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MODELING THE MECHANICAL DEGRADATION DUE TO MOISTURE ABSORPTION IN POLYMER MATRIX COMPOSITES

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This work aims to the development of a semi-empirical model for the mechanical degradation induced by moisture/water absorption in polymer matrix composite materials (PMCs). The final mathematical formulation is applicable to any composite system. Furthermore, both distilled and sea water immersion environments of different temperatures were considered. The extracted mathematical formulation was successfully applied to every single one case investigated taking into account four different micromechanical phenomena manifested during moisture uptake procedure; namely: matrix plastification, filling of internal voids with water molecules, hydrolysis of the interfacial or bulk matrix bonds and hydrogen bonds formation.

Keywords: composite materials, water uptake, humid ageing, semi-empirical modeling, degradation mechanisms

1. Introduction

Nowadays, composite materials are widely used almost in any technological field, from constructions and transportations to electronic devices, sports equipment and medicine, with emphasis to the so-called light structures. It seems like a new powerful worldwide developing material industry rises up. However, there are many questions to be answered and serious concerns to be alleviated and among them, long term durability and reliability under harsh conditions are of critical importance. More precisely, in many applications, composite materials face up to elevated temperatures, high relevant moisture levels and oxidation media. The conditions get harder if all the above phenomena coexist and, in any case, upon the time, the materials suffer from mechanical degradation. Numerous publications have focused exclusively on the investigation of the multiple effects of water immersion environment on the variation of the properties of various types of PMCs [1-5]. It would be of cardinal importance if the scientific society could predict in advance the long term evolution of the mechanical properties of a material system immersed in humid environment. In

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fact, there are too many experimental data available that prove this mechanical properties variation, but very little concerning its modeling. *To authors' knowledge, up-to-now, there is not a universal mathematical expression, existing in literature, predicting/describing the mechanical degradation induced by moisture/water absorption and applied to any composite system when being under any humid environment condition*. At first glance, it seems too complex to achieve such a target and maybe beyond today's knowledge. But, a first decisive step forward could be made if the whole degradation progress would be mathematically describable and to this direction, in this paper, a descriptive model is presented together with experimental work on two different glass strand mat reinforced polymer matrices (epoxy and polyester), immersed in natural seawater, as a first attempt of model application. Moreover, a series of experimental data taken from literature are used in order to serve the model validation and by this, to confirm the model's flexibility to fit to as many as possible different material systems and environmental conditions. The model combines clear mathematical and natural interpretation as well as experimental data, incorporating a number of different moisture/water absorption mechanisms, in a systematic approach to achieve a better understanding of the evolution of the whole phenomena investigated. In the present work, the application of the model is limited to fit only the variation of the elasticity modulus with possible future extension to other mechanical properties such as the aged composite materials strength.

2. Background

2a. Moisture absorption

Studying the effect of water absorption on PMCs behavior is of significant interest, especially when designing structures for highly aggressive environmental conditions. However, studying the ageing effects in such structures is not an easy task at all. It includes the effect not only of the amount of the absorbed moisture, the effect of water temperature and the time of immersion, but also the effect of the interaction of all these parameters together. Apart from pure scientific interest in understanding the net physical phenomenon, the practical goal of this kind of research is to minimize the probability of unexpected failure of structures. Moisture uptake in polymer composites mainly affects the properties of the matrix and fibre–matrix interface but also the fibers to some extent, depending on its propensity to absorb water [7].

2b. Diffusion mechanisms

There are three main different mechanisms for the water molecules to penetrate and diffuse into the PMCs:

(1) Direct diffusion, also known as Fickian diffusion, of water molecules through the matrix and, in some cases, through the fibers. The water molecules enter the polymer network via the free volume space in the transmolecular regions and among the high-density macromolecular chains.

(2) Capillary flow of water molecules, or water wicking, along the fibre/matrix interface followed by diffusion from the interface into the bulk resin with growing intensity as the compatibility between matrix and fibre gets worse.

(3) Accelerated diffusion through micro-cracks, micro-pores, defects and impurities in the material's structure. The term 'accelerated' refers to the fact that the holes coming from the manufacturing of the materials are bigger than free space voids coming from the polymerization.

It is highly expected that the above-mentioned mechanisms have a coordinated action with each other, leading to a deviation from the general accepted Fickian behavior.

