Evaluation of the barrier effect to humidity of surface treatments on composites

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Keywords: Composites, Relative Humidity, Dynamic Vapour Sorption, Dynamic Mechanical Analysis

Abstract

Composites are usually engineered to increase the mechanical properties of a polymer matrix. A good dispersion and adhesion to the matrix is essential for a good performance of the filler. Humidity is known to have a depletive effect on these properties.

Treating the surface of a composite with a layer capable of acting as a barrier to humidity seems to be an optimal solution.

In order to assess the barrier effect, we propose two complementary techniques: Dynamic Vapour Sorption (DVS) to measure the amount of water taken up by the sample and Dynamic Mechanical Analysis (DMA) with Relative Humidity control to assess the mechanical properties changes induced by humidity.

1 Introduction

The main purpose of a composite is to increase the mechanical properties of a polymer matrix by adding a filler, which can be in many different forms, including fibers (glass, carbon and others).

Very often, the improvements are measured and evaluated only as a function of temperature, as the vast majority of mechanical analyzers are capable of controlling only this parameter. However, it is known that Relative Humidity (RH) has a depletive effect on the mechanical properties of a composite, as it affects the adhesion of the filler to the polymer matrix. In addition to that, the composites might be used under RH conditions that are very different from the ones available in classical DMA equipments or dynamometers, where dry or normal air is employed.

Therefore, it is very important to study the mechanical properties of the composite under RH controlled conditions.

As water permeates the composite from the surface, applying a hydrophobic coating that may act as a barrier seems to be a practical idea to prevent or limit the effect of RH on the mechanical properties of the sample. In this work we present two different techniques to deposit such a layer on an epoxy/carbon composite and the preliminary results of the barrier effect of those layers assessed with two analytical techniques: Dynamic Vapour Sorption (DVS) Analysis, to measure the amount of water taken up from the sample, and Dynamic Mechanical Analysis (DMA) to study the effect of RH on the mechanical properties of the sample.

2 Materials and testing methods

2.1 Materials and coatings

The studied specimens are an epoxy/carbon composite. All samples are obtained from a single plate, about one millimeter thick, of cured epoxy filled with carbon fibers. Specimens for DVS analysis are cut in squares with a side of about 10 mm, while DMA specimens are slabs with a width of about 15 mm and a length of 50 mm.

One sample of each shape was left untreated as a reference.

One sample was coated with a Layer by Layer (LbL) process. This process is very simple as the sample is dipped into two different solutions (a positive and a negative one) several times to deposit a succession of bi-layers on its surface. When the sample is first dipped into the positive solution, a nanometric layer of the corresponding precursor will be deposited on its surface. Then the sample is washed to remove the excess of solution and it is dipped into the negative solution. A second, different layer is deposited over the first one. By repeating this process several times, it is possible to deposit a coating which thickness depends on the species chosen and the number of repetitions. In figure 1 we show a schematic of the LbL process.

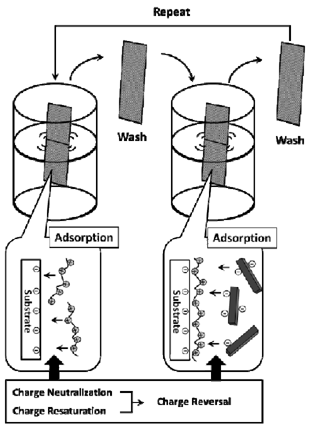

Figure 1 - A schematic description of the LbL process

To create a hydrophobic layer, a modified Polyethilemmine (0.1 w% diluted in 50/50 water/ethanol) and Nafion (0.1 w% diluted in 50/50 water/ethanol) were used as positive and negative layer, respectively. 10 bi-layers were deposited, with a 5 minute dipping time in each solution.

Another sample was coated with PECVD technique. The sample is put into a reaction chamber together with a gaseous precursor and other gases (Argon, Oxygen, etc.). A plasma is then generated in the chamber using a radio-frequency discharge between two electrodes: the discharge ionizes or breaks the precursor molecules. The activated molecules adhere on the sample forming a homogeneous and continuous film.

