Degradation of High Voltage Glass Fiber-Reinforced Polymer Matrix Composites by Aggressive Environmental Conditions

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University of Denver

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DEGRADATION OF HIGH VOLTAGE GLASS FIBER-REINFORCED POLYMER MATRIX COMPOSITES BY AGGRESSIVE ENVIRONMENTAL CONDITIONS

A Thesis
Presented to
the Faculty of the Daniel Felix Ritchie School of
Engineering and Computer Sciences
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In Partial Fulfillment
of the Requirements for the Degree
Master of Science

by
Tianyi Lu
August 2014
Advisor: Dr. Maciej Kumosa
Abstract

Polymer matrix composites reinforced with either E glass or ECR glass fibers-reinforced are used in a variety of high voltage electrical applications because of their advantages like lower weight and cost. However, they can be damaged by aggressive in-service conditions such as high temperature, ultraviolet radiation, moisture, ozone and corrosive environments. Different degradation mechanisms can develop in high voltage PMCs under those extreme environments, which, in turn, can affect the long term structural durability of the composites. A set of PMCs reinforced with ECR-glass and E-glass fibers embedded in four different resins has been investigated in this study. In addition, two PMC systems with surface coatings were also tested. The composites were supplied to the project by a US high voltage equipment manufacturer. The composites were subjected in four different tests to the individual and combined effects of UV radiation, elevated temperature, moisture, and nitric acid solutions. The surface degradation of the composites was subsequently analyzed using optical and scanning electron microscopy (SEM) techniques. Fourier transform infrared spectroscopy (FTIR) techniques are used to analyze chemical structure of the composites.
Acknowledgements

I am greatly indebted to a large group of people without whose help this thesis would not have been finished.

First of all, I would like to express my appreciation to my adviser Professor Maciej Kumosa for his invaluable guidance in my two years of graduate studies and research. I also appreciate the support of Professor Yun-bo Yi, Professor Paul Predecki, and Professor Davor Balzar for serving as the committee members in my final oral examination. Dr. Murugaverl, Balsingham from the Chemistry Department at DU gave me numerous suggestions on FTIR analysis.

Secondly, I thank all my lab mates, especially, Dr. Euripides Solis-Ramos. Euri helped me a lot with everything related to this thesis.

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Last but not least, I would like to give my special thanks to my family; their encouragement drives me until the end of my study. Also, thanks so much to my friends; they make me not lonely here. I enjoy all the happy time with them.

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Chapter One: General introduction

Glass fiber-reinforced Polymer (GRP) Matrix Composites are used in high-voltage insulators in a variety of electrical applications, which are significant for the operational safety and efficiency of transmission systems of electrical power. Therefore there is no surprise that these composites must meet particularly high requirements with respect to their reliability. Compare with conventional insulators made of ceramics or porcelain, as were extensively used as standard around middle of the 20th century, composite insulators become more predominant in recent years in the area of insulation technology for high-voltage overhead transmission lines and substations (Schmuck, 2013).

One of the most important reasons why composite insulators are widely used is because of their low weight. The weight of a GRP composite insulator is generally only about 10% of the corresponding porcelain one (Gubanski, 2005). Another main reason is related to less costly, which would include lower cost for transport and even tower construction (Gubanski, 2005). In addition, as the principal load-bearing component GRP rods have a higher mechanical strength to weight ratio, which would contribute to more competitive of these insulators than traditional ones (Hackam, 1999). However, outdoor applications have been limited due to susceptibility to unstable combinations of environmental degradations, such as high temperature, ultraviolet radiation, moisture,
ozone and corrosive environments. As Polymer Matrix Composites (PMCs) can be damaged by aggressive in-service conditions, the expected lifetime and their long-term reliability are not always certain.

The reasons of failure that may happen in GRP insulators are complicated to explain, as different degradation mechanisms can develop under those extreme environments, which could affect the long term structural durability and properties of the composites. PMCs are susceptible to environmental degradation. Depending on the type of their matrix and the type of reinforcement, the reactions against them always results in a very important issue-analysis that needs to be attended to in order to prevent their structural integrity in conjunction to their susceptibility to changes in thermo-physical, mechanical and chemical properties.

This study has been requested by the sponsor because of the concern for the degradation resistance of these new composites. As the study does not aim to make any service life predictions, the main goal of the study was to compare all supplied composites and select the “best one” which shows the best combination of properties after accelerated-extreme environmental testing. At same time, making an initial assessment of degradation issues in four types of matrix based PMCs.

The study was performed at the University of Denver between 2012 and 2014.
Chapter Two: Literature review

There are two major purposes of this literature review. The first is to understand the concept of high voltage glass fiber-reinforced polymer matrix composites and their main application in transmission systems. The second is to understand the degradation of polymer composites which usually caused by aggressive environment was complicated. We know that composites make up a very wide and significant class of engineering materials, but what about high voltage glass polymer composites, or what a role it plays in our world.

It is well know that composites or glass polymer composites in this work exhibit many different advantages, such as high specific strength, high stiffness and low weight. Despite these innate advantages, there are concerns about the in-service durability of these materials, especially when it correlated to their capability for sustained performance under aggressive environmental conditions. Review of the possible degradation mechanisms which are resulted from environment conditioning was a significant part of the literature search.

2.1 Introduction to composites

A composite, in general, can be defined as a combination of two or more chemically and physically different phases separated by a distinct interface (Sabu
Thomas, 2012). The different materials work together to give more useful structural or unique properties which are not attainable by any of the component alone. However, composite materials should be distinguished from alloys, which can be comprised of two more constituents but are formed naturally through processes such as casting (Chung, 2010). Usually, we can easily tell the different constituents apart within one composite as they do not dissolve or blend into each other (Composite materials). An example is glass fiber reinforced polymer we used in our tests.

Since proper combination of different materials generates properties that transcend those of the components, considerable composite materials can be designed or tailored to satisfy the generally and extremely service conditions by appropriately selecting their constituents, their distributions, their proportions, their degrees of crystallinity, their morphologies, as well as the structure and composition of the interface between constituents (Chung, 2010).

Due to this powerful tailor capability, composites are manufactured to optimize material properties, chemical, physical and mechanical (mainly strength) properties. In the later, optimization of thermal (softening and melting points, thermal expansion /thermal conduction, specific heat,), electrical (electrical conductivity/electrical permittivity, dielectric loss), and acoustical properties are become more note as well (Akovali, 2001).

People have been making and using composites for many thousands of years. One example is concrete, which was described by Vitruvius, writing around 25 BC in his Ten Books on Architecture. Concrete is a mix of sand and cement and has good compressive
strength. In recent times adding metal rods to the concrete has been discovered to increase its strength (Wikipedia) (Composite materials).

As everyone knows that there are a whole lot of benefits we can achieve from these wonder composites, which are becoming an essential part of today’s materials, but what exactly advantages they have. Again, wonderful tailor capability that allows us to develop products with low weight, low cost, High strength, high stiffness, chemical resistance and faster assembly. Nowadays, composite materials are broadly used as materials in making electronic packaging to medical equipment, and aircraft structures to home building (Shaw, 2010)

2.1.1 Classifications

Composites usually are constitutive of a reinforcing material embedded in a matrix. Therefore, matrices play a very important role in the properties of the composites.

In traditional, composites can be classified on the basis of their matrix material. Hence, the main classes are metal matrix composites (MMCs), ceramic matrix composites (CMCs), and polymer matrix composites (PMCs) (see Figure 2.1) (Avila, 2003). The classifications according to types of reinforcement are particulate composites, fibrous composites, and structural composites (Bunsell, 1974) (W. D. Callister, 1991).
2.1.2 Polymer matrix composites

According to the following experiment, we mainly focus on polymer matrix composites. Polymers are very different depending on the beginning ingredients, but almost based on carbon, hydrogen, oxygen and other nonmetallic elements. PMCs are one of the most developed composite materials, and there are several categories, each with widespread applications.

At present, the plastic consumption for matrices is roughly estimated at:

- 60–65% of thermosets. The unsaturated polyester share is estimated at 85%, that of epoxies 10% and the remaining 5% for all the other thermosets.

- 35–40% of thermoplastics, particularly polypropylene but also polyester and advanced thermoplastics such as polyetherimide, PEEK, etc. (Biron, 2014).

In this work, as the studied materials are thermoset PMCs, literature work will concentrate on the thermoset polymer composites.
Matrices

The matrix usually comprises 30%–40% of composite structure (Akovali, 2001), which normally provides two main functions, first is to uniform distribute load to the reinforcements, second is to protect the reinforcements against surface abrasion, environmental corrosion and mechanical damage. In addition, it is certainly that heat resistance and thermal properties of the matrix are also very important, which related to residual stresses in the composite.

Thermosetting resins: Thermosetting resins have chemically cross-linked or three dimension network structures with covalent bonds with all molecules. They cannot be reshaped once solidified by cross-linking process (Sabu Thomas, 2012). The mechanical properties depend on the molecular units making up the cross-linking processes in the cure. Thermosets are essentially brittle materials, but epoxies are in general tougher than unsaturated polyester or vinyl ester (Monteiro, 1986). The most commonly examples are epoxides, polyesters and vinyl ester, followed by polyimides and bismaleimides (Akovali, 2001) (D.Hull, 1996).

Since vinyl ester epoxy, polyester, epoxy and a proprietary material (R1) are investigated in this study, Details on these four thermosetting resins are discussed in later sections.

Thermoplastics: compare with thermosets thermoplastic polymers are not cross-linked. In other words, they comprise linear or branched chain molecules having strong intramolecular bonds (covalent bones). Opposite to thermosets, thermoplastics can be reshaped and softened by heat, and have remarkable ductility. Examples include
polyethylene (PE), polypropylene (PP), polystyrene (PS), nylons, polycarbonate (PC), polyamide-imides, polyether ether ketone (PEEK), and so on (Sabu Thomas, 2012).

Advantages and drawbacks of using thermoset and thermoplastic resins are shown in Table 2.1.

Table 2.1: Advantages and disadvantages of using thermoset and thermoplastic matrices.

<table>
<thead>
<tr>
<th>Application</th>
<th>Property</th>
<th>Thermoset Matrix</th>
<th>Thermoplastic Matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matrix</td>
<td>Formulation</td>
<td>Complex</td>
<td>More Simple</td>
</tr>
<tr>
<td></td>
<td>Melt Viscosity</td>
<td>Low (at the Beginning)</td>
<td>Rather High</td>
</tr>
<tr>
<td></td>
<td>Fibre Impregnation</td>
<td>Comparably Easy</td>
<td>Very Difficult</td>
</tr>
<tr>
<td></td>
<td>Cost</td>
<td>Low to Medium</td>
<td>Low to High</td>
</tr>
<tr>
<td>Prepreg</td>
<td>Tack/Drape</td>
<td>Good</td>
<td>Comparably Low</td>
</tr>
<tr>
<td></td>
<td>Shelf Life</td>
<td>Very Poor</td>
<td>Good</td>
</tr>
<tr>
<td>Composite</td>
<td>Processing Cycle</td>
<td>Very Long</td>
<td>Short to Long</td>
</tr>
<tr>
<td></td>
<td>Processing Temperature and Pressure</td>
<td>Moderate</td>
<td>High</td>
</tr>
<tr>
<td></td>
<td>Size of Products</td>
<td>Can be Very Large</td>
<td>Small to Medium</td>
</tr>
<tr>
<td></td>
<td>Resistance to Solvents</td>
<td>Good</td>
<td>Poor to Good</td>
</tr>
<tr>
<td></td>
<td>Damage Tolerance</td>
<td>Poor to Excellent</td>
<td>Fair to Good</td>
</tr>
<tr>
<td></td>
<td>Resistance to Creep</td>
<td>Good</td>
<td>Not Known</td>
</tr>
<tr>
<td></td>
<td>Interlaminar Fracture</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td></td>
<td>Toughness</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td></td>
<td>Ease of Fabrication</td>
<td>Labour Intensive</td>
<td>Less Labour Intensive</td>
</tr>
</tbody>
</table>

Reinforcements

The reinforcement materials are often fibers but can also be common ground minerals (Ali Mkaddem, 2008). However, ground minerals always used as ‘fillers’ to lower cost. Carbon, glass and aramid fibers are now used widely in PMCs.

Glass fibers: Most glass fibers is an amorphous materials comprise a silica (SiO₂) network, with additions of oxides of calcium, boron, sodium, iron, and aluminum (D.Hull, 1996). They are produced by a viscous drawing process, with the diameter around 5-20um (Sabu Thomas, 2012).

Advantages: Light weight, high tensile strength, high chemical resistance, or electrical insulation, Low price.
Various different types of glass fibers have been developed during the last decades, such as A-glass (A=alkali), E-glass (E=electrical), C-glass (C=chemical), S-glass(S=strength), D-glass (D=dielectric), M-glass (M=modulus), T-glass (T=thermal), L-glass (L=low-loss), R-glass (R=resistance) and Z-glass (Z=zirconia) (Sabu Thomas, 2012). Following Table 2.2 shows some properties of glass fibers.

Table 2.2: Properties of commercial glass fibers.
Source: (Sabu Thomas, 2012)

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>Glass fiber type</th>
</tr>
</thead>
<tbody>
<tr>
<td>General properties</td>
<td></td>
<td>A</td>
</tr>
<tr>
<td>Filament diameter</td>
<td>µm</td>
<td></td>
</tr>
<tr>
<td>Refraction index</td>
<td></td>
<td>1.512</td>
</tr>
<tr>
<td>Density</td>
<td>g/cm³</td>
<td>2.47</td>
</tr>
<tr>
<td>Elastic properties</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tensile modulus</td>
<td>GPa</td>
<td>73</td>
</tr>
<tr>
<td>Shear modulus</td>
<td>GPa</td>
<td>29.6</td>
</tr>
<tr>
<td>Poisson’s ratio</td>
<td></td>
<td>0.20</td>
</tr>
<tr>
<td>Tensile strength (virgin filament)</td>
<td>GPa</td>
<td>3.1</td>
</tr>
<tr>
<td>Tensile strength (roving)</td>
<td></td>
<td>2.76</td>
</tr>
<tr>
<td>Stain at failure</td>
<td>%</td>
<td>3.6</td>
</tr>
<tr>
<td>Chemical resistance</td>
<td></td>
<td>11.1</td>
</tr>
<tr>
<td>Weight loss after 1 h in boiling water</td>
<td>%</td>
<td>12–15</td>
</tr>
<tr>
<td>Weight loss after 1 h in boiling H₂SO₄ (1 N)</td>
<td>%</td>
<td>12–15</td>
</tr>
<tr>
<td>Weight loss after 1 h in boiling NaOH (0.1 N)</td>
<td>%</td>
<td></td>
</tr>
<tr>
<td>Thermal properties</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>W/(m K)</td>
<td>1.1</td>
</tr>
<tr>
<td>Specific heat capacity</td>
<td>J/(kg K)</td>
<td>9</td>
</tr>
<tr>
<td>CTE</td>
<td>10⁻¹⁰/K</td>
<td>300</td>
</tr>
<tr>
<td>Maximum use temperature</td>
<td>°C</td>
<td></td>
</tr>
<tr>
<td>Electrical properties</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Relative dielectric constant</td>
<td></td>
<td>6.9</td>
</tr>
<tr>
<td>Loss tangent at 10⁶ Hz</td>
<td>10⁻⁷</td>
<td>500</td>
</tr>
<tr>
<td>Volume resistivity</td>
<td>Ω m</td>
<td>10¹⁰</td>
</tr>
</tbody>
</table>

As the experiment relates to different aggressive conditions, corrosion and thermal properties of fibers are very important.

Corrosion Properties: Commonly, corrosion resistance of glass fibers is in general fully controlled by the fiber sizing. Noncoated fibers would extremely corrode in alkali or acid environments or even water would deteriorate the properties of the fiber. Specially developed glass compositions in C-glass and Z-glass have a higher corrosion resistance.
resistance compared to E-glass in acidic and alkaline environments, respectively. The corrosion resistance of fibers is determined by the measurement of glass fiber weight loss when boiling in alkali or acid liquids or distilled water for 1 h (Lowrie, 1967).