2c. Micromechanical phenomena

After long term immersion in a water medium, the material suffers from many chemical and physical changes as a result of multiple degradation mechanisms that take place through the time of aging. Consequently, a serious variation of the material's mechanical behavior is obvious**.** The different occurring mechanisms that may provoke these variations are the following:

(1) Filling of internal voids
(2) Hydrolysis
(3) Forming of hydrogen bonds
(4) Plasticization

It is well known, that during the first short period of immersion, the water molecules entering the composite material, occupy initially the internal voids situated both in bulk matrix and into the interphase region between the filler and the matrix. Little by little, the water molecules start to diffuse through the free volume space and a redistribution of internal stresses occurs. In fact, water invasion provokes swelling that firstly may lead to better filler-matrix adhesion as water molecules are situated mainly into the interphase region being under compressive stresses from the bulk matrix. However, as time passes, the bulk matrix also starts to suffer from swelling and thereafter, the interphase becomes thicker and as a result, less capable to transfer the external loads from the matrix to the filler. On the one hand, this filling of air trapped holes render the material from non-continuous to a continuous one, leading to stress continuity as well, but, on the other hand, this water presence assumes also a more aggressive stance for the material, that is to say the activation of hydrolysis reactions onto the weak interfacial bonds and secondary bonds of the bulk polymeric matrix network. The hydrolysis consequence is the formation of new free space to be captured by water molecules. All this procedure enhances the role of water as a plasticizer and favors the molecular mobility and the reduction of the degree of adhesion between the two main phases of the composite. Thus, the occurring plasticization leads to a more ductile material with a reduced glass transition temperature (T_g) as well. Furthermore, hydrogen bonds are formed between water molecules and macromolecular chains and this phenomenon is enhanced by the hydrolytic action of water that creates more free radicals on the secondary polymer network branches which results to the formation of additional hydrogen bonds. The intensity of the above-mentioned mechanisms depends on both the immersion temperature and time. To end up, the antagonistic nature of each phenomenon by itself and in coordination with the other occurring phenomena at the same time is much more than evident.

2d. Effect of water absorption on the macromechanical behavior of composites

The usual conception found in literature concerning the evolution of the mechanical behavior due to water uptake refers to matrix plastification as the one and only one parameter affecting the overall behavior of the composite, excluding all the rest of the mechanisms already mentioned above. However, as already observed and reported in authors' previous publications [6-8], the overall trend of variation of both the reduced static and dynamic modulus of polymeric particulate and fiber composites with time of immersion, follows a complex continues curve as that one schematically shown below in Fig.1.

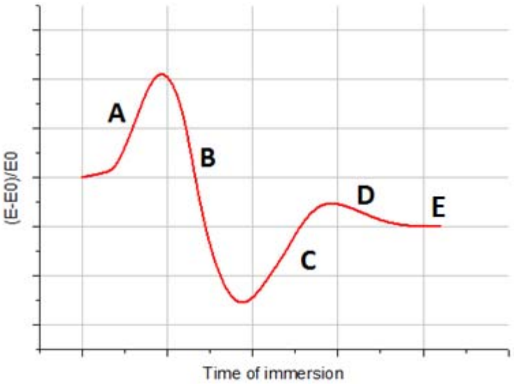


Fig. 1. Schematic curve for the variation of elasticity modulus as a function of immersion time

The complex shape of this curve is divided into four distinct regions, from A to E, which represent the possible increasing, decreasing and constant trends of the reduced elastic modulus variation and correspond to the different micromechanical phenomena already described above. The curve illustrated is absolutely schematic and could also be reversed without losing its physical interpretation. The main question that remained unanswered up-to now is the following one: Is there any universal law describing the observed behavior which would be valid irrespectively of the material tested and the environmental conditions? In the present paper we are presenting a semi-empirical model described by a mathematical formulation predicting such a behavior, the validation of which has been realized both through our own experimental results as well as through results taken from literature.