To create a barrier layer, Examethilsiloxane (HDMSO) was used as a precursor to deposit a layer of Polydimethilsiloxane (PDMS). The sample was first cleaned in an argon atmosphere (5 sccm, 50W), then activated in an oxygen atmosphere (20 sccm, 50W), then the layer was deposited by introducing HDMSO into the chamber (1:2 ratio with oxygen, 20 sccm total, 25W) and the sample was finally post-treated in Argon (20 sccm, 25W).

The deposition system is a laboratory scaled PECVD chamber, "Pico" model from Diener Electronic GmbH + Co. KG. The magnetron generator works at 40kHz and has a maximum power of 200W.

2.2 Equipment and methods

DVS is a technique based on thermo-gravimetry, where the weight of the sample is monitored over time as the RH of the environment is changed. To prevent a weight change due to the sample holder taking up water, the reference empty pan is exposed to the same temperature and RH profile as the sample. In figure 2 we show a schematic of the furnace and the RH controller. RH is controlled by accurately mixing two flows of nitrogen: one dry and one 100% wet.

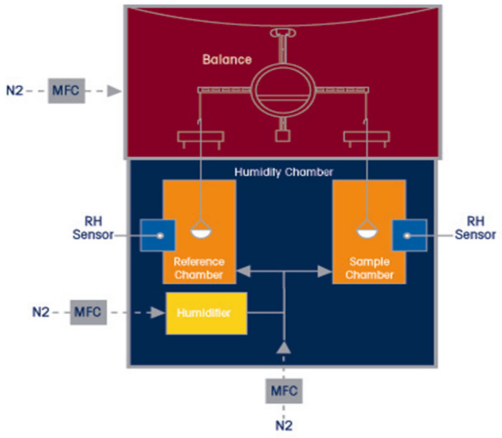

Figure 2 - A schematic of the DVS chamber with flow paths

Usually, the weight at the end of the step (that is, after equilibration) is plotted versus the RH of that step, in order to observe under equilibrium conditions the water amount taken up by the sample and the eventual amount of water retained at the end of the adsorption – desorption cycle.

First, the samples were dried in the DVS analyzer by setting the temperature at 60°C and the RH to 0% for two hours. Then the temperature was reduced to 25°C and the RH stepped up from 0% to 90% with 10% steps, each one lasting two hours. This is the so-called adsorption curve. After that, the RH was stepped down from 90% to 0%, with 10% steps, each one lasting two hours. This is the so-called desorption curve.

The DVS analyzer used for this work is a Q5000SA from TA Instruments.

DMA is a classic technique to measure the visco-elastic properties of a wide range of materials, due to the capability of applying small deformations, measuring small to large forces and employing different clamping geometries to comply with a wide range of stiffness values. Samples as soft as crude rubbers or as stiff as composites or metals can be easily analyzed. The main advantages of a DMA versus a dynamometer are the capability of applying oscillatory deformations of controlled amplitude and frequency and the temperature control. In this case we also employ an accessory that can control both the temperature and the RH to which the sample is exposed, thus adding another parameter to DMA analysis. RH is changed with a computer controlled humidifier, while temperature is controlled with Peltier elements. In figure 3 we show a picture of the DMA equipped with the RH controller.

Figure 3 - Q800 DMA (right) equipped with RH controller (left)

Typically, RH controlled DMA's are used to measure the plastifying effect of water on the glass transition of polymers and the depleting effect of water on mechanical properties such as the relaxation modulus. In figure 4 we show the shift to lower temperatures of the glass transition of Nylon 6, which is known to be significantly plasticized by water [1] as RH increases, while in figure 5 we show the reduction and instability of the relaxation modulus of unsupported Nafion 112, as both temperature and RH are increased.

