

COMPARATIVE STUDY OF THE EFFECT OF WATER EXPOSURE AND MECHANICAL FATIGUE ON THE ELASTIC MODULUS OF A UNIDIRECTIONAL GLASS-EPOXY COMPOSITE

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Abstract: The aging of a material exposed to any medium may take a few aspects. They have an overall impact on the evolution of its mechanical properties. The individual effect of each quantization allows to highlight the major factor of degradation of the medium. This study proposes a correlation between the influence of exposure to an aqueous medium and mechanical cycling on the elastic modulus of a glass-epoxy composite.

Keywords: glass/epoxy composite, water absorption, bending fatigue

INTRODUCTION

The aging of a structure is a major and essential problem in materials science. This results in slow and irreversible changes in the microstructure of the material due to its inherent instability, interactions with the environment or to mechanical stress and that leads inevitably to an end. To fight against this unchanging situation, the composites are a significant technological challenge for manufacturers.

The aim of this study is evolution of the elastic modulus of a glass-epoxy unidirectional composite subjected to the effect of a bending cycle after exposure to an aqueous medium.

The absorption and diffusion of water in epoxy resins are extensively discussed in the literature. Although the absorption of water is controlled by diffusion and obey Fick's law in one dimension, the process is strongly linked to the system studied.

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial^2 X^2} \quad (1)$$

C - constant water concentration during the absorption,

t- time,

x- diffusion direction of the water molecule,

$D \approx 3 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$ diffusion coefficient in the case of a glass-epoxy composite, it is almost constant in function of the thickness of the sample and is little influenced by the orientation of the fibers [1].

Generally the phenomenon can be described by the following curve:

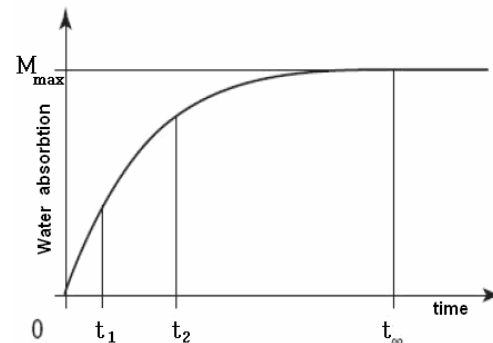


Figure 1. Kinetics of diffusion of water into a polymeric material [2]

From t_2 to t_∞ , two cases are possible depending on the used model.

- In case of the single phase absorption model described by Bonniau & al [3], the maximum water concentration is at the surface and remains constant during absorption. The absorption profile is continuous with the equilibrium M_{\max} stabilizes with the external environment. The step between 0 and t_2 involves the free water molecules.

- In case of more complex absorption which involves the cracking of the resin, it is possible to use the two-stage absorption model, Jacobs and Jones [4]. He considers the existence of two phases with different densities in the epoxy and shows that the distribution is due to free diffusion into a phase and a combined effect into a discontinuous phase without improving water absorption. Thus, the weight gain curve does not stabilize after t_2 and continues to increase gradually.

Both are valid when the following inequality is satisfied:

$$\frac{Dt}{e^2} < 0,05 \quad (2)$$

e- thickness of sample (diffusion distance)

This is possible for a very short exposure time.

The comparative study of Bonniau and Bunsell [3] highlights the impact of immersion in water on a series of glass-epoxy composite using three different hardeners. Under these conditions, for the diamine curing agent, the material becomes gradually white, opaque and cracks. The fast degradation is not equilibrium with the external environment.

If is known the absorption curve and the diffusion coefficient, it is possible estimation of time t_{sat} in which the resin alone is saturated with water.

$$t_{sat} = \frac{\pi}{16} \times \frac{e^2}{D} \quad (3)$$

For a glass-epoxy composite, the M_{max} value is around 0.6%.

There are two approaches to describe the water distribution mechanism:

- Free volume theory: In this case the diffusion of molecules is firstly determined by the number and size of holes in the resin and on the other hand by the existing attraction forces between the water and the polymer. Water migrates by capillary from cavity to cavity. These are present either between the macromolecules or in the fiber / matrix interfaces. Water is absorbed as a liquid and is considered free.

- The molecular approach: The high water absorption in epoxy resins involves hydroxyl (-OH) groups that are hydrophilic sites. Migration is performed by water passing from an -OH to an other -OH linked by double or even triple hydrogen bonds. The water which is not in a liquid state, it is called bound. Antoon et al. [5] show that these interactions are completely reversible.

