

MODELING OF LONG-TERM DEGRADATION OF E-GLASS REINFORCED COMPOSITES IN ORGANIC ENVIRONMENTS

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ABSTRACT

The present work establishes a chemical model of degradation that takes place in polymer composites materials after immersion in chemical environments. Composites were obtained by hand lay-up moulding, using polyester and vinylester resins and three different reinforcements of E-glass. Samples were immersed in organic solvents such diesel and unleaded petrol, during periods of time up to 20000 hours. Mechanical, physical, optical and structural properties were analyzed before and after immersion in solvents.

Flexural and tensile behaviour are the main mechanical properties evaluated, although they are supplemented with Barcol hardness and Charpy impact, obtaining complete mechanical information. The study has been completed with weight changes, morphology analysis of surface and cross-sections after and before immersion, by means of optical microscopy and scanning electron microscopy.

A mathematical model is obtained for each material degraded in organic environment. It can explain the different behaviour of glass fiber reinforced composite versus exposure time. The model divides every variation of mechanical properties as function of degradation time in two different stages: short and long term degradation.

At the first stage, mechanical properties remain constant, and in the second stage mechanical properties decrease for long time degradation, a life time in these types of environments is also obtained.

1. INTRODUCTION

Glass fiber polymers have received considerable attention as alternative to metals, like steel and aluminium, as alternative design and structural materials. It is used in areas with great technological development industries like aerospace, automotive, chemical, construction, civil and sport applications. Polymer reinforced composites have increased their applications due to advantageous characteristics, such as light weight, high strength, elevated strength-to-weight ratio, resistance to chemical attack and ease of handling [1-4].

Chemical resistance of compound becomes a critical factor in applications with a long-term contact. Different chemical solutions can produce degradation and a significant variation in composite mechanical properties, for instance, laminar structures destined to storage or conduction of chemical solutions like acids, alkalis or hydrocarbons.

Material can be subjected to microstructural and morphological transformations during its service life, leading to property changes due to physical and chemical aging. It is possible that the presence of moisture in the composite, whether by itself or in combination with other chemicals, can initiate undesirable structural changes within the fiber reinforcement and the matrix or the interface, and this can potentially reduce the durability of glass fiber reinforced composite.

A lot 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 inside 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].

This study aim to obtain a mathematical model about mechanical properties from polymer composites reinforced with glass fiber after immersion in organic environment. So establish

life time of the material (when changes in mechanical properties behaviour occurs) and characterization of different degradation behaviour.

2. EXPERIMENTAL

Materials

Two different types from thermosetting resin were studied. The first one was unsaturated polyester (UP) P4 TV-29 with glycol and/or phthalic base, 1.2 kg/m^3 of density. The second one was vinylester (VE) resin Atlac A-430.01, containing bisphenol-A and 1.2 kg/m^3 . Both resins provided by Basf. E-glass fiber is used as reinforcements, with a three different disposition. Mat (MAT), taffeta (TF) and multiaxial (MX) provided INP-96, S.L., JEMP Spain, G-Tensor Alcoy, S.L, each one. The properties of resins and reinforcements are presented in Table 1.

Table 1. Glass reinforced polyester specimens

Name	UPTF	UPMX	UPMAT	VETF	VEMX	VEMAT
Product Name	Polyester: P4 TV-29			Vinylester: Atlac A-430.01 (bisphenol-A)		
Molding	Manual					
E-glass Fiber	300 g/m ² 1:1 to 90°	770 g/m ² 1:1 to 0/45	300 g/m ²	300 g/m ² 1:1 to 90°	770 g/m ² 1:1 to 0/45	300 g/m ²
Matrix Resin	Polyester unsaturated 35% styrene			Vinylester 40% styrene		

Composite Materials Manufacture

Composite materials have been obtained by means of hand lay-up moulding. The resin is adjusted with the catalyst to 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. 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 °C, during three hours, in order to make sure resins reticulation. Laminates were obtained in a 30-cm square piece. According to the mechanical tests norm, correct dimensions of samples are obtained.

Exposure Environments

Chemical degradation is carried out following UNE 53-029-82 normative. Samples were immersed in different organic environments at room temperature in diesel and unleaded petrol. Mechanical properties were evaluated at different degradation time up to 20000 hours. Dimension, visual analysis, weight characterization and mechanical test were done the next day after removing the sample from the exposure environment. Samples were cleaned with

distilled water, drying 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.

