

# THERMAL ANALYSIS OF POLYMER RESIN MATRIX REINFORCED WITH E-GLASS FIBERS DEGRADATED IN NEUTRAL ENVIRONMENT

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## ABSTRACT

The present work aims to add a new type of thermal analysis like differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), to obtain a complete knowledge about degradation of glass fibers polymer composites. The composites were obtained by hand lay-up moulding, using two different resins, polyester and vinylester. Samples were immersed in neutral environment, like water and sodium chloride (3.5% w/w) for long term up to 19000 hours.

The study has been completed with the analysis of surface and cross-sections morphology by means of optical microscopy and scanning electron microscopy. Results of temperature peak position on TGA curves allows to determine degradation processes as well as the influence of reinforcements and type of resin.

## 1. INTRODUCTION

Chemical industries are interested in composite materials by their advantages of lightness, chemical properties and resistance to corrosion. Polyester resins reinforced with glass fiber have been adapted for construction of equipment with competitive cost, excellent mechanical properties and good corrosion behaviour [1-4].

A lot of works are focused on effect in the characteristics and properties of different resins, in watery and saline [5-12], acid, alkaline [12-14] and organic solvents [13-18]. Although ortophthalic polyester resins do not have satisfactory behaviour in the chemical solutions, vinylester are especially interesting in wet and acid environments [9, 14]. Applications of polyester resins in alkaline and alcoholic environments are not advisable in ortophthalic and limited in vinylester resin [18, 19].

Plastic components can fail via many different modes, including catastrophic mechanism, such as brittle fracture, ductile overload, creep rupture, environmental stress cracking, molecular degradation and fatigue. In the case that failure produces fracture, the determination of failure mode involves identifying how the crack was initiated and how is subsequently extended. This is usually obtained using a number of visual techniques, such as stereomicroscopy (OM) and Scanning Electron Microscopy (SEM), to study surfaces and cross sections. Non-catastrophic failure mode is also relevant, and this includes discoloration, distortion and contamination. By assessing the mode of the failure, is easy to establish the cause of material failure.

In many cases, a single cause cannot be identified because multiple integrated factors may have contributed to the failure. Factors that affect the behaviour of a composite can be classified into four categories: material, design, processing and service conditions [20].

Thermal analysis describes the techniques used in characterising materials by measuring a physical or mechanical property as a function of temperature or time, at a constant temperature or as a function of temperature. This dependency allows access to processing and performance information relating to resins and fiber- reinforced composites and can be used for quality assurance, process control, and new material-process development. Gel points, T<sub>g</sub>,

expansion/contraction properties, reaction rates and cure kinetics, effect of individual and combination of components, polymer stability, and material life predictions can be all determined by thermal analysis.

Thermogravimetric analysis (TGA) is used in the assessment of the composition of polymeric-based materials. The quantitative results obtained of TGA evaluation complement the qualitative information produced by FTIR analysis. The relative loadings of various constituents within a plastic material, including polymers, plasticizers, additives, carbon black, mineral fillers, and glass reinforcement can be obtained. A thorough knowledge of the decomposition and chemical reactions is required to properly interpret the results obtained. Non-combustible material remaining after TGA testing is often associated with the glass fiber reinforcement.

TGA data is used to compare the thermal and oxidative stability of polymeric materials. The relative stability can be evaluated by means of the onset temperature of decomposition of the polymer. Quantitatively, this temperature is not useful for comparing de long-term stability of materials, because materials are generally molten at the beginning of decomposition [20]. However, a comparison of the TGA thermograms can provide insight into possible degradation of the failed component material. Degradation experiments involving polymeric materials can also provide information regarding the kinetics of decomposition, and material life time.

This study aim to model polymer composites reinforced with glass fiber after immersion in neutral environment. This study is focused on variation of mechanical properties along time. It allows knowing life time of the material and characterisation of different degradation behaviour.

