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HAL Id: hal-00926859
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Submitted on 10 Jan 2014

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NANOINDENTATION CHARACTERIZATION OF VINYLESTER GLASS-FIBER COMPOSITES SUBMITTED TO DENSE UV- RADIATION EXPOSURE

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Abstract
The use of polymer matrix composites in building and construction has become increasingly attractive, though some issues are remaining, among which are the variations of mechanical properties following in outdoor environment, particularly due to dense UV-exposure. In this work, bulk vinylester as well as vinylester glass-fiber composite samples were exposed to UV-radiation using the SPHERE (Uv-radiation facilities located at NIST, Gaithersburg, Md, USA). Then, the Laser scanning confocal microscope (LSCM) allows the 3D visualization and the quantification of vinylester damage due to the UV exposure. Nanoindentation, which is a very helpful Non-Destructive Technique, was applied to measure the local Modulus and Hardness on exposed surfaces. The preliminary studies showed a huge standard deviation because of the roughness of samples generated after UV-exposure. Long and tedious statistical analyses encouraged the development of a new method based on testing under nanoindentation the cross sections of the samples. Doing so, not only the characterization of the evolution of mechanical properties with the exposure time can be carried out, but also the quantification of the depth affected by UV radiations.

Keywords: UV-degradation, nanoindentation, confocal microscope, composite, vinylester resin

1. Introduction

Composite materials are challenging materials for use as structural parts in civil engineering and construction. Their main advantages are pertaining to their excellent corrosion resistance and strength-to-weight ratio in comparison with steels, high stiffness, relatively good resistance to environmental agents and fatigue, good processability and ease of installation. These advantages have led them to be considered over more conventional materials such as steels and reinforced concrete as structural parts. Polymer composite materials can be applied for rehabilitation of structural components systems. They also have shown promising potential as construction materials in new infrastructure components.

However, despite the substantial advantages of composites, some critical issues remain regarding their environmental durability and long-term performance. It should be noted that previous research on thermosetting resins, glass fibers and their composites has shown significant losses in their mechanical properties and integrity when exposed to aggressive conditions for prolonged periods of time, such as the Hygrothermal Exposure and Sustain Strain (Heibling & Karbhari, 2008). Indeed the outdoor environment can be
detrimental to organic polymers: moisture, acid rain, temperature cycling and ultraviolet (UV) radiation can lower the overall performance of a polymer.

One of the main performance that outdoor composite applications should exhibit is the ability to withstand long term exposure without any mechanical properties loss. Attempts at linking field and laboratory exposure results and at predicting the service life of a polymeric material exposed in its service environment have been a high priority research topic of the polymeric materials community for over a century (Martin et al., 2005). The inability to generate accurate, precise, and timely service life estimates for polymeric systems exposed in their intended service environments hinders product innovation as well as the timely introduction of new polymeric materials into the market.

At present, the only accepted way of generating a performance history for a new product is to expose it for many years at one or more "standard" field exposure sites such as Florida or Arizona. Performance data generated from such experiments, however, are neither repeatable nor reproducible, since the weather never repeats itself over any time scale or at any location (Martin et al., 2005). Laboratory weathering experiments are typically designed to simulate and accelerate outdoor degradation by exposing materials for extended periods of time to high UV irradiance, elevated temperature, and relative humidity environments. However, the lack of rigorous temporal and spatial experimental control over each of the weathering factors comprising an exposure environment within and among laboratory exposure devices has made it impossible to correlate results between laboratory devices and to link laboratory and field exposure data.

The French National Project DECID2 that aims at erecting a large dimensions platform entirely made out of smart composites (DECID2) has been approved in 2008. A composite combination based on E-glass fibers and vinylester matrix was chosen as constituent materials. Among the critical issues of the project is the assessment of the mechanical properties of composites that have undergone heavy UV-radiation exposure. The UV-radiation tests (150W/m²) have been carried out at NIST (Gaithersburg, Md.) under 2 and 4 weeks, which caused significant roughness that happened on the surface of the specimens. The roughness was characterized mainly using nanoindentation, a suitable NDT technique, as well as Laser Scanning Confocal Microscopy (LSCM).