Mechanical Tests

Tensile and flexural tests were made in an universal tests machine INSTRON 4204, equipped with 50 mm gauges and 50 kN load cells for tensile tests, according to UNE 53-280-79, and 1 kN load cells for three points flexural tests 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 tests has been made on rectangular samples by means of Charpy tests 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.

Weight Changes

Short time immersed samples were weighed on an electric balance with resolution 0.1 mg. The samples were removed from the chemical solutions at set dates and times. Prior to weighting, the specimens were dried in a chamber at room temperature with silica gel, during almost 24 hours, after being weighted.

Microstructure Characterization

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.

3. RESULTS & DISCUSSION

The treatment of diesel and unleaded petrol mechanical results will take to unify as organic environments due to the fact that similar behaviour have been observed. The aim is modeling similar behaviours and establishing times that show different tendencies or accused changes in mechanical properties. Life time is the time when change in mechanical behaviour occurred for these types of composites.

Properties of the materials are modeled, dividing behaviour of mechanical properties as function of exposure time in two different stages: short and long term degradation, where mechanical properties increase their value or remain constant and a second stage where properties decrease for long time degradation.

Weight Changes

In general, weight of composites increase after immersion in chemical hydrocarbon solvents, due to sorption of fluid. It is possible to explain weight changes: weight gain is due to sorption of solvent, and weight loss is due to solution of low-molecular components in 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 and 2, for the unleaded petrol environment and resin-reinforcements combinations analyzed.

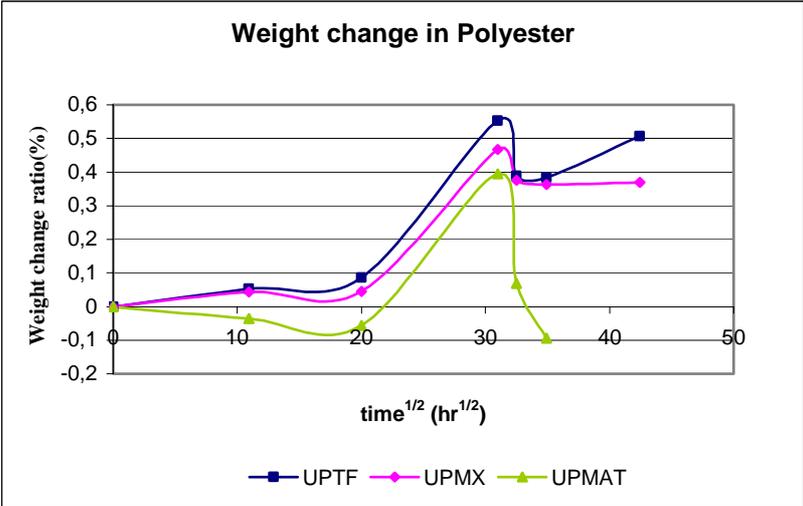


Fig. 1. Polyester weight changes in unleaded petrol

The initial increase of the weight is caused by diffusion of solvent in polyester matrix and penetration through surface cracks, as shown SEM micrographs Fig. 9 (a).

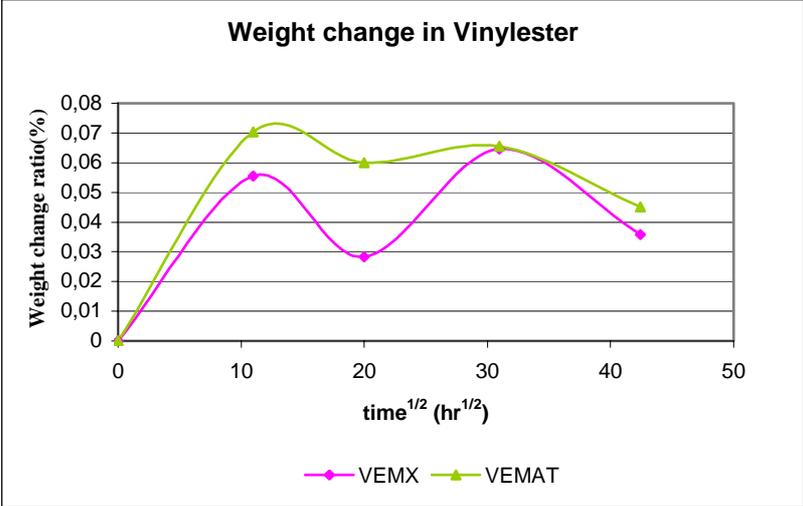


Fig. 2. Vinylester weight changes in unleaded petrol

The Fig. 2 shows an important increase of weight during short immersion times for vinylester resin.