**Thermal Properties:** The specific heat capacity of glass fibers is slightly lower compared to the value of its bulk glass equivalent, and mainly depends on the glass composition. An value between 700 and 800 J/(kg K) is found in literature (Bunsell A., 1988). The thermal conductivity of E-glass fibers is around 1.1W/ (m K). The coefficient of thermal expansion varies for the different glass compositions and is found between $2 \times 10^{-6}$ and $9 \times 10^{-6} \text{ K}^{-1}$ (see Table 2.2).

Generally, glass fibers have a very high thermal and electrical resistance and are hence often used in electronic and electrical components. In the testing, E-glass and ECR-glass fibers were embedded in four types of thermosetting polymers. The results may be affected by E-glass and ECR-glass fibers which should be considered carefully.

**Carbon fibers:** Carbon fibers, which are commonly around 7um, can be obtained at high temperature (1200–1400 °C) by the pyrolysis of organic precursor fibers (polymer) such as rayon, polyacrylonitrile (PAN), or pitch (Akovali, 2001).


A great deal of scientific effort has been directed toward improving and analyzing their performance in particular composite systems (Morgan, 2005) (Schwartz, 1992).
Different methods such as electrochemical and plasma techniques are used to increase the roughness of fibers’ surface (Sabu Thomas, 2012).

**Aramid fibers:** Aramids are aromatic polyamides and the most common two members of this family are Kevlar and Nomex, which were first introduced in the early 1970s (Akovali, 2001). Unique properties of Kevlar fiber over other fibers are shown in Table 2.3.

Advantages: low density, high strength, high modulus, toughness, and thermal stability, chemical inertness, good creep resistance. Disadvantage: flame resistant (can be ignited), low electrical conductivity.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Nylon 66</th>
<th>Kevlar 29</th>
<th>Kevlar 49</th>
<th>E-Glass</th>
<th>Steel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity</td>
<td>1.14</td>
<td>1.44</td>
<td>1.45</td>
<td>2.55</td>
<td>7.86</td>
</tr>
<tr>
<td>Tensile strength (MPa)</td>
<td>1000</td>
<td>2750</td>
<td>2760</td>
<td>1700</td>
<td>1960</td>
</tr>
<tr>
<td>Tensile modulus (GPa)</td>
<td>5.52</td>
<td>82.7</td>
<td>131</td>
<td>68.9</td>
<td>200</td>
</tr>
<tr>
<td>Elongation at break (%)</td>
<td>18</td>
<td>5.2</td>
<td>2.4</td>
<td>3.0</td>
<td>2.4</td>
</tr>
</tbody>
</table>

2.2 High voltage glass-reinforced polymer matrix composites

Polymer matrix composites are one specific material used in electrical power engineering. They can be conductive or insulating which depends on combination of fiber and resin. However, the crucial property of glass fiber reinforced polymer matrix composites (GFRP) here is insulation resistance.

The first fiber reinforced composites for electrical insulation purpose was asbestos reinforced phenolic resin compound introduced in 1915. Glass fiber reinforced composites containing unsaturated polyester as the matrix resin was developed in 1943.
Since then, electrical grade GFRPs have become established as structural insulating material because of their combination of high electrical insulating properties and mechanical strength. With the help of improved production techniques and technical innovations, these GFRP dielectrics are finding increased applications in the electrical power system, such as overhead high voltage transmission lines.

Here, high voltage is considered any voltage over approximately 110,000 volts in electric power transmission engineering. This is a classification based on the design of apparatus and insulation. Voltages above 230 kV are considered extra high voltage and require different designs compared to equipment used at lower voltages (Wikipedia, Electric power transmission).

### 2.2.1 Reinforcing fibers and polymer matrices

Usually, glass fibers have a quite high electrical resistance (see Table 2.4), so they are able to be used in electrical and electronic components.

On the other hand, the polymeric insulating materials used in electrical engineering have a very high molecular weight and consist of two or more polymeric compounds of several structural monomers normally bound together by covalent bonds.
Reinforcing fibers: E-glass (Electrical) and ECR-glass (Electrical Corrosion Resistance) are two main fibers broadly used in composite dielectrics. They help increase mechanical strength and provide high electrical insulating properties at same time.

E-glass was developed as a second form of glass fibers, named after its electrical insulation properties. This type was the first to be produced in filaments and today still forms more than 90% of all produced glass fibers worldwide for glass fiber-reinforced composites (Bunsell A., 1988).

E-glass is a glass composition that imparts among others strength, stiffness, corrosion resistance, low electrical conductivity, and essentially isotropic properties. The designation E-glass is specified by a compositional range for each inorganic oxide and
element in the glass (see Table 2.5). Therefore, physical and chemical properties vary to a limited extent depending on the exact composition (Bingham, 2010).

Table 2.5: Typical physical properties of E-glass.

<table>
<thead>
<tr>
<th>Property</th>
<th>Range of published valuesa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density – bulk (g/cm³)</td>
<td>2.54–2.62</td>
</tr>
<tr>
<td>Coefficient of thermal expansion – bulk (m/m/K)</td>
<td>4.9–6.0 × 10⁻⁶</td>
</tr>
<tr>
<td>Specific heat – bulk (kJ/kg K)</td>
<td>0.8</td>
</tr>
<tr>
<td>Softening temperature (°C)</td>
<td>830–916</td>
</tr>
<tr>
<td>Thermal conductivity – bulk (W/m K)</td>
<td>1.0</td>
</tr>
<tr>
<td>Refractive index – bulk</td>
<td>1.547–1.560</td>
</tr>
<tr>
<td>Tensile strength – filament (GPa)</td>
<td>3.1–3.8</td>
</tr>
<tr>
<td>Tensile modulus – filament (GPa)</td>
<td>76–81</td>
</tr>
<tr>
<td>Elongation at break – filament (%)</td>
<td>4.5–4.9</td>
</tr>
<tr>
<td>Poisson’s ratio</td>
<td>0.18</td>
</tr>
<tr>
<td>Dielectric strength – bulk (kV/mm)</td>
<td>10.3</td>
</tr>
<tr>
<td>Volume resistivity – bulk (ohm cm)</td>
<td>10¹⁵</td>
</tr>
</tbody>
</table>

Table 2.6 shows chemical compositions of E-glass and ECR-glass.

ECR-glass means chemically resistant modified E glass, which is a boron-free glass contained 2.5% TiO₂ and 2.9% ZnO. ZnO increases the acid resistance and ZrO₂ increases both acid and base resistance (Bingham, 2010).
Table 2.6: New ECR-glass variants with ZnO, TiO\(_2\), and 0.0–0.5% Li\(_2\)O.
Source: (Bingham, 2010).

<table>
<thead>
<tr>
<th>Examples</th>
<th>E-glass</th>
<th>ECR-glass</th>
<th>New ECR-glass variants Without Li(_2)O</th>
<th>With 0.45% Li(_2)O</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO(_2), wt%</td>
<td>59.45</td>
<td>58.1</td>
<td>59.00</td>
<td>58.70</td>
</tr>
<tr>
<td>Al(_2)O(_3), wt%</td>
<td>12.29</td>
<td>11.5</td>
<td>12.00</td>
<td>12.90</td>
</tr>
<tr>
<td>CaO, wt%</td>
<td>23.55</td>
<td>21.7</td>
<td>22.50</td>
<td>22.40</td>
</tr>
<tr>
<td>MgO, wt%</td>
<td>2.55</td>
<td>2.0</td>
<td>3.40</td>
<td>3.49</td>
</tr>
<tr>
<td>TiO(_2), wt%</td>
<td>1.10</td>
<td>2.8</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>Na(_2)O, wt%</td>
<td>0.90</td>
<td>1.0</td>
<td>0.90</td>
<td>0.90</td>
</tr>
<tr>
<td>ZnO, wt%</td>
<td>–</td>
<td>2.9</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>Li(_2)O, wt%</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Fe(_2)O(_3), wt%</td>
<td>0.25</td>
<td>0.1</td>
<td>0.20</td>
<td>0.20</td>
</tr>
<tr>
<td>RO (CaO + MgO)</td>
<td>26.10</td>
<td>23.7</td>
<td>25.90</td>
<td>25.80</td>
</tr>
<tr>
<td>SiO(_2)/RO</td>
<td>2.28</td>
<td>2.45</td>
<td>2.28</td>
<td>2.28</td>
</tr>
<tr>
<td>Lggs FT, °C</td>
<td>1258</td>
<td>1235</td>
<td>1234</td>
<td>1231</td>
</tr>
<tr>
<td>Liquidus, °C</td>
<td>1173</td>
<td>1166</td>
<td>1175</td>
<td>1161</td>
</tr>
<tr>
<td>Delta T, °C</td>
<td>85</td>
<td>69</td>
<td>59</td>
<td>50</td>
</tr>
<tr>
<td>Reference/Ex.</td>
<td>[13, 14]</td>
<td>[32, 33]</td>
<td>[7, 10]</td>
<td>[7, 10]</td>
</tr>
</tbody>
</table>

**Acid corrosion to glass fibers:**

Commonly, when E-glass fibers are subjected to acid environment, the oxides which are preferentially extracted from these fibers on acid leaching, e.g., with dilute H\(_2\)SO\(_4\) or HCl (Wallenberger, 1999) (Jones, 2006), are B\(_2\)O\(_3\), Na\(_2\)O, Al\(_2\)O\(_3\), CaO, MgO, Fe\(_2\)O\(_3\), and only a very small amount of SiO\(_2\). Ultimately, a porous silica fiber structure remains after acid leaching of a borosilicate E-glass fiber.

On the other hand, various oxides in E-glass fiber also exhibit influences in improving or impairing different properties. The high SiO\(_2\) content translates into high acid resistance. The low Al\(_2\)O\(_3\) content translates into reduced strength and stiffness. The high Na\(_2\)O content translates into a lower viscosity. The absence of B\(_2\)O\(_3\) translates into lower cost (Bingham, 2010).
**Polymer matrices:** Some high molecular polymers have quite insulation resistance because there is no free electron or ion which is basic requirement to form current. Of course, very high electric fields can free electrons from atoms (dielectric breakdown).

Compared to conventional ceramics, also known as “porcelain” in one of its forms, polymer materials has much lower density. Therefore, the products are remarkable lighter and easier to handle and install. The reduced weight also permits the use of lighter and less costly structures.

According to classification, the polymers are divided into thermosets and thermoplastics. Both of them have insulation resistance. But thermoplastics usually have relatively poor thermal resistance and their properties deteriorate rapidly at higher temperatures. In contrast, thermosets, in general, are more stable compared to thermoplastic materials in thermal properties. Hence thermosets are extensively used in electrical engineering for insulation purposes (Ravindra A., 2011). For example, epoxy resin as one of the most widely used materials in electrical engineering shown in Figure 2.2 has better insulation resistance than PVC at high temperature (Ravindra A., 2011).

![Figure 2.2: Specific insulation resistance variation with temperature of solid insulating materials. Source: (Ravindra A., 2011).](image)
2.2.2 The studied polymer matrices

There are four types of insulation resistant resins investigated in this study. All of samples are thermosetting polymers (Epoxy, Vinyl ester, Polyester and a proprietary material). In general, the price of epoxy and vinyl ester epoxy are relative higher than polyester and R1 is cheapest (Biron, 2014).

*Epoxy resin:* Epoxy resins, also known as polyepoxides are a class of reactive pre-polymers and polymers which contain epoxide groups (an oxygen atom united with two carbon atoms) (see Figure 2.3).

![Figure 2.3: Characteristic group for epoxies. Source: (Akovali, 2001)](image)

*Chemical process of curing:* Epoxy curing involves two phenomena, polymerization and cross-linking. During the initial stage of curing, polymerization is favored because in the case of catalyzed homo-polymerization terminal epoxides are the most reactive, and in the case of co-reactive agents primary reactions are more reactive than secondary ones. Then, after the molecular weight of the growing polymer approaches infinity, all monomers are connected by at least one bond and a network is formed. At this point, called the gel point, the polymer behaves like a very high-molecular-weight thermoplastic. From the gel point, cross-linking becomes the dominant phenomenon due to the lack of free monomers. Crosslinking involves interchain bonding of intrachain reactive sites, either intrachain epoxides or secondary sites on co-reactive agents. The cross-linking reactions produce a growing network and reduce the mobility of the chain segments. The
growth of the network results in mechanical and thermal stabilization of the structure, resulting in increasing modulus and glass transition and degradation temperatures. For example, a rubber transforms into a glass. In a glassy state, the mobility of reactants is severely restricted, so reaction becomes much slower until all the reactive sites available are exhausted (Hanna Dodiuk, 2014).

The most important Epoxy resin used as electrical insulating material, the so-called “Bisphenol-A Epoxy resin”, prepared by reaction of acetone and phenol is shown in Figure 2.4. Epoxy resins can be characterized by Fourier transform infrared (FTIR) analysis. In FTIR spectra, peaks at 890 cm\(^{-1}\) to 910 cm\(^{-1}\) are attributed to an epoxy group. A hydroxyl group is indicated by a broad band at 4000cm\(^{-1}\). (Ratna, 2009).

![Figure 2.4: The diglycidyl ether of bisphenol A (DGEBA). Source: (Hanna Dodiuk, 2014)](image)

Advantages of epoxy matrix in composites: Good mechanical properties; low shrinkage during cure (lowest within thermosets); resistance to numerous organic solvents and other chemicals; good adhesion to most fiber, fillers; good resistance to creep and fatigue; good electrical properties.

Drawbacks: Sensitivity to moisture (after moisture absorption (1%–6%), there usually is a decrease in the following: heat distortion point, dimensions and physical properties); difficulty in combining toughness and high-temperature resistances; high
CTE as compared to other thermosets; susceptibility to UV degradation (chalking); Cost (Donenov, 1992)

**Polyester (unsaturated):** Polyesters are macromolecules made by reacting a diacid or dianhydride with a dihydroxy compound (diols). Unsaturated polyesters (UPE) differ from saturated polyesters, in which maleic anhydride or fumeric acid is used in addition to a saturated diol, which provides unsaturation in the structure (C=\(C\) double bonds) (see Figure 2.5). Here, unsaturated polyester is considered to be used in composite matrix.

\[
\text{Figure 2.5: Synthesis of the unsaturated polyester backbone.}
\]
\text{Source: (Hanna Dodiuk, 2014)}

Besides unsaturated polyester resins are the most widely used cross-linkable polymeric materials for composites, comprising in excess of 80% of all thermoset resins (Hanna Dodiuk, 2014). Figure 2.6 shows chemical structure of one typical cross-linked unsaturated polyester resin.
Figure 2.6: Schematic representation of the chemical structure of styrene cross-linked unsaturated polyester resin chains based on the basic building blocks phthalic acid (yellow background), propylene glycol (blue background), and styrene (red background).

Source: (Hanna Dodiuk, 2014).

Functional groups are identified by FTIR analysis from the characteristics peaks: carboxylic acid (1710 cm\(^{-1}\)), ester (1730 cm\(^{-1}\)), double bond (1640 cm\(^{-1}\)), ether (1100–1250 cm\(^{-1}\)) and hydroxyl (3350–3500 cm\(^{-1}\)) (Ratna, 2009).

Advantages: Interesting price/property ratios; good mechanical and electrical properties; resistance to a great number of chemicals; resistance to light, weathering and water in spite of surface deteriorations (water resistance for boats); possibilities of transparency and food contact for suitable grades; ease of some manual processing methods.

Drawbacks: Natural flammability (but fire retardant grades); significant shrinkage of the current grades (but low shrink grades are also marketed); industrialization and reproducibility difficulties for some processes; limited behavior to bases, acids and
boiling water except for special grades; decomposition by the oxidizing strong acids; attack by some solvents.