## **2. EXPERIMENTAL**

### **Materials**

Two different types of resins were studied. The first one was unsaturated polyester P4 TV-29 with glycol and/or phthalic base,  $1.2 \text{ kg/m}^3$  of density and 35% styrene content. The second one was vinylester resin Atlac A-430.01, containing bisphenol-A,  $1.2 \text{ kg/m}^3$  of density and 40% styrene content. Both resins were provided by Basf. E-glass fiber was used as reinforcements, with a different disposition. Mat specific weight is  $300 \text{ g/m}^2$ , provided by INP-96, S.L. Taffeta disposition is 1:1 to  $90^\circ$  with the same specific weight, provided by JEMP Spain. Multiaxial disposition has continuous fibre 1:1 0/45 with  $770 \text{ g/m}^2$  specific weight, provided by G-Tensor Alcoy, S.L. Different resins and reinforcements studied were: polyester taffeta (UPTF), polyester multiaxial (UPMX), polyester mat (UPMAT), vinylester taffeta (VETF), vinylester multiaxial (VEMX) and vinylester mat (VEMAT).

### **Composite Materials Manufacture**

Composite materials have been obtained by hand lay-up moulding. The resin is adjusted with the catalyst at the beginning of the process, using a metallic surface as a mould where a first fine layer of resin is extended. Four layers of reinforcements are placed in the case of mat and taffeta, and two for the multiaxial reinforcements, alternating with resin layers, to obtain a similar specific reinforcement weight. Excess resin was removed by applying a roller to the upper sheet.

Polymerization of resins took place at room temperature during 24 hours, for unsaturated polyester, and additional cured treatment was carried out in an oven for vinylester resin at  $130^\circ\text{C}$ , during three hours, in order to ensure resin reticulation. Laminates were obtained in form of a 30-cm square piece.

## **Exposure Environments**

Chemical degradation is carried out following UNE 53-029-82 normative. Samples were immersed in neutral environment at room temperature in water and sodium chloride (3.5% w/w) for long term up to 19000 hours. Solutions pH were 7.71 and 6.32 at 20 °C. Dimension, visual analysis and weight characterization were done the next day after removing the sample from the exposure environment. Samples were cleaned with distilled water, dried with paper and remained in a dryer with silica gel at least during 24 hours, before being observed, evaluated and tested. Visual inspection of colour changes and superficial deterioration was observed by stereomicroscopy.

## **Weight Changes**

Uptake experiments were carried out for a short time exposure samples at ambient temperature. Samples were periodically removed from solution and cleaned with distilled water. Prior to weighting, the specimens were dried in a chamber at room temperature with silica gel during almost 24 hours. Afterwards these were weighted in the electric balance with 0.1 mg resolution. Water and solution sorption was calculated as the change in mass with respect to the initial dry mass of the sample.

## **Mechanical Testing**

Tensile and flexural tests were made in an universal testing machine INSTRON 4204, equipped with 50 mm gauges and 50 kN load cell for tensile testing according to UNE 53-280-79, and 1 kN load cell for three points flexural testing according to UNE-EN ISO 14125:1999. In the latter case a support span to depth ratio of 16 ( $L/d=16$ ) and were loaded at the rate of 2 mm/min. Impact testing has been made on rectangular samples by means of Charpy testing machine, equipped with a hammer of 7.5 and 15 J, in agreement with UNE EN ISO 179-1-2001. Each value for flexural, tensile and impact reported is an average of three replicate runs. Hardness tests were made with Barcol hardness, in accordance with UNE 53270:1976.

## **Microstructure Characterisation**

Observation of sample surface was carried out by means of stereomicroscopy (OM) with magnification between 10x and 63x.

Scanning Electron Microscopy (SEM) was carried out with a JEOL 6300 microscope, working at 10 kV and 15 cm of working height, equipped with microanalysis (energy dispersive X-ray analysis from Link Isis of Oxford Instruments). Samples were coated with gold layer during 90 seconds, as a conducting material. The effect of degradation in surface and the failure mode was analysed using both techniques.

## **Thermal analysis**

### *Differential Scanning Calorimetry*

By means of DSC analysis, non satisfactory results were obtained, as only using a scanning calorimetry with a modulated signal allows obtaining some results and this equipment was not available. So thermal analyses were focused on thermogravimetric ones, as better results than DSC could be obtained.

### *Thermogravimetric Analysis*

Thermogravimetric Analysis (TGA) is a thermal analysis technique that measures the amount and rate of change in weight of a material as a function of temperature or time in a controlled atmosphere. The weight of the evaluated material can decrease due to volatilization or decomposition or increase because of gas absorption or chemical reaction. Thermogravimetric

analysis can provide valuable information regarding the composition and thermal stability of polymeric materials. This can be done to compare between different materials or an accelerated means for life time predictions.