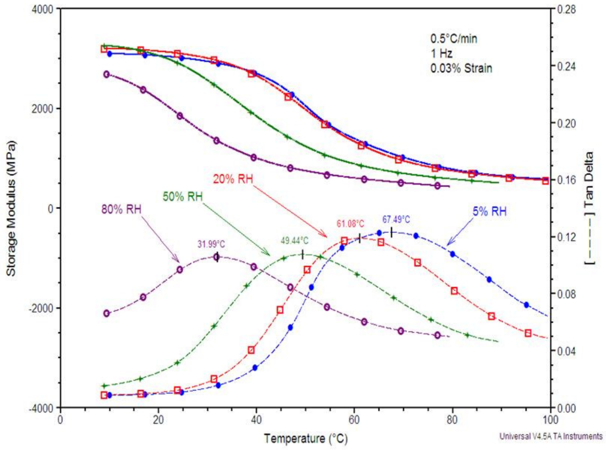

Figure 4 - Shift of the Glass Transition temperature in Nylon as a fuction of the RH

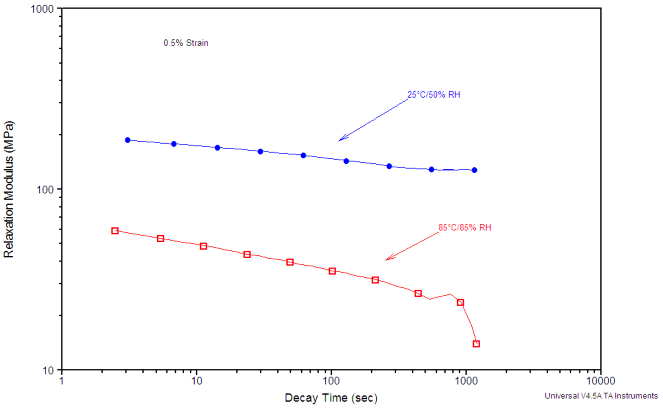

Figure 5 - Reduction of the relaxation modulus of unsopported Nafion 112 as RH and Temperature are increased

At this moment, the composite specimens are under evaluation and the final data will be presented in the oral presentation.

The DMA used in this work is a Q800 equipped with the recently introduced [2] RH controller from TA Instruments.

3 Results and conclusions

3.1 DVS results

In figure 6 we show the adsorption and desorption curves of the three specimens: the composite "as prepared" (TQ), the sample coated via plasma, and the sample coated with the Layer by Layer (LbL) technique.

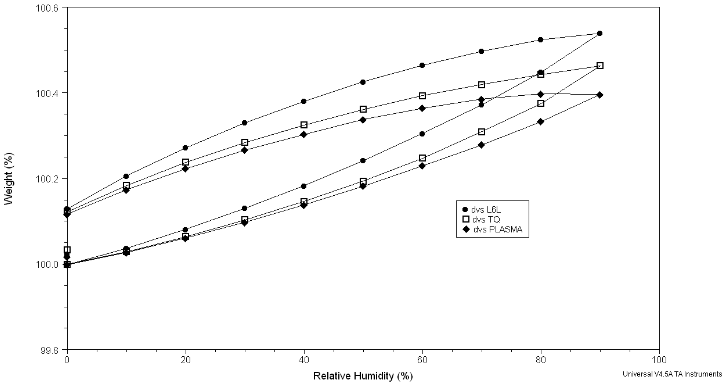

Figure 6 - Adsorption (lower) and desorption (upper) curves for the three samples

It is clear that in all cases, the amount of water taken up is small (no more than 0.5%), but the plasma coated specimen shows the lowest uptake at high RH values. The LbL coated sample shows a greater amount of water uptake with respect to the TQ sample. All samples show a small amount of water retained after the cycle, which seems to be independent on the coating technique. This should be water that made it through the coating and is permanently retained by the composite.

The Plasma coated sample has a more homogenous and continuous coating of PDMS on it, so it is reasonable to expect a better protection towards water. The LbL coated sample has a more porous barrier on it. In addition to that, Nafion is known to have some interaction with water, which will be more deeply investigated with the DMA tests.

References

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