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Thermal aging effect on the mechanical properties of polyester fiberglass composites

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Abstract
In this work, the mechanical properties of polyester fiberglass , which is subjected to accelerated thermal aging, have been evaluated for different periods (30, 60, 90 and 120 days). The aging temperature was fixed to 80 °C. It has been observed that the mechanical properties of this material are strongly affected by thermal aging. As the aging time increases, the elastic modulus decreases of about 50% and the stress at break decreases of approximately 22%. This can be explained by the changes undergone by the microstructure of the matrix and by the fiber-matrix debonding and fiber degradation. The experimental results obtained by tensile test performed on test samples for the studied material are then compared with those got by numerical simulations.

Keywords: Thermal aging, mechanical properties, tensile test, polyester fiberglass composite

1. Introduction
Current knowledge concerning the aging effect on the mechanical behavior of polyester fiberglass composites leads to oversized nesign and therefore expensive.Composite materials are often presented as the materials of the future in reason of their potential for innovation that offer. reinforced polyester glass fiber composites are increasingly used in several areas such as aerospace, automotive, shipbuilding and offshore oil [1].These materials present many advantages; low weight, high stiffness-to-weight and strength-to-weight ratios. Unsaturated polyester resins reinforced with glass fibers are widely used for the construction of large structures (i.e. Pools, tanks, pipes, containers, car bodies, roofs....) in aggressive environments (chemical, humidity, thermal) . Properties of fiber reinforced polymer are relatively well known by scientists and engineers, but there are still many concerns about their durability and their performance under severe environmental conditions [2].Several environmental factors can cause the ageing that occurs within fibers reinforced polymers, such as moisture [3–5], water absorption [6–8] and elevated temperature [9, 10].The environmental effect on two different epoxy resins with woven glass reinforcement was studied by Sookay et al. [11].The mechanical behavior of fiber reinforced polymer composites can be strongly influenced by the temperature and material microstructure [12]. Fiber reinforced polymer composites are sensitive to temperature variations as a result of induced thermal stresses between the fibers and polymer matrix [13] which arises due to their distinct thermal expansion coefficients. At elevated temperatures, differential thermal expansion of fiber and matrix may lead to the formation of micro cracks at the fiber/polymer interface [14]. The fiber–matrix interface also becomes sensitive to aggressive reactions under the exposure of high temperature environment, which can lead to the degradation of both of the fibers and the matrix [15].
The polyester fiber glass composite studied in this paper will be used in the manufacture of bath tubs and tanks.
To perform this study the material has been aged in oven at temperature about 80 °C, for an overall duration of 120 days. The change of the mechanical properties has been checked every 30 days (monthly interval). The elastic modulus and the Failure stress have been measured and compared. Then, the experimental results have been compared with those obtained with numerical simulations.

2. Experimental procedures

2.1. Materials

The studied composite material is an orthotropic laminate. It is protected from the surrounding environment by a pigmented resin layer: the gelcoat EUROGEL GCP. This laminate consists of 6 plies stacked fiberglass-polyester. The used resin is unsaturated orthophthalic polyester SIRESTER FS 0993LP. It is diluted to styrene, moderately reactive and has a low viscosity. Its properties are given in Table 1. The role of the resin is to tie the fibers (cohesion role), and to ensure the transmission of the stresses. Furthermore, the matrix ensures the strength of the material in the transverse direction of the reinforcement. The woven fibers provide a mechanical strength to the material (traction, compression, fatigue ....) as shown in figure 1. The reinforcement is a planar fabric of fiber glasses (woven fiber glasses of "E" type) as cross taffeta of basis weight 500g/m^2, those properties are given in Table 2. The catalyst is a peroxide solution, called PMEC50 (solution with 50% by weight of methyl ethyl ketone peroxide). Two types of specimens were prepared: samples with 2% of catalyst and samples with 3% of catalyst. With the addition of the catalyst, hardening at room temperature takes only a few hours. Table 3 shows the properties of the resin after the addition of catalyst.