In addition, significant improvement in hydrolytic stability, chemical resistance, and resistance to yellowing on exposure to ultraviolet radiation can also be obtained by substituting neopentyl glycol (NPG, see Figure 2.7) for propylene glycol.

![Figure 2.7: Chemical structure of neopentyl glycol. Source: (Hanna Dodiuk, 2014)](image)

**Vinyl ester**: vinyl esters (VE) are the reaction products of epoxy resins (difunctional or multifunctional) with unsaturated carboxylic acids such as acrylic acid and methacrylic acid (Launikitis, 1982) (see Figure 2.8).

![Figure 2.8: Reaction schemes for the synthesis of a VE resin. Source: (Ratna, 2009)](image)

Unlike UPE resins, unsaturation occurs only at the end in VE resins resulting in fewer crosslinks compared with UPE resin networks. Because of fewer crosslinks and
ether linkages in the structure, VE resin networks exhibit better flexibility, impact strength, tensile strength compared with UPE resins.

On the other hand, during the reaction of epoxy resins with carboxylic acid, several hydroxyl groups are formed along the VE chain. These hydroxyl groups allow H-bonds to form with the similar groups present in the glass fiber. That is why VE resins offer better adhesion with glass fibers or other polar substrates as compared with UPE resin. However, such adhesion occurs more in epoxy resins because more hydroxyl groups are present. VE resins offer much better corrosion resistance compared with general purpose UPE resins. The better corrosion resistance originates from the large number of atoms between the ester groups, low concentration of ester groups, and the steric hindrance offered by the pendent methyl group of methacrylic acids (Ratna, 2009).

In electrical industries, VE resin-based FRP are used to make components for electricity generating stations, transmission system, and televisions.

Technologically, vinyl ester resins are some kind of a compromise between unsaturated polyester resins and epoxy resins. Hence, VEs exhibits lots of advantages, especially for chemical and heat resistance. Besides, we can use aliphatics in the enchainment to replace aromatics improves the UV-resistance of the vinyl ester resin (Hanna Dodiuk, 2014).

**Proprietary Material R1:** Material R1s are polymers containing proprietary linkages (R2) and are available in thermoplastic and thermosetting forms.
Different R1s may have quite different properties, which we can synthesis them by selecting different polyol, polyisocynate, extender and modifier. According to the stiffness and cross-linking density, R1 can be classified into two main categories: rigid R1 and elastic R1 (see Figure 2.9).

In our GFRPs provided by sponsors, solid R1 is used as matrix, which is formed by react an isocyanate (MDI) with a polyol (diols). Figure 2.10 shows main chemical reactions involved to prepare R1s.

Branching and cross-linking are most commonly accomplished by the use of higher-functionality polyols. These are most conveniently based upon a triol or hexol backbone, which, in turn, help prepare rigid R1.

Figure 2.11 shows the spectrum of R1 by FTIR. Some characteristic peaks are shown in Figure.
All polymers can be depolymerized, R1s are no exception. There are several ways R1s can be depolymerized chemically, among them: hydrolysis, thermolysis, photolysis, pyrolysis and solvolysis (Naturalium, 2004).

For hydrolysis, ester, proprietary group (R3), and R2 are most susceptible to degradation (see Figure 2.12). The ester reverts to the precursor acid and alcohol; the urea bond can hydrolyze to form a carbamic acid and an amine. The carbamic acid normally is unstable and typically undergoes further reaction. The R2 linkage, although somewhat less susceptible, may undergo hydrolysis to yield a carbamic acid and the precursor alcohol.

\[
\begin{align*}
\text{Ester} & \quad \overset{\text{R-C-O-R'}}{\longrightarrow} \quad \text{R'-OH + H}_2\text{O} \\
\text{Carbamic acid} & \quad \overset{\text{R-C-OH + HO-R'}}{\longrightarrow}
\end{align*}
\]
For thermooxidation the ether is the weak link. Thermooxidation proceeds via a free radical mechanism. During thermooxidation degradation, the order of stability is: Ester > R3 > R2 >> ether (Naturalium, 2004).

Advantages: Broad range of moduli from very flexible to rigid materials; liquid state of suitable grades; ease and diversity of the processing methods; interesting price/property ratios; fair oil and fuel behaviors; fair or good mechanical and thermal resistances for suitable grades; possibilities of transparency and fire-proofing.

Drawbacks: Sensitivity to hydrolysis, acids and bases of the polyester types particularly; sometimes limited resistance to aging; natural combustibility; limited continuous use temperature for some grades; rather slow processing.

2.2.3 High voltage applications and experience

One of the most significant applications of HV PMCs is composite insulators which have become a popular alternative to porcelain in the manufacture of high voltage insulators (L. Kumosa, 2004) (see Figure 2.13).

Figure 2.13: schematic of a high voltage composite (non-ceramic) insulator.
Source: (L. Kumosa, 2004)
The concept of the composite insulator was actually developed in the USA in the 1950s. However, this technology was not taken seriously until the 1970s, when major progress had been made in aspects of the fiber reinforced materials, which form the basic core of the composite insulators, and the polymer, which form the housing of these insulators (Schmuck, 2013). When construction and material selection of composite insulators are designed appropriately, they will have great performances which conventional porcelain insulators cannot exhibit.

A further advantage of the composite insulator is its low weight, which facilitates transport and assembly and allows construction of lighter towers. In the case of high-voltage lines, the weight of conventional insulators may account for almost 20% of the entire vertical load on a tower. By contrast, composite insulators allow a weight saving of up to more than 90% compared to conventional insulators. The sensitivity of the composite structure to impact loads caused by power arc, dynamic mechanical forces is much lower than that of a conventional insulator (Schmuck, 2013). Figure 2.14 shows reasons for using composites insulators.

![Figure 2.14: Reasons for use of composite insulators. Source: (CIGRE, 2000)](image)
Act as key importance of transmission systems of electrical power for the operational safety, composite insulators should meet specific high requirements in terms of reliability.

The first transmission line insulators made of organic materials were those used more than 50 years ago in the USA. Many of them had to be replaced after a short period of use due to various problems. Building on this experience, the first “real” composite insulator then followed. A few years later, manufacturers from different countries, like Germany, the US, France and England began to manufacture composite insulators in the form we know today (Schmuck, 2013) (see Figure 2.15)

![Figure 2.15: Installed composite insulators according to the survey. Source: (CIGRE, 2000)](image)

The early polymer insulating materials (first and second generation of composite insulators) did not provide the expected service life of at least forty years. It was primarily because of inadequate UV, tear or hydrolytic resistance, corrosive resistance and thermal resistance. Even though the use of polymeric materials for outdoor HV insulators in the power industry has been rapidly increasing with the development in
material science, aggressive environment conditions are still a serious problem to reliability of outdoor PMCs insulators.

2.3 Overview of testing and certification

When it comes to service time of one composite product, the ability to predict its failure rate would be highly beneficial and significant. The composite should be tested in real time and in similar environments where the products will be exposed. Unfortunately, this is not always possible. Sometimes, in order to achieve final result quickly, laboratory accelerated tests will be conducted with a simulated environmental conditions.

Since composites degradation caused by environments is extremely complicated, it is difficult to predict service lifetime. A lot of results we see are that the design of this product is total failure or basic eligible. In addition, a PMC product is highly dependent upon the manufacturer, the additive package, and its processing history. Slight composition and manufacturing changes can cause drastic changes in performance and results.

In this work, based on the PMC application in HV insulators, physical and chemical failures caused by different environment factors are carefully considered. Finally, ultraviolet irradiation, moisture, acid corrosion, thermal stability are selected to be simulated factors and conducted in our tests.

2.3.1 Ultraviolet (UV) radiation

Ultraviolet (UV) light is electromagnetic radiation with a wavelength shorter than that of visible light, but longer than X-rays. And only 3% of total ultraviolet in vacuum
reaches ground, which are consisted by 95% UVA (400-315nm) and 5% UVB (315-280nm), other short wave UV is blocked by oxygen, a great deal (>97%) of mid-range ultraviolet is blocked by the ozone layer (Wikipedia).

The UV components of solar light incident on the earth surface are in the 280-400 nm band. The energy of these UV photons is comparable to the dissociation energies of polymer covalent bonds, which are typically 290-430 KJ/mole (Bhavesh G. Kumar, 2002).

Table 2.7: Bond strength in polyatomic molecules.
Source: (Lide, 1995) (Pauling, 1970)

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond Strength* (dissociation energy) (kJ/mole)</th>
<th>Bond strength (eV/bond)</th>
<th>Bond Energy** (kJ/mole)</th>
<th>Molecule</th>
<th>Bond Length* (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-C</td>
<td>376</td>
<td>3.9</td>
<td>348</td>
<td>CH₃-CH₃</td>
<td>0.154</td>
</tr>
<tr>
<td>C=C</td>
<td>733</td>
<td>7.6</td>
<td>615</td>
<td>H₂C=CH₂</td>
<td>0.13</td>
</tr>
<tr>
<td>C≡C</td>
<td>965</td>
<td>10</td>
<td>812</td>
<td>HC≡CH</td>
<td>0.12</td>
</tr>
<tr>
<td>C-H</td>
<td>439</td>
<td>4.55</td>
<td>415</td>
<td>H-CH₃</td>
<td>0.11</td>
</tr>
<tr>
<td>C-N</td>
<td>298</td>
<td>3.09</td>
<td>292</td>
<td>C₆H₅CH₂-NH₂</td>
<td>0.15</td>
</tr>
<tr>
<td>C-O</td>
<td>277</td>
<td>2.87</td>
<td>350</td>
<td>CH₃⁺</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>OC(CH₃)₂CH₂</td>
<td></td>
</tr>
<tr>
<td>C=O</td>
<td>532</td>
<td>5.51</td>
<td>725</td>
<td>O=CO</td>
<td>0.12</td>
</tr>
<tr>
<td>C-F</td>
<td>472</td>
<td>4.89</td>
<td>441</td>
<td>F-CH₃</td>
<td>0.14</td>
</tr>
<tr>
<td>C-Cl</td>
<td>350</td>
<td>3.63</td>
<td>328</td>
<td>Cl-CH₂Cl</td>
<td>0.18</td>
</tr>
<tr>
<td>O-H</td>
<td>437</td>
<td>4.53</td>
<td>463</td>
<td>H-OCH₃</td>
<td>0.1</td>
</tr>
<tr>
<td>O-O</td>
<td>157</td>
<td>1.63</td>
<td>143</td>
<td>CH₃O-OCH₃</td>
<td>0.15</td>
</tr>
<tr>
<td>O-Si</td>
<td>536</td>
<td>5.56</td>
<td>432</td>
<td>HO-Si(CH₃)₃</td>
<td>0.16</td>
</tr>
<tr>
<td>N-H</td>
<td>383</td>
<td>3.97</td>
<td>391</td>
<td>H-N(CH₃)₂</td>
<td>0.1</td>
</tr>
<tr>
<td>N-O</td>
<td>175</td>
<td>1.81</td>
<td>175</td>
<td>CH₃O-NO</td>
<td>0.12</td>
</tr>
<tr>
<td>F-F</td>
<td>158</td>
<td>1.64</td>
<td>158</td>
<td>F-F</td>
<td>0.14</td>
</tr>
<tr>
<td>H-H</td>
<td>436</td>
<td>4.52</td>
<td>436</td>
<td>H-H</td>
<td>0.074</td>
</tr>
</tbody>
</table>

* Values from Handbook of Chemistry and Physics, 76th ed. 1995-96
Note: bond energy values are negative for forming bonds (energy is released) and positive for breaking bonds (energy absorbed).

Table 2.7 shows different covalent bonds which have various bond strengths. In order to compare the bond strengths (in eV/bond) with UV photon energies (in eV/photon), energies for different wavelength of UV photons were calculated.

\[ v = f \times \lambda \]  

(2.1)

where:

- \( v \) radiation velocity (in vacuum)
- \( f \) radiation frequency
- \( \lambda \) radiation wavelength

According to quantum theory, electromagnetic waves carry discrete amount of energy, the magnitude of which depends on their frequency, as stated by Planck’s Law:

\[ E = h \times f \]  

(2.2)

where:

- \( E \) energy of radiation
- \( f \) frequency of radiation
- \( h \) Planck’s constant

Eq. (2.2) can be used for calculating the energy of radiation of known wavelength.

The excitation energy per mole can be obtained by multiplying the molecular excitation energy by Avogadro’s number:

\[ E = Nh_f = \frac{Nh c}{\lambda} = \frac{119586}{\lambda} \left[ \frac{kJ}{mol} \right] \]  

(2.3)

where:

- \( E \) energy of radiation of a given wavelength
- \( N \) Avogadro’s number = 6.022 × 10^23 in mol⁻¹
- \( h \) Planck’s constant = 6.626 × 10⁻³⁴ J s
- \( f \) frequency of radiation
- \( c \) velocity of light = 2.998 × 10^8 m/s
- \( \lambda \) wavelength of radiation in nm

By Eq. (2.3), we can calculate the energy of various wavelengths of photons. The results are shown in Table 2.8.
Table 2.8: Photon energy distributions by various wavelengths

<table>
<thead>
<tr>
<th>Wavelength (μm)</th>
<th>280</th>
<th>290</th>
<th>320</th>
<th>350</th>
<th>380</th>
<th>400</th>
</tr>
</thead>
<tbody>
<tr>
<td>Each photon (eV)</td>
<td>4.43</td>
<td>4.27</td>
<td>3.88</td>
<td>3.54</td>
<td>3.32</td>
<td>3.10</td>
</tr>
<tr>
<td>Energy (KJ/mole)</td>
<td>427</td>
<td>412</td>
<td>374</td>
<td>342</td>
<td>320</td>
<td>299</td>
</tr>
</tbody>
</table>

The conversion factors are: 1kJ/mole = .010365eV/bond

If the photon energy is greater than or equal to the bond strength then bond breakage can take place. Thus the UVB will break this bond but the UVA will not.

According to Table 2.7 and 2.8, it can be seen that the energy of UV photons can be comparable to the dissociation energies of polymer covalent bonds such as C-C bond.

Generally, all the chain scission caused by UV exposure is a result of oxidation initiated by high energy photon radiation. Hydroperoxides are one significant intermediate which may result in chain scission and crosslinking.

### 2.3.2 Diffusivity and moisture

Pure polymer and composites have quite different diffusivity and moisture problem since fibers involved. Interface between fiber and matrix makes diffusion extremely undefended and complex. Under certain situation such as specific geometrical dimension of samples, diffusion rules still work. Unfortunately, according to the proportion of width, length and thickness of our specimens, diffusion rules (Fick’s law) are not work.

Since moisture resistance highly depends on chemical structure of resin which we are not being told by sponsor, it is difficult to tell which composite has a better moisture
resistance. But commonly, hydroxyl group helps in water absorption. Hydrolysis may also occur slowly in ester group.

### 2.3.3 Chemical corrosion

Corrosion is normally defined as the interaction of a material with its environment through which a chemical or electrochemical reaction takes place thereby degrading the material. In this study, nitric acid corrosion is a key issue which is used to simulate acid rain in our real environment. Acid provides active hydrogen ions which may cause oxidation reaction in the composites.

### 2.3.4 Thermal stability

As all specimens are thermoset polymers, this means they have relative high thermal resistance. In our testing, the maximum temperature is 80°C, which is below glass transition temperatures. So it is not necessary to consider decomposition process of composites during UV radiation and thermal tests. Since thermal resistance highly depends on chemical structure of resin which we are not being told by sponsor, it is difficult to tell which composite has a better thermal reliability.

### 2.3.5 Example

Following Figure 2.16 shows an example of vinyl ester epoxy resin. It is well known that different chemical structures of polymer may lead to various physical and chemical properties. So if we do not know the chemical structure, it would be hard to analysis some physical or chemical performances.
Figure 2.16: Schematic representation of the chemical structure of vinyl ester epoxy resin.