The sorption behavior of fluid can be classified according to five different types of fluid sorption in addition to the linear Fickian behavior that were identified by Weitsman [20]. Polyester resin can follow a “two-stage diffusion” behavior, related to change in sorption conditions between stages whereas vinylester resin follows a curve that is related to irreversible damage and degradation [21].

Mechanical Properties

Flexural Tests

The main values of flexural tests were measured with an universal testing machine in a 3-point bend test. The flexural strength and modulus were analyzed as function of immersion time for different samples and environment. Due to the fact that hydrocarbons solvents have a similar flexural behaviour, allows us working at the same time with two solvents.

The flexural strength and modulus have a slightly increase or remain constant after degradation during 2500 hours (~104 days) in organic solvents as shown Fig. 3 an 4.

The values of flexural behaviour have dropped near to 86% in strength and 90% in modulus for long term degradation; being less significant for vinylester resin.

Using different linear models for each stage with different behaviour (short and long term degradation) allows us obtaining a mathematical model for flexural properties, with 8% as estimated error between model and experimental results, as shown Fig. 3 and 4.

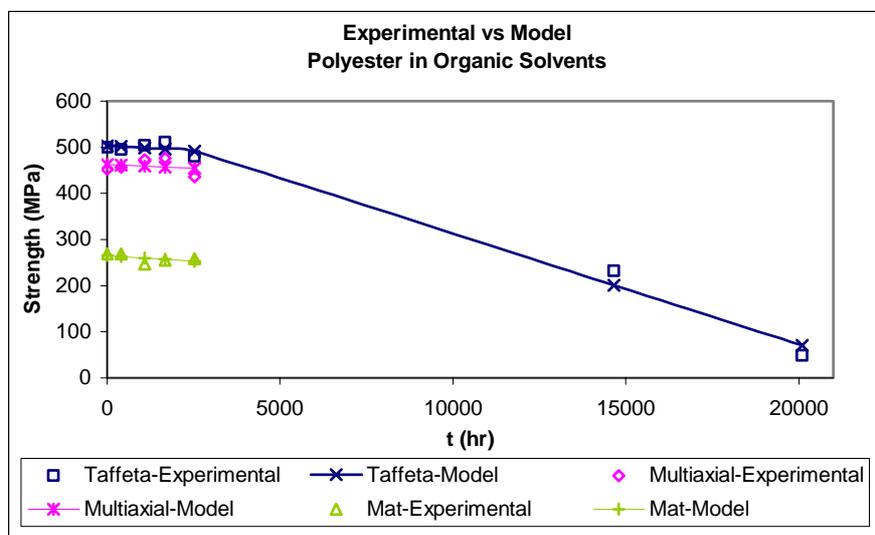


Fig. 3. Flexural strength in organic solvents

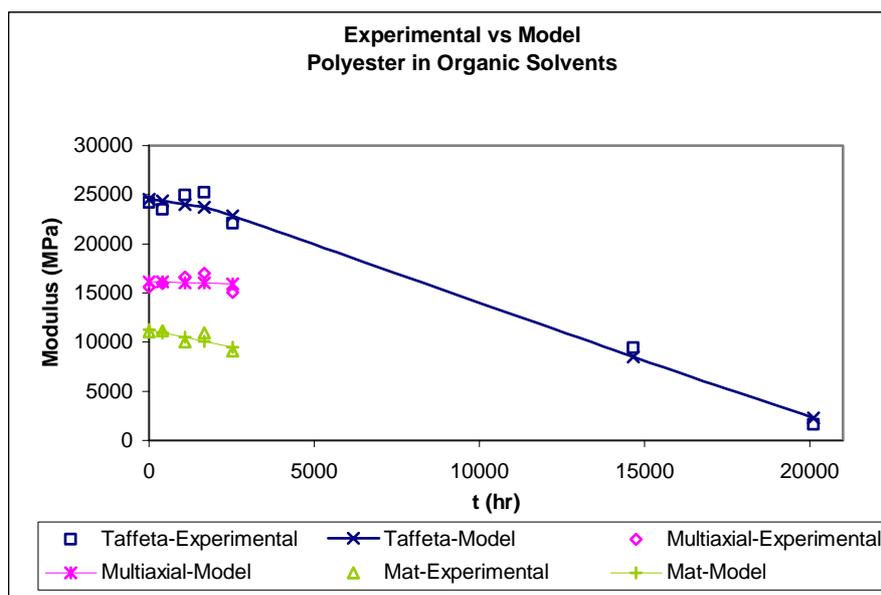


Fig. 4. Flexural modulus in organic solvents

Tensile Tests

Tensile tests were measured with an universal testing machine with a 50 kN load cell, and rate of 2 mm/min. The tensile strength and modulus were analyzed as function of immersion time. As well as with flexural properties, in this case is possible to work with both hydrocarbons solvents together.

The tensile strength and modulus have a slightly increase or remain constant after degradation during 2500 hours (~104 days) in organic solvents as shown Fig. 5 and 6.

The values of tensile behaviour dropped near to 40% in strength and 55% in modulus for long term degradation; being less significant for vinylester resin. That allows obtaining a mathematical model for tensile properties, with 7% as estimated error between model and experimental results, using different linear models for short and long term degradation, as shown Fig 5 and 6.