**Materials & Methods**

1.1. Materials

The high initial fabrication cost issues of composites were solved partially through the use of lower cost resins (e.g. Vinylester), fibers (e.g. E-glass) and the use of non-autoclave process routes such as pultrusion. E-glass fibers are often preferred as reinforcements due to their higher strain to failure and better impact resistance coupled with a significantly lower cost as compared to other available fibers such as carbon fibers. Matrices used in civil infrastructure are typically restricted by temperature. This is the reason why vinylester resins are appearing as an attractive choice since they combine the superior mechanical
performances and environmental durability of epoxies, while being more economical, with the better handling, faster curing, and lower viscosity characteristics associated with polyesters.

1.2. Specimen preparation

Vinylester sample and composite manufactured by pultrusion with a 66% glass-fiber volume fraction and vinylester matrices (Figure 1) are cut using a diamond wheel and polished, respectively with 600, 800 and 1200 grain sizes with diamond past grades: 15 µm, 9 µm, 6 µm, 3 µm, 1 µm and 0.05 µm. Then the samples are exposed in the SPHERE (Figure 2). To study the cross sections, some samples are cut, mounted on epoxy and polished with the same protocol (Figures 1c and 1d).

1.3. UV radiation exposure – The SPHERE

Developed under the auspices of the NIST Coatings Service Life Prediction Consortium, the NIST 2m integrating sphere provides a source of collimated ultraviolet radiation in the 290 nm to 400 nm region of the spectrum (Brown et al., 2000). Visible and infrared components of the input radiation are largely removed by dichroic mirrors or filters. The exposure was carried out in an extreme condition. The samples were initially exposed at 55°C, with a humidity of 75% for about 2 days, and then changed to 35°C for 4 days and finally decrease humidity of 50% for the remainder of the exposure. The received flux is about 150W/m². On set of samples was removed from integrating sphere after 2 weeks and another set after 4 weeks. The third set doesn’t receive UV exposure.

1.4. Nanoindentation – Instrumented Indentation Testing (IIT)

The instrument of the indenter is measured using an electromagnetic coil and displacement of the indenter is measured using a capacitive plate transducer. Measurements were performed using a commercial available nanoindenter (MTS Nanoinstruments, NanoXP). The load and displacement resolutions are reported to be 50 nN and 0.04 nm, respectively. Indentation was conducted with a 10 µm radius, 90° diamond cone indenter and a Berkovich indenter (Figure 2). The two different tips allow a comparison of results but the Berkovich indenter is preferred to the visualization on LSCM. The two tip area functions were determined using a fused silica standard over the experimental indentation depth. Loading was performed at a constant strain rate of 0.05 s⁻¹. The depths used on this study were 500 nm, 750 nm and 1000 nm. To devoid any interaction, the indents were spaced at least 50 µm apart.

Two methods are used to determine the stiffness, S: Unloading Method where the stiffness corresponds to the unloading slope of the load-displacement curve and CSM Method which is using Equation (1) (Oliver et Pharr, 1992). This last technique consists on applying a small oscillation to the force signal at a high frequency (45 Hz) during indentation loading. The amplitude of the force oscillation is kept small (5 nm). The contact stiffness is measured by the displacement response at the excitation frequency. The Young’s modulus and Hardness are then derived from the contact stiffness. The main advantage of this technique is that the modulus and hardness can be evaluated as a function of indentation depth (Figure 3). A
constant value of local Modulus and Hardness is reached after a penetration of about 200 nm. We should keep in mind that during the first oscillations the local plastic behavior under the indenter is not yet achieved. Hence, the slope of the unloading part is very sharp and the value of modulus and hardness is overestimated. When the applied load exceeds the transition force, the local plastic behavior takes place and the elastic response upon unloading leads to the right estimate of the mechanical characteristic, reflected by a plateau value (Drissi Habti et al., 1998).

\[ S = \left[ \frac{1}{\frac{P_{os}}{h(\omega)} \cos \varphi - (K_s - m \omega^2)} - K_f^{-1} \right]^{-1} \] (1)

Where \( P_{os} \) is the peak value of the harmonic force, \( h(\omega) \) is the magnitude of the indenter displacement when the harmonic force is applied, \( \omega \) is the frequency of the harmonic force applied, \( \varphi \) is the half-included angle of the indenter tip, \( m \) is the mass of the indenter, \( K_s \) is spring constant of leaf springs supporting the indenter, and \( K_f \) is the stiffness of the indenter.