① Relate to physical properties such as thermal resistance

② Relate to infiltrating property

③ Relate to ductile properties such as impact resistance

④ Relate to active property

⑤ Relate to chemical resistance
2.4 Thesis statement

Based on individual and combined effects of aggressive environment (UV radiation, elevated temperature, moisture, and nitric acid solutions), some foundational research was done to analyze different outcomes of high voltage composite insulation rod, which will help explain different mechanisms of degradation in composites.
Chapter Three: Experimental procedure

3.1 Materials

The GRP composites tested in this project are listed in Table 3.1. The materials were supplied for this research by sponsor. The manufacturer did not agree to release the chemical structure of the resin as well as nanocoating.

<table>
<thead>
<tr>
<th>Label</th>
<th>Composites</th>
<th>Matrix</th>
<th>Fiber (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A</td>
<td>Vinyl ester Epoxy</td>
<td>ECR-Glass 1</td>
<td>75% glass</td>
</tr>
<tr>
<td>3A</td>
<td>Vinyl ester Epoxy</td>
<td>E-Glass 1</td>
<td>75% glass</td>
</tr>
<tr>
<td>4b</td>
<td>Vinyl ester Epoxy</td>
<td>ECR-Glass 2</td>
<td>80% glass</td>
</tr>
<tr>
<td>6</td>
<td>Polyester</td>
<td>ECR-Glass 2</td>
<td>80% glass</td>
</tr>
<tr>
<td>10</td>
<td>Epoxy</td>
<td>ECR-Glass 2</td>
<td>80% glass</td>
</tr>
<tr>
<td>11</td>
<td>Proprietary material (R1)</td>
<td>ECR-Glass 2</td>
<td>80% glass</td>
</tr>
<tr>
<td>1AN</td>
<td>Nano-coated Vinyl ester Epoxy</td>
<td>ECR-Glass 1</td>
<td>75% glass</td>
</tr>
<tr>
<td>11N</td>
<td>Nano-coated R1</td>
<td>ECR-Glass 2</td>
<td>80% glass</td>
</tr>
<tr>
<td>5</td>
<td>Polyester</td>
<td>E-Glass 1</td>
<td>80% glass</td>
</tr>
<tr>
<td>9</td>
<td>Epoxy</td>
<td>E-Glass 1</td>
<td>80% glass</td>
</tr>
</tbody>
</table>

3.2 Specimens preparation

Samples of the nominal size 50×80×6 mm were dry-cut with special care to ensure minimum damage to the composites during cutting. The edges of the samples were sealed with a thin layer of an RTV, and subsequently dried in an oven at 80°C for five days before the test.
3.3 Ultraviolet testing in Theory and practice

3.3.1 Ultraviolet chamber

A Q-LABQUV/SPRAY/RP chamber (as shown in Figure 3.1) was used to simulate the environmental conditioning. Although UVB lamps can degrade GRPs faster, UVA lamps are especially useful for comparing different types of polymers, which provides the best possible simulation of sunlight in the critical short wavelength region from 365 nm down to the solar cutoff of 295 nm. Intensity is controlled around 1.5 W/m² which is nearly double higher than noon summer sunlight for fast test result.

![Q-LABQUV/SPRAY/RP chamber](image)

Figure 3.1: Q-LABQUV/SPRAY/RP chamber

3.4 Performed Ultraviolet tests

3.4.1 UV radiation tests

The GRP composites tested under UV radiation condition are listed in Table 3.2. Six PMCs and two new nano-coated composites were investigated in this part of the project. All samples followed the previously mentioned preparation procedure.
Table 3.2: Description of the studied glass fiber reinforced polymer composites under hot dry UV.

<table>
<thead>
<tr>
<th>Label</th>
<th>Composites</th>
<th>Fiber (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A</td>
<td>Vinyl ester Epoxy</td>
<td>ECR-Glass 1, 75% glass</td>
</tr>
<tr>
<td>3A</td>
<td>Vinyl ester Epoxy</td>
<td>E-Glass 1, 75% glass</td>
</tr>
<tr>
<td>4b</td>
<td>Vinyl ester Epoxy</td>
<td>ECR-Glass 2, 80% glass</td>
</tr>
<tr>
<td>6</td>
<td>Polyester</td>
<td>ECR-Glass 2</td>
</tr>
<tr>
<td>10</td>
<td>Epoxy</td>
<td>ECR-Glass 2</td>
</tr>
<tr>
<td>11</td>
<td>Proprietary material R1</td>
<td>ECR-Glass 2</td>
</tr>
<tr>
<td>1AN</td>
<td>Nano-coated Vinyl ester Epoxy</td>
<td>ECR-Glass 1, 75% glass</td>
</tr>
<tr>
<td>11N</td>
<td>Nano-coated R1</td>
<td>ECR-Glass 2</td>
</tr>
</tbody>
</table>

The UV chamber was used in the hot dry UV testing. The tests were carried out for 1008 hours (42 days) of UV radiation with the wavelength ranging from 315 to 400 nm (UVA) at 1.50 W/m². The tests were conducted at 80 °C and the relative humidity (RH) in the chamber was 3 ± 2%. The weight of the specimens was determined every 100 hours. The surface conditions of the specimens were analyzed using the JEOL model JSM 5800 LV Scanning Electron Microscope (SEM) and an optical Olympus BX51M microscope.

3.4.2 Water condensation tests

The same six composites and two nano-coated composites, as tested under UV radiation condition, were investigated in this part of the project. In addition, two E-glass fiber composites were investigated (see Table 3.3). All samples followed the previously mentioned preparation procedure.
Table 3.3: Description of the studied glass fiber reinforced polymer composites under water condensation condition

<table>
<thead>
<tr>
<th>Label</th>
<th>Composites</th>
<th>Fiber (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A</td>
<td>Vinyl ester Epoxy</td>
<td>ECR-Glass 1, 75% glass</td>
</tr>
<tr>
<td>3A</td>
<td>Vinyl ester Epoxy</td>
<td>E-Glass 1, 75% glass</td>
</tr>
<tr>
<td>4b</td>
<td>Vinyl ester Epoxy</td>
<td>ECR-Glass 2, 80% glass</td>
</tr>
<tr>
<td>6</td>
<td>Polyester</td>
<td>ECR-Glass 2 80% glass</td>
</tr>
<tr>
<td>10</td>
<td>Epoxy</td>
<td>ECR-Glass 2 80% glass</td>
</tr>
<tr>
<td>11</td>
<td>R1</td>
<td>ECR-Glass 2 80% glass</td>
</tr>
<tr>
<td>1AN</td>
<td>Nano-coated Vinyl ester Epoxy</td>
<td>ECR-Glass 1, 75% glass</td>
</tr>
<tr>
<td>11N</td>
<td>Nano-coated R1</td>
<td>ECR-Glass 2 80% glass</td>
</tr>
<tr>
<td>5</td>
<td>Polyester</td>
<td>E-Glass 1 80% glass</td>
</tr>
<tr>
<td>9</td>
<td>Epoxy</td>
<td>E-Glass 1 80% glass</td>
</tr>
</tbody>
</table>

The UV chamber was used in the water condensation testing. The tests were carried out for nearly 2000 hours in the hydrothermal environment. The tests were conducted at 60 °C and the relative humidity (RH) in the chamber was 92 ± 2%. The weight of the specimens was determined every 100 hours. The surface conditions of the specimens were analyzed using the JEOL model JSM 5800 LV Scanning Electron Microscope (SEM).
3.4.3 UV & condensation cyclic exposure tests

The same six PMCs were investigated in this part of the project (see Table 3.4).

Table 3.4: Description of the studied glass fiber reinforced polymer composites under UV/water condensation condition

<table>
<thead>
<tr>
<th>Label</th>
<th>Composites</th>
<th>Matrix</th>
<th>Fiber (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A</td>
<td>Vinyl ester Epoxy</td>
<td>ECR-Glass 1, 75% glass</td>
<td></td>
</tr>
<tr>
<td>3A</td>
<td>Vinyl ester Epoxy</td>
<td>E-Glass 1, 75% glass</td>
<td></td>
</tr>
<tr>
<td>4b</td>
<td>Vinyl ester Epoxy</td>
<td>ECR-Glass 2, 80% glass</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Polyester</td>
<td>ECR-Glass 2 80% glass</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Epoxy</td>
<td>ECR-Glass 2 80% glass</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>R1</td>
<td>ECR-Glass 2 80% glass</td>
<td></td>
</tr>
</tbody>
</table>

Again, the UV chamber (Figure 3.1) was used to simulate the environmental conditions. The tests were conducted on a set of specimens (six PMC) for 1008 hours of exposure. Each cycle of exposure in the chamber consisted of 16 hours of UVA (400nm – 315 nm) radiation 1.50 W/m² at 80°C followed by 8 hours of deionized (DI) water condensation at 60°C. The Relative Humilities (RH) under the UV and water condensation were 33 ± 2% and 92 ± 2%, respectively. This sequence of environmental conditions was applied in identical series until it reached 1008 total hours of exposure.

3.5 Thermal stability tests

The same six PMCs and two nano-coated composites were investigated in this part of the project (see Table 3.2). All samples followed the previously mentioned preparation procedure.
A Model 40GC Lab Oven was used to simulate the thermal environment. The tests were conducted for 1008 hours (42 days) at 80 °C and the relative humidity (RH) in the oven was 3 ± 2%. The weight of the specimens was determined every 100 hours. The surface conditions of the specimens were analyzed using the JEOL model JSM 5800 LV Scanning Electron Microscope (SEM).

3.6 Mass change tests

After the tests, the specimens were weighed using an Ohaus Voyager Electronic Scale (200 gram maximum mass limit). It should be noted that the weight measurements of specimens were made when a correspondent cycle ended to avoid the interruption of the established cycles. The percent weight changes as a function of time were calculated using the well-known equation:

\[
\% \text{ weight change} = \frac{W_f - W_i}{W_i} \times 100 \quad (3.1)
\]

where \(W_f\) is the final weight of the tested sample and \(W_i\) is the initial weight of the dried specimens at room temperature.

The specimens were initially weighed at room temperature and no discernible difference on the basis of the sealant was observed. Also, for each composite no specific variations of thickness or fabric architecture in their components were observed. These results were used to generate baseline data and, hence, achievable direct comparison (mass change curves) on the basis of their general structure after the exposure.
3.7 Performed nitric acid exposure tests

3.7.1 Nitric acid exposure tests

The same composites as in the water condensation tests were investigated here for their resistance to nitric acid exposure. All samples followed the previously mentioned preparation procedure. The details of the matrix and the fibers of the composites are presented in Table 3.1.

The specimens were partially submerged with only one side of each specimen being exposed to 0.063 mol/L (pH = 1.2) and 1 mol/L (PH = 0) nitric acid for two weeks at room temperature. After the exposure, all specimens were dried at room temperature for seven days before subsequent SEM surface characterizations using the SEM.

3.7.2 UV tests followed by nitric acid exposure.

The same composites as in the UV radiation tests were investigated here for their resistance to nitric acid exposure after UV radiation. All samples followed the previously mentioned preparation procedure. The details of the matrix and the fibers of the composites are presented in Table 3.2.

The specimens were partially submerged with only one side of each specimen being exposed to 0.063 mol/L (pH = 1.2) and 1 mol/L (PH = 0) nitric acid for two weeks at room temperature. After the exposure, all specimens were dried at room temperature for seven days before subsequent SEM surface characterizations using the SEM.
3.7.3 **UV & condensation tests followed by nitric acid exposure.**

The same composites as in the UV & condensation tests were investigated here for their resistance to nitric acid exposure after combined effect of UV and condensation. All samples followed the previously mentioned preparation procedure. The details of the matrix and the fibers of the composites are presented in Table 3.4.

The specimens were partially submerged with only one side of each specimen being exposed to 0.063 mol/L (pH = 1.2) nitric acid for two weeks at room temperature. After the exposure, all specimens were dried at room temperature for seven days before subsequent SEM surface characterizations using the SEM.

### 3.8 Fourier transform infrared spectroscopy

A Shimadzu IRAffinity-1 Spectrometer was used to analyze the chemical structure changing of the specimens after nearly 1000 hours of UV radiation. As our specimens are glass fiber reinforced thermoset polymer composites, it is difficult to make them to powders. So here, we set cleaned specimens on the crystal in the equipment directly.

### 3.9 Microscope

A JSM 500 LV scanning electron microscope (SEM) was used to evaluate the surface degradation of the specimens after 1000 hours of exposure. All specimens were prepared and mounted using conventional procedures for electron and optical microscope observations.
Chapter Four: Results

4.1 UV radiation tests

Figure 4.1 shows the changes in weight for the composites during the 1000 hours of exposure. It can be seen that the specimens exhibited immediate loss in weight from the very first hours of testing. All PMCs after 1000 hours of exposure lost between 0.03 to 0.06 % of their weight.

For the new Nanocoated composites there was a significant exception in weight change behavior for one sample. Specimen 11N (Nanocoated R1 ECR-Glass 2) showed a loss in weight up to 50 % more than the rest of the composites. The percent of weight loss (0.1%) was similar to those obtained for the composites after 1000 hours of exposure to UV/water condensation. However, the 1A Nano-coated specimen exhibited the same behavior as the rest of the composites with a very similar weight loss tendency.
Table 4.1 shows the resulted average mass changes after longer exposure times (500 and 1000 hours) for comparison purposes. As it can be seen that the least degraded specimen after the UV exposure for 1000 hours was the specimen 10 (Epoxy ECR-Glass 2) with only 0.029% followed by specimen 6 (Polyester ECR-Glass 2) with 0.037% weight loss. In contrast, the most severe degradation was observed in 11N (Nano-coated R1 ECR-Glass 2) with a 0.1% weight loss.
Table 4.1: Average percent mass changes of six PMCs after 500 hours and 1000 hours in the UV chamber.

<table>
<thead>
<tr>
<th>Composite</th>
<th>500 h</th>
<th>1000 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A</td>
<td>-0.03372</td>
<td>-0.05046</td>
</tr>
<tr>
<td>3A</td>
<td>-0.03278</td>
<td>-0.0485</td>
</tr>
<tr>
<td>4b</td>
<td>-0.0288</td>
<td>-0.04558</td>
</tr>
<tr>
<td>6</td>
<td>-0.02131</td>
<td>-0.03707</td>
</tr>
<tr>
<td>10</td>
<td>-0.01993</td>
<td>-0.02994</td>
</tr>
<tr>
<td>11</td>
<td>-0.04311</td>
<td>-0.05908</td>
</tr>
<tr>
<td>1AN</td>
<td>-0.02927</td>
<td>-0.04932</td>
</tr>
<tr>
<td>11N</td>
<td>-0.06615</td>
<td>-0.10215</td>
</tr>
</tbody>
</table>

4.1.1 Surface morphology after UV exposure.

In Figure 4.2 several micrographs are shown of composite surfaces before and after dry hot UV exposure. The micrographs were obtained using an optical microscope. The images exhibited different contrasts in colors ranging from opaque to light yellow. Photo-yellowing effects happened generally in all the samples, especially for those PMCs that have double bonds or conjugated double bonds (Fink J.K. 2008). From the results of the surface yellowing effect, Epoxy ECR-Glass 2 (composite 10) exhibited the best photo-yellowing resistance (see Figure 4.2(f)). This may be happening because they have less double bonds but more ether bridges in the network of the epoxy matrix than the others. Also, significant changes in surface roughness were observed for all specimens in on their exposed surfaces.
(a) 1A-Vinyl ester Epoxy ECR-Glass 1 and (b) 1AN-Nanocoated Vinyl ester Epoxy ECR-Glass 1.

(c) 3A-Vinyl ester Epoxy E-Glass 1

(d) 4b-Vinyl ester Epoxy ECR-Glass 2
Figures 4.2 (a) to (h): Typical surface characteristics after 1000 hours of exposure to dry hot UV.

