EPON® resin 828/ dicyandiamide bonded joints had lost at least 50% and up to 97% of their original strength after only one week of exposure. It is thus concluded that the realistic lifetime of an EPON® resin 828/ dicyandiamide bonded joint is about one week, and sandblasting would be recommended as the substrate surface pretreatment method.

It was observed for the EPON® resin 828 / EPI-CURE® 3090 bonded joints with the corroded substrate that there was a 57% loss in the shear strength after one week of exposure in a NaCl solution. The bonded joints with the acetone wiped substrate had lost 65% of their original shear strength after one week of exposure in a NaCl solution. Therefore, it is suggested that protective oxide layers should be formed just before the bonding procedure to ensure longer lifetime of a bonded joint. The EPON® resin 828 / EPI-CURE® 3090 bonded joints with the corroded steel lost 60% and 77% of their original shear strength after two weeks and four weeks of exposure in the NaCl solution respectively. It is estimated that the service lifetime of an EPON® resin 828 / EPI-CURE® 3090 bonded joint with corroded substrate is up to two weeks.

The surface analysis results show that failure always occurred cohesively within the oxide layers if oxides were present on the substrate surface prior to the bonding procedure. This observation can be made for both resin systems and for all experimental variables, such as exposure time and environments. Thus, it is concluded that the oxide layers are the weak components in the bonded joints and that an optimum substrate surface morphology is critical to the performance of the bonded joints. If the loosely bounded oxides were not removed before the bonding procedure, the lifetime and the performance of these bonded joints will be severely limited. However, some mechanical interlocking between the adhesive and the substrate is essential to optimize the mechanical strength of the bonded joints. It has been shown that a substrate with a rougher surface morphology can provide a better mechanical interlocking with adhesives than one that is relatively featureless in its surface morphology. It has also been shown that the steel substrate with oxide layers formed shortly before the bonding procedure has rougher surface morphology than one that was polished. Therefore, it is suggested that loosely bounded oxides should be removed and that a protective oxide layer should be formed prior to bonding to ensure maximum lifetime and performance of the bonded joints.

The procedure for repairing a damaged pipe is proposed here. The epoxy resin can be mixed and placed in a dispenser before the diver enters the water if the gel time of the resin is reasonably longer than the working time of the diver. Once the diver has located the damaged pipe, he or she should prepare the surface for bonding. Some suggested surface pretreatment methods include scrubbing with a scrubbing pad and sandblasting. The diver then dispenses the resin and applies it over the damaged site. The repaired site should be inspected within 24 hours after the repair to make sure that no further repair is necessary. The respired site should also be inspected periodically until a new pipe is installed to avoid any catastrophic failure.

Using adhesives as a temporary underwater pipe repair method is a promising possibility. However, more studies are needed to understand the failure mechanisms of the bonded joints in more depth, to prolong the lifetime of the bonded joints, and to predict the lifetime of the bonded joints more accurately.

Chapter 6 : Future Work

Several experiments are suggested in this section for future work in the area of applying adhesives in underwater pipe repair.

The strength of the epoxy system can be improved by reinforcing the system with fibers. Once the strength of the epoxy system is increased, the strength of a bonded joint will likely be more superior. Moisture uptake experiment of the reinforced adhesive patch would be suggested. DMA would also be useful in determining the effect of environments on the properties of the adhesive patch. More surface pretreatment methods can be used to study the effects of substrate surface morphology on the mechanical properties of the bonded joints. It would be beneficial to determine the optimum surface condition for forming a strong bond that can help to prolong the lifetime of a bonded joint. Other aging solution can also be used to study the effects of environmental factors on the bonded joints. The solution can be made more corrosive by increasing the concentration of a NaCl solution. Other mechanical tests that can simulate the real service conditions should also be performed. A blister test that involves the delamination of the adhesive patch by a fluid or gas pressure can simulate the real service environment more closely.

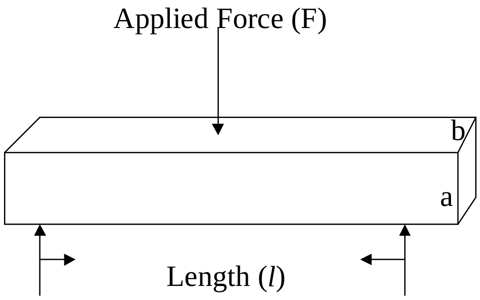
Hopefully, these suggested experiments will enhance our knowledge in enabling us to enact highly effective temporary pipe repairs in underwater applications.