3. Model presentation

From mathematical point of view, the final expression predicting the experimental points' variation for the modulus of elasticity as a function of time of immersion, is constituted of two superposed exponential functions. This mathematical expression, is the one given by eq. (1) and predicts the reduced elastic modulus of the material considered. In this equation, E_c refers to the ''current'' value of the elasticity modulus while E_0 refers to the initial dry-state value. The value of $y(\infty)$ is considered as the value of the reduced elastic modulus of the saturated material. In order to ensure a physical meaning of the expression two boundary conditions were used. The first refers to zero time, i.e. when the material is dry and no property variations have happened yet. This condition is shown in eq. (2). The second, refers to saturation level when typically, after very long time of immersion, no more interaction between aqueous environment and composite material is under progress. For this reason, the time derivative of the equation for long immersion times gets also value equal to zero as shown in eq. (3). Two coefficients are used as well. Coefficient T refers to the time corresponding to an abrupt change in the slope of the curve (i.e. from decreasing to increasing). This phenomenon appears with remarkable consistency in every single elastic modulus curve examined in this work from either experimental work done in the lab or taken from literature. Furthermore, coefficient C_1 is a fitting factor that, for every one case investigated, takes values, both positive and negative always in the range between zero and one. Although C_1 value is determined by the user, the too short range of values, for every application case, creates the prospective of investigating its origins, in a way to be able to pre determine it, and by this way reduce the model input factors.

$$y=\frac{E_c-E_0}{E_0}=C_1*\left(\frac{t}{T}\right)*e^{\left(-\frac{t}{T}\right)}-y(\infty)*\left[e^{\left(-\frac{t}{e*T}\right)}-1\right] \qquad (1)$$

$$y(0)=0 \qquad (2)$$

$$\left.\frac{dy}{dt}\right|_{t\to\infty}=0 \qquad (3)$$

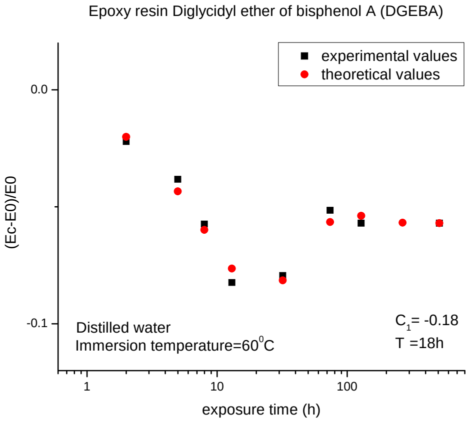
4. Materials and methods

During the study there have been investigated two of the most commonly applied composite materials in maritime and naval constructions; Glass/Epoxy and Glass/Polyester. Both composites were reinforced with an E-glass strand mat satin woven fabric supplied by Seal Co. (Italy). A satin weave has each warp and weft yarn going over one yarn and under a number of yarns. The Epoxy resin used was a CY219 supplied by Renlam and the Polyester resin was thixotropic polyester supplied by Five Stars. The specimens have been manufactured using a simple wet hand lay-up technique. In both cases, three layers of glass mat have been used. After fabrication the specimens were cured at 60^{o}C for 24 hours. Specimen dimensions were 100mm x 12,8mm with 3mm in thickness with variance less than 4%. Specimens have been immersed in sea water in a thermostatic bath at 40^{0}C for time durations of 2, 4, 8, 16, 20, 24, 48, 96, 192, 288, 384, 552, 720 and 1008 hrs. The experimental procedure consisted with the removal of three specimens out of the bath and carefully air dry surface moisture, before weighing them carefully by means of a balance of high accuracy. Each time, the amount of water uptake was measured. The flexural modulus of the composites was then determined for each immersion time using a three-point bending test method. The extracted experimental curves are shown below (Fig. 2b.-c.).