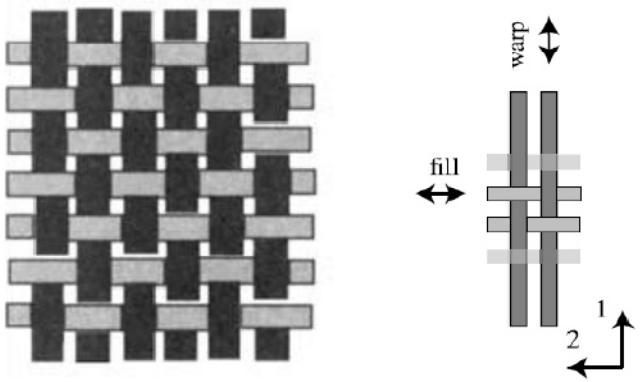


Figure 1: Schematic representation of woven fabric architecture [17]

Table 1: Mechanical properties of polyester resin

Elasticity modulus [GPa]	Shear modulus [GPa]	Poisson ratio [-]	Density [g/cm^3]
3.4	1.2	0.4	1.10

Table 2: Mechanical properties of fiberglass

Elasticity modulus [GPa]	Shear modulus [GPa]	Poisson ratio [-]	Density [g/cm^3]
72	29	0.25	2600

Table 3: Mechanical properties of polyester resin after the addition of catalyst

Flexural modulus [GPa]	Barcol hardness	Flexural strength [MPa]	Temperature of deflection under load (LDT) [°C]
3.4	40	105	75

2.2. Elastic behavior of the material

The advantage of the polyester fiberglass composites and composite materials in general is that they are designed and dimensioned such that the mechanical stresses are applied in the fiber direction. It follows that the propertie are different according to the loading direction, thus the material is anisotropic. The studied material is orthototropic. For an orthotropic laminate material, only six independent elastic constants are needed to describe the elastic behavior. If the isotropic axis is in the direction 3, the independent elastic parameters are: three Young modulus (E1, E2 and E3), two Poisson's coefficients (ν12 and ν13) and a shear modulus (G13).
The following relationships must be satisfied:

$$\frac{\nu_{ij}}{E_i} = \frac{\nu_{ji}}{E_j} \qquad i,j = 1,2,3 \tag{1}$$

$$\frac{\nu_{13}}{E_1} = \frac{\nu_{31}}{E_3} \tag{2}$$

The compliance matrix can be written as follows (formula (3)) (Voigt's notation):

$$S = \begin{pmatrix} \frac{1}{E_1} & \frac{-\nu_{12}}{E_1} & \frac{-\nu_{13}}{E_1} & 0 & 0 & 0 \\ \frac{-\nu_{23}}{E_2} & \frac{1}{E_2} & \frac{-\nu_{21}}{E_2} & 0 & 0 & 0 \\ \frac{-\nu_{31}}{E_3} & \frac{-\nu_{32}}{E_3} & \frac{1}{E_3} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{G_{23}} & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{1}{G_{13}} & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{1}{G_{12}} \end{pmatrix} \tag{3}$$

Figure 2 defines the principal axes for a typical woven fiber reinforced lamina. Axis 1 is along the fiber length and represents the longitudinal direction of the lamina; axes 2 and 3 represent the transverse in-plane direction and the thickness direction respectively.

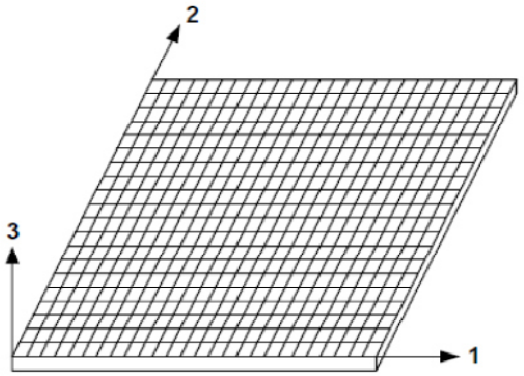


Figure 2: Laminate reference axes.