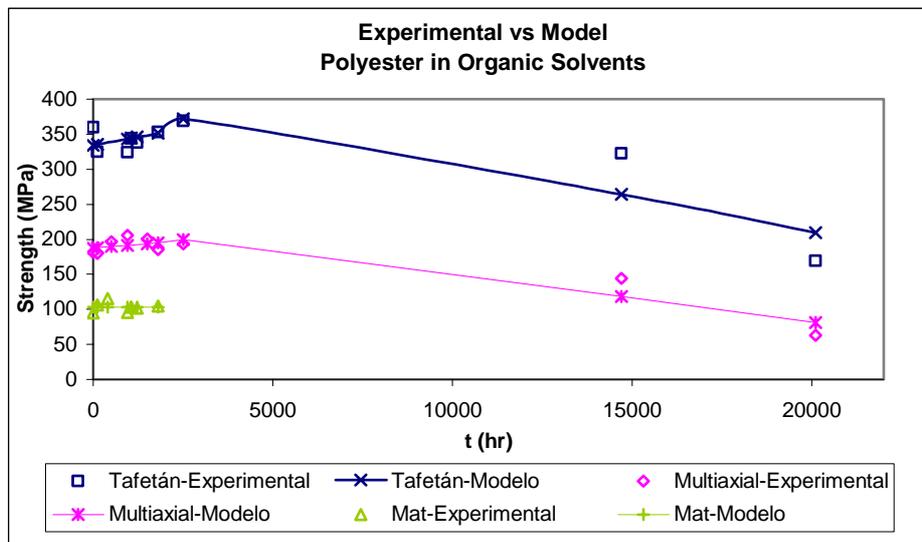


Fig. 5. Tensile strength in organic solvents

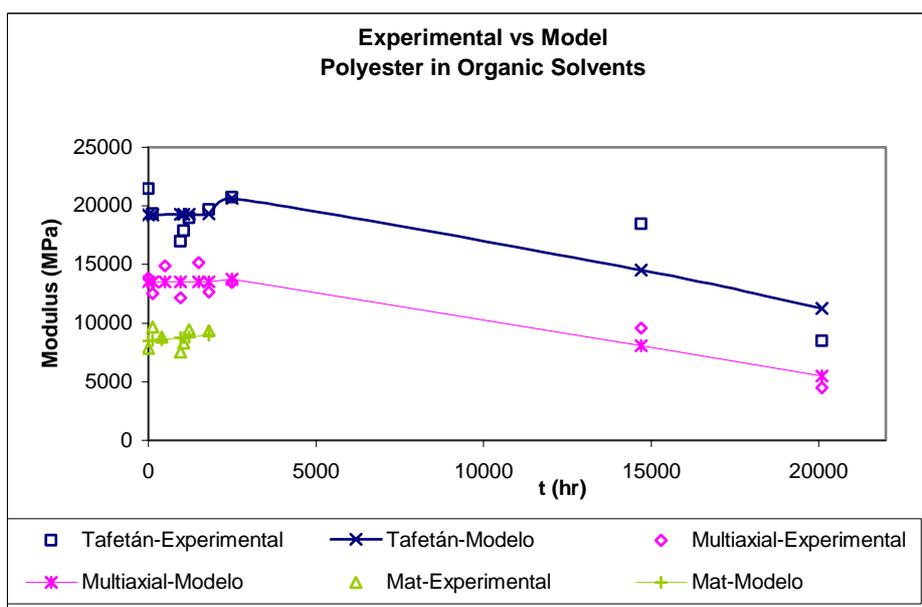


Fig. 6. Tensile modulus in organic solvents

Hardness and Impact Test

These mechanical tests are used as supplementary information about degradation effect in mechanical behavior. The most relevant aspects are: hardness has an important decrease for polyester and it is constant for vinylester; the impact energy in Charpy test has a great increase during first 1000 hours (~42 days), and then remain constant for polyester, and continues increasing for vinylester.

Infrared Spectroscopy

Transmission infrared spectra were measured using a Fourier transform infrared spectrometer Nicotet 510, 10 scans were collected and averaged at a resolution of 4 cm^{-1} . The samples were scraped from the surfaces of samples, without reinforcement, and ground using a mortar. The pellet method with potassium bromide was used to obtain IR spectra. Pellet was heated approx. $165\text{ }^{\circ}\text{C}$, during 10 minutes to avoid ambient moist uptake in sample. Fig. 7 and 8 shows the spectra obtained.

The peaks shown in the spectrum are indicative of organic material, as the peaks at 3450 cm^{-1} , $1725/1625\text{ cm}^{-1}$ (doublet) and 1050 cm^{-1} can be attributed to hydrogen bonded O-H stretching, carboxylate stretching (COO^-) and O-H bending, respectively. Peak at 2950 cm^{-1} is an evidence of C-H stretching [22].

Stretching 3450 cm^{-1} O-H decrease in the intensity in polyester, opposite effect take place in vinylester; $1250\text{-}1113\text{ cm}^{-1}$ ester C-O stretching decrease in both resins and a minor change in 1625 cm^{-1} C=O peak occurs. Fig. 7 and 8 shown IR spectra obtained for diesel.