The data obtained can include volatiles, inorganic filler and carbon black contents, the onset of thermal decomposition and the volatility of additives such as antioxidants or plasticizers [21]. The loss of additives can damage the material structure so decomposition profiles are excellent indicators of change.

Specific determination of thermal stability is difficult, however, because of the interaction of various aging phenomena. Because decomposition mechanisms are often diffusion controlled, sample geometry and fillers can affect the observed test results. Therefore, the data obtained on small test specimens may not be extrapolated to larger structures.

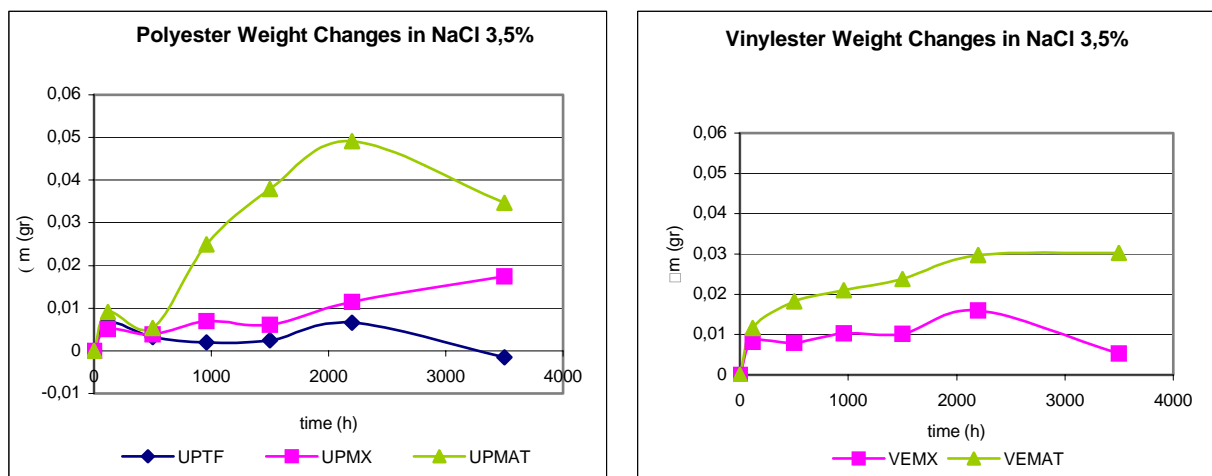
Thermogravimetric analysis was carried out on a TGA-SDTA instrument 851e (Mettler-Toledo), at a heating rate of 20 °C/ min in a nitrogen atmosphere. Mass loss was characterized in the range from 30 °C to 500 °C and typical samples weight was 5-7 mg.

### 3. RESULTS & DISCUSSION

#### Weight Changes

In general, weight of composites increase after immersion in chemical aqueous solutions, due to sorption of the fluid. Weight changes are possible to be explained as follows: weight gain is due to sorption of solution, and weight loss is due to solution of low-molecular components into the liquid environment [12] like the loss of styrene obtained in DSC results [5].

Weight changes as a function of exposure time are given in Fig. 1, for the environments and resin-reinforcement combinations analyzed.



**Figure 1.** Weight changes of polyester and vinylester in sodium chloride

The initial weight increase is caused by diffusion of water and penetration through surface cracks being more significant in the polyester matrix than in the vinylester one, as seen on the SEM micrographs Fig. 4 (a) and (d).

The decrease of the weight in NaCl solution occurs after 2200 hours in the polyester resin. This mass loss is attributed to the hydrolysis and subsequent dissolution of the resin, being more significant than in vinylester.

