Final Technical Report

Project Title: Sustainable Energy Solutions
Task 4.2: UV Degradation Prevention on Fiber-Reinforced Composite Blades

Award Number: DE-FG36-08GO88149
Recipient: Wichita State University

Project Location(s): Wichita State University
Wichita, Kansas 67260

Project Period: June 1, 2008 – December 31, 2009
Date of Report: March 1, 2010
Written by: Ramazan Asmatulu, Ph.D.

Program Manager:
Debbie Weems
Technical Project Officer
Inventions and Innovations Program
United States Department of Energy
Golden Office
1617 Cole Boulevard
Golden, CO 80401-3393

Principal Investigators:

Subcontractors:

Cost-Sharing Partners: Wichita State University
Acknowledgment: This material is based upon work supported by the Department of Energy under Award Number DE-FG36-08GO88149.

Disclaimer: This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.
FINAL TECHNICAL REPORT

Sustainable Energy Solutions
DE-FG36-08GO88149

Task 4.2
UV Degradation Prevention on Fiber-Reinforced Composite Blades

Project Director
Ramazan Asmatulu, Ph.D.,
Assistant Professor, Mechanical Engineering

Wichita, Kansas

PI: Janet M. Twomey, Ph.D.
Professor, Industrial and Manufacturing Engineering
EXECUTIVE SUMMARY

Use of wind energy has expanded very quickly because of the energy prices, environmental concerns and improved efficiency of wind generators. Rather than using metal and alloy based wind turbine blades, larger size fiber (glass and carbon) reinforced composite blades have been recently utilized to increase the efficiency of the wind energy in both high and low wind potential areas. In the current composite manufacturing, pre-preg and vacuum-assisted/heat sensitive resin transfer molding and resin infusion methods are employed. However, these lighter, stiffer and stronger composite blades experience ultraviolet (UV) light degradation where polymers (epoxies and hardeners) used for the blades manufacturing absorb solar UV lights, and cause photolytic, thermo-oxidative and photo-oxidative reactions resulting in breaking of carbon-hydrogen bonds, polymer degradation and internal and external stresses. One of the main reasons is the weak protective coatings/paints on the composite blades. This process accelerates the aging and fatigue cracks, and reduces the overall mechanical properties of the blades. Thus, the lack of technology on coatings for blade manufacturing is forcing many government agencies and private companies (local and national windmill companies) to find a better solution for the composite wind blades. Kansas has a great wind potential for the future energy demand, so efficient wind generators can be an option for continuous energy production.

The research goal of the present project was to develop nanocomposite coatings using various inclusions against UV degradation and corrosion, and advance the fundamental understanding of degradation (i.e., physical, chemical and physiochemical property changes) on those coatings. In pursuit of the research goal, the research objective of the present program was to investigate the effects of UV light and duration on various nanocomposites made mainly of carbon nanotubes and graphene nanoflakes, contribute the valuable information to this emerging field of advanced materials and manufacturing and advance the Kansas economy through creation of engineering knowledge and products in the wind energy.

The proposed work was involved in a multidisciplinary research program that incorporates nanocomposite fabrication, advanced coating, characterization, surface and colloidal chemistry, physicochemistry, corrosion science, and analysis with a simple and effective testing methodology. The findings were closely related to our hypothesis and approaches that we proposed in this proposal. The data produced in the study offered to advance the physical understanding of the behavior of nanostructured materials for the prevention of UV light at different exposure time and salt fogging. Founding of this proposal enabled the first UV resistive nanocomposite corrosion coating effort in Kansas to impact the local and national windmill industry. Results of this program provided valuable opportunities for the multidisciplinary training of undergraduate and graduate students at Wichita State University (WSU), as well as a number of aircraft companies (e.g., Cessna, Hawker Beechcraft, Spirit, Boeing and Bombardier/Learjet) and other local and regional industries.
Comparison of the Actual Accomplishments with the Goals and Objectives of the Project

UV light and other environmental factors (e.g., oxygen, pollutants and moistures) are introduced to the fiber reinforced polymeric composites during the service, causing physical, chemical and physicochemical degradations. This reduces the lifetime and limits the applications of the composite based wind blades. In order to minimize UV and other environmental factors on the composite blades, new studies are focusing on functional coating systems. The objective of this work is to improve the durability of turbine blades through new materials: nano-composite coatings. During this work, we have performed a number of UV and salt exposure tests on coated samples and analyze the results using optical microscope, SEM, contact angle measurement and AFM techniques. Our findings clearly show that the hypothesis and approaches that we proposed in this proposal meet the goals and objectives.
1. INTRODUCTION

1.1 Motivation

Thin films have potential benefits in wind mill industry where UV and corrosion protection, and wear resistance improvements are imperative. However, these organic films have yet to be perfected and failures due to the degradation caused by UV lights and other environmental factors are potential hazards. These hazards can cost the US economy millions of dollars and cause serious accidents [1]. In the present program, the principal investigator (PI) studied to understand the mechanisms of the UV degradation and improve the performance of protective coatings, which in turn will advance the service life and safety. In addition, the novel coating process could be economic, environmentally friendly, and easy to use compared to other methods currently employed by the industry.