There are two main physical effects of water on the resin, namely the plasticizing and swelling of the polymer. Generally the effects are reversible after drying the wet part.

Plasticization is a modification of the polymer structure. Two consequences are attributed to this degradation:

- The reduction of the glass transition temperature, which can lose up to 20 °C, according to the system resin/hardener. Knowing the mass fraction of water absorbed the new temperature can be determined in two ways. The first approach is based on a relationship derived from the free volume theory [6], the second uses the configurational entropy theory and provides a better prediction.

- The change of the mechanical properties: After 20 days of exposure the tensile strength decreases few MPa, the elastic modulus also decreases.

When the storage of composite is carried out in wet condition the matrix absorbs water but not the fibers. The hydrogen bonds between hydroxyl groups of the resin are broken and a molecule of water slips between polymeric chains, increasing the distance between them. The volume of the sample increases.

The fiber / matrix bonds significantly influences the amount of water accumulated at the interface [7]. During conditioning at high humidity, a layer about 3 nm of water can be formed which is enough to cause a large loss of adhesion and thus contributes to the reduction of mechanical properties. If this phenomenon is present, adhesion becomes insufficient and delamination occurs. The speed of water penetration increases due to the new empty space, accelerating the degradation mechanism. Nguyen et al. [8] noted the presence of debonding at the interface of untreated fibers after only 75 hours of exposure.

The chemical aging occurs when chemical structure of the material has undergone chemical degradation [9]. This can happened during thermo chemical treatments, oxidation or chemical attack. Generally, the chemical aging overlaps and interferes with the physical aging. Its effects are irreversible has as effect the disappearance of the stabilization region in the curves of physical properties variation.

The change in properties is due to physical and chemical effects after exposure to water. The loss of mechanical properties is initially linked to resin plasticization and reduction of adhesion forces at the fiber/matrix interfaces. Bowditch et al. [10] observed a 46% decrease of the tensile strength after 80 days immersion in water at 40°C. It also shows that these degradations are increase significant with the increase of the exposure time and temperature.

EXPERIMENTAL

The material studied is a composite plates made by an epoxy resin reinforced with unidirectional glass fibers E which has as origin a bidirectional fabric (density of 300 g/m²). The strands from one direction have been removed and finally the reinforcement was unidirectional (6 plies with 150g/m²).

The plate was made by hand lay-up method, and due to difficulties in impregnation of fiber bundles with resin, the material had fabrication defects such as air voids, defects inherent after this type of processing procedure. More than that the individual fibers from glass strands are not completely covered by resin and finally

the mechanical characteristics of composite are less than that of a material provided by industry.

The specimens were cut out from the plate at different orientation according to fiber direction, noted T_x , and those exposed in aqueous medium T_{xa} .

- x is the angle in degrees between the orientation of fibers in the matrix and cut off direction of specimen. The reference being fixed in the direction of the length, 0 means that the fibers are parallel and 90 that are perpendicular.

a - test piece was subjected to the aqueous medium for 5 weeks.

In this study, the aqueous medium was chose to replicate the environment of the Mediterranean sea.

After exposure, the water absorption was relative constant, samples weight increasing with 1,7÷1.9%. The medium is designed in the lab by adding 35.15 grams of salt in a liter of water. The salt comes directly from the blast of salt Mediterranean. As it has received no treatment thereafter, the aqueous solution has the following composition:

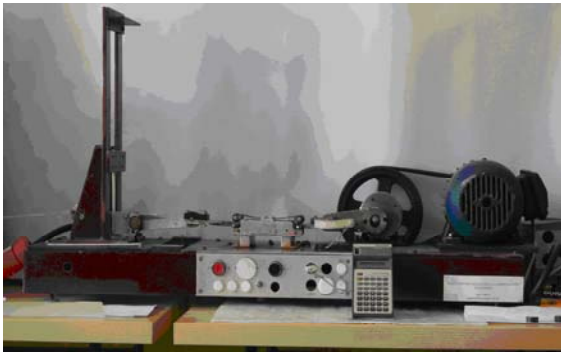


Table 1. Mass concentration of salts in solution

Salt	Mass concentration (g.L ⁻¹)	Salt	Mass concentration (g.L ⁻¹)
NaCl	27,2	CaSO ₄	1,26
MgCl ₂	3,8	K ₂ SO ₄	0,86
MgSO ₄	1,65	CaCO ₃	0,12

