

# Effect of Hygrothermal History on Water and Mechanical Properties of Glass/Vinylester Composites

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**ABSTRACT:** The effects of hydrothermal aging on the mechanical and viscoelastic properties of vinylester (VE)/unidirectional glass-fiber composites are reported. The studies are done by means of a dynamometer (INSTRON) and a dynamic mechanical thermal analyzer (Perkin Elmer). The studies are carried out at three different temperatures: 20, 40, and 60°C. The adhesion between the fibers and matrix is studied by scanning electron microscopy (SEM) microphotographs. Flexural strength, flexural modulus, storage modulus in the glass state ( $T_g - 50$  K), in rubber state ( $T_g + 50$  K), and the glass transition temperatures are also investigated. These parameters are determined in the case of the matrix and composites materials, for the initial and final states. The diffusion coefficients are calculated by using the simplest Fick's equation.

**KEY WORDS:** mechanical properties, diffusion coefficient, water absorption, vinylester, glass fibers, composites.

## INTRODUCTION

**G**LASS-FIBER REINFORCED UNSATURATED vinylester (VE) composites, which are commonly used in several applications, exhibited a very interesting relationship of their mechanical properties and their cost [1–3]. In automotive, aeronautical, and aerospace industries, the long-term stability measured by their mechanical properties is of great interest. In these applications, they are in contact with liquids or vapors that affect

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the long-term properties of the material. Hence, in the use of composite materials, the environmental aspects have to be taken into account [4,5].

Water aging may affect the matrix behavior through variation in chemical and physical properties. The extent of the effect depends on the chemical structure of the matrix, the temperature, and environmental humidity exposure [6,7].

In the case of composite materials, water not only affects the matrix but also attacks the fiber–matrix interface which is the determining factor in the reinforcement of glass-fiber/polymer matrix composites in wet environments [8].

The most common water entrance mechanism into a composite material is diffusion. Although two other mechanisms are possible: the capillarity along the fibers, the interface and transport by microcracks [9]. The last mechanism can be activated after a material damage produced by water exposure.

Water entrance into a polymer matrix leads to several effects: plasticization of the matrix due to the interaction between their polar groups and water molecules, microcraze formation due to environmental stress, leaching of the unreacted monomer, and sometimes to resin degradation. Relatively short exposure times lead to almost reversible plasticization that produces a decrease in the glass transition temperature ( $T_g$ ). The extent to which this temperature falls depends on the amount of water absorbed and it can be described by the free volume theory [10,11].

The long-term behavior of composite materials as environmental effect can be evaluated by real time observations exposed to natural conditions for several years. However, accelerated aging tests seem to be useful by means of organizational and economic reasons [12].

Investigations on the history of dependence of water absorption in resins and composites rarely appear in scientific literature. The reversibility of wet/dry cycle, the damage induced by the absorption process, the effect of this damage on the later stages of the absorption process and on subsequent cycles, is of practical interest [13].

The aim of this work was to study the effect of cyclic absorption process on the mechanical properties of glass-fibers/VE composites.

## EXPERIMENTAL

### Materials

The composite matrix used was a vinyl ester resin (VE, Derakane 350 from Dow Chemicals), provided by Poliresinas San Luis, Bs. As., Argentina. This resin used as a composite matrix contains about 45 wt% styrene. It can be cold-cured using methyl ethyl ketone peroxide (MEKP, Pergot 50) and 2.5% cobalt naphthenate solution (CN, Fluka). The composition of the VE mixture was the following: 100 g of VE, 0.5 wt% CN, and 1.5 wt% MEKP. The E-unidirectional glass fiber of 300 g/m<sup>2</sup> which was used as reinforcement was provided by Vetrotex.

The VE samples were cast at room temperature between glass plates separated by a rubber of thickness 3 mm. The plates were cured with a slow temperature program 1 h at 40°C, 1 h at 80°C, 2 h at 100°C, and 8 h at 140°C.

The glass fiber composites were prepared by manual hand-lay-up with 60% of fiber mass fraction. The plates were cured with the same temperature program as the matrix.

The fiber content was determined by burning the composite samples following the ASTM D678 recommendations.

## Methods

Matrix and composite samples of  $120 \times 20 \times 2 \text{ mm}^3$  were cut from plaques. These samples were immersed in distilled water at 20, 40, and 60°C. The samples were removed from the bath at fixed times and were carefully dried with an absorbent paper. Their weight change was determined by means of a microbalance calculated at 10 mg. At least four specimens of each material were used. Tests were carried out in two cycles.

The first cycle was completed when a constant water content was reached. After that, the samples were dried in an oven at 110°C till a constant weight is reached and then the samples were put in water again. The weight change was determined again until a constant weight is observed.

In order to determine mechanical and dynamical mechanical properties, all the samples were dried in an oven at 110°C until constant weight is reached.