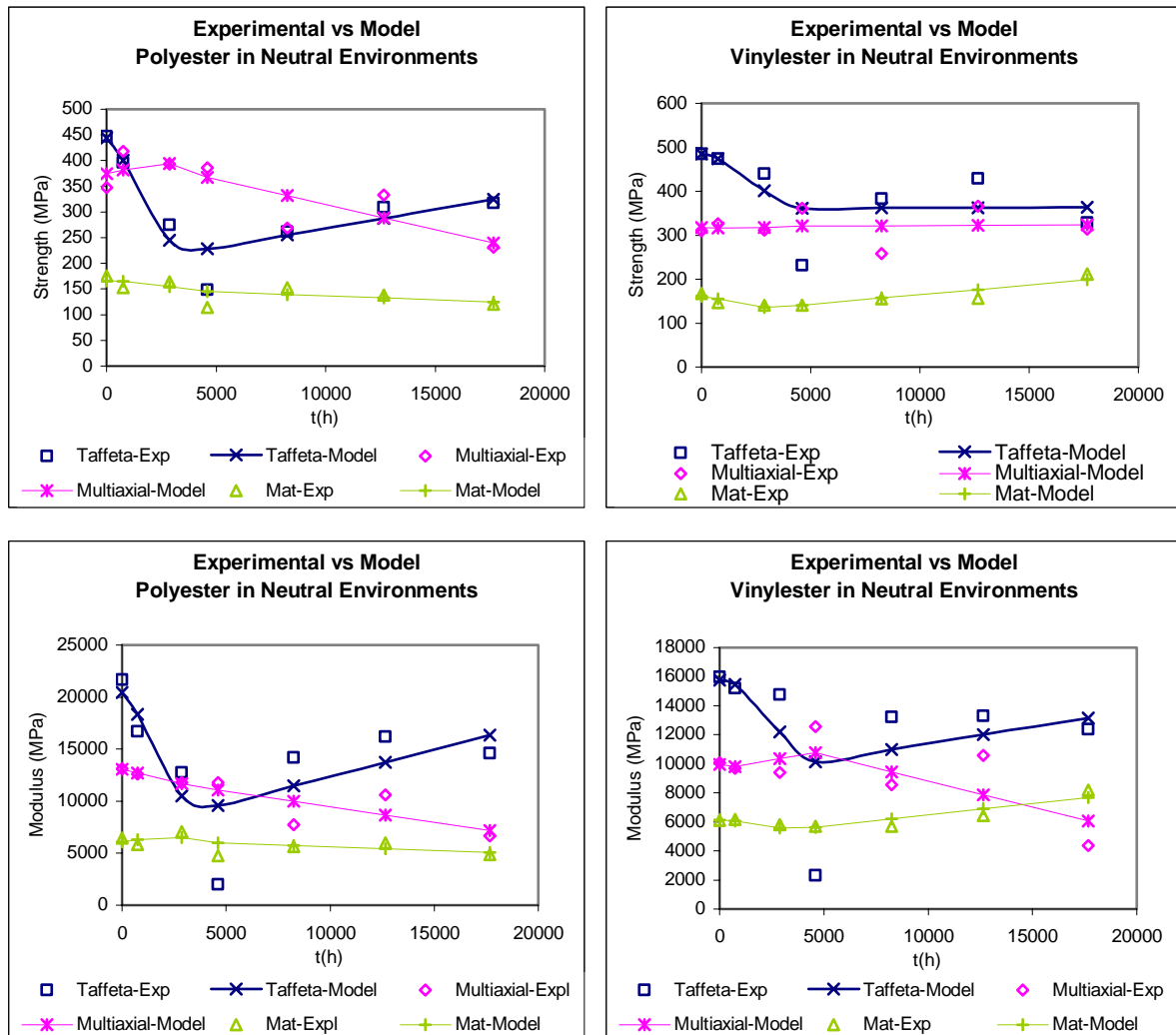
## Mechanical Testing

As a similar mechanical behaviour was observed in both environments (water and sodium chloride solution) the results are treated together as neutral environment.

### Flexural testing

The main values of flexural tests were measured with an universal test machine in a 3-point bend test. The flexural strength and modulus were analyzed as function of time immersed for different samples and environments studied. Finally, it was concluded that water and sodium chloride have a similar flexural behaviour that allows be treated together.

An overall decrease in strength and modulus was most important in the first 2800 hours (~120 days) in neutral environments as shown Fig. 2.