2.3. ***Preparations of the composites***

The unidirectional composites with crossed plies were prepared by contact molding. The volume fraction of fiberglass is 40% and the volume fraction of resin is 60%. The aluminum mold surfaces are 500x 500 mm²; they are coated with an unmoldingMOLD WIZ-F57 CN. Six fiber sheets of dimension 380 x 250 mm² are pre-cut in a roll for each test tube to develop. The molding method consists in sequentially depositing on one face of the mold a resin layer, then a reinforcing layer(See figure 3).The surface of the mould is thoroughly cleaned to be ready for the use, by removing any dust and dirt from it.The impregnation is made of the reinforcement by a manual operation using a roller or brush (doubling and rolling) to remove the larger bubbles. This operation is repeated several times to obtain the desired thickness of the test tube. So, in our case 6 plies (0 ° and 90 ° to the fibers directions) were superposed.The against mold is put in place without any clamping. The hardening is done at room temperature. A Plates with thickness of 3.2 mm are obtained.

2.4. ***Aging conditions***

The studied material is placed directly after post-hardening in an oven at 80°C to accelerate the aging phenomenon. The overall duration of aging time is 120 days. The sampling is done every 30 days to control the change of the mechanical properties. The mechanical tests are run after the sample is removed from the oven, once the sample has reached an equilibrium temperature, but not too long after to avoid uncontrolled structural evolution.

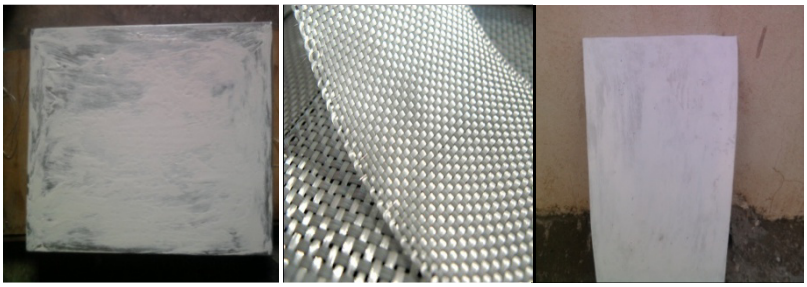


Figure 3:Preparation of polyester fiberglass composites.

*2.5. **Tensile testing***

The tensile tests were performed on an INSTRON 5569 machine at a fixed crosshead speed of 2mm.min^{-1}. The specimens are cut into rectangular shapes, according to the standard ISO574-4 for composite materials, with the following dimensions: Width = 25 mm, length = 250 mm and thickness = 3.2 mm (See figure 4). The Modulus is calculated from the slope of the stress–strain curve.

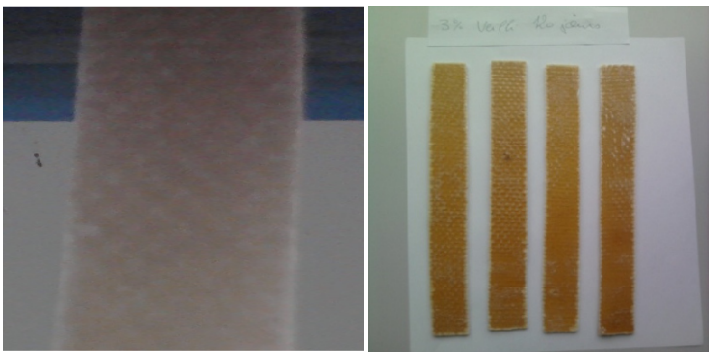


Figure 4: Tensile test pieces of glassfiber polyester.

3. Results and discussion

3.1. Young modulus determination

The mechanical properties of the unaged laminates made in the laboratory are determined, this is required to characterize the initial properties of the material.

Figure 5 and Figure 6 show a representative stress–strain curve of the studied material for samples with 2% and 3% of catalyst, respectively.It is found that the aging time (at 80 °C) affects the mechanical properties.There is no plastic domain.