During this program, in order to understand the exact mechanism(s) of the UV degradation, inorganic nanoparticulates were incorporated into polymeric coating materials, and then UV light and salt fog were exposed for the polymeric degradation. Understanding of the degradation process improved the coating performance and corrosion efficiency on composite and metal surfaces, as well as mechanical strengths of composites (tensile strength, elongation, abrasion and impact resistances, etc.).

1.2 General Background

Protective coating is frequently utilized for the purpose of composite and metal surface protection against environmental attacks. These organic films including polyurethane, polyamide, polyester, resin and epoxy play a crucial role as a barrier layer to avoid the transportation of corrosive species, such as chlorine and hydroxyl ions, water, oxygen, pollutants and pigments. These unwanted elements have high affinity to react with the surfaces when they interact with the interfaces of the materials [1-3].

Coating materials undergo physical, chemical and physicochemical deteriorations by environmental interactions. These degradations of polymeric materials can develop in the form of swelling by radiations (solar UV lights, electron beams, x-ray, β-ray and γ-ray), water absorption (causing a reduction in hardness and stiffness), dissolution, cross-linking, oxidation and color changes due to the heat, acid rain, oxidative environments (O₂ and O₃), and other factors [4-10]. Additionally, at elevated temperatures some gas species may be evolved from the coatings, so this process can reduce the strength, molecular weight (MW), gloss, density and glass transition temperature (T_g) and increase the porosity and surface roughness of the polymeric coatings. The combined effects of the degradation can also take place on the organic materials. Finally, the process alters mechanical, electrical, thermal and optical properties, as well as other chemical and physicochemical properties of the materials [7,8]. Figure 1 shows major atmospheric influences on an organic coating and corrosion formations on a metal substrate [11-14].
1.3 UV Degradation

The sun has high intensity UV lights, which cause free radical formations on the polymer surface [2]. These radicals are simply groups of atoms/molecules with an excess of electrons, which desire to pair with the other electrons in the polymer structure. Therefore, this process breaks the covalent bonds of polymer molecules into small molecules and initiates the cross-linking reactions (extra polymerization) or oxidation [7]. Figure 2 illustrates the free radical formation and cross-linking of a polymer with UV lights [15]. In the long period of UV light exposures, these polymers can be overly cured at wavelength ranges of 300 nm to 400 nm, which in turn cause shrinkage/expansion, and hence increase the internal stresses and brittleness of the polymers [6].
Because of the long term UV exposures, synthetic and naturally occurring polymeric coatings cannot function against environmental attacks. Especially at higher levels of cross linking, polymeric materials can degrade and eventually crack propagation can take place on the protective coatings. Therefore, composites, metals and alloys under the coatings can be degraded or dissolved as oxide or other compounds in aqueous media [1-3].

2. EXPERIMENTAL

2.1 Materials

For the coatings of specimens, Corrosion Resistant Epoxy Primer P/N 10P30-5, Curing solution or Hardener P/N EC-275, and Exempt Solvent Reducer or Thinner P/N TR-115 were used in the experiments. These chemicals were purchased from ANAC Aerospace. Figure 3 shows the coating units of primer, thinner and hardener. In order to mix the coatings, they were shaken by a pneumatic paint shaker to avoid the agglomeration or settlement.

![Paint used for making nanocomposite coatings](image)

**Figure 3:** Paint used for making nanocomposite coatings: a) Thinner or Exempt Solvent Reducer P/N TR-115, (b) Epoxy Primer P/N 10P30-5, and (c) Hardener or Curing solution P/N EC-275.