Because in water were immersed the sample after cut out procedure (not entire plate), the absorption model which can be approximated with relation (1) cannot be applied. The lateral faces, in which fiber strands are sectioned, are also in contact with water. The probability of water absorption increases and the entire material can be associate with a underwater region from a hand made composite lite boat which have been crushed. Fatigue tests were performed by using a bending machine (Fig.2) which can apply a constant displacement cyclic loading (frequency 3.7Hz, displacement $d=35\text{mm}$) on the samples exposed and no exposed on the aqueous solution

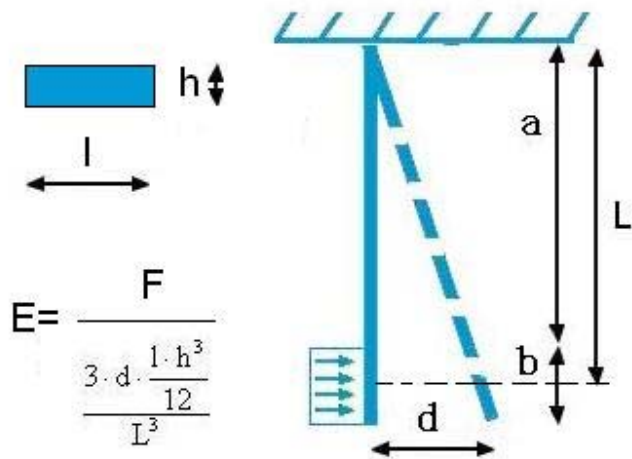


Figure 2. Bending machine and calculus procedure for longitudinal elastic modulus

The tests were carried out on non-standard samples (rectangular beam with following dimensions: width $l=15\text{mm}$, thickness $h=2\text{mm}$, $L=12\text{mm}$).

Fatigue or water absorption has as effect a continuous reduction of stiffness (and hence the strength characteristics) due to progressive accumulation of defects or plasticization of resin.

Because the significant defects influence on material stiffness, the elastic modulus is a parameter which can be used for characterization of global material degradation.

The effect of stiffness variation could be monitored by using a degradation parameter D described by relation (4) which is in fact the relative reduction of elastic modulus.

$$D = \frac{(E_i - E_n)}{E_i} \times 100 \quad (4)$$

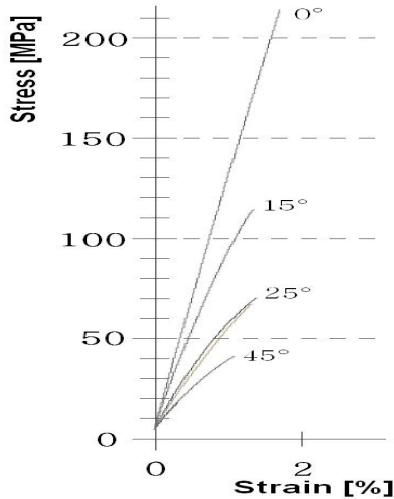
D – degradation parameter

E_i – initial elastic modulus

E_n – elastic modulus after n cycles

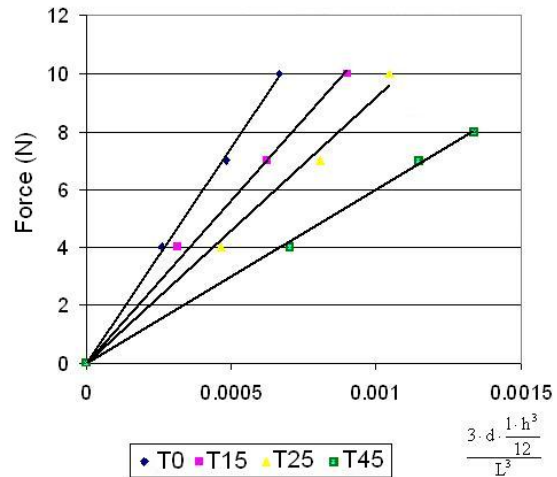
A preliminary traction test which is standard for elastic modulus measurement was performed in order to confirm the values of Young modulus obtained by

bending tests. The resulting curves which are shown in Fig. 3 provide information on the elastic modulus (slope of the curves) of each fiber orientation. In order to remain in the elastic region of the tensile curve, the



a

elastic modulus has been estimated in the region where the strain is between 0.05% and 0.25% for traction tests (a) and for displacement between 0 and 15 mm in case of bending test (b).



b

Figure 3. Traction test results (a) and curves provided by bending test (b)

Because the calculated values provided by both technique were in a good agreement the estimation of elastic modulus by bending test is validate.