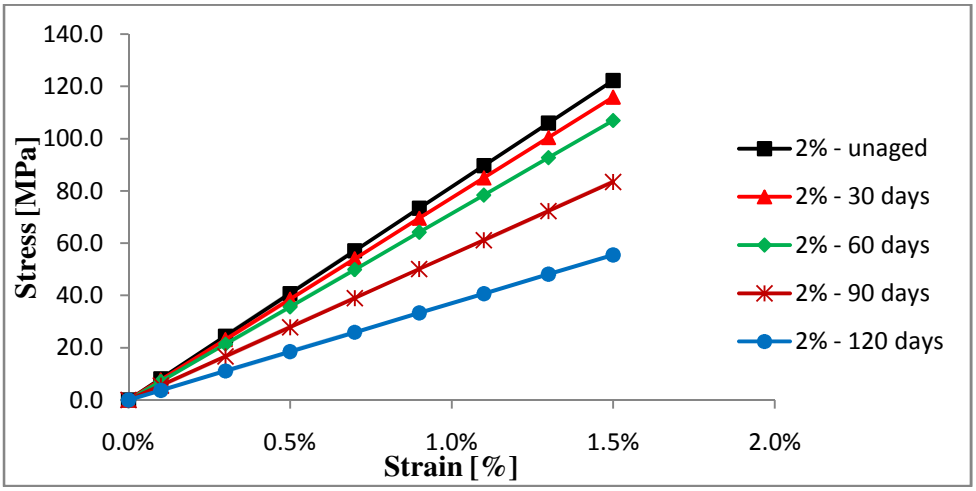


Figure 5: Experimental curve of the tensile test for polyester fiber glass composites with 2% of catalyst.

Young's modulus (E) is measured during the tensile test according to the direction 1 (see Figure 2). It is determined from the slope of the linear part of the stress–strain curve. The Young's modulus for the composites

with 2% and 3% of catalyst decrease progressively with aging time as shown in Figure 7. These curves show the influence of the catalyst concentration and the aging time on the elastic modulus. Aging time tends to decrease the Young's modulus while the catalyst concentration improves it. Above 55 days of heat treatment, an abrupt decrease of the slope is observable for both catalyst concentrations.The initial Young's modulus is E= 8.15 GPa for the composite with 2% of catalyst and E=8.3 GPa for the one with 3%.

When the sample moves from the unaged stage to aged one (i.e. 120 days at 80 °C), the Young's modulus decreases by 55% for the composite with 2% of catalyst and 47% for the composite with 3% of catalyst. In fact, at the end of the aging protocol the Young's modulus becomes E= 3.7 GPa for sample with 2% and E=4.4 GPa for the sample with 3% of catalyst. It can be thus considered that the catalyst tends substantially to improves the Young's modulus of the material.

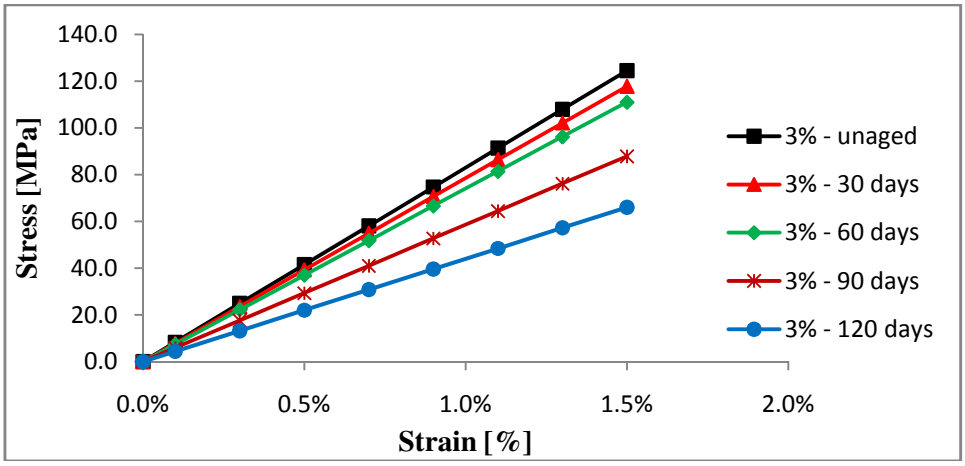


Figure 6 : Experimental curve of the tensile test for polyester fiber glass composites with 3% of catalyst.