(e) Polyester ECR-Glass 2

(f) Epoxy ECR-Glass 2

(g) R1 ECR-Glass 2

(h) 11N Nano-coated R1 ECR-Glass 2

Non-exposed section

Exposed section

Non-exposed section

Exposed section

Non-exposed section

Exposed section

Non-exposed section

Exposed section
In the case of the R1 samples (11 and 11 N) severe discoloration was observed on the surface of the specimens, as shown in Figure 4.3. An explanation for this effect would be that when R1 absorbs energy of UV radiation, it is isomerized to the enol-form which has more than 3 conjugated double bonds and, therefore, is colored by the chain scission reaction and also is the main result of photodegradation. Homolysis of C-N bond occurs on irradiation above 340 nm and degradation of hydroperoxides is confirmed by FTIR. (Wypych, G. 2008). For the current test conditioning the radiation was between 315 nm to 400 nm.

![Figure 4.3: Optical images of specimen 11 (R1 ECR-Glass) after UV exposure for 1000 h. (a) and (b) exposed and non-exposed sections.](image)

More surface degradations features were detected during subsequent SEM observations. Figure 4.4 (a)-(h) shows with more detail the matrix degradation - the exposed surfaces clearly revealed the well-reported microcracking and chalking phenomena.
As brittleness alone will not produce microcracking unless elastic stresses exists in the matrix and exceeds its fracture strength. On cooling from 80°C we would expect the matrix to go into axial tension which could be the cause of the microcracking but the cracks should then be perpendicular to the fibers, i.e. normal to the maximum tensile stress direction. Some of the cracks in Fig. 4.4 (b) and (h) are perpendicular to the fibers but others are not. This suggests that another mechanism is also acting. Perhaps the volumetric shrinkage caused by reduction in free volume at 80°C and chain scission is producing shrinkage of the matrix, which would produce biaxial tension, therefore biaxial cracking. It looks like only the coated specimens are showing pronounced cracking.

The non-exposed areas are showing sections where the fibers are still covered by the matrix. Whereas, on exposed areas, the micrographs are showing partial degradation in the matrix. The removed layer of the matrix seemed to be 20 um after dry hot UV radiation. Also, this phenomenon was observed only on the exposed surfaces of samples. The fibers also seem to have maintained their structural integrity after the exposure, and there was no evidence of cracks along their surfaces.

Previous research reported that degradation on polymers surfaces is a time dependent effect where the photochemical reactions (by UV radiation) are sometimes restricted to the surface of the polymers within a layer around 10 um, (Fink J.K. 2008). Up to three times more was observed in the current exposure specimens.

Figure 4.4 (h) shows the surface of specimen 11 N (Nano-coated R1 ECR-Glass 2). It can be seen in this micrograph that the Nano-coated layer was severely degraded by UV radiation. The coating appears to be removed by an exfoliation process. This
considerable volume of removed coating could be the main reason for the high percent of weight loss observed during the exposure. At the same time, the underlying polymer does not seem to have any cracks.

(a) 1A Vinyl ester Epoxy ECR-Glass 1 - 75% glass.

1) low magnification ×300 and 2) high magnification ×1500
(b) 1AN Nano-coated Vinyl ester Epoxy ECR-Glass 1 75% glass.
1), 2) and 3) low magnification ×300 and 4) high magnification ×1500

(c) 3A Vinyl ester Epoxy E-Glass 1 75% glass.
1) low magnification ×300 and 2) high magnification ×1500

(d) 4b Vinyl ester Epoxy ECR-Glass 2 80% glass.
1) low magnification ×300 and 2) high magnification ×1500
(e) 6 Polyester ECR-Glass 2.
1) low magnification ×300 and 2) high magnification ×1500

(f) 10 Epoxy ECR-Glass 2.
1) low magnification ×300 and 2) high magnification ×1500

(g) 11 R1 ECR-Glass 2.
1) low magnification ×300 and 2) high magnification ×1500
Figure 4.4 (a) to (h): SEM images of PMCs from exposed and non-exposed sections to UV radiation. The images are showing the matrix degradation by the UV radiation.

4.2 Water condensation tests

Figure 4.5 shows the percentage of weight gain as a function of square root of time during 1900 hours of exposure to water condensation environment (92% humidity air?). This figure shows that this process is controlled by diffusion.

It can be seen that the specimens exhibited immediate increase in weight from the very first hours of testing and increasing tendency even after 1900 hours in chamber.
Based on the curve slope, specimens may keep gaining mass before reaching a saturation point. All PMCs after 1900 hours of exposure gained between 0.05 to 0.28% of their weight. Comparatively, the percentage of mass gain of specimen 11 (R1 ECR-Glass 2) is 4 times higher than that of specimen 10 (Epoxy ECR-Glass 2) after 1900 hours of condensation exposure in Figure 4.5. The smaller mass gain for this test can be attributed to a better moisture resistance performed by PMCs. Since no UV exposure involved in the test, there were no soluble low molecular products of photo oxidation reactions from the UV exposed surfaces. So the main factor of weight loss can be ignored in this test.

![Figure 4.5: Mass changes of specimens during the water condensation test.](image)

Table 4.2 shows the resulted average mass changes after longer exposure times (500, 1000 and 1900 hours) for comparison purposes. As it can be seen that the best moisture resistant specimen after the condensation exposure for 1900 hours was the specimen 9 (Epoxy E-Glass 1) with only 0.05%, which is followed by specimen 10.
(Epoxy ECR-Glass 2) with 0.068% mass gain. In contrast, Specimen 11 (R1 ECR-Glass 2) exhibited the highest percentage in mass gain after 1900 hours (Figure 4.6).

Table 4.2: Average percent mass change of PMCs after 500, 1000 and 1900 hours in the UV chamber.

<table>
<thead>
<tr>
<th>Composites</th>
<th>500h</th>
<th>1000h</th>
<th>1900h</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A</td>
<td>0.12886</td>
<td>0.17104</td>
<td>0.226428</td>
</tr>
<tr>
<td>3A</td>
<td>0.12888</td>
<td>0.19012</td>
<td>0.246792</td>
</tr>
<tr>
<td>4b</td>
<td>0.04721</td>
<td>0.06458</td>
<td>0.094613</td>
</tr>
<tr>
<td>6</td>
<td>0.04773</td>
<td>0.06415</td>
<td>0.096692</td>
</tr>
<tr>
<td>10</td>
<td>0.03193</td>
<td>0.04245</td>
<td>0.06807</td>
</tr>
<tr>
<td>11</td>
<td>0.14715</td>
<td>0.20092</td>
<td>0.276716</td>
</tr>
<tr>
<td>1AN</td>
<td>0.13313</td>
<td>0.18851</td>
<td>0.245886</td>
</tr>
<tr>
<td>11N</td>
<td>0.09543</td>
<td>0.15711</td>
<td>0.214319</td>
</tr>
<tr>
<td>5</td>
<td>0.1196</td>
<td>0.14618</td>
<td>0.206426</td>
</tr>
<tr>
<td>9</td>
<td>0.03046</td>
<td>0.03573</td>
<td>0.050345</td>
</tr>
</tbody>
</table>

Figure 4.6: average percent mass change after 1900 hours condensation exposure.
4.2.1 Desorption tests after condensation experiments

After three specific periods of exposure (300, 500 and 1900 hours), as shown in Figure 4.7, the specimens were subjected to drying in a conventional oven at a constant temperature of 80 ± 2 °C. The specimen weights were monitored every 48 hours for 50 days (1400 hours) and then a series of desorption curves were obtained for their interpretation, as shown in Figure 4.8. The mass changes were determined using equation (3.1).

Figure 4.7: Mass changes during 1900 hours of exposure to water condensation. The arrows show the selected times (300, 500 and 1900 hours) to evaluate the dry/desorption effect of the samples.
Figure 4.8: Desorption curves after selected exposure times: (a) 300, (b) 500 and (c) 1900 hours.
Figure 4.8 shows that the moisture initially absorbed in the absorption test is more rapidly lost than it was absorbed. Then there is a further mass loss with time which is most pronounced with samples 11, 1AN and 11N i.e. the R2s and the nanocoated vinyl ester. This suggests that the moisture absorption is affecting the structure of the polymer e.g. by hydrolysis of R2 and urea groups and ester groups. Subsequent desorption is faster since chains have been broken so chain segments are shorter therefore more mobile.

Specimen 11N (Nanocoated R1 ECR-Glass 2) and 1AN (Nanocoated vinyl ester epoxy) showed a similar tendency but a higher mass loss rate than the others during desorption tests. It can be understood that degradation of coating which was partial removed during condensation exposure tests lead to a higher weight loss. Also, another mechanism may due to degradation of matrix, such as hydrolysis of R2, urea groups and ester groups.

It should be noted that, after 1400 hours of drying, the average percent mass loss of Figure 4.8(a) and Figure 4.8(b) are quite close to each other (around -0.045%). Nevertheless, percentage of average mass loss in Figure 4.8(c) is up to 35% more than the others. Details are shown in Figure 4.9. One possible reason for this result due to the short moisture exposure may not affect the physical and chemical structure of composites. In contrast, after a longer moisture exposure (1900 hours), degradation gradually affected the structure of composites, which eventually result in higher desorption rate and higher mass loss.
4.2.2 Surface morphology after condensation exposure

From the following micrographs (see Figure 4.10), it can be seen that all composites suffer various degrees of degradation after 1900 hours of water condensation. Matrix disintegration seems occurred among all composites, especially in vinyl ester epoxy composites and epoxy composites. Also, degradation caused by water condensation can still be fast in local areas.

In Figure 4.10(e) and (g), fiber cracking was found in E-glass composite; it seems that E-glass does not have an outstanding moisture resistance at high temperature. In Figure 4.10 (i), microvoids were observed in matrix, which explains why composite 11 gained more weight than the rest of composites. In Figure 4.10 (c), it can be seen that osmotic blisters were produced after 2000 hours in hydrothermal environment in composite 3A (Vinyl ester epoxy E-glass). Additionally, the same kind of blisters seems to be present in 4.10 (a), (f), (i) and probably (j).

Figure 4.10 (b) and (j) show the surface of specimen 1AN (Nanocoated Vinyl ester epoxy ECR-Glass 1) and 11 N (Nanocoated R1 ECR-Glass 2). It can be seen that
the nanocoated layer was severely damaged by water condensation. Otherwise, after coating layer was removed, lots of scratches were observed on the surface, which may due to the specimen surface was abraded before the nanocoating was applied, in order to increase adhesion.

(a) 1A Vinyl ester Epoxy ECR-Glass 1 - 75% glass. 1) low magnification ×300 and 2) high magnification ×1500

(b) 1AN Nano-coated Vinyl ester Epoxy ECR-Glass 1 75%. 1) low magnification ×300 and 2) high magnification ×1500
(c) 3A Vinyl ester Epoxy E-Glass 1 75% glass. 
1) low magnification ×300 and 2) high magnification ×1500

(d) 4b Vinyl ester Epoxy ECR-Glass 2 80% glass. 
1) low magnification ×300 and 2) high magnification ×1500

(e) 5 Polyester E-Glass. 
1) low magnification ×300 and 2) high magnification ×1500
(f) 6 Polyester ECR-Glass 2.
1) low magnification ×300 and 2) high magnification ×1500

(g) 9 Epoxy E-Glass.
1) low magnification ×300 and 2) high magnification ×1500

(h) 10 Epoxy ECR-Glass 2.
1) low magnification ×300 and 2) high magnification ×1500
4.3 Thermal stability tests

The main purpose of thermal stability tests is used to compare with UV radiation. Testing conditions have been introduced in chapter 3.

Figure 4.11 shows the percentage of weight loss as a function of time during 1000 hours in high temperature environment. It can be seen that the specimens exhibited immediate loss in weight from the very first hours of testing. All PMCs after 1000 hours
of exposure lost between 0.012 to 0.045 % of their mass. Combined with Table 4.3, composite 11 and 11N exhibited the highest percentage in weight loss, which is two times that of the rest of composites. On the other hand, composite 4b and 10 showed only a 0.012% mass loss with respect to the maximum average weight loss (0.024 %) from other specimens. Furthermore, from the tendency of both composite 4b and 10, it can be seen that they are not losing weight any more. Comparisons of UV radiation and thermal tests will be discussed in chapter 5.

For the two nanocoated composites there was a significant different behavior in keeping weight. From Figure 4.11, it can be seen that there is a sudden tendency changing around 300 hours for composite 11N. After 300 hours in oven, composite 11N shows a drop in thermal resistance ability (without error bars on the points, it is difficult to argue that 11N shows any sudden changes in slope). In contrast, composite 1AN behaved stable and there is no obvious drop in weight change.

![Average mass changes for all tested PMCs during 1000h in Oven](image)

Figure 4.11: Mass changes during 1000 hours in thermal environment condition.
Table 4.3: Average percent mass changes of PMCs after 500 hours and 1000 hours in the oven.

<table>
<thead>
<tr>
<th>Composite</th>
<th>500 h</th>
<th>1000h</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A</td>
<td>-0.021</td>
<td>-0.028</td>
</tr>
<tr>
<td>3A</td>
<td>-0.0186</td>
<td>-0.0232</td>
</tr>
<tr>
<td>4b</td>
<td>-0.0095</td>
<td>-0.0121</td>
</tr>
<tr>
<td>6</td>
<td>-0.0145</td>
<td>-0.0202</td>
</tr>
<tr>
<td>10</td>
<td>-0.0103</td>
<td>-0.0123</td>
</tr>
<tr>
<td>11</td>
<td>-0.0284</td>
<td>-0.044</td>
</tr>
<tr>
<td>1AN</td>
<td>-0.0086</td>
<td>-0.0139</td>
</tr>
<tr>
<td>11N</td>
<td>-0.0193</td>
<td>-0.041</td>
</tr>
</tbody>
</table>

4.4 UV & condensation cyclic exposure tests

As shown in Table 4.4, after early cycles of exposure, positive mass gains were noticed for most of the composites, except for 4b (Vinyl ester Epoxy ECR-Glass 2, 80% glass) and 6 (Polyester ECR-Glass 2), which exhibited a slightly reduction in their masses. Afterwards, the mass of the two composites increased just like in the other four cases until they reached a maximum absorption value (after approximately 96 hours). It can be seen that 1A (Vinyl ester Epoxy ECR-Glass 1, 75% glass) and 3A (Vinyl ester Epoxy E- Glass 1, 75% glass) specimens gained mass up to 50 % more than the rest of the composites. Also, for these two composites, their rates of mass increases appear to be higher than for the other composites. According to the data in Table 4.4, the transitions from the mass gains to mass losses occurred somewhere between 100 and 200 hours of the test. The maximum absorption peaks followed by their reduction are shown in Figure 4.12.
Table 4.4: Average percent mass changes of after 200 hours of exposure to UV and condensation.

<table>
<thead>
<tr>
<th>Composite number</th>
<th>24 h</th>
<th>48 h</th>
<th>96 h</th>
<th>192 h</th>
<th>264 h</th>
<th>312 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A</td>
<td>0.0013</td>
<td>-0.0002</td>
<td>0.0098</td>
<td>0.0093</td>
<td>0.0019</td>
<td></td>
</tr>
<tr>
<td>3A</td>
<td>0.0006</td>
<td>0.0044</td>
<td>0.0098</td>
<td>0.0097</td>
<td>-0.0003</td>
<td></td>
</tr>
<tr>
<td>4b</td>
<td>-0.0023</td>
<td>0.0010</td>
<td>0.0025</td>
<td>-0.0008</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>-0.0007</td>
<td>-0.0037</td>
<td>0.0042</td>
<td>0.0028</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0.0007</td>
<td>-0.0006</td>
<td>0.0038</td>
<td>-0.0035</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>0.0029</td>
<td>0.0004</td>
<td>0.0029</td>
<td>-0.0060</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 4.12: Mass changes of PMCs after 250 hours of exposure to UV and H2O condensation.