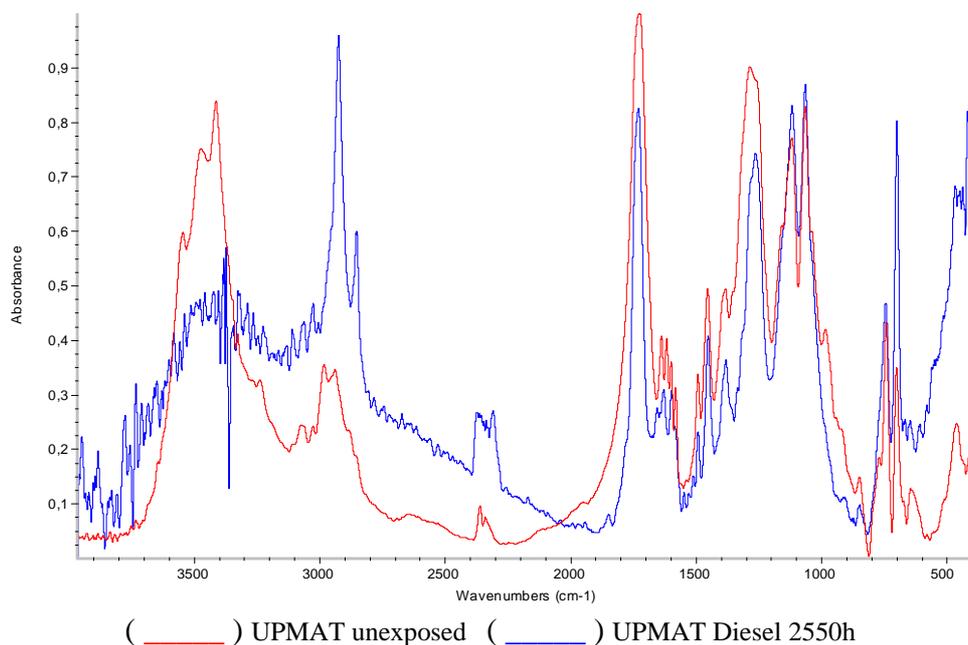


Fig. 7. Polyester infrared spectra

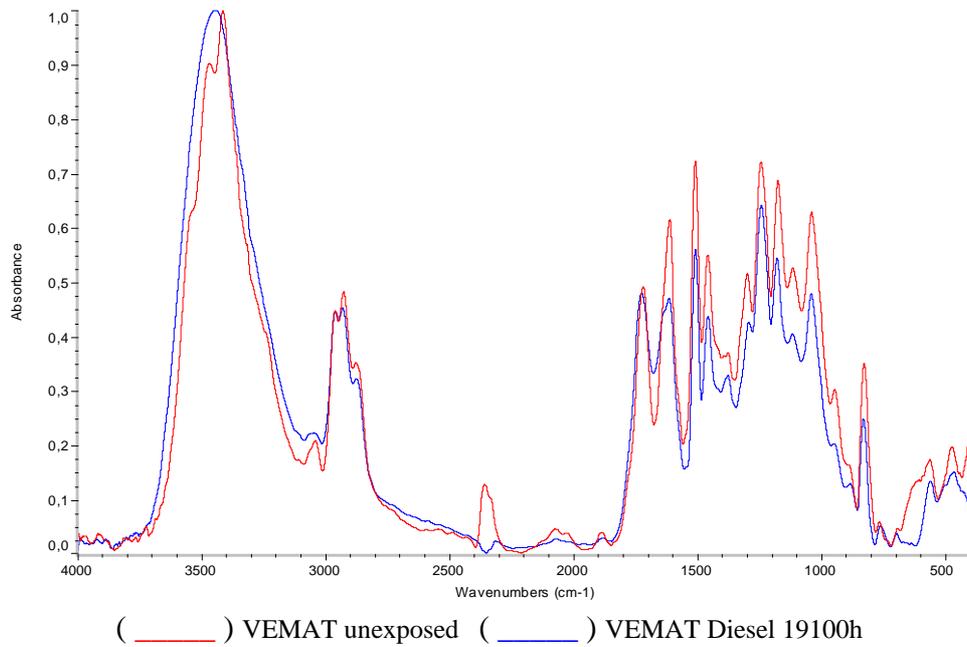
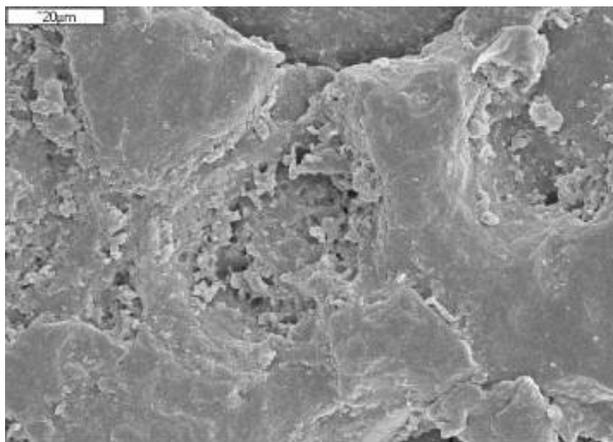


Fig. 8. Vinylester infrared spectra

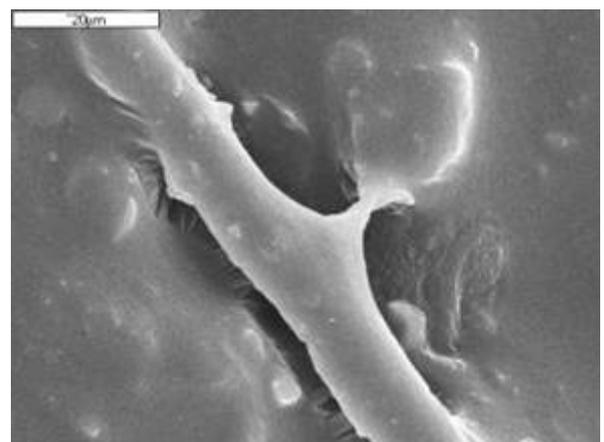
Scanning Electron Microscopy

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

The study by SEM does not reveal attack in fiber-glass of reinforcement, only single attack on the resin, as the fiber surface is essentially clean and this implies adhesive failure at the interface [23, 24] as shown Fig. 9 and 10.