2.2 Nanoscale Inclusions

Multi wall carbon nanotubes (MWCNT) and graphene platelets were chosen for the polymeric nanocomposite fabrication. MWCNTs were purchased from Materials and Electrochemical Research (MER) Corporation, with 140 +/- 30 nm diameter and 7 +/- 2 micron length, with purity >90%. Graphene platelets were purchased from Angstron Materials, LLC. with at least 75% of the z dimension less than 10 nm. Specific surface area (BET) and D50 are 90.4 m²/g and 6 µm, respectively. These inclusions were used in the experiments without further modification. Figure 4 shows the images of MWCNTs and graphene platelets [1,16].
As is known, nanoparticles tend to aggregate due to their intermolecular interactions, such as electrostatic, hydrophobic, and van der Waals, which makes the dispersion process difficult in polymeric matrices [17]. Hence, effective utilization of nanoparticles in these applications strongly depends on their ability to homogeneously disperse throughout the matrix and achieve good interfacial bonding, which will directly affect the performance of the inclusions. For this reason, ultrasonic vibration, high-shear mixing, and mechanical stirring were utilized to disperse the inclusions into the matrix materials.

2.3 Prepreg Glass Fiber Composite Fabrication

A standard vacuum bag lay-up process was used in the fabrication of prepreg lay-up. 12 prepreg plys that consist of glass fiber and resin were cut and placed on the smooth and clean Al plate with the same fiber direction. The prepreg was purchased from Cytec. Tacky type, release film, breather and vacuum bag were used during the vacuuming at 25 inHg. The prepreg lay-up was initially heated up to 82 °C (gel temperature) for cross-linking, and kept at this temperature for 15 minutes, and then the heat was further increased to 121 °C for final curing for two hrs. The heating and cooling rates were 5 °C/ min. The prepared composites were machined into appropriate size and shape before the further processing.

2.2 Methods

2.2.1 Nanocomposite preparation

Nanocomposite coatings were prepared by dispersing MWCNTs and graphene platelets in the Epoxy primer. Inclusions were mixed with the solvent reducer and sonicated for 30 minutes to ensure a good dispersion. Epoxy primer was shaken on a pneumatic paint shaker and placed on a hot plate. Then the inclusions/solvent mixtures were slowly added drop wise into the epoxy primer and the resulting solution
was stirred on the hot plate for 24 hours at room temperature. After 24 hours, curing solution was added to the mixture and stirred for 15 minutes to produce the uncured nanocomposite coating. Mixtures of 0.25%, 0.5%, 1% and 2% MWCNT or graphene were prepared and corresponding test samples were painted at different thickness. Figure 5 shows the SEM images of MWCNTs into the epoxy primer. The SEM images clearly show that the MWCNTs were well dispersed in the epoxy primer.

![Figure 5: SEM images of MWCNTs dispersed into the epoxy primer.](image)

High Volume Low Pressure (HVLP) Spray Gun Kit was purchased from Central Pneumatic, Model# 94572. This gravity feed spray gun can likely give more reliable coverage than conventional spray guns for uniform coatings. 1 mil (25.4 µm) and 3 mil coating thicknesses were applied on the samples. The spray gun used to coat the panels is shown in Figure 6a. Coating thickness of the dried samples was measured with an eddy current paint thickness gauge.

### 2.2.2 UV Chamber

QUV Accelerated Weathering Tester (or UV Chamber) was purchased from the Q-panel Company. The ultraviolet ray lamp used in this tester was UVA-340 lamps which can produce only the ultraviolet
portion of the spectrum. This lamp is a simulation of short-wave sunlight where higher UV damage can be seen on the polymeric coating. QUV chamber can produce photodegradation in a few days or weeks that can occur in outdoors in several months or even years. It also has the moisture simulation system, so materials can be tested under controlled humidity. Figure 6b shows the ultraviolet ray chamber used for testing nanocomposite coated surfaces.

Figure 6: a) High volume low pressure (HVLP) spray gun for nanocomposite coating, and b) QUV Accelerated Weathering Tester used for the UV degradation of polymeric coatings.

2.2.2 Water Contact Angle Goniometer

Water contact angle goniometer (KSV Instruments Limited, Model# CAM 100) with compact video mode was used to measure the water contact angle values before and after UV exposure. Computer software used for measuring contact angle is provided by KSV Instrument Limited which can precisely calculate and record contact angle values as well as can take the images of the water droplets. The KSV Cam 100 used in this project is shown in Figure 7a.
2.2.3 Metallurgical Microscope

The inverted metallurgical microscope employed to inspect the surface of the samples was purchased from OLYMPUS, Model# GX41. The magnification settings extend from 5X to 100X in this microscope and it is suitable for simple polarization observations as well as bright field. A standard 6V-30W halogen lamp is attached to this microscope to receive a high-brightness image even with dark sample. Computer software was also supplied by the OLYMPUS to observe and record microscopic images. Figure 7b shows the metallurgical microscope utilized to take microscopic images.