1.5. Surface morphology - LSCM

A Zeiss model LSM510 reflection laser scanning confocal microscope (LSCM) was employed to characterize the surface morphology (topographic profile) and to measure the Roughness of the specimen. LSCM uses coherent light (HeNe 1 laser, 543 nm) and collects light exclusively from the focal plane while rejecting light out of the focal plane. The images are processed using the software provided by Zeiss. The size resolution of the vertical direction (z-axis) is determined by the numerical aperture of the objective and the pinhole. By moving the focal plane, single images (optical slices) can be combined to build up a three dimensional stack of images that can be digitally processed.

2. Theoretical background

Instrument Nanoindentation improves on macro and micro static indentation tests by indenting at the nanoscale with a very precise tip shape, high spatial resolutions to place the indents, and by providing real-time load-displacement (into the surface) data while the indentation is in progress (Figure 4).

As the indenter is driven into the material, both elastic and plastic deformations cause the formation of a hardness impression. As the indenter is withdrawn, only the elastic portion of the displacement is recovered. It is this recovery which allows one to determine the elastic properties of a material (Oliver and Pharr, 1992, Anthony and Fischer-Cripps, 2004, Cook and Oyen, 2007). For the following calculations, we limit the scope of the discussion to isotropic continuum whose dimensions are very large relative to the depth of the indent and whose surfaces are smooth and frictionless. Furthermore, we assume that there is no time-dependence in the material response. We also assume there are no piling-up or sinking-in and
no fracture during the indentation. Finally, indentation study can be exploited only if the stress is hydrostatic which means that the area under study is orthogonal to the axis of the nanoindentor. Under these conditions, hardness and local modulus can be defined:

\[
H = \frac{P}{A}
\]

\[
E_r = \frac{\sqrt{\pi}S}{\beta 2\sqrt{A}}
\]

\[
\frac{1}{E_r} = \left(\frac{1 - \nu_s^2}{E_s} + \frac{1 - \nu_i^2}{E_i}\right)
\]

Where \( H \) is the hardness, \( P \) the load, \( A \) the contact surface, \( E_r \) the reduced modulus, \( S \) the stiffness, \( \beta \) a tip correction factor (\( \beta = 1 \) for a cylindrical contact, \( \beta = 1.034 \) for a Berkovich pyramid), \( E_s \) and \( E_i \) are the sample and the indentor modulus, respectively, \( \nu_s \) and \( \nu_i \) are the sample and the indenter Poisson's ratio, respectively.

3. Results and discussion

3.1. Microstructural analysis

Before characterizing mechanical properties, LSCM checking allows the visualization of unexposed and exposed surfaces and provides information about the structure and damage. Figure 5a highlights the difference of roughness between unexposed and exposed surfaces. During the UV radiation on the SPHERE, only the middle of the sample is under irradiation. While the roughness is about 0.1 µm for unexposed surfaces, it is about 0.6 µm and 1 µm for respectively the 2 and 4 weeks exposed surfaces. Rosu et al. (2008) exposed vinylester samples with fairly the same spectrum emission and temperature and with a received flux twice as large (300 W/m²). They noticed that the gloss index variation and optical microscopy micrographs show the roughness increase on the surface of vinylester sample after 200h irradiation time, whereas as-received sample shows a smooth surface.

The roughness that is recorded after irradiation is mainly due to the particles added to the vinylester. Indeed, during irradiation, vinylester matrix was subject to ablation while the additive particles remain intact. Figure 5b shows the micrographies of this mechanism on composite. The fiber as well as the particles remain intact, thus the damage can be characterized by the height difference between the fiber and the matrix. It is negligible for an unexposed sample, about 5 µm for the 2 weeks exposed samples and 10 µm for the 4 weeks exposed samples. Some observations were made on areas with various fibers densities and the matrix ablation was on the same order, no matter the fiber density was.