Appendix A: Derivation Of Equations

The equations that were used to analyze shear strengths and axial strengths from a three-point bend test were derived in the following section.

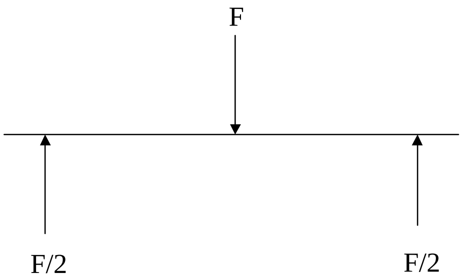
Substrate Only – No Adhesive

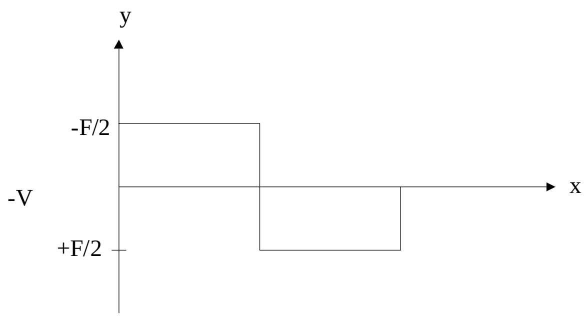
In this section, only substrate will be analyzed.



$$A = a * b$$

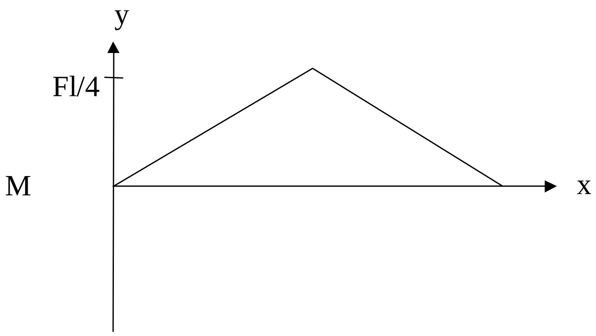
$$I = \frac{1}{12} * b * a^3$$





$$V = -\frac{F}{2}, x \le \frac{l}{2}$$

$$V = \frac{F}{2}, x \ge \frac{l}{2}$$



$$M = \frac{F}{2} * x, x \le \frac{l}{2}$$
$$M = \frac{F}{2} * (l - x), x \ge \frac{l}{2}$$

$$\sigma_x = \frac{M * y}{I}$$
$$\sigma_{x,maximum} = \sigma_x\left(x = \frac{l}{2}, y = \pm\frac{a}{2}\right) = \pm\frac{F * l}{4} * \frac{a}{2} * \frac{12}{ba^3} = \pm\frac{3Fl}{2ba^2}$$
$$\tau_{xy} = \frac{V * Q}{I * b}$$
$$Q = \int_y^{a/2} \bar{y} dA = b * \int_y^{a/2} \bar{y} d\bar{y} = b * \left[\frac{y^2}{2}\right]_y^{a/2} = \frac{b}{2} * \left[\frac{a^2}{4} - y^2\right]$$
$$\tau_{xy} = \pm\frac{F}{2} * \frac{b}{2} * \left[\frac{a^2}{4} - y^2\right] * \frac{12}{ba^3} * \frac{1}{b} = \pm\frac{3F}{ba^3} * \left[\frac{a^2}{4} - y^2\right]$$
$$\tau_{xy,maximum} = \tau_{xy}(y = 0) = \pm\frac{3F}{4ba}$$

Solve for deflection in the substrate,

$$EI\frac{d^2y}{dx^2} = M$$

Use symmetry and solve for $x \le \frac{l}{2}$

$$EI\frac{d^2y}{dx^2} = \frac{F}{2}x$$
$$\frac{d^2y}{dx^2} = \frac{F}{2EI}x$$
$$\frac{dy}{dx} = \frac{F}{2EI} * \frac{x^2}{2} + C_1 = \frac{F}{4EI}x^2 + C_1$$