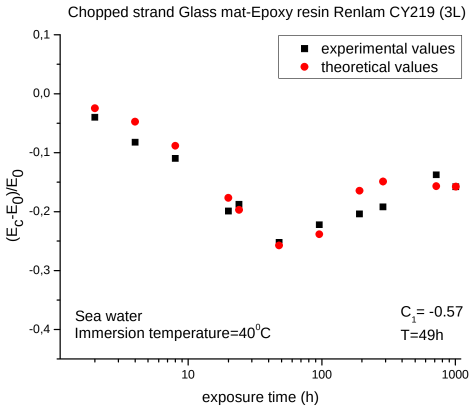
5. Model validation

In order to strengthen the potentiality of the model developed, many experimental works were borrowed from the literature for further model application. In this way, the application cases range was expanded also to pure epoxy resin (Fig. 2a.) [7], epoxy resin/unidirectional glass fabric 8-layer laminate (Fig. 3a) [11], vinylester/glass woven fabric 5-layer laminate (Fig. 4a.) [9], epoxy/unidirectional flax fabric 11-layer laminate (Fig. 3b.) [11], polypropylene/wood floor composites (Fig. 3c.) [10] and epoxy/iron particles composites with different filler volume fractions (Figs 4b.-d.) [6]. In the end, ten different cases were considered. Judging from the type of the curves shown below, the presentation of the results is divided into three different groups. Each one of the groups contains curves with the same general behavior, that is to say, same alternating trends that composite materials seem to follow before end up with a constant plateau. The classification by shape of the curves serves two purposes: On the one hand, the mechanical behavior similarity between different material systems and immersion medium conditions is shown. On the other hand, the fact that all these phenomenally different expressions of water uptake phenomenon come under a universal mathematical formulation is practically proved as well. The explanation that lies behind this agreement achieved has to do with the nature of all above mentioned mechanisms and the time consideration of the experiment. In fact, depending on the materials and the immersion conditions, the above-analyzed antagonistic trends are demonstrated with major or minor effect on the overall mechanical behavior variations and at the same time, the time interval for every one mechanism action changes.

<u>Group A</u>



a.



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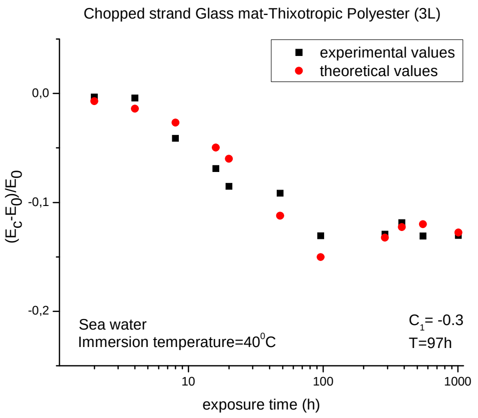
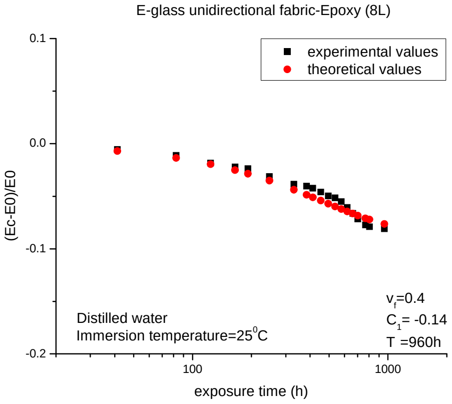


c.

Fig. 2. : Variation of elasticity modulus as a function of immersion time for a. Epoxy resin ,b. Glass chopped strand mat fabric/Epoxy resin and c. Glass chopped strand mat fabric/Polyester specimens.

Group B



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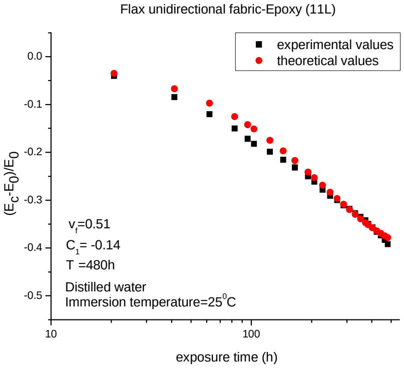

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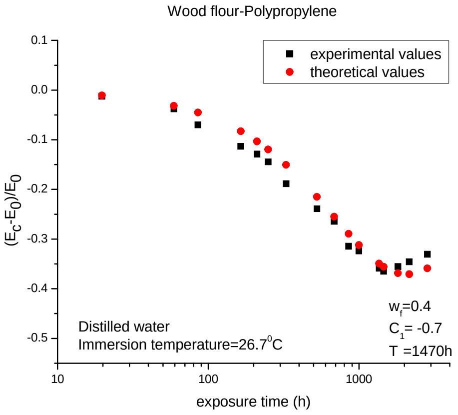
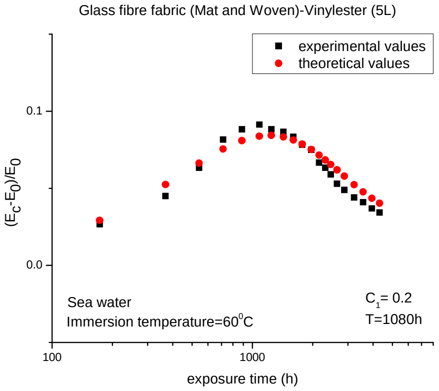


c.