The preliminary traction experiments have proved that, with increasing the angle between fibers and loading direction the nonlinear behavior increases. Sample T0 has a cvasilinear curve, which is characteristic for loading in fiber direction knowing that the glass fiber has a linear stress-strain curve. For the rest of samples the

plastic behavior increases with the angle between fibers direction and loading direction.

RESULTS AND DISCUSSION

In Fig. 4 are shown the evolution of elastic modulus and degradation as function of number of cycles in case of samples unexposed on aqueous medium.

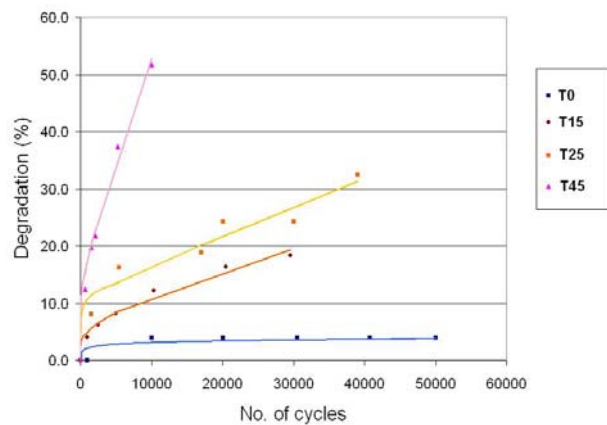
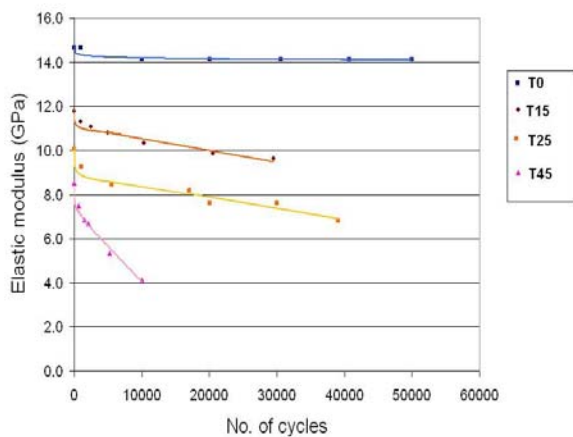
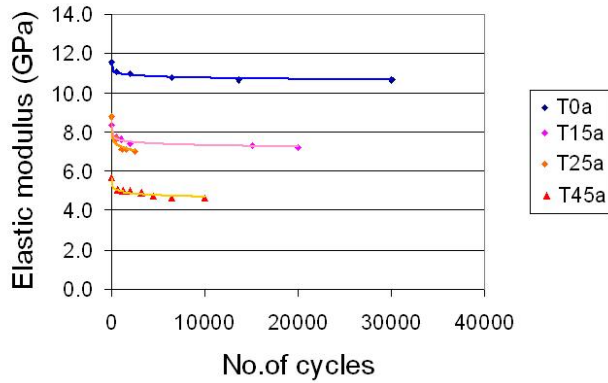


Figure 4. Elastic modulus and degradation evolution with number of cycles

Curves as a function of number of cycles for the unexposed water samples show a normal evolution. The rate of deterioration increases with the angle of the fibers. This is explained by the fact that if fibers tend to

have an inclination close to 90° and the sample mechanical behavior behaves close to pure matrix, and therefore less resistant to the stress. The process of damage accumulation is faster and the degradation

parameter increases with angle at the same number of cycles.



In Fig. 5 are shown the evolution of elastic modulus and degradation as function of number of cycles in case of samples exposed on aqueous medium.