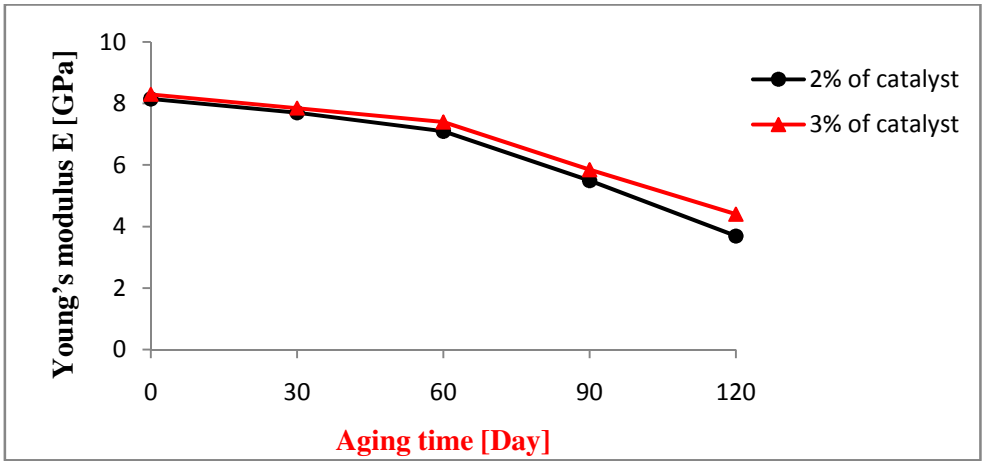


Figure 7: Young's modulus variation according to aging time at 80 °C for polyester fiberglass composites with 2% of catalyst and 3% of catalyst.

3.2 ***Evolution of the failure stress***

Figure 8 shows the variation of the failure stress versus aging time for polyester fiberglass composites with 2% and 3% of catalyst. In both cases the failure stress decreases with aging time. In general, the failure stress of the matrix is lower than that of the fibers. Indeed, the breaking by cracking occurs earlier for the resin than for the glass fibers.

In machine direction, the tensile failure stress cannot be calculated from the mixtures law, because the deformation of the matrix at break is greater than that of the fibers. However in the elastic domain of the fibers, the material remains homogenous.When the breaking of a fiber occurs, the load is transmitted by the interface by shearing to the matrix, broken fibers retain partially their ability to carry the load for a short distance (20 to 100 times the fiber diameter, critical length).When the average length of the broken fibers is below the critical

length, the breaking of the material occurs, with a loosening of the fibers. With ageing (120 days, 80 °C) the failure stress decreases by 31% for the samples with 2% of catalyst and by 21% for the samples with 3% of catalyst.
Before aging the failure stress is of about 130 MPaforthe samples with 2% of catalyst and 140MPa for the samples with 3% of catalyst. For the last stage of aging, the failure stress decreases till 90 MPa for the samples with 2% of catalyst and 110 MPa for those of 3%. As for the modulus, it can be considered that the catalyst tends to slightly improve the failure stress of the material.

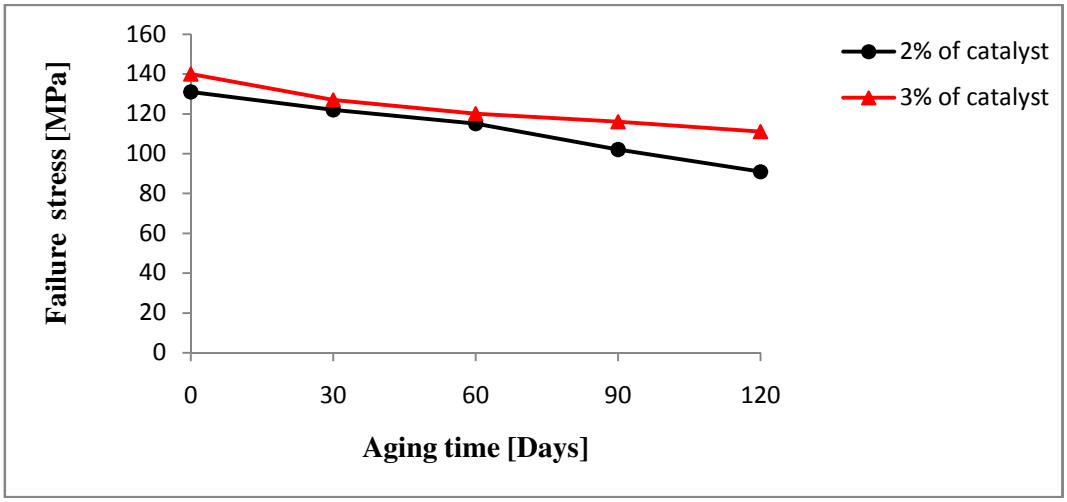


Figure 8 : Failure stress variation according to to aging time at 80 °C for polyester fiber glass composites with 2% of catalyst and 3% of catalyst.