First boundary condition: slope at midspan is 0

$$\frac{dy}{dx}_{x=l/2}=0, C_1=-\frac{Fl^2}{16EI}$$

$$\frac{dy}{dx}=\frac{F}{4EI}\left[x^2-\frac{l^2}{4}\right]$$

$$y=\frac{F}{4EI}\left[\frac{x^3}{3}-\frac{l^2}{4}x\right]+C_2$$

Second boundary condition: displacement at end (x = 0) is 0, $C_2 = 0$

$$y=\frac{F}{4EI}\left[\frac{x^3}{3}-\frac{l^2x}{4}\right]=\frac{Fx}{4EI}\left[\frac{x^2}{3}-\frac{l^2}{4}\right]$$

$$x=\frac{l}{2}$$

$$y=\frac{Fl^3}{48EI}$$

$$E=\frac{Fl^3}{48Iy\left(l/2\right)}$$

Epoxy Bonded Joint

It is assumed that the plane sections remain plane. Although, there is a slight deformation at the ends of the epoxy bonded joints, the structure generally remains plane.

$$\varepsilon_{xx}=-\frac{y}{R}$$

Hooke's Law

$$\varepsilon_{xx}=\frac{1}{E}*\left[\tau_{xx}-\upsilon\left(\tau_{yy}+\tau_{zz}\right)\right]$$

It is assumed that the plane stresses are zero. $\tau_{yy} = \tau_{zz} = 0$

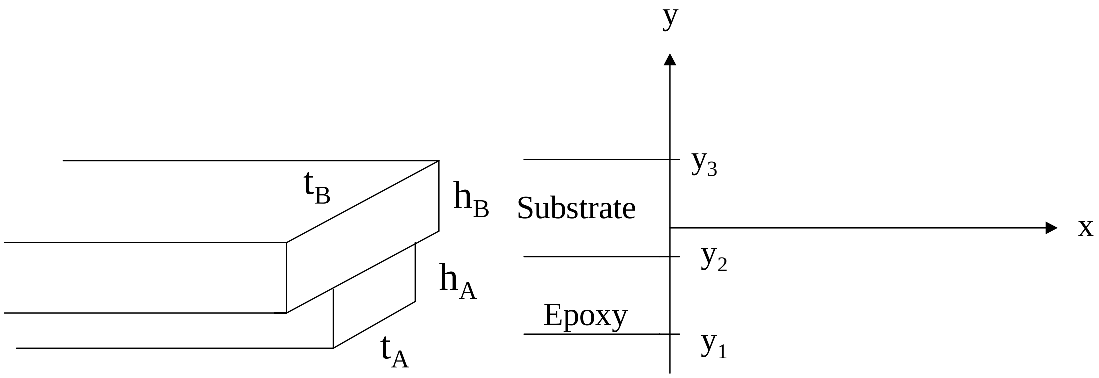
$$\varepsilon_{xx}=\frac{\tau_{xx}}{E}$$

$$\tau_{xx}=-\frac{Ey}{R}$$

$$\varepsilon_{yy}=\varepsilon_{zz}=\frac{\upsilon y}{R}$$

Locate the neutral surface of the epoxy bonded joint:

$$\int\tau_{xx}dA=0$$



$$0=\int_{y_1}^{y_3}\tau_{xx}dA=\int_{y_1}^{y_3}-\frac{Ey}{R}dA=\int_{y_1}^{y_2}-\frac{E_A}{R}ydA+\int_{y_2}^{y_3}-\frac{E_b}{R}ydA$$

$$E_At_A\int_{y_1}^{y_2}ydy+E_Bt_B\int_{y_2}^{y_3}ydy=0$$

$$E_At_A\frac{y_2^2-y_1^2}{2}+E_Bt_B\frac{y_3^2-y_2^2}{2}=0$$

$$y_1=y_2-h_A$$

$$y_3=y_2+h_B$$

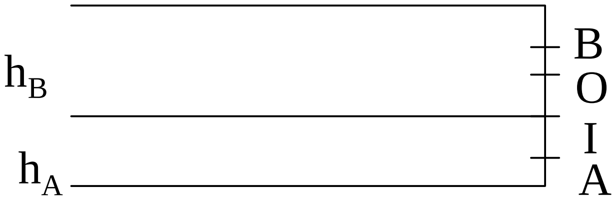
$$E_At_A\left[y_2^2-(y_2-h_A)^2\right]+E_Bt_B\left[(y_2+h_B)^2-y_2^2\right]=0$$