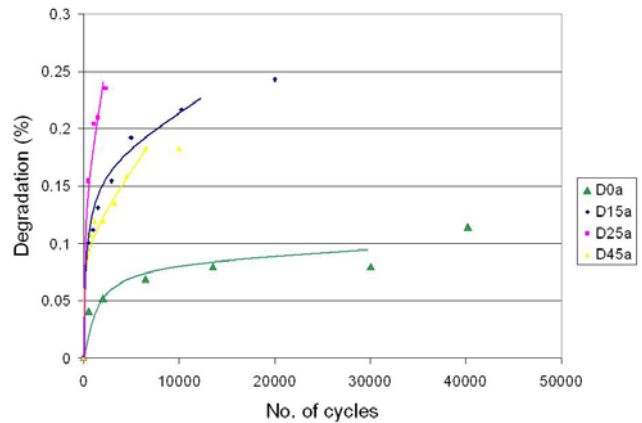


Figure 5. Elastic modulus and degradation evolution with number of cycles for exposed samples

In the case of the specimens exposed to water, three things are highlighted :

- First the chemical effect of water on the resin decrease the stiffness of material for all sample orientation
- The degradation rate seems to be less than degradation rate in case of unexposed samples.
- The rate of degradation for sample T45a is less than T15a and T25a. This suggests that the specimen 45° has a better resistance to the loading condition.

The degradation parameter from Fig. 5 has been calculated in assumption that the initial elastic modulus is the one that has been measured at first bending cycle after water exposure.

In order to find answers in Fig. 6 is shown the variation of elastic modulus for all samples as function of number of cycles having as reference the elastic modulus of dry sample.

It can be seen that the global degradation increase when angle increases. In case of water exposed samples there are two degradation stages, an initial reduction of stiffness due to resin plasticization, which is equivalent with a dramatic decreasing of elastic modulus and after that classical bending fatigue.

However, the elastic modulus is lower, but the deterioration is slower after the water exposure.

Water absorption make the composite more flexible so for the same displacement level the stress is lower and mechanical damage is slower.

In order to quantify this effect in Fig. 7 and Fig.8 are presented the elastic modulus and degradation variation for each orientation of fiber and both exposed and unexposed samples.

As we can observe in Fig. 7 a and b elastic moduli after water exposure are around 80% from values characteristic for dry samples.

In case of samples T0,T15, even T25 (Fig. 8a) water absorption for five weeks is equivalent with a degradation $D=0.2$.

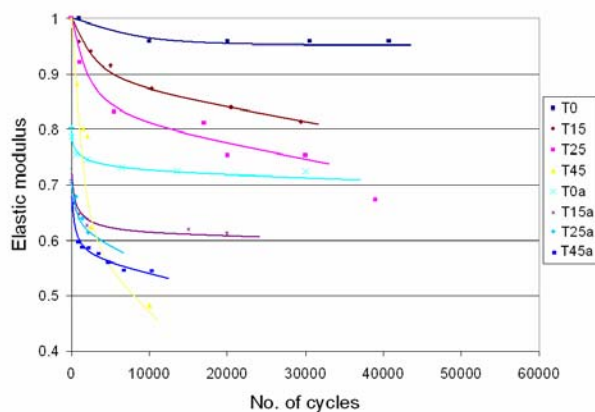


Figure 6. Normalization of elastic modulus variation

This kind of conclusion cannot be accepted and is necessary a global analysis (degradation from dry specimen to bending fatigue after water exposure).