**Figure 2.** Flexural strength and modulus in neutral environments

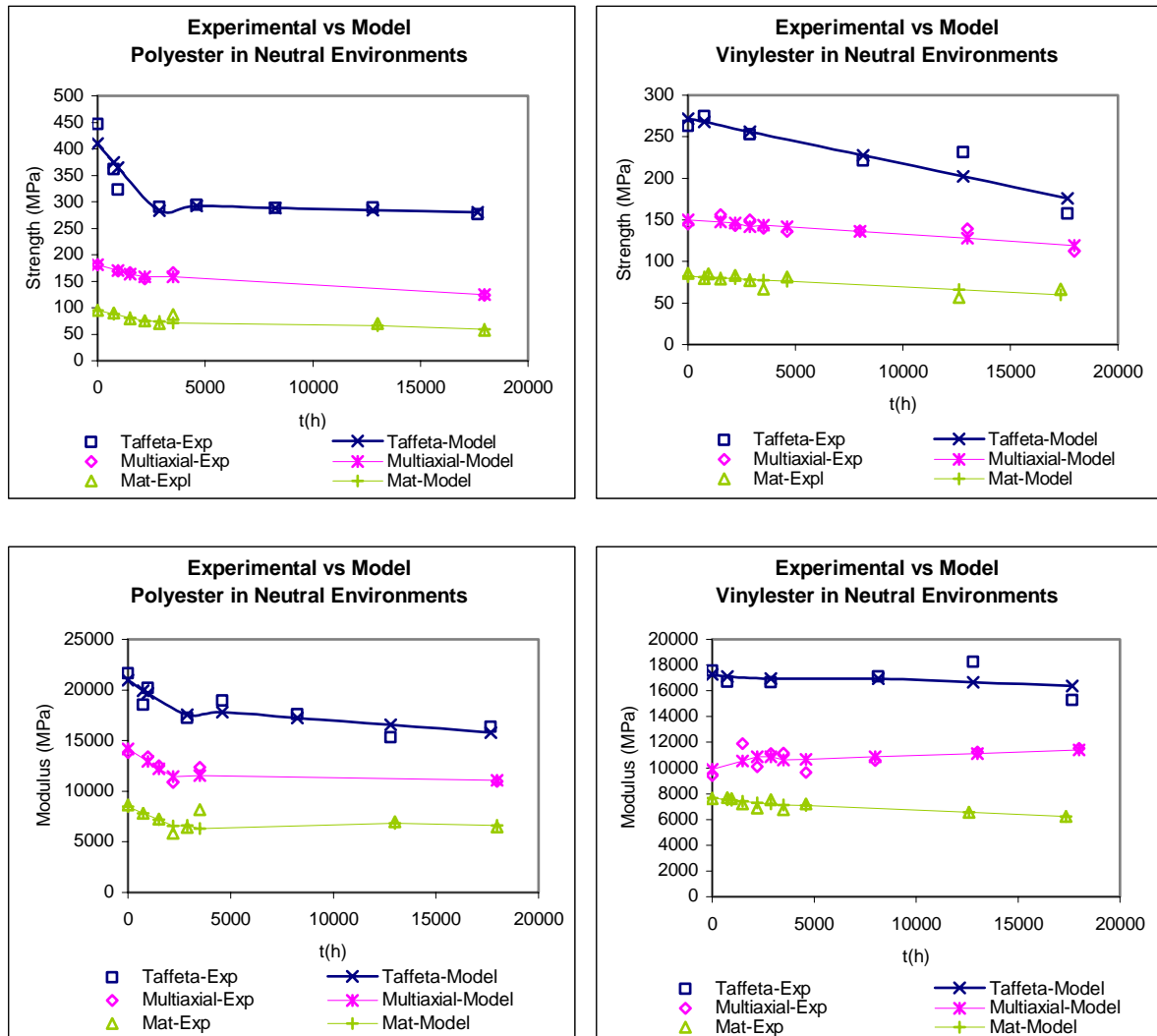
The values of strength and modulus have dropped near to 40% in strength and 37% in modulus for intermediate term degradation, being less significant for vinylester resin.

These results allow obtaining a mathematical model for flexural properties, using different linear adjustments for stages with different behaviour (short and long term degradation as shown Fig 2). The linear mathematical model has 5% as estimated error between model and experimental results.

### Tensile testing

The main values of tensile tests were measured with an universal test machine with a 50kN load cell, and rate of 2mm/min. The tensile strength and modulus were analyzed as function of time immersed, for different samples and environments studied, arriving at the conclusion that water and sodium chloride have a similar tensile behaviour.

The reduction in strength and modulus was most important in the first 2800 hours (~120 days) in neutral environments, like in flexural properties, as shown Fig. 3. Reduction in strength is considered to be a clear indicator of polymer degradation [22].



**Figure 3.** Tensile strength and modulus in neutral environments

The values of strength and modulus have dropped near to 30% in strength and 20% in modulus for intermediate term degradation, being less significant for vinylester resin.