$$E_At_A\left[y_2^2-y_2^2+2y_2h_A-h_A^2\right]=E_Bt_B\left[y_2^2-y_2^2-2y_2h_B-h_B^2\right]$$

$$y_2\left[E_At_A2h_A+E_Bt_B2h_B\right]=E_At_Ah_A^2-E_Bt_Bh_B^2$$

$$y_2=\frac{E_At_Ah_A^2-E_Bt_Bh_B^2}{2\left[E_At_Ah_A+E_Bt_Bh_B\right]}$$

Moment of inertia of each section with respect to neutral axis



Axial Stress

$$M(x) = -\int_{y_1}^{y_3} \tau_{xx} y dA = \frac{1}{R}\int_{y_1}^{y_3} Ey^2 dA$$

$$M(x) = \frac{1}{R}\left[E_B \int_{y_2}^{y_3} y^2 dA_B + E_A \int_{y_1}^{y_2} y^2 dA_A \right] = \frac{1}{R}\left[E_B I_B + E_A I_A\right]$$

$$R = \frac{E_B I_B + E_A I_A}{M}$$

$$\tau_{xx} = \frac{-EyM}{E_B I_B + E_A I_A}$$

$$\tau_{xx,A} = -\frac{My}{\left(\frac{E_B}{E_A}\right) I_B + I_A}$$

$$\tau_{xx,B} = -\frac{My}{I_B + \left(\frac{E_A}{E_B}\right) I_A}$$

Maximum axial stress in adhesive occurs with a combination of maximum moment of inertia (x=l/2) and minimum y ($y=y_2-h_A$).

$$\tau_{xx,max} = -\frac{Fl}{4} * \frac{(y_2 - h_A)E_A}{I_B E_B + I_A E_A}$$

If $E_B I_B >> E_A I_A$, $y_2=-h_B/2$ and

$$\tau_{xx,max} \cong \frac{Fl}{4} * \frac{\left(\frac{h_B}{2} + h_A\right) E_A}{I_B E_B}$$

Interfacial Shear Stress

$$-\int \tau_{xx_1} dA_1 + \int \tau_{xx_2} dA_2 - \overline{\tau_{xy}} t_B dx = 0$$

$$\tau_{xx_1} = -\frac{My}{I_B + \frac{E_A}{E_B} I_A}$$

$$\tau_{xx_2} = -\frac{My}{I_B + \frac{E_A}{E_B} I_A} - \frac{d}{dx}\left[\frac{My}{I_B + \frac{E_A}{E_B} I_A}\right]_{A_1} dx$$

$$-\overline{\tau_{xy}}t_B dx - \int \frac{d}{dx}\left[\frac{My}{I_B + \frac{E_A}{E_B} I_A}\right] dA dx = 0$$

$$-\overline{\tau_{xy}}t_B dx - \int \frac{y}{I_B + \frac{E_A}{E_B} I_A} \frac{dM}{dx} dA dx = 0$$

$$\frac{dM}{dx} = -V$$

$$-\overline{\tau_{xy}}t_B + \frac{V}{I_B + \frac{E_A}{E_B} I_A} \int y dA = 0$$

$$\overline{\tau_{xy}} = \frac{V}{I_B + \frac{E_A}{E_B} I_A} \int_{y_2}^{y_3} y dy$$

$$\overline{\tau_{xy}} = \frac{V}{I_B + \frac{E_A}{E_B} I_A} * \frac{1}{2}\left[y_3^2 - y_2^2\right]$$

$$\overline{\tau_{xy}} = \frac{V}{2} * \frac{\left[2y_2 h_B + h_B^2\right]}{I_B + \frac{E_A}{E_B} I_A}$$

VITA

Michelle K. Lian

The author, Michelle Kuo-Ling Lian, was born July 25, 1973 in Taipei, Taiwan. She is the daughter of Mr. and Mrs. Jeng Lian. She and her family immigrated to the United States in the spring of 1990. Michelle graduated from high school in Kissimmee Florida in 1991. Michelle then went on to attend the University of Florida where she earned a Bachelor of Science degree in Materials Science and Engineering, with honors, in 1996. Michelle decided to pursue a Masters of Science in Materials Science and Engineering at Virginia Polytechnic Institute and State University under the guidance of Dr. Brian Love. Michelle completed her graduate degree in the summer of 1998.