*3.2 **SEM micrographs***

The scanning electron micrographs (SEM) of fiberglass composite polyester are shown in Figure 9. The temperature causes a degradation of the glass fiber polyester composite, by fiber-matrix debonding and fiber degradation. The effects of the thermal aging will be well observable if the material is exposed to relatively high temperatures, and it can be considered as the main cause of the matrix failure at long-term.

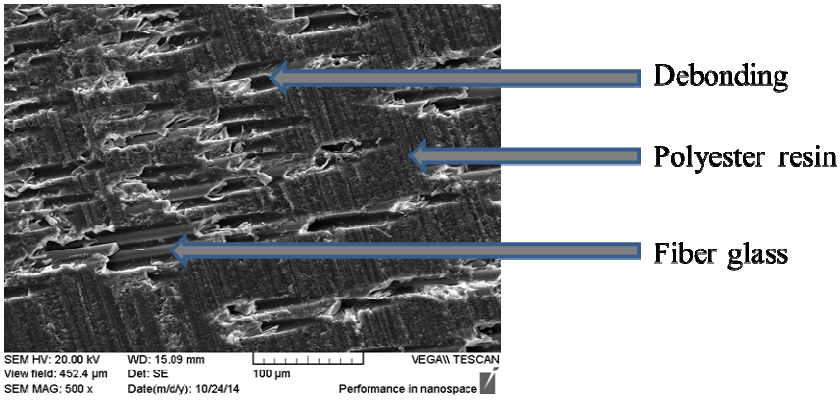


Figure 9 : SEM micrograph of a sample aged during 90 days at 80 °C

4. Numerical modeling and numerical simulations

*4.1 **Material Characterization***

The material elastic properties of the laminate of test specimens are determined through the law of mixtures. These properties are Young's moduli (E_1 – in direction 1, E_2 – in direction 2, E_3 – in direction 3), Poisson's ratios (ν_{12}, ν_{13}, and ν_{23}), inplane shear modulus (G_{12}) and transverse shear moduli (G_{13} and G_{23}) as referred in Figure 2. The elastic constants of the unidirectional composite are calculated using the law of mixtures by the relations of equation (4) [16].

$$
\begin{aligned}
E_1 &= E_f V_f + E_m V_m \\
E_2 &= E_m \left[\frac{E_f + E_m + (E_f - E_m) V_f}{E_f + E_m - (E_f - E_m) V_f} \right] \\
\upsilon_{12} &= \upsilon_f V_f + \upsilon_m V_m \\
\upsilon_{23} &= \upsilon_f V_f + \upsilon_m V_m \left[\frac{1 + \upsilon_m - \upsilon_{12} \frac{E_m}{E_1}}{1 - \upsilon_m^2 + \upsilon_m \upsilon_{12} \frac{E_m}{E_1}} \right] \\
G_{12} &= G_m \left[\frac{G_f + G_m + (G_f - G_m) V_f}{G_f + G_m - (G_f - G_m) V_f} \right] \\
G_{23} &= \frac{E_2}{2(1 + \upsilon_{23})}
\end{aligned}
\tag{4}
$$

Where the indices *m* and *f* denote matrix and fiber, respectively. After calculating, the elastic constants of the unidirectional composite and the elastic constants of the woven fabric composite material are estimated using the relations of equation (5) [17] and the results are listed in table 4.