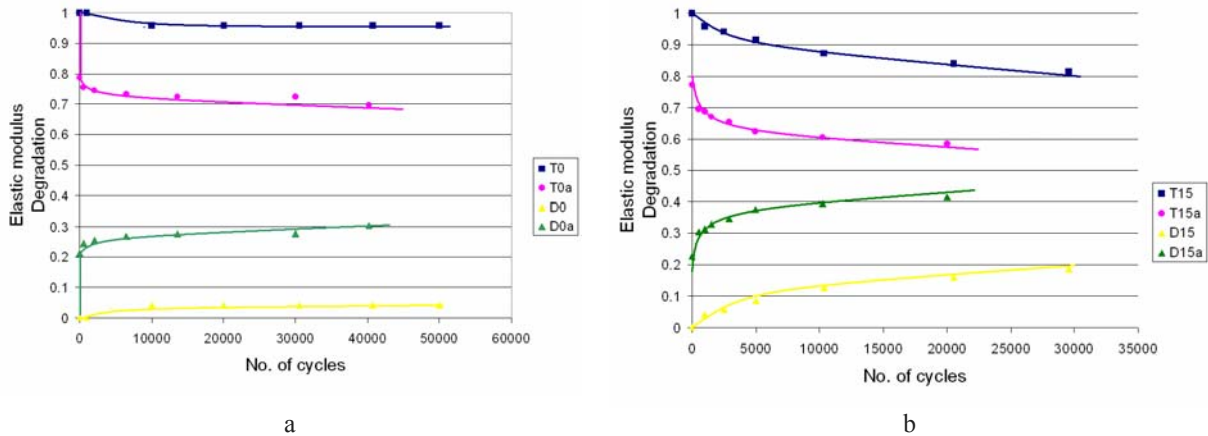


Figure 7. Normalized elastic modulus and degradation evolution with number of cycles for exposed and unexposed samples with fibers oriented at 0° (a) and 15° (b)

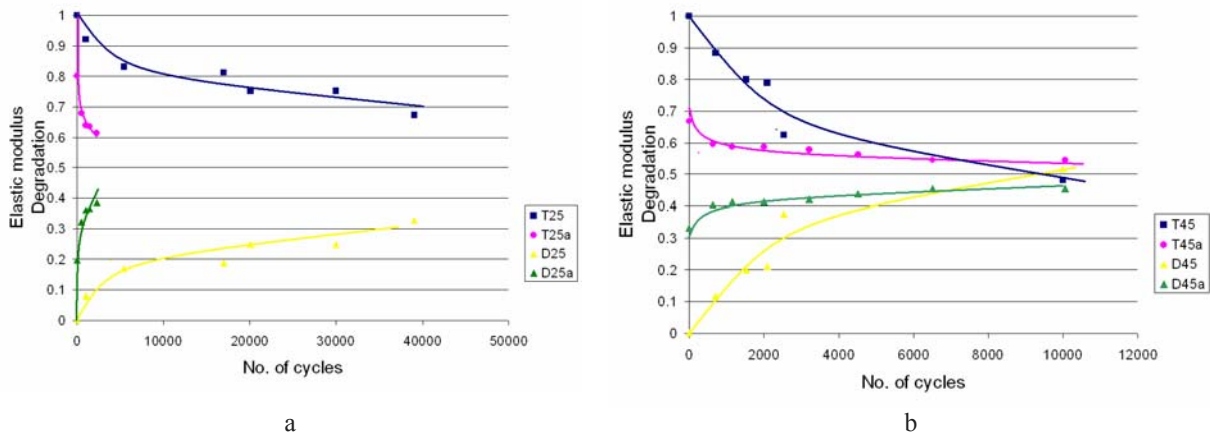


Figure 8. Normalized elastic modulus and degradation evolution with number of cycles for exposed and unexposed samples with fibers oriented at 25° (a) and 45° (b)

In case of samples T45 (Fig. 8 .b) water absorption for five weeks is equivalent with a degradation around $D=0.3$. It is interesting to observe that for samples T45 and T45a, after a number of cycles (7500) the elastic modulus of water exposed sample remains superior to dry sample.

That is result of resin plasticization (reduction of stiffness has as effect a reduction of stress in bending test which is performed at constant deformation) and a subsequent better behavior in bending fatigue at great values of number of cycles.

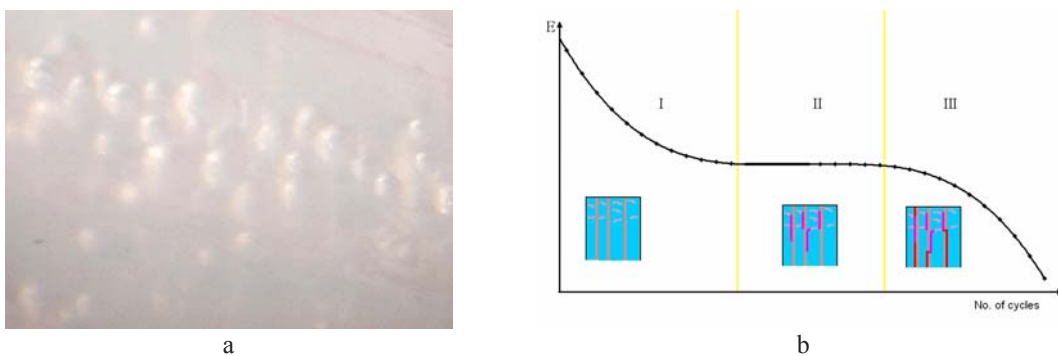


Figure 9. Air bubble between successive fiber layers (a) Schematically representation of defects propagation in fatigue test (b)

The large number of specimens tested allowed correlation between the changes in elastic modulus with the formation of cracks. Because the samples are provided from the plates with a lot of void defects (Fig.9) the degradation is accelerated.