That allows obtaining a mathematical model for tensile properties, using different adjustments model for each stage, as shown Fig 3. The mathematical linear model has 4% as estimated error between model and experimental results.

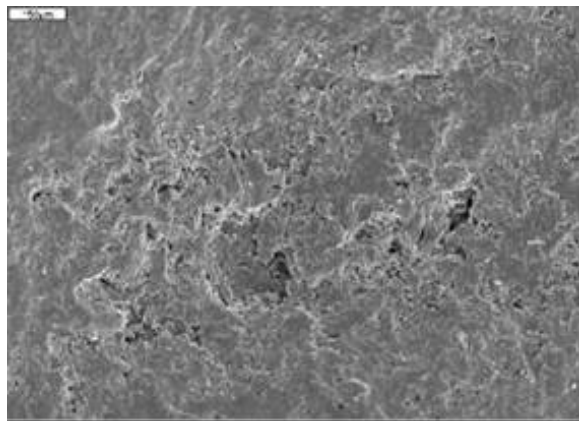
### *Hardness and Impact Testing*

These mechanical tests are used as supplementary information, for tensile and flexural, about degradation effect in mechanical behaviour. Important hardness decreases occur in the first 2200 hours, being more significant for polyester. After 2200 hours hardness became higher.

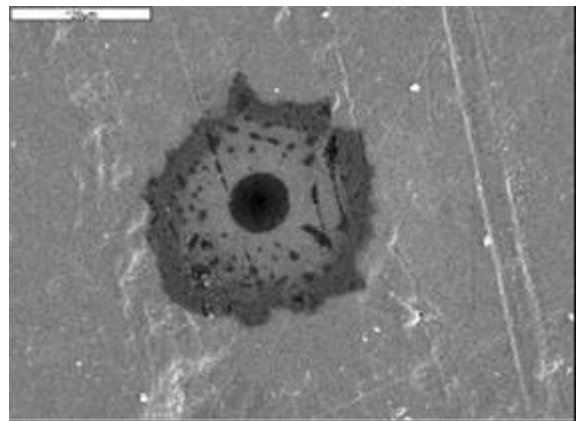
### **Scanning Electron Microscopy**

To evaluate the state of deterioration, surfaces and fractures of materials were observed with scanning electron microscopy (SEM). Samples for the SEM were cut (10x5 mm in size) from the tested samples. Before being analyzed, the surfaces and cross-section were coated with gold.

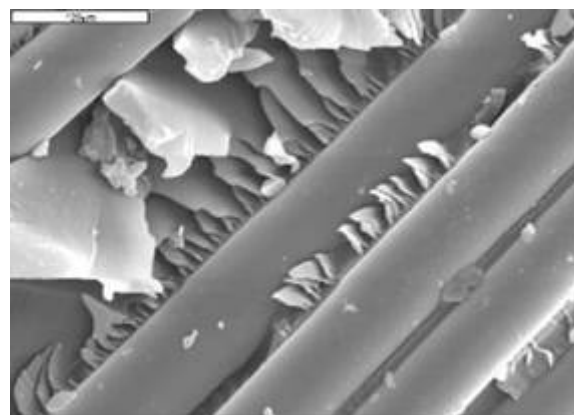
In neutral solutions, water and sodium chloride, reduction of mechanical properties is due to degradation of the matrix by hydrolysis and plasticization. The study by SEM does not reveal attack in fibber-glass of reinforcement, only a single attack on the resin, as shown Fig. 4. It is characteristic for sodium chloride to show black spot on the surface, that it can be black fungi on the surface [12], that effect is shown in Fig. 4 (b).