2.2.4 Atomic Force Microscope

Model MFP-3D-SA Stand Alone Atomic Force Microscope (AFM) purchased from Asylum Research was used to take AFM images. This provides us micro and nanoscale degradation on the coatings. A standard Si₃N₄ cantilever tip was used during the scanning of the samples surfaces. The Atomic Force Microscope located at WUS is shown Figure 8a.

2.2.6 Corrosion Chamber

Corrosion Test (Salt Fog) Chamber purchased from Singleton Corporation was used for Salt Fog, Humidity and Water Fog. The prepared samples were exposed to a series of different environments in a repetitive cycle that reproduces cyclic outdoor conditions. This provides the best possible laboratory simulation of natural corrosion and degradation. Figure 8b shows the corrosion chamber used for the present study at 4% salt concentration.
2.2.7 Coating Thickness Gauge

PosiTTest DFT Combo coating thickness gauge was used to measure the coating thickness of prepared samples. It measures coating thicknesses both on steel (magnetic) and aluminum (nonmagnetic). It can recognize the substrate automatically and measures the coating thickness.

2.2.8 Tensile Testing

A tensile test (or tension test) was used to determine the mechanical properties (e.g., elastic modules, ultimate stress, elongation, etc.) of the composite panels. MTS tensile testing unit was utilized in the present work.

3. RESULTS AND DISCUSSION

3.1 Nanocomposite Coating on Al Surface

In the first set of experiments, CNT based nanocomposite coatings were sprayed on the Al substrates (2.5x7.5 cm). Optical images were taken for all the samples before and after UV exposure and corrosion tests. It is expected that adding carbon nanotubes into the primer, color of the primer should change, as well. UV and salt fog unexposed aluminum samples with different weight percent carbon nanotubes are shown in Figure 9. The number at the top right corner indicates the sample numbers. The bottom three numbers indicate carbon nanotubes percentage, duration of UV exposure (days) and salt fog exposure (days), respectively. For example, sample number 42 is coated with 0.5% carbon nanotubes-epoxy nanocomposite coating and it is UV and salt fog exposed for 0 day (or unexposed). It is seen in Figure 8 that the color of the MWCNT containing nanocomposite coating becomes darker by increasing the weight percents of the carbon nanotubes in the coating materials.
Samples coated with various CNTs were exposed to UV light. Figure 10 shows the exposed and unexposed coatings on the panels. After the UV exposure, colors of the samples that have lower inclusions were significantly changed; however, the color changes on the nanocomposite coated samples were very low. Especially, it is very hard to visually distinguish the color change on 1% and 2% MWCNT containing nanocomposite samples. This clearly indicates a big surface degradation of the primer coated samples.

### 3.1.1 Contact Angle Measurements

The contact angle measurements of 1 mil and 3 mil thick coatings are given in Tables 1 and 2, respectively, as a function of CNT contents and UV exposure times. At 0 day UV exposure, the average contact angle values of 0%, 0.25%, 0.5%, 1% and 2% nanocomposite coatings were closer to each other, and stayed between 85° and 91°. There is a very little contact angle improvement at high CNT loadings. The contact angle
values of primer coatings gradually decreased by increasing UV exposure times on the samples. For example, the contact angle values of both 1 mil and 3 mil primer coatings were initially 85°, and then reduced to 11° after 16 days of UV exposure.

**Table 1:** Contact angle measurements of 1 mil thick coating with different percentage of CNTs under various UV exposures.

<table>
<thead>
<tr>
<th>UV Exposed Days</th>
<th>0% CNT</th>
<th>0.25% CNT</th>
<th>0.5% CNT</th>
<th>1% CNT</th>
<th>2% CNT</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>84.78</td>
<td>84.08</td>
<td>85.26</td>
<td>86.07</td>
<td>91.38</td>
</tr>
<tr>
<td>4</td>
<td>74.90</td>
<td>78.82</td>
<td>78.72</td>
<td>81.33</td>
<td>91.12</td>
</tr>
<tr>
<td>8</td>
<td>52.32</td>
<td>74.07</td>
<td>74.12</td>
<td>75.43</td>
<td>89.67</td>
</tr>
<tr>
<td>10</td>
<td>28.75</td>
<td>53.12</td>
<td>66.09</td>
<td>68.56</td>
<td>86.69</td>
</tr>
<tr>
<td>12</td>
<td>21.07</td>
<td>35.54</td>
<td>41.90</td>
<td>57.81</td>
<td>62.14</td>
</tr>
<tr>
<td>16</td>
<td>11.52</td>
<td>29.68</td>
<td>33.12</td>
<td>40.30</td>
<td>43.04</td>
</tr>
</tbody>
</table>

**Table 2:** Contact angle measurements of 3 mil thick coating with different percentage of CNTs under various UV exposures.