(a)



(b)

Fig. 9. SEM images of surfaces immersed 14600 hours in unleaded petrol:

(a) UPTF, x1000; (b) VEMAT, x1500

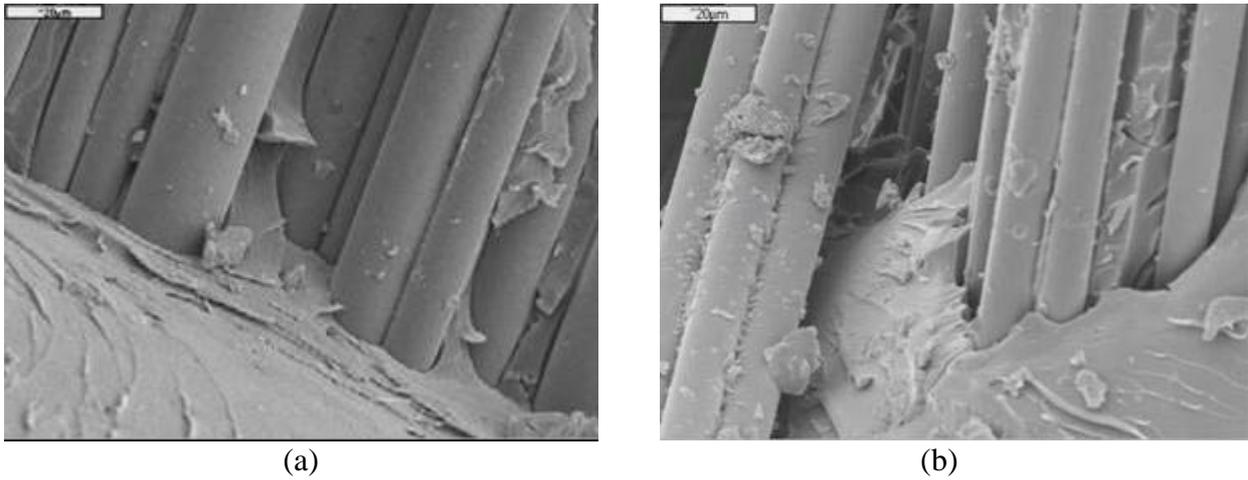


Fig. 10. SEM images of cross-sections degraded 14000 hours:
 (a) VETF in diesel, x1000; (b) VEMAT in unleaded petrol, x1000

Visual Observations

Optical microscopy gives other complementary information about external aspect of samples, color surfaces changes and external cracks that helps to understand the degradation effect. The attack caused by organic solvents is centered in matrix resin and attack organic layer of coupling agents in fibers; it explains the great decrease in mechanical properties, as shown Fig. 3-6.

4. CONCLUSIONS

Results obtained allow determining that diesel and unleaded petrol have not a significant effect in mechanical properties during the first 2500 hours. The reinforced vinylester as resin have better behavior in mechanical and physical properties.

In organic solvents, diesel and unleaded petrol, reduction of mechanical properties is due to degradation, plasticization of the matrix and interface failure. Mechanical properties have an important decrease after 2500 hours, the loss of modulus and hardness is correlated with matrix plasticization. SEM images showed that degradation is focused on the matrix and in fiber-matrix interface. Also, chemical changes are produced in resin where a surface decolouration is observed.

Infrared spectra shows that vinylester is less susceptible to the degradation than polyester due to the fact that ester functional groups are terminal and shield by methyl groups, whereas in polyester they are distributed along the main chain, being more easily accessed for reaction. Influence of type reinforcement in degradation process is clearer for vinylester than polyester resin. Similar degradation results are obtained for orderly reinforcements in vinylester, taffeta and multiaxial, and different behaviour in mat reinforcement.

Material life time has been established in 2500 hours, making possible differentiate two stages in degradation behaviour, lower and upper than life time. Behaviour has been modeled by means of linear models, with a low estimated error between model and experimental results, for each stage defined. In the first stage mechanical properties have a moderate increase or remain constant, and during the second stage, for long-term degradation, an important decrease of properties occurs.

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