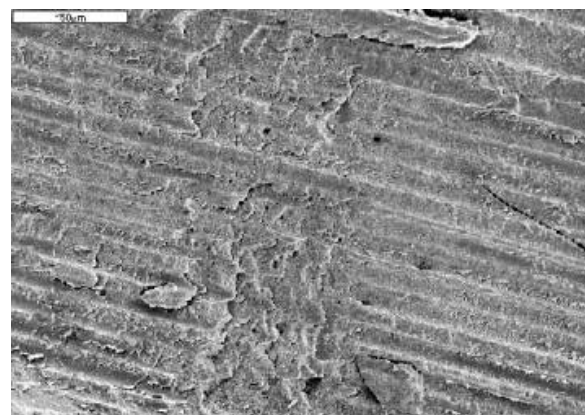
a) VEMAT - Water – 12300 hr - X250



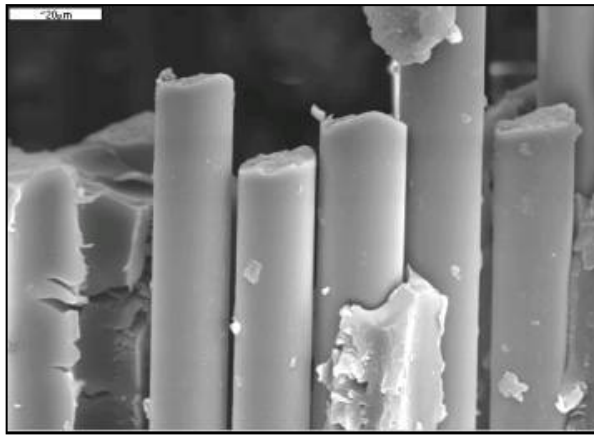
b) UPTF – NaCl 3.5% - 13000 hr - X1500



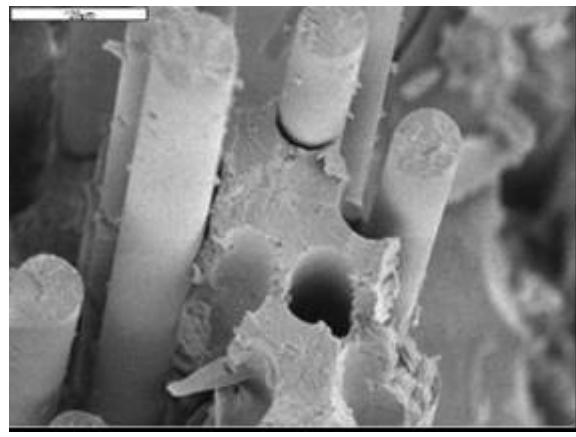
c) VEMX - Water – 750 hr – X1500



d) UPMAT – NaCl 3.5% - 13000 hr - X500



e) VEMX - Water - 750 hr - X1000



f) UPMAT - NaCl 3.5% - 13000 hr - X1500

**Figure 4.** Surface and cross-section SEM micrograph immersed in water and sodium chloride

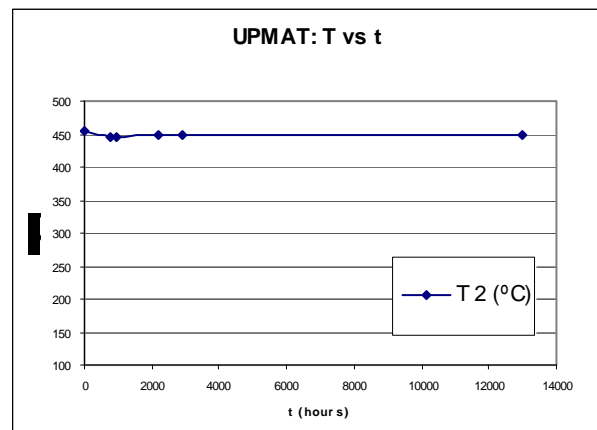
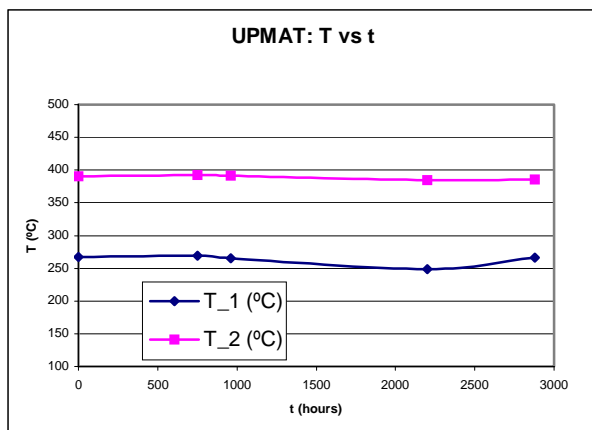
### Visual Observations

Optical microscopy gives other complementary information about external aspect of samples, colour surface changes and external cracks that helps to understand the degradation effect [20]. The attack caused by neutral environments is focus on matrix resin and in resin-fiber interface due to the fact that fiber surface appears clear, because an adhesive failure occurs.