<table>
<thead>
<tr>
<th>UV Exposed Days</th>
<th>0% CNT</th>
<th>0.25% CNT</th>
<th>0.5% CNT</th>
<th>1% CNT</th>
<th>2% CNT</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>85.31</td>
<td>85.15</td>
<td>84.89</td>
<td>85.97</td>
<td>89.33</td>
</tr>
<tr>
<td>4</td>
<td>74.45</td>
<td>82.54</td>
<td>83.48</td>
<td>85.34</td>
<td>89.18</td>
</tr>
<tr>
<td>8</td>
<td>48.17</td>
<td>72.95</td>
<td>79.72</td>
<td>83.05</td>
<td>88.48</td>
</tr>
<tr>
<td>10</td>
<td>28.11</td>
<td>45.39</td>
<td>67.34</td>
<td>74.33</td>
<td>86.66</td>
</tr>
<tr>
<td>12</td>
<td>23.92</td>
<td>24.06</td>
<td>57.07</td>
<td>62.13</td>
<td>69.84</td>
</tr>
<tr>
<td>16</td>
<td>11.63</td>
<td>12.48</td>
<td>34.53</td>
<td>49.45</td>
<td>54.00</td>
</tr>
</tbody>
</table>
Figure 1: Contact angle values of 0 and 1% CNT nanocomposite coatings obtained at 0, 8 and 16 days of UV exposure times. The film thickness is 3 mil.

Contact angle values are greater at higher loadings of CNTs in coatings after the same duration of UV exposure (Tables 1 and 2). At 0 day of the UV exposure, contact angle values of 0.5% and 2% CNTs coatings were 85 and 89° for the 3 mil samples, respectively. After 16 days of UV exposure, the contact angle values of these two samples were reduced to 34° and 54°. The 2% CNT content sample has an approximately 43° higher contact angle value than the base case (primer coating only). This improvement should increase the performance of the nanocomposite coatings against UV degradation and corrosions. Figure 11 clearly shows the water contact angle measurements of the samples obtained using the Goniometer.

The water contact angle values of 0, 4, 8, 10, 12 and 16 days of UV exposure on the 1 mil and 3 mil coating respectively for various carbon nanotubes content are graphically shown in Figures 12 and 13. The data clearly points out the change in hydrophobicity of the coated surface, and then the hydrophobicity is
gradually lost with UV exposure time. For the coating without CNTs, the coated surface became highly hydrophilic after 16 days of UV exposure. On the other hand, CNT based nanocomposites were less hydrophilic after 16 days of UV exposure, as well.

Figure 12: Change in contact angle values of 1mil thick coatings as a function of CNT and UV exposure time.
3.1.2 Atomic Force Microscopy

In order to determine the degradation levels of the coatings at micro and nanoscale, our team used atomic force microscopy (AFM) studies on the coated samples. Figure 14 shows the AFM surface images and roughness (or height) of 3 mil nanocomposite coatings at 0 and 16 days of UV exposures. The images reveal that surface morphologies of coated samples are entirely changed after the UV exposure. At 0 day UV exposure, surface is smooth and shiny where higher contact angle is achieved, while at 16 days of UV exposure, the surface smoothness and glossyness are reduced or completely disappeared, where a lower contact angle or hydrophilic surface obtained. This may be because of the fact that the radicalized polymer chains under UV lights interact with oxygen, hydroxyl and other species, causing rougher and hydrophilic surfaces.
Figure 14: AFM surface images and surface roughness of 3 mil coatings with different percentages of carbon nanotubes at 0 and 16 days of UV exposures.
Figure 15: a) Primer only coated surface after 80 days corrosion chamber without UV exposure and b) primer only coated surface after 16 days UV exposure and 80 days salt fogging.

Figure 15a shows AFM image of primer only coated surface which has not been exposed to UV light, but kept in the corrosion chamber for 80 days. From the Figure 15a, the surface is destroyed and pitting at large scale is formed on the polymeric coating. Figure 15b shows the primer only coated surface which has been exposed to 16 days UV light and 80 days of salt fog. From the image, smooth place on the surface of the coating cannot be seen, and the surface is completely damaged. This will eventually accelerate the further degradation and corrosion formation on the surface of the composites.
Figure 16: a) 0.5% MWCNT coated surface after 80 days corrosion without UV exposure, and b) 0.5% MWCNT coated surface after 16 days of UV exposure and 80 days corrosion.