$$
\begin{aligned}
\left(\frac{1}{E_1}\right)^{WF} &= \left(\frac{2}{E_1} \frac{E_1 (E_1 + (1 - \upsilon_{12}^2) E_2) - \upsilon_{12}^2 E_2^2}{E_1 (E_1 + 2E_2) + (1 + 2\upsilon_{12}^2) E_2^2} \right)^{UD} \\
\left(\frac{\upsilon_{12}}{E_1}\right)^{WF} &= \left(\frac{4}{E_1} \frac{\upsilon_{12} E_2 (E_1 - \upsilon_{12}^2 E_2)}{E_1 (E_1 + 2E_2) + (1 + 2\upsilon_{12}^2) E_2^2} \right)^{UD} \\
\left(\frac{\upsilon_{13}}{E_1}\right)^{WF} &= \left(\frac{1}{E_1} \frac{E_1 (\upsilon_{12} + \upsilon_{23} + \upsilon_{12}\upsilon_{23}) + \upsilon_{12}^2 E_2}{E_1 + (1 + 2\upsilon_{12}) E_2} \right)^{UD} \\
\left(\frac{1}{E_3}\right)^{WF} &= \left(\frac{(1 - \upsilon_{23}^2) E_1^2 + (1 + 2\upsilon_{12} + 2\upsilon_{12}\upsilon_{23}) E_1 E_2 - \upsilon_{12}^2 E_2^2}{E_1 E_2 (E_1 + (1 + 2\upsilon_{12}) E_2)} \right)^{UD} \\
\left(\frac{1}{G_{12}}\right)^{WF} &= \left(\frac{1}{G_{12}}\right)^{UD} \\
\left(\frac{1}{G_{13}}\right)^{WF} &= \left(\frac{1 + \upsilon_{23}}{E_2} + \frac{1}{2G_{12}} \right)^{UD}
\end{aligned}
\tag{5}
$$

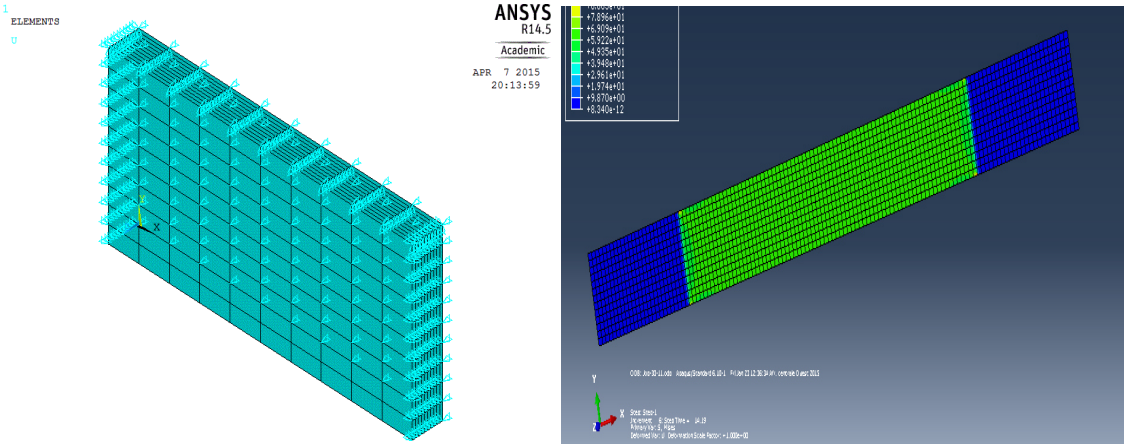
Where *UD* and *WF* denote unidirectional fiber and woven fiber, respectively.

Table 4: elastic properties of woven fabric composite laminate

Elastic modulus E_1=E_2 [GPa]	Elastic modulus E_3 [GPa]	Poisson ratio ν_{12} [-]	Poisson ratio ν_{13} [-]	Shear modulus G_{13} [GPa]
19.7	8.2	0.20	0.72	2.5

*4.2. **Numerical simulations***

The study of tensile was performed in 3D on a rectangular plate. For symmetry reasons, the model consists to a quarter of the plate. Thus, the perpendicular displacements to the symmetry plane are locked. The ANSYS 14.5code, and Abaqus 6.11 based on FEM, are used for the numerical simulations. For the ANSYS the structure is meshed with SOLID45 elements. The SOLID45 is used for the 3-D modeling of solid structures and the number of elements is about 4400.The element is defined by eight nodes having three degrees of freedom at each node: translations in the nodal x, y, and z directions. Figure10 shows the meshed structure.