### Thermogravimetric Analysis

The TGA thermograms illustrate the sample weight, usually in percent of original weight, on the y-axis as a function of temperature on the x-axis. The weight-change transitions are highlighted by plotting the corresponding derivative on an alternative y-axis. The weight of the evaluated material can decrease due to volatilization, decomposition or increase because of gas absorption or chemical reaction. Mass changes at sample temperatures between 250°C and 300°C can be correlated to changes in molecular structure and is believed to reflect the extent of matrix depolymerization which may have occurred. Above 380 °C, mass loss is rapid and severe for almost all organic materials.

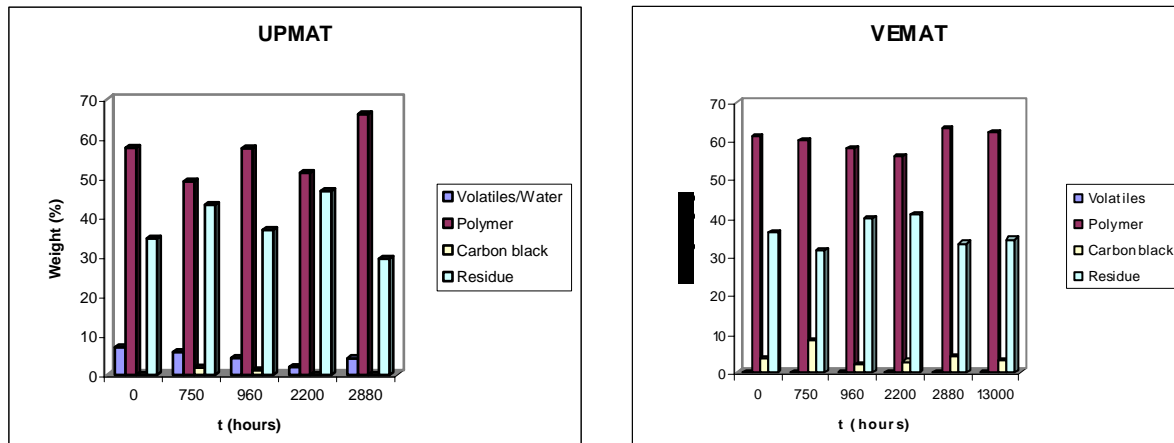
Polyester thermograms are characterized by two significant temperatures when weight-change transitions take place. At first, volatiles compounds disappear, and second, where polymer decomposition takes place. For vinylester resin only the last weight-change transition appears. T-t curves (temperature-time) were represented by using significant temperatures obtained using TGA results for different degradation time, as shown Fig. 5.



**Figure 5.** T-t curves



It has been found that polyester is more susceptible to degradation than vinylester due to more significant deviation respect to horizontal tendency that is observed before 2800 hours. After that tendency is constant. Decrease of weight-change transition temperatures is attributed to the matrix plasticization, hydrolysis and subsequent dissolution of the matrix and it is consistent with degradation of the polymer network structure [23].



**Figure 6.** Percent weight loss as function of exposure time

#### 4. CONCLUSIONS

Mechanical properties decrease as function of exposure time. It is possible differentiate mechanical behaviour in two stages. At first stage an aggressive degradation takes place and the greatest loss of mechanical properties occurs. The reduction in flexural and tensile properties, strength and modulus, was most important in the first 2800 hours, neutral life time. During second stage a general stabilization of properties takes place for long time degradation. These behaviours allow obtaining mathematical linear models.

The study by SEM, in neutral environments, does not reveal attack in fiber-glass, only a single attack on the resin and in resin-fiber interface, due to the fact that fiber surface appears clear, because an adhesive failure occurs. Modulus at tensile and flexural test decrease due to hydrolysis and plasticization of resin matrix, as it is observed a decrease of composite hardness.

Decrease of weight-change transitions temperature, observed in thermograms, is attributed to matrix plasticization, hydrolysis and dissolution of the matrix and it is consistent with degradation of the polymer network structure. In general vinylester has been found to be less susceptible to hydrolysis than polyester, due to the fact that ester functional groups in vinylesters are terminal and shielded by methyl groups, whereas in polyester they are distributed along the main chain, making them more accessible for reaction; being vinylester compounds more hydrolytically stable than unsaturated polyesters.

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