Figure 16a shows the AFM image of the 0.5% MWCNT coated surface exposed to 80 days salt fog. Some pits are still visible on the surface, but those are very smaller in size comparing the previous samples. Hence, undoubtedly the surface quality of the 0.5% MWCNT coated samples is better than those of 0% and 0.25% MWCNT coated surface after 80 days of corrosion test. Figure 16b exhibits the 0.5% MWCNT nanocomposite coated surface after 16 days of UV and 80 days of salt fog exposures. Once again, the surface destruction is very less for 0.5% MWCNT nanocomposite coated surface than 0% and 0.25% MWCNT containing nanocomposite coated surface. This improvement was also seen on the 1% and 2% CNT based nanocomposite coatings.

4.5 Changes in Coating Thickness

It was found that the coating thickness of all samples remains the same after the UV degradation, but is changed after the 80 days of the salt fog exposure in the corrosion chamber. Coating thickness measurement was performed on 3 mil thick coatings. Figure 17 shows the percent reduction in coating thickness of 0%, 1% and 2% MWCNT containing samples after different duration of the UV exposure and 80
days of the salt fogging. At 0% MWCNT coating, percent reduction between 0 and 8 days of UV exposure is at lower level, and then significantly increased. At 16 days of UV exposure and 80 days of salt fog, nearly 23% of film is removed from the surface. However, at 1% and 2% MWCNT coatings, the film thickness reductions are 13% and 7%, respectively, at the same UV and corrosion test conditions. This indicates that in the presence of nanoscale inclusion, film thickness also stays more stable, which may be another reason of receiving higher performance against UV light and salt fog.

![Graph showing percent reduction in coating thickness](image)

**Figure 17:** Percent reduction in coating thickness of different coatings after different UV exposure time and 80 days of salt fogging.

### 3.2 Nanocomposite Coating on Composite Surface

In the second part of the study, graphene platelets were dispersed in the same epoxy primer and sprayed on the glass fiber reinforced composites. The following experiments were applied on the coated samples:

#### 3.2.1 Contact Angle

Table 3 gives the contact angle values of 3 mil thick coating on glass fiber composite panels at various graphene loadings and UV exposure times. As can be seen, at 0 day UV exposure, the average contact angle values of 0%, 0.25%, 0.5%, 1% and 2% graphene nanocomposite coatings are between 75° and 80°; however, after 16 days UV exposure, contact angle values are gradually reduced to 10°, 11°, 13°, 14° and 20°, respectively. Another word, contact angle values are a little increased by graphene addition into the
polymeric coating and block the water penetration into the coating and composite structure. As the thickness of the nanocomposite coatings increases, contact angle values also increase, which may be because of the lesser substrate surface effects and/or lower degradation levels. The contact angle values of these nanocomposite coatings are graphically shown in Figure 18. These data point out that the surface hydrophobic properties of coatings were improved by adding graphene in the polymeric coating and increase the coating resistance against the UV lights and corrosion.

Table 3: Contact angle measurements of 3 mil thick coating with different percentage of graphene under various UV exposures.

<table>
<thead>
<tr>
<th>UV Exposed Days</th>
<th>0% graphene</th>
<th>0.25% graphene</th>
<th>0.5% graphene</th>
<th>1% graphene</th>
<th>2% graphene</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>75.52</td>
<td>82.15</td>
<td>84.62</td>
<td>85.53</td>
<td>85.68</td>
</tr>
<tr>
<td>4</td>
<td>68.58</td>
<td>80.33</td>
<td>82.31</td>
<td>83.52</td>
<td>84.26</td>
</tr>
<tr>
<td>8</td>
<td>47.86</td>
<td>50.98</td>
<td>54.43</td>
<td>56.37</td>
<td>59.74</td>
</tr>
<tr>
<td>12</td>
<td>20.34</td>
<td>26.75</td>
<td>27.63</td>
<td>28.77</td>
<td>30.45</td>
</tr>
<tr>
<td>16</td>
<td>10.54</td>
<td>19.47</td>
<td>19.54</td>
<td>20.86</td>
<td>25.57</td>
</tr>
</tbody>
</table>

Figure 18: Change in contact angle values of graphene based coatings on the glass fiber composites at various UV exposure time