3.2. Nanoindentation on exposed specimens
Figures 6 shows the results of nanoindentation tests for each vinylester sample and each method. The order of magnitude of these results can be compared with the previous nanoindentation data for UV-exposed vinylester presented by Signor et al., (2003). Our results give mean modulus in the range 4 to 5 GPa, while Table 1 that summarizes Signor et al., results, shows mean modulus (estimated with nanoindentation) ranging between 1.23 and 3.75 GPa.

<table>
<thead>
<tr>
<th>Exposure time (h)</th>
<th>$E_{\text{estimated}}$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.23 ± 0.47</td>
</tr>
<tr>
<td>1000</td>
<td>3.75 ± 1.32</td>
</tr>
<tr>
<td>4000</td>
<td>2.32 ± 0.64</td>
</tr>
</tbody>
</table>

Table 1 : Nanoindentation data for UV-exposed vinylester (Signor et al., 2003)

For exposed samples, the standard deviation is not negligible and does not stand for to conclude about the evolution of properties. Indeed, some assumptions are not fully available: firstly the material is not smooth in particular exposed samples. We have to keep in mind that the roughness is rather important, thus creating inevitably some deviation from the assumption of the hydrostatic applied stress that has to apply in indentation tests. Secondly, the vinylester is not an isotropic material, there are some additive particles. We can get around the second dilemma by ruling out the indentations made on particles; these can be identified with LSCM. But the roughness cannot be removed by polishing the surface because it is resulting from UV-radiation that actually needs to be characterized.

The first idea to find an alternative method is based on Bouzaki’s works (2003). This author plots the distributions of the number of measurements versus the maximum indentation depth. In our case, for each spot, 40 measurements are programmed (that is four times more than previous tests). Unlike Bouzaki’s work, the depth is controlled and the number of measurements is plotted versus the maximum load of indentation. If we assume that the roughness directly influences depth as it is shown on the Bouzaki’s article; load being proportional to square of depth, the roughness influences square root load (Figure 7). Indeed the results give Gaussian distribution but even this method can provide interesting pieces of information, the measurement and analysis are time-consuming. Furthermore the behavior evolution is not easily noticeable; thus it does not seem to be the best way to continue this study.

3.3. Cross section

The second solution is to cut, mount on epoxy and polish a cross section of the sample in order to indent a row through the thickness (Figure 8). This method is directly inspired by Forster et al. works (2009), whose line of indents allows the characterization of multilayer coatings. Thus, in our case, the polishing can be done without removing the layer affected by UV radiation. Furthermore the depth to which the UV radiation impacts the material can be
predicted. Two different tests were programmed: the sample is put at about 10°, respectively 20°, angles between the exposed surface and the indent row. 60, respectively 50, indentations (about 30% on Epoxy and 70% on Vinylester) were programmed on this row with a 15 µm, respectively 40 µm, between each indent. In the first case (Figure 9), the smaller increase of distance between the edge and the indentation was chosen so that the most continuous behavior could be obtained and determine the depth of the possible edge effects. And in the second case (Figure 10), a larger distance is chosen to allow the ability to go deeper into the material and determine the depth affected by the UV radiation.

As a beginning, differences between epoxy and vinylester indent were observed; i.e. there is a significant break between the two materials. In the two cases, the mechanical properties of the unexposed sample are almost constant. So, we can assume that the material is homogeneous and the edge effects are negligible on the vinylester. The edge effect assumption can be translated to exposed samples.

It can be seen that near the surface, the higher is the exposure time, the higher are the mechanical properties. A decrease as a function of depth is thereafter recorded on the exposed sample. The local mechanical properties tend towards a plateau-like value corresponding to the values of the unexposed sample mechanical properties. Thus, it is evident that the damage layer formed due to UV degradation is confined to approximately 500 µm from the surface while the material underneath the degraded layer remained unaffected. Goel (2008) reported the same conclusion with the analyse of modulus evolution on polypropylene (PP) matrice exposed to UV-radiation.