Figure 4.13 shows the percentage of weight gain-loss as a function of time during 1000 hours of exposure to UV and water condensation. When the specimens reached the saturation point in absorption, which was shortly after 100 hours, an opposite effect was evident. That is, for all tested composites, the weight loss tendency increases with time. The specimens exposed to this environmental condition show the losses in mass with the maximum values between 0.08 and 0.1%. Moreover, the specimen mass was still decreasing steadily at the end of the duration, which suggested that the mass loss would have continued further with more exposure to UV radiation and condensation.
A remarkable distinction in mass loss behavior was observed in specimen 6 (Polyester ECR-Glass 2), which exhibits only a 0.02% mass loss with respect to the maximum average mass loss (0.09%) from other specimens. In fact, for this particular specimen, its real mass loss started after 500 hours. It was found that after it reached the maximum weight gain (0.042 %), the specimen was almost stable with respect to time after 500 hours. Subsequently, a loss in mass started to be more and more evident up to a mass loss of 0.02%.

The question that arises here is: in Fig 4.13 just the sum of UV alone plus moisture alone? We can see that UV alone produces a mass change of between -.1% and -.03% after 1000hrs (see Fig 4.1) while moisture alone produces a mass change of between .2% and .03% after 1000hrs (see Fig 4.5). Since the UV exposure in each cycle is twice that of the moisture exposure, we should double the above values for the UV exposure. So, after 1000hrs the sum of the two effects is roughly zero. However Fig 4.13 shows clearly that average mass change for all the samples except 6 is around -.09% for the combined UV plus moisture cycling. This indicates that moisture/UV cycling amplifies the mass loss due to UV over and above that of UV alone.
Table 4.5 shows the resulted average mass changes after longer exposure times (500 and 1000 hours) for comparison purposes. Again, specimen 6 was the only one that started to lose weight after 500 hours due to exposure to UV and water condensation environments. Also, it should be noted that this specimen generally exhibited the smallest fluctuation in its mass during the exposure with respect to time. On the other hand, composite 1A (Vinyl ester Epoxy ECR-Glass 1, 75% glass) and 3A (Vinyl ester Epoxy E-Glass 1, 75% glass) exhibited the highest percentage in weight loss (up to 0.1%) and the largest fluctuation in their mass under the same testing conditions. As mentioned before, one of the reasons was that at the initial period of time, these two specimens gained mass up to 50% more than the others and then, after 1000 hours, the weight loss was significantly higher than the others. (is this result with specimen 6 reproducible?)
Table 4.5: Average percent mass changes after 500 and 1000 hours of exposure to UV and condensation.

<table>
<thead>
<tr>
<th>Composite</th>
<th>500 h</th>
<th>1000 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A</td>
<td>-0.0210</td>
<td>-0.1060</td>
</tr>
<tr>
<td>3A</td>
<td>-0.0282</td>
<td>-0.1030</td>
</tr>
<tr>
<td>4b</td>
<td>-0.0314</td>
<td>-0.0889</td>
</tr>
<tr>
<td>6</td>
<td>0.0026</td>
<td>-0.0187</td>
</tr>
<tr>
<td>10</td>
<td>-0.0283</td>
<td>-0.0760</td>
</tr>
<tr>
<td>11</td>
<td>-0.0290</td>
<td>-0.0823</td>
</tr>
</tbody>
</table>

4.4.1 Desorption tests after UV and condensation experiments

After five specific periods of exposure (100, 200, 300, 500 and 1000 hours), as shown in Figure 4.14, the specimens were subjected to drying in a conventional oven at a constant temperature of 80 ± 2 °C. The specimen weights were monitored every 48 hours for 50 days (1200 hours) and then a series of desorption curves were obtained for their interpretation, as shown in Figure 4.15. The mass changes were determined using equation (1).
Figure 4.14: Mass changes during 1000 hours of exposure to UV/condensation. The arrows show the selected times (100, 200, 300, 500 and 1000 hours) to evaluate the dry/desorption effect of the samples.
(b) after 200h

(c) after 300h

(d) after 500h
Figure 4.15: Desorption curves after selected exposure times: (a) 100, (b) 200, (c) 300, (d) 500 and (e) 1000 hours.

The desorption tests at 80°C have shown that the percentage of mass gain (moisture absorbed by UV and water condensation) by the composites at early periods of time was gradually decreasing during the first 100 hours of drying. Generally, for this time, the observed values of weight loss reached 0.02%, and the slopes of the curves are showing a significant rate of desorption during the drying process.

Specimen 11 (R1 ECR-Glass 2) showed the same tendency but with a higher rate of mass loss (up to 0.03%) than others during the same time of drying. Possibly some of the reasons for the higher mass loss (desorption) for this specimen could be caused by the rapid moisture diffusion out of the composite in which its main structure already had been attacked by the environmental tested cycles (rapidly degradation by UV and water condensation on early times of exposure.) Also, another mechanism that would be enhanced to get this high rate of desorption could be due to the drying temperature effect,
in which the temperature of 80 °C is promoting the easy removal of some volatiles from the composite during the drying process.

It can be seen in Figures 4.15 that the specimens were losing their mass faster with time. After 300 hours of drying, the curves are showing values of 0.04% of mass loss in average. The same graphs are showing that the values are increasing for longer drying times. Consequently, for all specimens at longer times of drying (after 500 hours), the weight losses are more noticeable, up to 50% increments in weight loss –from 0.04% at 300 hours to 0.08% at 500 hours. The composites maintain the same tendency to losing weight but with slightly gradual decrements. Figure 4.15 (d) and (f) show the rate of desorption in which the slope of their curves are more moderate (low slope) than the initial ones at early times of drying. The level of absorbed moisture by the UV and H₂O condensation already disappeared and only the drying temperature is causing effects in the weight loss of the composites.

It should be noted again that specimen 6 (Polyester ECR-Glass 2) exhibited the lowest value of weight loss (0.05%) in comparison with the rest of the composites (0.2% on average) after 1000 hours of drying. Comparing the graphs in Figure 4.15 (e) and Figure 4.13, for this particular specimen, there is only 0.03% difference in its value of mass change with respect to 1000 hours. Besides, one is after exposure to UV and H₂O condensation and the other is after 1000 hours of drying. Nevertheless, it could be assumed that this composite structure is more resistant to the testing environmental conditioning than the others and that this composite maintains an enhanced thermal stability after longer periods of exposure at 80 °C.
4.4.2 Surface morphology after UV/condensation exposure

Visual observations of the exposed specimens showed similar patterns of degradation on the surfaces of composites. At lower magnifications the discoloration of the samples was evident; there was considerable yellowing of the specimens. At higher magnifications and for comparison purpose, the SEM images - Figures 4.16 to 4.21, only (a)’s - of non-exposed and exposed areas are showing how the degradation (erosion process) affected each side of their surface sections. The non-exposed areas are showing sections where the fibers are covered by the matrix phase. The micrographs showed that the fibers are well covered by the matrix and presents good adhesion of the matrix to the fiber. However, once the sections are more and more exposed this adhesion with the matrix gradually changes until it leaves them completely clean without any remaining matrix. On the other hand, in the exposed areas, the micrographs are showing strong degradation effects. In some cases, the matrix phase was completely removed by the erosion effect.

In comparison to the exposed sections from the UV tests (Figures 4.4 (a) to (h)), the removed layer of the matrix seemed to be more deep (approximately 30 um) after UV/condensation cyclic exposure than after the exposure to hot dry UV radiation, which was less than 20 um thick.

In addition, the micrographs showed that matrix-fiber deboning was present in some composites, as shown in Figure 4.21 (b). The resulted debonding fiber-matrix interface appaers to be more similar to cracks which grow along the matrix beside the fibers. The fibers seem to have maintained their structural integrity after the exposure
testing, and there was no evidence of cracks along their surfaces. Also, at this level of magnification, no microcracking or micropores were evident in the matrix. However, this degradation was found only on the exposed areas and was limited at subsurface level. Additionally, previous processing anomalies, such as surface roughness and misaligned fibers, could be contributing to enhancing the degradation on exposed surfaces.

Figures 4.19 (a) and (b) show the surface of specimen 6 (Polyester ECR-Glass 2). It can be seen that matrix degradation was much less severe than for the other composites. Also, Figure 4.19 (b) shows that the composite still maintains, partially, its matrix with a considerable level of adhesion to the fibers after the exposure.

Figure 4.16: SEM images of unexposed (a) and exposed (b) surfaces of Vinyl ester Epoxy with ECR-Glass 1 after 1000 h of UV/condensation exposure.
Figure 4.17: SEM images of unexposed (a) and exposed (b) surfaces of Vinyl ester Epoxy with E-Glass 1 after 1000 h of UV/condensation exposure.

Figure 4.18: SEM images of unexposed (a) and exposed (b) surfaces of Vinyl ester Epoxy with ECR-Glass 2 after 1000 h of UV/condensation exposure.

Figure 4.19: SEM images of unexposed (a) and exposed (b) surfaces of Polyester ECR-Glass 2 after 1000 h of UV/condensation exposure.
Figure 4.20: SEM images of unexposed (a) and exposed (b) surfaces of Epoxy ECR-Glass 2 after 1000 h of UV/condensation exposure.

Figure 4.21: SEM images of unexposed (a) and exposed (b) surfaces of R1 ECR-Glass 2 after 1000 h of UV/condensation exposure.

4.5 Nitric acid exposure testing

As mentioned in Chapter 3, all specimens were partially submerged with only one side of each specimen being exposed to 0.063 mol/L (pH = 1.2) and 1 mol/L (PH = 0) nitric acid for two weeks at room temperature. After the exposure, all specimens were dried at room temperature for seven days before subsequent SEM surface characterizations using the SEM.
4.5.1 0.063 mol/L nitric acid exposure

Typical examples of surface characteristics from all tested composites except nanocoated ones before and after the low concentration acid exposure are shown in Figure 4.22. Remarkable distinctions in surface characteristics were observed in specimen 5 (Polyester E-Glass 1) and 9 (Epoxy E-Glass 1), which are noticeable fiber cracks. On the other hand, specimen 9 (Epoxy E-Glass 1) exhibited degradation of matrix on the surface after exposure.

No major damage to the rest of composites by the acid was found. Slight degradation in some localized areas was observed, mainly on exposed fibers, as shown in Figure 4.22 (d) and (e).

(a) 1A Vinyl ester Epoxy ECR-Glass 1-75% glass.
   1) before exposure  and 2) after exposure
(b) 3A Vinyl ester Epoxy E-Glass 1 - 75% glass.
1) before exposure and 2) after exposure

(c) 4b Vinyl ester Epoxy ECR-Glass 1 - 80% glass.
1) before exposure and 2) after exposure

(d) 6 Polyester ECR-Glass 2.
1) before exposure and 2) after exposure
(e) 10 Epoxy ECR-Glass 2.
1) before exposure and 2) after exposure

(f) 1 R1 ECR-Glass 2.
1) before exposure and 2) after exposure

(g) 5 Polyester E-Glass 1.
1) before exposure and 2) after exposure
4.5.2 1mol/L nitric acid exposure

Similar to the results of low concentration acid testing, but more severe fiber cracks were found in specimen 5 and 9, as shown in Figure 4.23(g) and (h). No major damage to the rest of composites by the acid was observed. Most importantly no evidence of fiber cracking was detected in the ECR-glass fiber composites.
(b) 3A Vinylester E-Glass 1.

(c) 4b Vinyl ester Epoxy ECR-Glass 2.

(d) 6 Polyester ECR-Glass 2.
(e) 10 Epoxy ECR-Glass 2.

(f) 11 R1 ECR-Glass 2.

(g) 5 Polyester E-Glass 1.

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For specimens with nanocoating which are 1AN and 11N, both of them were degraded on the surface after two weeks nitric acid exposure (see Figure 4.24). Cracks developed in the coating even in low concentration solution, but it seems that 1AN had a better nitric acid resistance than 11N in which nanocoating already had been partially removed. Comparatively, concentrated acid contribute to more severe cracks in both coating than dilute acid.

(a) 1AN Nanocoated Vinlyester Epoxy ECR-Glass 1 75% glass.
1) after low concentration acid exposure and 2) after high concentration acid exposure.
4.6 UV radiation tests followed by nitric acid exposure

Same to the nitric acid exposure testing, two concentrations of nitric acid solution were used in the tests, which are low one with 0.063mol/L and high one with 1mol/L.

4.6.1 0.063 mol/L nitric acid exposure

Typical examples of surface characteristics from all tested composites after UV exposure and the low concentration acid exposure are shown in Figure 4.25. Remarkable distinctions in surface characteristics were observed in specimen 1AN (Nano-coated Vinyl ester epoxy ECR-Glass 1) and 11N (Nano-coated R1 ECR-Glass 2) from Figure 4.25 (b) and 4.25 (h), which are noticeable matrix cracks. What’s more, lots of scratches were found on the ECR glass fibers, same to the images in water condensation part, scratches were manually made to increase roughness which may help get a stronger interfacial adhesion.

On the other hand, specimen 6 (Polyester ECR-Glass 2) exhibited obvious
interfacial debonding in Figure 4.25(e). From Figure 4.25(f) and (g), microvoids were found in the matrix of specimen 10(Epoxy ECR-glass2) and 11(R1 ECR-glass 2). No major damage to the rest of composites by the acid was found.

(a) 1A Vinyl ester Epoxy ECR-Glass 1 75% glass.  
1) low magnification ×300 and 2) high magnification ×1500

(b) 1AN Nanocoated Vinyl ester Epoxy ECR-Glass 1 75% glass  
1) low magnification ×300 and 2) high magnification ×1500
(c) 3A Vinyl ester Epoxy E-Glass 1 75% glass.
1) low magnification ×300 and 2) high magnification ×1500

(d) 4b Vinyl ester Epoxy ECR-Glass 2 80% glass.
1) low magnification ×300 and 2) high magnification ×1500

(e) 6 Polyester ECR-Glass 2.
1) low magnification ×300 and 2) high magnification ×1500
(f) 10 Epoxy ECR-Glass 2.
1) low magnification ×300 and 2) high magnification ×1500

(g) 11 R1 ECR-Glass 2.
1) low magnification ×300 and 2) high magnification ×1500

(h) 11N Nano-coated R1 ECR-Glass 2.
1) low magnification ×300 and 2) high magnification ×1500

Figure 4.25 (a) to (h): SEM images of PMCs from exposed sections to 0.063mol/L nitric acid.
4.6.2 1mol/L nitric acid exposure

Similar to the results of low concentration acid testing, but severe fiber cracks were found in specimen 3A, as shown in Figure 4.26(c). As interfacial debonding were found in specimen 1A, 1AN 3A and 6, it seems high concentration acid lead to a strong debonding effect. On the other hand, severe matrix cracking were observed in specimen 11N. No major damage to the rest of composites by the acid was observed. Most importantly no evidence of fiber cracking was detected in the ECR- glass fiber composites.

(a) 1A Vinyl ester Epoxy ECR-Glass 1 75% glass
1) low magnification ×300 and 2) high magnification ×1500

(b) 1AN Nanocoated Vinly ester Epoxy ECR-Glass 1 75% glass
1) low magnification ×300 and 2) high magnification ×1500
(c) 3A Vinyl ester Epoxy E-Glass 1 75% glass.
1) low magnification ×300 and 2) high magnification ×1500

(d) 4b Vinyl ester Epoxy ECR-Glass 2 80% glass.
1) low magnification ×300 and 2) high magnification ×1500

(e) 6 Polyester ECR-Glass 2.
1) low magnification ×300 and 2) high magnification ×1500
Figure 4.26 (a) to (h): SEM images of PMCs from exposed sections to 1mol/L nitric acid.
4.7 UV/condensation tests followed by nitric acid exposure

Figures 4.27 (a) to (f) show the surface degradation developed to the composites after the UV/condensation followed by the exposure to the acid (0.063mol/L). Comparing with Figures 4.16-4.21 (Chapter 4.4) no obvious evidence can be found of any additional damage from the acid. Similar the main conclusions from UV & condensation testing, the Polyester-ECR composite had the smallest amount of surface damage after the UV/condensation – acid testing (see Figure 4.27d).