3.2.2 AFM Images
Figure 19: AFM surface images and surface roughness of 3 mil coatings with different percentages of graphene at 0 and 16 days of UV exposures.
In order to determine the surface degradation levels of the coatings at micro and nanoscale, AFM was used. Figure 19 shows the AFM surface images and roughness (or height) of 3 mil nanocomposite coatings at 0 and 16 days of UV exposures. The images clearly prove that surface morphologies of coated samples are entirely changed after the UV of exposure. At 0 day UV exposure, the surface is smooth and shiny where higher contact angle is achieved, while at 16 days of UV exposure, the surface smoothness and glossyness are reduced or completely disappeared, where a lower contact angle or hydrophilic surface formed. This may be because of the fact that the radicalized polymer chains under UV lights interact with the species, resulting in rougher and hydrophilic surfaces.

3.2.3 Mechanical Properties of Composites

Mechanical properties of glass fiber reinforced composites were studied using the tensile testing unit (MTS). The composite panels were machined in dog-bone shape, and then coating materials were sprayed by the air nozzle sprayer. Figure 20 shows the coated and uncoated composite specimens that were used for the tensile testing. Figure 21 also illustrates the elastic modules values of the composite samples as a function of salt fogging. The elastic modules values of the uncoated composite panels are around 19.8 GPa at 0 day UV exposure and various salt fogging between 0 and 40 days; however, the elastic modules values were significantly reduced after 16 days of UV exposure. The UV exposure and salt fogging did not make significant changes on the 2% graphene coated composites. This confirms that the nanocomposite coating stabilize the strength of the composites, which may be useful for the composite wind mill blades.

![Figure 20: The coated and uncoated composite specimens that were used in the tensile testing.](image)
Most of the wind turbine blades are made of glass and carbon fiber reinforced composites; however, these composite blades experience UV degradation where polymers (epoxies and hardeners) used for the blades manufacturing absorb solar UV lights, and cause photolytic, thermo-oxidative and photo-oxidative reactions resulting in breaking of carbon-hydrogen bonds, internal and external stresses and polymer degradations. One of the main reasons is the weak protective coatings/paints on the composite blades. This process accelerates the aging and fatigue cracks, and reduces the overall mechanical properties of the blades. Thus, our new coating system that has higher contact angle, mechanical strength and UV resistance values will open up new possibilities to extend the lifetime of the composite blades.

4. BENEFITS OF THE PROJECT
The initial experimental results highly encouraged us to focus on nanostructured materials fabrication and characterization for the prevention of UV light. In the present program, experimental and theoretical studies on the use of nanoscale inclusions in polymeric coating were conducted. This research enhanced the fundamental understanding of process, which, to date, is very limited in terms of UV degradation. These materials can also be used to address other close related problems, such as nondestructive testing of coating, prevention of corrosion, repairing of composites, etc. The specific benefits that support the objectives of the proposed project follow:

- Verified the parameters affecting the UV degradation,
- Determined the appropriate materials, methods, and their specifications,
- Built up creative, reliable, and sustainable methods for various applications,
- Increased the professional knowledge of engineers and faculty members through hands-on experience,
- Had an opportunity to conduct an interdisciplinary research program to enhance research and teaching activities locally and nationally,
- Had a potential advancement for the Kansas economy through creation of engineering knowledge and products in the area of wind energy.
- Had a chance to publish the data produced by undergraduate and graduate students in national and international conferences and prestigious journals. Currently, two conference and one journal papers are under preparation.

5. CONCLUSIONS

CNT and graphene based nanocomposite coatings were developed against UV degradation and corrosion. It is observed that a small weight percentage of carbon nanotubes and graphehens in the polymeric coating increase the film resistance against UV light. With the addition of 2% CNT there was no change in contact angle even after 10 days UV exposure. This proves that the hydrophobicity of the coated surface was not decreased, where water uptake into the film may be lesser. The microstructure of UV exposed and UV unexposed samples was also studied in detail. The primer only coated samples exposed to the 16 days of UV exposure revealed a great surface degradation. AFM study gave a better surface morphology at micro and nanoscale. The surfaces of the samples were shiny and smooth prior to the UV exposure and salt fogging, but these properties were destroyed completely after the exposures. However, degradation and surface property change are much lesser on the nanocomposite surfaces. Overall, it is concluded that CNT and graphene play a vital role in protecting of polymeric coatings against UV degradation and corrosion, and protect the mechanical properties of composite blades for a longer service life.