Fig. 3. : Variation of elasticity modulus as a function of immersion time for a. Glass UD fabric/Epoxy resin ,b. Flax UD fabric/Epoxy resin and c. Wood floor/Polypropylene specimens.

Group C



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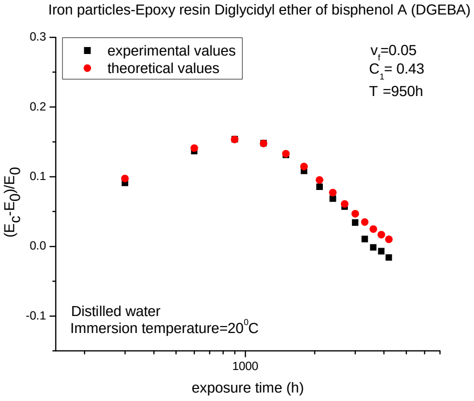

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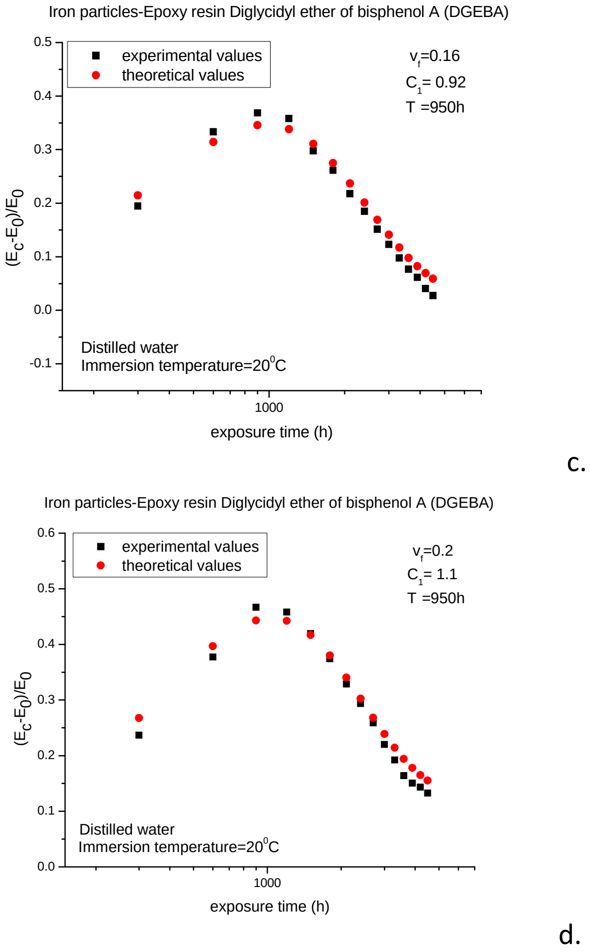

Fig. 4. : Variation of elasticity modulus as a function of immersion time for a) Glass fabric/Vinylester, b. Iron Particles/Epoxy resin (v_f=0.05%), c. Iron Particles/Epoxy resin (v_f=0.16%) and d. Iron Particles/Epoxy resin (v_f=0.2%).

As it is obvious from the figures above, a very similar behavior characterizes each one of the curve groups and for each and every separate experimental curve a very good mathematical approach has been achieved. Thus, to the time, the model can be considered as absolutely validated.

6. Conclusions

A mathematical description of experimental data for many different composite materials and immersion conditions into different types of water (seawater/distilled water) has been performed followed by respective physical explanations of the different mechanisms incorporated at different time intervals and characterized by non stable and univocal behavior. As it is obvious from the diagrams shown above, a very satisfactory agreement between experimental points and theoretical approach as derived from the model can be observed. A consideration of different modulus variation due to water absorption curves that constitute a part of a general more complex curve was also introduced. The part of the general curve representing the specific behavior of a material after immersion into water, depends on the interaction of the incorporated water absorption mechanism, its effect on the mechanical properties variation as well as on the selected time intervals of observation/measurements during water absorption experimental procedure, and finally on the total time duration of immersion.

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