Further analysis at higher magnifications on the matrix, in Figure 4.27(f), showed the presence of micropores or voids along the exposed surface with visible debonding of matrix-fibers. The presence of microvoids, which was not seen previously in UV/condensation tests due to the level of magnification analysis, developed due to the effect of UV/H₂O condensation (priori to acid exposure).

Another important feature shown in Figure 4.27 (d) displays the surface of specimen 6 (Polyester ECR-Glass 2), which presented the best resistance to UV/H₂O condensation effect. This image confirms such a characteristic by showing that the deep degradation was shorter than the rest of the composites. The composite still maintained part of their matrix and with a considerable level of adhesion of the matrix to the fibers after the exposure.
(a) 1A Vinyl ester Epoxy ECR-Glass 1 75% glass.
1) low magnification ×300 and 2) high magnification ×1500

(b) 3A Vinyl ester Epoxy E-Glass 1 75% glass.
1) low magnification ×300 and 2) high magnification ×1500

(c) 4b Vinyl ester Epoxy ECR-Glass 2 80% glass.
1) low magnification ×300 and 2) high magnification ×300
(d) 6 Polyester ECR-Glass 2.
1) low magnification ×300 and 2) high magnification ×1500

(e) 10 Epoxy ECR-Glass 2.
1) low magnification ×300 and 2) high magnification ×1500
(f) R1 ECR-Glass 2.
1), 2) low magnification ×300 and 3), 4) high magnification ×1500

Figure 4.27 (a) to (f): SEM images of exposed sections of six PMC after UV/H2O condensation followed
Chapter Five: Discussion

5.1 UV radiation tests

As we known from UV results section (Chapter 4.1), all specimens lost an average of 0.045% by weight after 1000 h of exposure. Further, from the tendency of curves, it can be seen that specimens will keep losing weight. This immediate decrease in specimen at beginning weight may be attributed to the expulsion of volatiles and rare residual moisture, which occurred early during exposure to UV radiation at 80 C. Then, degradation of matrix caused by UV radiation and oxidation at high temperature may become the main reason.

According to the results of mass changing tests, Chapter 5.1.1 – 5.1.3 makes corresponded comparisons based on the same matrix or fiber.
5.1.1 Comparison of nanocoated and non-nanocoated specimens

Figure 5.1: Mass changes of nanocoated and non-nanocoated PMCs during the UV radiation test.

According to the result of FTIR spectra, surface materials of the coating for composite 1AN and 11N are same. However, we do not know what nanoparticles the sponsor used in the coating resin by FTIR. Here, further experiment is suggested such as NMR. For both nanocoated composites, severe degradation of coating was observed on the UV exposed surfaces in Fig 4.4(b) and (h) (Chapter 4.1) and almost all the coating was removed eventually.

From the variation of mass changing of specimen 11 and 11N upon to time of UV exposure, it is obvious that nanocoating of R1 started to be removed after 150 hours of UV exposure. However, nanocoating of specimen 1A behaved relative better, which the curve kept along with specimen 1A, than specimen 11, indicating that the interfacial adhesion strength of specimen 1AN is large than that of specimen 11N. The reason may
be vinyl ester has more hydroxyl groups than R1 which can form hydrogen bonds that provide more strength between coating layer and matrix.

Regardless of nanocoating, specimen 1A and 11 exhibited similar results in both curve tendency and percentage of weight loss. For vinyl ester epoxy, under the condition of UV exposure, oxygen from air participated to generate the hydroperoxides (D. Rosu, 2006). The presence and the accumulation of hydroperoxides on the surface of specimen 1A, their instability and fragmentation led to products with low molecular weight and the high volatility. The loss in weight is an indication for photodegradation, with elimination of volatile compounds (CO, CO₂, H₂O, etc.) (Dan Rosu, 2008). For R1, similar to vinyl ester epoxy, hydroperoxides are formed by the reaction of Photo-Fries rearrangement (see Figure 5.2). As hydroperoxides are instable, the degradation of hydroperoxides led to homolysis of C-N bond and formed lots of low molecular weight and high volatile products such as carbonyl groups and hydrolyzed esters (Wypych, 2011).

Figure 5.2: Formation of hydroperoxides.
Source: (Gardette, Mailhot, Posafa, Rivaton, & Wilhelm, 1999)
5.1.2 Comparisons of E-glass or ECR-glass vinyl ester epoxy specimens

Figure 5.3: Mass changes of the same matrix PMCs during the UV radiation test.

Figure 5.3 shows the specimens with same matrix but different glass fibers exhibited similar weight loss. On the basis of tendency and percentage of weight change, four different composites presents quite close results to each other, indicating glass fibers did not affect the photodegradation of matrix. This is confirmed by SEM images, E-glass and ECR-glass fibers maintained their structural integrity after the exposure. Also, as previous literature work tells us glass fibers are inorganic materials comprise a silica network, which has a high thermal and chemical resistance, it can be seen that glass fiber were not affected much by UV radiation.
5.1.3 Based on ECR-glass fiber, different matrix specimens

Figure 5.4: Mass changes of the same ECR-glass fiber PMCs during the UV radiation test.

Figure 5.4 shows the specimens with ECR-glass fiber but different matrix exhibited different weight loss. As we do not know what exact matrix resins are, it is difficult to explain why the composites displayed those differences in weight loss. Based on the limited information offered by sponsor, certain and accurate explanations may not be gained. Here, we have to make some conjectures.

In Figure 5.4, specimen 11 exhibited a 0.06% weight loss with respect to the average weight loss (0.043%). As one possible monomer structure of R1 shown in Figure 5.5, it can be seen that a methylene group exists in this MDI polymer, which makes the reaction of formation of hydroperoxides occur easily (Figure 5.2). Furthermore, this mechanism explains why our R1 composites may be more vulnerable to photoxidation (Wypych, 2011). On the other hand, previous research reported that R1 can be depolymerized chemically by pyrolysis or thermolysis (Szycher, 2012). It is provide a possible reason why R1 lost so much in weight.
Specimen 4b (Vinyl ester epoxy ECR-glass 2) exhibited a 0.048% weight loss in Figure 5.4. Same to the result of specimen 1A (Vinyl ester epoxy ECR-glass 1), by the formation and decomposition of hydroperoxides which as a result of the involvement of the oxygen under high energy light radiation, lots of volatile products such as CO, CO₂ and H₂O are eliminated from specimens. At the same time, chain scission in molecular chain may occur in the composite which will make it brittle (Dan Rosu, 2008) (Signor, VanLandingham, & Chin, 2003). Here, nanoindentation experiment is quite suggested to be conducted before and after UV exposure for matrix brittle.

Specimen 6 (Polyester ECR-glass 2) and 10 (Epoxy ECR-glass 2) presented a close weight loss after UV exposure. We have no information of chemical composition from manufacturer, hence for the purpose of the final usage which is the core of composite insulator cycloaliphatic epoxides may be recommended to be used as resin in specimen 10.

Specimen 10 exhibited a 0.03% weight loss with respect to the average weight loss (0.043%). In the range of 300-330 nm, epoxy composite may absorb energy of radiation which leads to formation of radicals, chain scission and molecular weight reduction, as shown in Figure 5.6. Eventually, benzene, styrene and benzoic acid, all these small volatile products from chain scission reactions will be expelled from composite (Monney, Bole, Dubois, & Chambaudet, 1999). On the other hand,
photodegradation of specimen surface may not a uniform thickness reduction when it is amine-cured epoxy but it is an inhomogeneous erosion process with formation of localized nanometer-micrometer depressions and pits (Rezig, 2006). Therefore, the surface of composite 10 was quite rough after UV radiation in Figure 4.25(f) (Chapter 4.6.1). Also, chalking phenomenon is a typical result of photodegradation which may be related to brittleness of surface (see Figure 4.4(f), Chapter 4.1.1).

![Formation of radicals under UV radiation.](image)

Figure 5.6: Formation of radicals under UV radiation. Source: (Wypych, 2011)

The percentage of weight loss of specimen 6 is 0.036% with respect to the average weight loss 0.043%. For specimen 6 (polyester ECR-glass 2), how much it is affected by UV radiation depends a lot on chemical structure. Previous study reports that substituting neopentyl glycol for usual glycol makes outstanding properties in UV resistance, yellowing resistance, and chemical resistance (Hanna Dodiuk, 2014).

Here, as common unsaturated polyester, the reason why polyester lost less weight than the average can be explained by that specimen 6 may undergo either chain scission or crosslinking reactions under UV radiation at the same time. According to the previous research that the absorption of UV radiation leads to scission reactions centered around the ester linkage. Then free radicals from scission reactions may either recombine or they may abstract hydrogen from polymer molecules which leads predominantly to chain
scission (Wypych, 2011). On the other hand, one drawback of polyester is thermal instability, which may be the reason why it lost more than epoxy in both UV radiation test and heat test.

### 5.1.4 Yellowing phenomena

Yellowing phenomena occurred in all tested specimens (see Figure 5.7). The mainly reason is photo-oxidation resulted in the formation of chromophoric chemical species, which absorbed in the visible range of light.

In the case of the R1 samples (specimen 11), severe discoloration was observed on the surface of the specimens, as shown in Figure 5.8. An explanation for this effect would be oxidation of methylene between benzene rings in chemical chain. The formed conjugated double bond is main reason of discoloration in the tested R1.
5.1.5 FTIR

FTIR spectroscopy is a technique which allows quantifying the chemical changes in the materials after UV radiation (F. Posada, 2000). A Shimadzu IRAffinity-1 Spectrometer was utilized to determine spectra under the same condition, which provided a 2 cm\(^{-1}\) resolution.

From the following Figure 5.9 to 5.12, it can be seen that the spectra exhibit remarkable changes upon specimen exposure to UV radiation. No band or peak was found in the 1300-4000 cm\(^{-1}\) region, even after increasing the number of scans from 32 to 128. It is indicate that there is something happened on the surface of specimen. After exposure to UV radiation, surface was terribly damaged which resulted in layers of matrix were removed. Eventually, glass fibers were exposed outside which makes surface rough. The unexpected results may attribute to this coarse surface.

In the case of initial specimen 6 (see Figure 5.9), a broad peak around 3300 cm\(^{-1}\) are not observed, this means this particular polyester may not have OH groups. The bands at 2900-2990 cm\(^{-1}\) can be caused by asymmetric and symmetric stretching of CH\(_2\) group. A strong peak at 1730 cm\(^{-1}\) can be attributed to stretching of C=O group. The absorbance at 1580-1610 cm\(^{-1}\) in the spectrum of polyester could be attributed to the aromatic structures, which is characteristic to the stretching vibration of the double bonds in the
aromatic ring. Another point is that we do not find a peak at 1630-1680 cm\(^{-1}\) region which presents double bonds (-C=C-), this means, the polyester are well cured and all the carbon double bonds are reacted totally with hardener.

Figure 5.9 FTIR spectrums of Specimen 6 (Polyester) before (purple line) and after UV radiation (blue line).

Regardless of the result of after UV radiation, non-exposed specimen 10 showed a clear spectrum (see Figure 5.10). As a broad peak around 3300 cm\(^{-1}\) are not observed, this means epoxy composite do not have or have little of OH groups. As previous studies reported that hydroxyl group was primarily characterized by a broad peak at 3200-3400 cm\(^{-1}\). One reason may be the testing method limited to get a detail and accurate result. The bands at 2900cm\(^{-1}\), 2890cm\(^{-1}\) and 2880cm\(^{-1}\) can be attributed to asymmetric and symmetric stretching of CH\(_2\) group. A strong peak at 1750 cm\(^{-1}\) can be caused by stretching of C=O group, which is also a proof that cycloaliphatic epoxides may be used as main resin. Two peaks at 1250 cm\(^{-1}\) and 1510 cm\(^{-1}\) present oxirane ring stretching vibration of the epoxy (Bhavesh G. Kumar, 2002). Peaks of double carbon bonds in aromatic ring can be found at 1590-1670 cm\(^{-1}\).
Actually, vinyl ester epoxy is a combination of epoxy and polyester in chemical structure. A weak but broad band at 3400 cm$^{-1}$ means hydroxyl groups were exist in specimen 3A. The other peaks are quite similar to polyester or epoxy (see Figure 11).
For R1 sample, same result in which the spectra disappear after UV exposure were achieved in several tests. However, different spectrum as shown in Figure 5.12 was obtained in which some evident peaks after the exposure still there.

In Fig 5.12, the spectra did not exhibit appreciable changes after specimen exposure to UV radiation. The spectrum of non-radiated R1 specimen presents a characteristic band at 3310 cm\(^{-1}\), which corresponds to the stretching vibration of N-H group (Silverstein RM, 2005). The bands at 2890 cm\(^{-1}\), 2850 cm\(^{-1}\) and 2830 cm\(^{-1}\) can be attributed to asymmetric and symmetric stretching of CH\(_2\) group (B., 2004). The peak at 1710 cm\(^{-1}\) corresponds to C=O stretching vibration in the R2 bond (Rosu, 2009). The absorbance at 1580 cm\(^{-1}\) in the FTIR spectrum of R1 could attributed to the coupling N-H bending vibration with C-N stretching vibration in the -C-NH group (Silverstein RM, 2005) (B., 2004). The weaker vibration band at 1310 cm\(^{-1}\) corresponds to the combination between N–H bending vibration and C–N stretching vibration (Silverstein RM, 2005). The skeletal vibration of -C= in the aromatic ring from 1600 cm\(^{-1}\) can be coupled with the absorbance from 810 cm\(^{-1}\) (Lin-Vien D, 1991).

As a result of UV action on specimen 11, it can be noted that shape changing of peak signal. In the region 3400-3200 cm\(^{-1}\), there is an obvious decrease in absorbance. The decrease of the intensity of the band characteristic of the stretching vibration of N–H group (3310 cm\(^{-1}\)), indicates the loss of the R2 structures as a result of UV radiation (Romanova V, 2002).
Spectra of three specimens (Specimen 1A, 3A and 4b) which were same in matrix exhibit similar spectrum (see Figure 5.13). This means glass fibers do not affect the distribution of peaks from different chemical structures. The only different is the intensity of peaks, which specimen 4b is much lower than the other two, indicating that volume fraction of glass fibers in composite may affect the reflection of infrared radiation.
5.2 Thermal stability tests.

The main purpose of thermal test is used to compare with the result of UV radiation. Under the same exposure time and temperature, the only difference is UV exposure.

5.2.1 Thermal tests vs. UV radiation tests

Comparing Fig. 4.1 (Chapter 4.1) with Fig. 4.11 (Chapter 4.3), the curves are similar except that the mass loss with UV is about 2 times as large as without UV. This shows that the UV is having some additional degradation effect over and above that of just the dry heat alone.

<table>
<thead>
<tr>
<th>Composite</th>
<th>UV + Heat</th>
<th>Heat</th>
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</thead>
<tbody>
<tr>
<td>1A</td>
<td>-0.05046</td>
<td>-0.02800</td>
</tr>
<tr>
<td>3A</td>
<td>-0.0485</td>
<td>-0.02316</td>
</tr>
<tr>
<td>4b</td>
<td>-0.04558</td>
<td>-0.02212</td>
</tr>
<tr>
<td>6</td>
<td>-0.03707</td>
<td>-0.02019</td>
</tr>
<tr>
<td>10</td>
<td>-0.02994</td>
<td>-0.01226</td>
</tr>
<tr>
<td>11</td>
<td>-0.05908</td>
<td>-0.04399</td>
</tr>
<tr>
<td>1AN</td>
<td>-0.04932</td>
<td>-0.01389</td>
</tr>
<tr>
<td>11N</td>
<td>-0.10215</td>
<td>-0.04098</td>
</tr>
</tbody>
</table>

Table 5.1: Comparison of average percent mass changes after 1000 h

Both UV and temperature play an important role in mass loss of composites during 1000 hours of testing time. It can be seen that thermal tests lost less weight than UV radiation in Table 5.1. By comparing the result of specimen 11 after UV test with thermal test, it seems composite 11 are more dominated by temperature rather than UV exposure. Specimen 11 (R1 ECR-glass 2) may not have good thermal resistance based on literature review, so oxidation may occur to the surface of matrix at 80C which results in
thermal degradation or decomposition. Another possibility may that specimen 11 contains various volatiles or low molecular weight oligomer inside of matrix that were developed during manufacture and began to move out slowly to the surface at 80C.