6. FUTURE WORK
Effects of UV exposure and salt fogging can be evaluated for a longer period of time for better understanding of the complex mechanisms and outcomes. Instead of using continuous UV exposure, experiment can be carried out with alternate UV exposure and salt fog exposure together. Experiment can be also carried out on other composite materials, such as carbon fiber reinforced and Kevlar fiber reinforced which may be more susceptible to corrosion and degradation.

Other types of inorganic inclusions (nanosheets, nanotubes and nanoparticles) and organic coating materials can also be tested as barrier materials against UV degradation and corrosion. Carboxyl and amine functionalization and dispersion can be done on the nanoscale inclusions. As is known, effective utilization of nanomaterials in coating materials strongly depends on their ability to disperse homogeneously throughout the matrix and to achieve good interfacial bonding, which will affect the overall performance of these novel materials.

ACKNOWLEDGMENT

The author gratefully acknowledges the Department of Energy for the support of this work (DE-FG36-08GO88149).

REFERENCES


11. R. Asmatulu, R. Claus, J. Mecham, S. Corcoran," Corrosion Protection of Surfaces by Nanocomposite and Urethane Top Coatings” *Smart Structures and Materials* 2005 Proceedings of SPIE Vol. 5761 40-


Products Developed and Technology Transfer


Journal Paper:

Conference Proceedings:
2) Zhang, B. and Asmatulu, R. “Change in Surface Hydrophobicity of Composites under Harsh Environment,” to be submitted to SAMPE Fall Technical Conference 2010, October 11-14, Salt Lake City, UT.

Thesis:
1) Mahmud, G.A. “increasing the coating resistance against uv degradation and corrosion using nanocomposite coating,” Wichita State University, December, 2009.

Presentations:
2) “Effects of Sun Light on the Polymeric Composites” Nanotechnology Entrepreneurship Forum, Friday, April 23, 2010, Pittsburg State University (to be presented).
B) Web site / Internet sites The project website is: www.wichita.edu/sustainability

C) Technologies/Techniques: A nanocomposite coating technology was developed for the UV degradation of the composites.

G. Students Funded
Mahmud, G.A.; Safdari, M.; Cooper, B.; Anwar, R.; Abedin, F.; Ceylan, M.; Revuri, S.

---

College of Engineering Wichita State University
Wind Energy Research Symposium
March 26th, 2009
1:00 – 5:00pm Room 307, NIAR

(www.wichita.edu/sustainability)

Supported by the Department of Energy (DOE DE-FG36-08GO88149)

Over the past year the College of Engineering has engaged in research activities that draw from aviation design and manufacturing research to target issues critical to the widespread deployment of wind energy. This symposium will include presentations and posters summarizing the research and findings of faculty and students supported by a Department of Energy award.

Schedule of Presentations

<table>
<thead>
<tr>
<th>Time</th>
<th>Topic</th>
<th>Presenter</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:00-1:20</td>
<td>Posters</td>
<td>Students</td>
</tr>
<tr>
<td>1:20-1:40</td>
<td>Welcome and Introductions</td>
<td>College of Engineering: Dean Zulma Toro-Ramos</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Project PI: Dr. Twomey</td>
</tr>
<tr>
<td>1:40-2:00</td>
<td>Network Monitoring and Control</td>
<td>Dr. Jewell</td>
</tr>
<tr>
<td>2:00-2:20</td>
<td>Wind Turbine Reliability and Maintainability</td>
<td>Dr. Steck</td>
</tr>
<tr>
<td>2:20-2:40</td>
<td>Environmental Impacts of Wind Energy Systems using Life Cycle</td>
<td>Dr. Overcash</td>
</tr>
<tr>
<td>2:40-3:00</td>
<td>Break/Posters</td>
<td></td>
</tr>
<tr>
<td>3:00-3:20</td>
<td>Fiber-Reinforced Composite Blade UV Degradation Prevention using Nanotechnology</td>
<td>Dr. Asmatulu</td>
</tr>
<tr>
<td>3:20-3:40</td>
<td>Intelligent Manufacturing of Hybrid Carbon-Glass Fiber-Reinforced Composite Wind Turbine Blades</td>
<td>Dr. Minaie</td>
</tr>
<tr>
<td>4:00-4:20</td>
<td>Wind Energy Supply Chain/ Co-Generation Technologies (PEM Fuel Cells)</td>
<td>Drs. Yildirim and T.S. Ravi</td>
</tr>
<tr>
<td>4:20-4:30</td>
<td>Wrap-up</td>
<td>Dr. Twomey</td>
</tr>
<tr>
<td></td>
<td>Posters</td>
<td>Students</td>
</tr>
</tbody>
</table>