Initially small cracks parallel to the width of the race are formed in the matrix. Their number is growing constantly and size until they meet the fibers. Once stopped the crack follows the fibers propagate through the interface. This step is more or less long, it depends on the length of the fibers is substantially constant part of the module. Finally, the crack runs through the whole ply and delamination occurs and the mechanical properties fall drastically.

In our case is difficult to identify delamination because all fibers have the same orientation and interface between plies became diffuse.

Because samples were water exposed after cutting and lateral face are not covered with resin the strands sectioned in these region have had a contribution in water absorption.

This area exposed to ink, show the ink infiltration and proved the existence of long channels along the glass fibers. This has as effect a sharp drop in the mechanical properties of the specimen and explains the difference between the characteristics of industrial composite and the value of the handmade ones.

This also explains the mode of water propagation in the composite. As the sides of the tests were not coated with resin after cutting the water as the ink, preferably have penetrated here by following the fiber / matrix interfaces without cohesion.

The presence of bubbles in the composite is derived from the impregnation stage with a brush, it is at this point that the air has been incorporated in the matrix. On the one hand they weaken the mechanical properties of the material because it is less dense than expected.

So as part of this study, it is possible to conclude that a glass-epoxy composite handmade has the same type of fatigue behavior as an industrial composite. However, the manufacturing process leaves more easily runs to the formation of defects including poorly impregnated fibers and air bubbles which leads to a severe reduction in the modulus of elasticity and a lower life expectancy.

CONCLUSIONS

The main goal of this work was to compare the mechanical performance of a handmade glass-epoxy composite with and without exposure to salt water.

Fiber / matrix interfaces are the Achilles heel of these structures because at this level the cracks appear, spread and cause the collapse of the part.

In order to analyze substantial range of unidirectional composites, fiber directions 0° , 15° , 25° , 45° were tested.

The bending test performed at constant displacement consists of an undefined number of cycles resulting in the gradual reduction of the elastic modulus of the specimen and deterioration in the nth cycle.

The analysis of the experimental data leads to the conclusion that a handmade glass-epoxy composite has the same answer in bending fatigue that an industrial composite.

Water absorption during five weeks leads to a reduction of elastic modulus between 20 and 30%.

However, the manufacturing process involves the formation of defects such as poorly impregnated fibers and air bubbles which causes a severe decrease in the modulus of elasticity and the durability.

Throughout this study, despite is a good correlation between theory and practice, however further investigations are needed to complete it.

Chemical analyzes must be done on the wet specimens to demonstrate the effective presence of water on the resin macromolecules. The differential scanning calorimetry would highlight free water and thermogravimetry would detect smaller molecules present in the resin which would be present due to hydrolysis.

REFERENCES

- [1] W. R. Broughton, M. J. Lodeiro, *NPL Report CMMT 2000, 064*.
- [2] A. Apicella, L. Nicolais, G. Astarita, E. Drioli, *Polymer* 1981, 22, 1064.
- [3] P. Bonniau, A. R. Bunsell, *Journal of Composite Materials* 1981, 15, 272.
- [4] P. M. Jacobs, E. R. Jones, *Journal of Materials Science* 1989, 24, 2343.
- [5] M. K. Antoon, J. L. Koenig, T. Serafini, *Journal of Polymer Science: Polymer Physics Edition* 1981, 19, 1567.
- [6] E. L. McKague, J. D. Reynolds, J. E. Halkias, *Journal of Applied Polymer Science* 1978, 22, 1643.
- [7] T. NGUYEN, D. BENTZ, E. BYRD, *Journal of Coatings Technology* 1994, 66, 39.
- [8] T. Nguyen, E. Byrd, D. Alsheh, W. McDonough, J. Seiler, *Materials Research Society Symposium Proceedings* 1995, 385.
- [9] B. MORTAIGNE, *Techniques de l'ingénieur. Plastiques et composites* 2005.
- [10] M. R. Bowditch, *International Journal of Adhesion and Adhesives* 1996, 16, 73.