For nanocoated composites, we can see only high temperature did not cause much damage to coatings. Furthermore, by comparing mass change of 1AN (0.014%) with 1A (0.028%) after 1000 hours in oven, nanocoating seems to help composite keep its weight. This is an indication that the coating plays an important role as “septum” which protect composite from oxidation.

5.3 Water vapor condensation tests

As shown in Figure 4.5 (Chapter 4.2), all the specimens exhibited immediate gain in weight from the very first hours of testing and increasing tendency even after 1900 hours in chamber. All specimens were absorbing water very slow in the condensation environment.

According to the results of mass changing tests, Chapter 5.3.1 – 5.3.3 makes corresponded comparisons based on the same matrix or glass fiber.
5.3.1 Comparison of nanocoated and non-nanocoated specimens

For both Nano-coated composites, severe degradation of coating was observed on the condensation exposed surfaces. In figure 5.14, specimen 11N (Nano-coated R1 ECR-Glass 2) showed a gain in weight up to 25% less than specimen 11, which can be understood as a result of nano-coating degradation after water condensation exposure. However, specimen 1AN (Nano-coated Vinyl ester Epoxy ECR-Glass 1) exhibited the same behavior as specimen 1A and with a very similar weight gain tendency. That mean specimen 1AN should absorb more moisture than Specimen 1A under same exposure condition. It is supposed that exposed surfaces were severe damaged when coating was removed, which lead to an extremely rough surface. From SEM images, lots of scratches were observed on the surface after 1900 hours of water condensation exposure (Figure 4.10(b)). These micro structures may absorb and contain lots of water.
5.3.2 Comparisons of E-glass or ECR-glass vinyl ester epoxy specimens

Figure 5.15: Mass changes of the same matrix PMCs during the water condensation test.

Figure 5.15 shows the specimens with same matrix but different glass fibers exhibited diverse moisture absorptions. Although specimen 1A, 1AN, 3A and 4b are all vinyl ester epoxy matrix based composites, the 4b specimen (Vinyl ester Epoxy ECR-Glass 2, 80% glass) exhibited a noticeable different behavior in moisture absorptions that gained in weight up to 66% less than the rest of composites.

From SEM images (Fig. 4.10(a), Chapter 4.2), interfacial debonding was observed on the surface of specimen 1A, which may contribute to absorption of moisture. Also osmotic blister formation, as suggested in Figure 5.16 may be resulting from the high solubility of the hydrolysis products. These blisters would provide easy desorption paths for absorbed moisture.

Another physical reason may be that volume fraction of glass fiber is different.
Specimen 4b is 80%, whereas the others are 75%. Lower volume fraction of matrix may mean less damage caused by condensation in matrix. Manufacture process may also have some change as volume fraction is different. If cure reaction of the vinyl ester epoxy resin proceeded more slowly in specimen 4b than the others thereby enabling it to organize its linear macromolecular chains in a more compact structure with higher conversion rates. As a result, this vinyl ester epoxy composite had a lower water diffusion coefficient.

Figure 5.16: osmotic blister in specimen 3A after 1900 hours of condensation testing.
5.3.3 Comparisons of epoxy and polyester specimens with same fiber

Figure 5.17: Mass changes of the same matrix or same fibers PMCs during the water condensation test.

Figure 5.17 shows diverse moisture absorptions between two different polymer matrices with same fibers and two different fibers with same matrix (see following Tables) composites. Comparing specimen 6(Polyester ECR-Glass 2) with 10 (Epoxy ECR-Glass 2) shows that polyester absorbed more moisture than epoxy, specimen 5(Polyester E-Glass 1) and 9 (Epoxy E-Glass 1) did as well. Commonly, polyester composite has better water resistance than epoxy’s, as it has been widely used in pipes, tanks, fishing boats (Tatna, 2009). However, here, polyester and epoxy exhibited in an opposite way, which may be explained by the interface between fiber and matrix. It’s well known that interface can absorb water which can be dominated sometimes. Epoxy has a more hydroxyl groups allow H-bonds to form with the similar groups present in the glass fiber that provide better adhesion with glass fibers than polyester. Another possible
reason is special epoxy with high moisture resistant ability was used in this particular composite.

5.4 UV & water condensation cyclic exposure tests

When the specimens were cyclically exposed to both UV radiation and condensation the change in specimen weight were completely unexpected, as shown in Fig 4.13 (Chapter 4.4). The weight of specimens increases first then decreases after about 100 hours of exposure time. The weight loss continued at a steady rate for the remainder of the test. One of the reasons for the weight loss effect would be that condensation due to the presence of water can also remove soluble products of photo oxidation reactions from an ultraviolet radiated surface and thereby exposing fresh surfaces that will be susceptible for further degradation by ultraviolet radiation, which could be interpreted as continuous erosion process due to cyclic exposure effect. This was confirmed by SEM as discussed in the Chapter 4.4.2. Basically, degradation of matrix was similar to the result of UV radiation, but as water was participated physically or chemically, which may play a role of catalyst or reactant in the degradation process of polymers.

Comparing the variation of weight change at the end of tests as well as tendency of curves it can be seen that specimen 6 presents a noticeable distinction in weight loss behavior which exhibits only a 0.02% weight loss with respect to the maximum average weight loss (0.09%) from other specimens. By literature work, polyester has an advantage in resistance to light, weathering and water, which are outstanding comparing to other composites. Although hydrolysis may occur at 80C by the influences of water
during the test, the reaction is limited because its segments are hard to move freely in the crosslinking structure.

In contrast, specimen 1A (vinyl ester epoxy ECR-glass 1) and 3A (vinyl ester epoxy E-glass) exhibited the highest percentage in weight loss (up to 0.1%) and the largest fluctuation in their mass under the same testing conditions. Generally, the design of vinyl ester epoxy is to combine advantages of both polyester and epoxy resin as it is a reaction product of polymerization of polyester and epoxy resin. However, the result indicted that this product is a failure when it was subjected to cyclic exposure of UV radiation and condensation. There are various possibilities. One of the reasons may proportion problem of two main reactants in product design which relate to the degree of curing reaction.

Specimen 11 (R1 ECR-glass 2) exhibited 0.08% in weight loss. Comparing to the result of UV radiation 0.06%, it seems that water condensation have a positive effect on degradation of the material. Previous research reported that water can react with excess isocyanate and produces carbon dioxide and amine very easily (Ratna, 2009).

5.4.1 Desorption tests: moisture exposure vs. UV/condensation cyclic exposure test

The desorption behavior is more complicated. If we just look at moisture absorption alone (Fig 4.7) and subsequent moisture desorption (Fig.4.8) and just consider 2 specimens: 11 and 10; we see that after 300hrs and after 500hrs of moisture exposure, the mass loss after 1400 hrs of desorption is greater than the mass increase due to
moisture absorption. The actual approximate numbers I read off the figures are as follows:

After 300hrs absorption: 11 increases 0.12% and on desorption drops 0.2%
After 500hrs absorption: 11 increases 0.15% and on desorption drops 0.26%.
After 300hrs absorption: 10 increases 0.02% and on desorption drops 0.05%
After 500hrs absorption: 10 increases 0.03% and on desorption drops 0.05%

This clearly indicates that volatile hydrolysis products are leaving these specimens as well as the water absorbed.

If we now look at the 1400hr desorption after moisture plus UV cycling (Fig.4.15):
After 300hrs cycling: 11 drops 0.07% and 10 drops 0.02%
After 500hrs cycling: 11 drops 0.1% and 10 drops 0.02%

These drops are considerably smaller than those due to moisture alone. One reason is that the actual moisture absorption time in the cycled tests was only about 1/3 as long since the UV was on for 16hrs (33%RH) and the moisture exposure was on for 8hrs during each cycle.

5.5 Nitric acid tests

The results of nitric acid tests are quite different based on testing conditions. Two kinds of glass fiber are involved in our testing, which are E-glass fiber and ECR-glass fiber. In the case of 1N concentration acid, lots of cracking were observed in E-glass fiber while no cracking in ECR-glass fiber (see Fig 4.23), which is something that was expected, since E-glass has reduced resistance to corrosion environments.
Following series of SEM images Figure 5.18 (a) to (f) show final surface characterization after different aggressive conditions. We can see specimen that subjected to UV & condensation and UV & condensation followed by acid exhibited most severe degradation. That is because UV radiation and condensation operate in a synergistic manner that leads to extensive matrix erosion (Bhavesh G. Kumar, 2002). Besides Fig 5.18 (c) and (e) shows numerous microvoids in matrix. The reason may due to degradation of matrix, such as hydrolysis of R2, R3 groups and ester groups.
Figure 5.18 (a) to (f): SEM images of exposed sections of specimen 11 (R1 ECR-glass) under different conditions.

Microcracking was caused by the polymer matrix becoming more brittle due to the increased crosslinking resulting from photo-oxidation reaction induced by UV radiation (Wypych, G. 2008). Comparing Figure 5.19 (a) with (c), Fig. 5.19 (c) presents severe matrix cracking which is not observed in Fig. 5.19 (a). This may due to reactions of crosslinking and chain scission on surface of specimen increase the brittleness of the matrix during UV radiation. Then after the affection of strong nitric acid, microcracking began to grow on the surface of matrix.
Figure 5.19 (a) to (c): SEM images of exposed sections of specimen 11N (nanocoated R1 ECR-glass) under different conditions.

(a) After UV exposure

(b) After 1N nitric acid exposure

(c) After UV radiation followed by 1N nitric acid exposure
Chapter Six: Conclusions

6.1 Dry hot UV exposure

All composites showed weight losses with the maximum values between 0.03 and 0.06%. The results showed approximately 20% less degradation in the matrix by dry hot UV than UV/H$_2$O condensation after the same time of exposure.

The least degraded specimen was specimen 10 (Epoxy ECR-Glass 2) with only 0.029% followed by specimen 6 (Polyester ECR-Glass 2) with 0.037% of its weight lost.

For the nano-coated composites, specimen 11N (Nano-coated R1 ECR-Glass 2) showed the highest loss in weight - up to 50% more than the rest of the other composites. The weight loss was 0.1% compared to 0.05% for the rest of the composites. For the 1ANnano-coated, it exhibited the same tendency in weight loss as the rest of the composites.

The exposed surfaces of the composites presented characteristic yellowing effects. Epoxy ECR-Glass 2 (composite 10) exhibited the best photo-yellowing resistance whereas the most affected surface was of the R1 samples 11 and 11 N. Significant changes in surface roughness were also observed.
The examination by SEM revealed that the matrix degradation clearly presented the well-reported microcracking and chalking phenomenon but 10 m less deep than was found in the samples after UV/H$_2$O condensation (30 m).

The degradation was observed only on the exposed surfaces and the fibers maintained their structural integrity. There was no evidence of cracks along their surfaces.

### 6.2 Water condensation exposure

All composites showed weight gains with the maximum values between 0.05 to 0.28%. The percentage of weight gain of specimen 11(R1 ECR-Glass 2) is 0.28%, which is 4 times higher than that of specimen 10(Epoxy ECR-Glass 2) after 1900 hours of condensation exposure.

Specimen 10(Epoxy ECR-Glass 2) exhibited the lowest weight gain (with only 0.068% mass gain)

For the nanocoated composites, specimen 11N (Nanocoated R1 ECR-Glass 2) showed gain in weight - up to 20% less than specimen 11. The weight gain was 0.21% compared to 0.27% for the rest of the composites. For the 1ANnano-coated, it exhibited the same tendency in weight gain as composite 1A.
The examination by SEM reveals that all composites suffer varying degrees of degradation after 2000 hours of water condensation. Matrix disintegration seems occurred among all composites, especially in vinyl ester epoxy composites and epoxy composites

### 6.3 UV & condensation cyclic exposure tests

After about 100 hours, the composites reach a maximum point of moisture saturation. After that, no further mass gain was detected. 1A (Vinyl ester Epoxy ECR-Glass 1, 75% glass) and 3A (Vinyl ester Epoxy E-Glass 1, 75% glass) specimens gained weight up to 50% more than the rest of the composites.

Specimen 6 (Polyester ECR-Glass 2) exhibited the lowest weight loss (with only 0.02% mass gain) with most of the gain occurring after 500 hours.

The rest of the composites exhibited significant losses in weight with the maximum values between 0.08 and 0.1%. The most degraded composites were 1A (Vinyl ester Epoxy ECR-Glass 1, 75% glass) and 3A (Vinyl ester Epoxy E-Glass 1, 75% glass).

The exposed surfaces of the composites presented characteristic discolorations with considerable yellowing alterations.

SEM showed that the composites exhibited severe degradation to the matrix and
to the matrix/fiber interfaces. Major loses to the matrix were observed, in some places up to 30um deep. The fibers, however, appeared to be free from any visible surface damage.

SEM observations also showed that specimen 6 (Polyester ECR-Glass 2) had the lowest level of degradation and partially maintained its matrix with a considerable level of adhesion to the fibers after the exposure.

After 1000 hours of drying at 80 ºC, specimen 6 (Polyester ECR-Glass 2) presented the lowest value of weight loss (0.05%) compared to the rest of the composites (0.2% in average). The specimen maintains a good thermal stability after longer periods of exposure.

6.4 Thermal stability tests

All PMCs after 1000 hours of exposure lost between 0.012 to 0.045 % of their weight. Composite 11 and 11N exhibited the highest percentage in weight loss (0.045%), which is double times than the rest of composites.

Composite 4b and 10 showed only a 0.012% weight loss with respect to the maximum average weight loss (0.024 %) from other specimens.

6.5 Nitric acid exposure tests

No major differences in surface characteristics were found in the samples before
and after the acid exposure (0.063mol/L). Slight degradation in some localized areas was observed, mainly on exposed fibers.

Specimen 1AN and 11N degraded on the surface after two weeks nitric acid exposure. Cracks developed in the coating even in low concentration solution.

### 6.6 UV/condensation followed by nitric acid exposure

No additional acid degradation was found on the surfaces previously damaged by UV/condensation tests.

### 6.7 Dry UV followed by nitric acid exposure

Specimen 1AN (Nano-coated Vinyl ester epoxy ECR-Glass 1) and 11N (Nano-coated R1 ECR-Glass 2) exhibited noticeable matrix cracks after two weeks in acid solution (0.063mol/L).

No evidence of fiber cracking was detected in the ECR- glass fiber composites but not in the E-glass fiber.

Specimen 11 (R1 ECR-glass 2) exhibited numerous microvoids on the surface of matrix after acid solution exposure.
References

Composite materials. Advancing the Chemical Sciences :
http://www.rsc.org/Education/Teachers/Resources/Inspirational/resources/4.3.1.pdf
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### Appendix: Acronyms and Symbols

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Full Form</th>
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<tbody>
<tr>
<td>A-glass</td>
<td>Alkali-glass</td>
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<tr>
<td>CMCs</td>
<td>Ceramic matrix composites</td>
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<tr>
<td>C-glass</td>
<td>Chemical-glass</td>
</tr>
<tr>
<td>D-glass</td>
<td>Dielectric-glass</td>
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<td>Electrical-glass</td>
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<td>ECR-glass</td>
<td>Electrical Corrosion Resistance-glass</td>
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<tr>
<td>FTIR</td>
<td>Fourier transforms infrared spectroscopy</td>
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<td>GFRP</td>
<td>Glass fiber reinforced polymer matrix composite</td>
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<td>GPC</td>
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<td>Polyether ether ketone</td>
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<td>Room temperature vulcanization silicone</td>
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<td>Scanning Electron Microscope</td>
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<td>Thermal-glass</td>
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<tr>
<td>UPE</td>
<td>Unsaturated polyesters</td>
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UV        Ultraviolet
VE        Vinyl esters
ZnO       Zinc oxide
Z-glass   Zirconia-glass