(a) (b)

Figure 10:(a) The meshed structure with SOLID45 element, (b)Traction simulation results by abaqus.

Figure 11 shows the comparison between experimental results and those obtained by numerical simulation. It depicts the stress according to the strain for an unaged polyester fiber glass with 3% of catalyst.A difference between the numerical simulation and experiment was observed. This difference is relatively low for the simulation with ANSYS and Abaqus. The results obtained by the two numerical models that are presented in the following table, seem reasonable, despite the defects acquired by the composite during the manufacturing process, particularly air bubbles and uncertainties experimental devices used.

Table 5: Comparison of the ultimate properties obtained by simulation (ABAQUS and ANSYS) and experimentally

ANSYS simulation 3%		ABAQUS Simulation 3%		Experimental 3% unaged	
strain	stress	strain	stress	Strain	Stress
0,00%	0	0,05%	4,20469	0,1%	8,1
0,13%	9,99375	0,10%	8,41153	0,3%	24,3
0,25%	19,9875	0,17%	14,7258	0,5%	40,5
0,63%	49,9687	0,28%	24,2064	0,7%	56,7
0,95%	74,9531	0,45%	38,4477	0,9%	72,9
1,27%	99,9375	0,72%	59,8557	1,1%	89,1
1,59%	124,922	1,09%	92,071	1,3%	105,3
		1,67%	140,627	1,5%	121,5

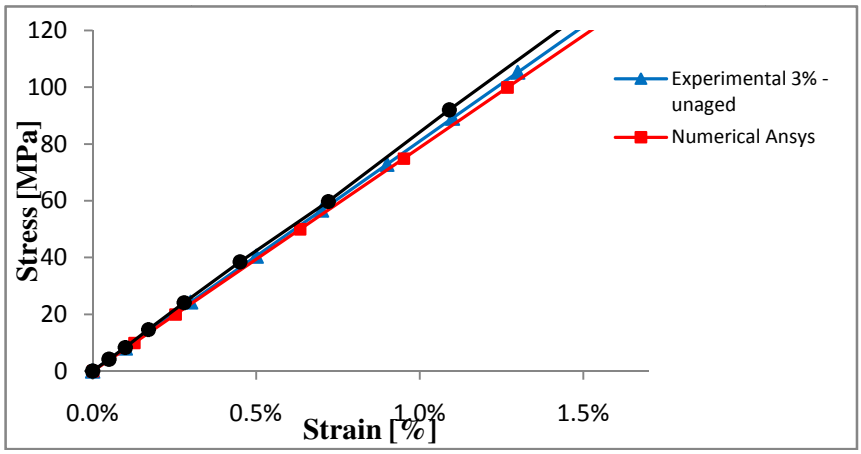


Figure 11 : numerical and experimental comparison for unaged samples with 3% of catalyst

Conclusion

This paper presents a mechanical characterization of polyester fiberglass composites thermally aged at a temperature of 80 °C well above the Tg (53.17°c) of the matrix. A sampling has been performed every 30 days and for each aging stage a tensile test has been carried out.

The variations of the elastic modulus and the failure stress have been investigated on two types of samples, the first with a catalyst concentration of 2% and the second with 3%. It has been found that the mechanical properties of the polyester fiberglass composite are strongly affected by the thermal aging. The young's modulus and the stress sensibly decreased due to the effect of temperature. The Young's modulus decreased significantly with aging time (it goes from 6% after 30 days to 55% after 120 days for the sample with 2% of catalyst and from 5% after 30 days to 47% after 120 days with 3% of catalyst). This, leave us consider that it is of prime importance to protect polyester fiberglass composite structures against exposure to high temperatures to avoid undesirable loss of performances in their environment of use. In the present work a comparison between stress-strain curves obtained experimentally with those simulated by numerical models for enlarged samples have shown a good result. In the forthcoming communications it will be presented the same type of work, but this time for aged samples and physico-chemical characterizations will be carried out to make possible to link the changes of the mechanical properties to that of the microstructure. Creep experiment can be regarded as a good approach to characterize mechanically the material. It will bring additional information thanks to other mechanical greatnesses, which will show the progressive material degradation. This technique is already developed in our laboratory by one of our colleagues working on polyethylene film degradation.

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