### 3.4. Composite indentation

Nanoindentations carried out on exposed matrix within composite samples exhibit mechanical properties higher than the neat vinylester (Table 2). Compared to the results of Goel’s work about neat and PP composite, there is more change in the modulus, and hardness in our case, in damaged areas of the matrix inside the composite than in damaged areas of neat polymer. Goel suggested this is probably because of the acceleration of the damage caused by the addition of more chromophores in terms of functional groups present in the sizing applied to the glass fibers for better bonding with neat PP (or vinylester).

<table>
<thead>
<tr>
<th></th>
<th>Neat vinylester</th>
<th>Vinylester on composite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modulus</td>
<td>5 GPa</td>
<td>10 GPa</td>
</tr>
<tr>
<td>Hardness</td>
<td>0.25 GPa</td>
<td>0.5 GPa</td>
</tr>
</tbody>
</table>

Table 2: Mean values of Hardness and Modulus estimated by nanoindentation testing on vinylester exposed samples.

### 4. Summary

The following conclusions can be drawn from this work.
• Confocal imaging showed an ablation of the matrix. Further experiments will be conducted with longer UV-exposure time to check whether we will be having an increasing ablation with time of exposure.

• Huge standard deviation in local mechanical properties was coming from the surface roughness on the exposed samples caused by UV-radiations. Thus, direct nanoindentation cannot be exploitable. The first idea was to plot statistical distribution by increasing indentation number. This statistical analysis gave Gauss distribution but was not accurate enough and needs a lot of data. The second solution was to mount and polish a cross-section of the sample in order to indent through the thickness. Because the dispersion is very small, it can be concluded that this method is more efficient than the the previous one.

• Nanoindentation results showed that modulus and hardness of the degraded region, around 0.5 mm from the surface, increased with the increase in the exposure time.

• Vinylester present in composite underwent more modulus change near the surface region as compared to neat Vinylester.

Acknowledgements: MDH would like to thank deeply the BFR Laboratory of NIST for the their precious support, as well as the French Department of Industry and the Local Government (Region Pays de La Loire) for the financial support of DECID2 National Project.

References


Figure 1: (a) Vinylester specimens: the orange parts are exposed during 4 weeks and the yellows part is unexposed because they are protected during the exposure. (b) Composite Vinylester with E-Glass fiber exposed during 4 weeks. (c) Vinylester section sample with 4 weeks exposure and mounted on Epoxy resin. (d) Composite section sample 4 weeks exposure and mounted on Epoxy resin.

Figure 2: Indentation on epoxy resin at 1000 nm with a Berkovich tip.
Figure 3: Evolution of the CSM Local Modulus (a) and Hardness (b) as a function of the penetration depth with a Berkovich tip on vinylester sample.

Figure 4: Load vs. displacement performed on polished unexposed neat vinylester sample and composite sample.
Figures 5: (a) 2D and 3D unexposed and 2 weeks exposed vinyl ester micrography (1.64mmx1.64mm), (b) 3D unexposed (a), 2 (b) and 4 (c) weeks exposed vinyl ester-flass fiber composite micrography (164µmx164µm). Characterization of vinyl ester collapse.

Figure 6: Modulus (a) and Harness (b) with the two tips, the two depths, the two Methods on the three samples (unexposed, 2 and 4 weeks of exposure). Error bar show the standard deviation for each test (10 indentations for each test).
Figure 7: Statistical analysis of square root load for 2 and 4 weeks exposed Vinylester samples, indentation with Berkovich tip at 1000 nm depth.
Figure 8: Successive zooms of indentation row – schema and LSCM micrographs
Figure 9: Local modulus (a) and hardness (b) versus the distance between indent and vinylester edge for unexposed and 4 weeks exposed sample, Berkovich tip with a 1000 nm depth.
Figure 10: Local modulus (a) and hardness (b) versus the distance between indent and vinylester edge for unexposed, 2 weeks and 4 weeks exposed sample, Berkovich tip with a 750 nm and 1000 nm