Specimens for dynamical mechanical tests, with a nominal dimension of  $20 \times 2 \times 1 \text{ mm}^3$  were cut from the resin and composite samples. The measurements were done in a Perkin Elmer DMA-7 at a temperature range of 10–250°C, a heating rate of 5°C/min, and a frequency of 1 Hz. The static and dynamic stresses used were 2.4 and 2.15 MPa, respectively. The span used was 20 mm.

Flexural tests were carried out using an Instron 4467 and the crosshead speed was chosen according to ASTM D790-93 recommendations. An average value of at least four samples was determined.

Scanning electron microscopy (SEM Phillips 500) was performed on fracture surfaces from the flexure specimens.

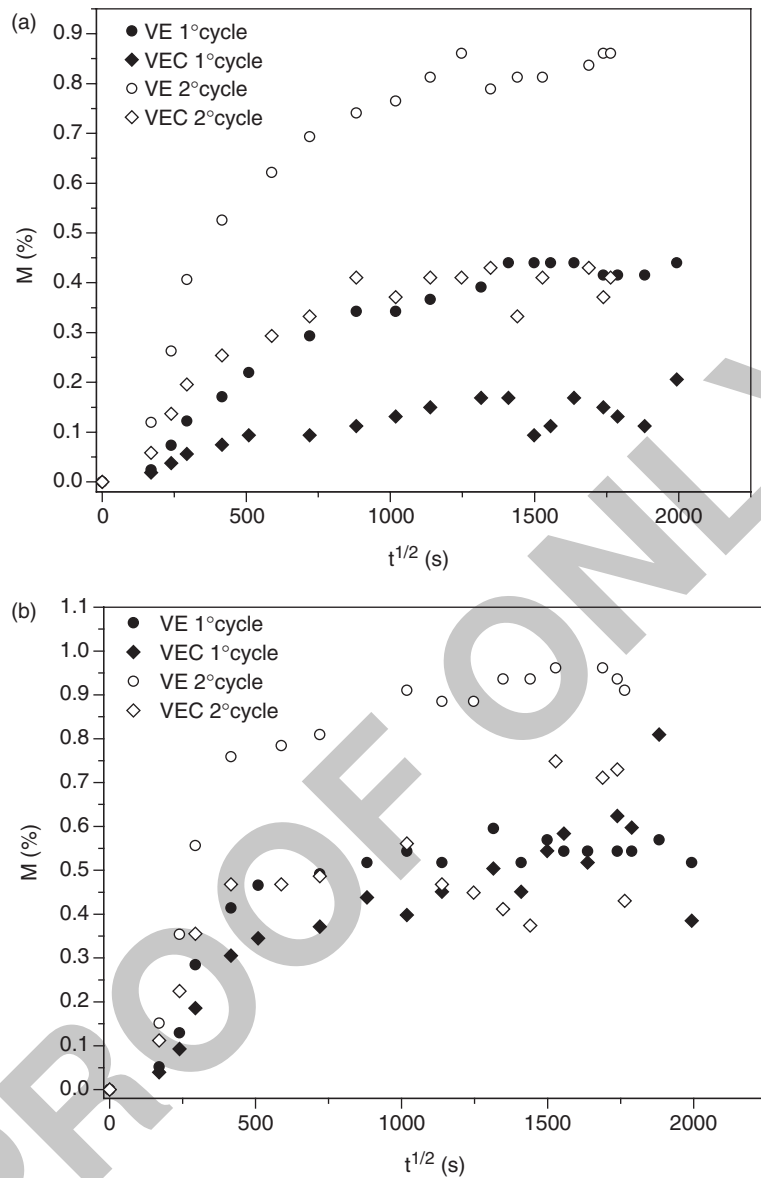
## RESULTS AND DISCUSSION

### Water Absorption Behavior

Weight change (percent) during water absorption was determined by using the following equation:

$$M\% = \frac{M_t - M_0}{M_0} \times 100 \quad (1)$$

where  $M_t$  is the mass at a time  $t$  and  $M_0$  is the weight of the dry sample. The weight changes of studied materials during immersion in water at different temperatures for first and second cycles are shown in Figure 1. In the case of composite material, no significant interfacial capillary flow occurs during the initial Fickian step where water absorption occurs mainly by diffusion through the matrix network. At longer immersion times, a positive deviation from Fick's law was attributed to interfacial degradation and cracking (as shown in Figure 3).



**Figure 1.** Specimen water uptake as a function of the square root of the time in seconds for different materials at different bath temperatures: (a) 20°C, (b) 40°C, and (c) 60°C.

The VE samples gained weight during immersion. The weight continuously increased with immersion time. The water equilibrium concentration,  $M_{\infty}$ , was taken as the maximum in the curves. The values of this parameter are shown in Table 1. If we consider a perfect adhesion between fibers and matrix and without voids, we can calculate:

$$M_{\infty c} = M_{\infty m} \text{ wt\%matrix} \quad (2)$$

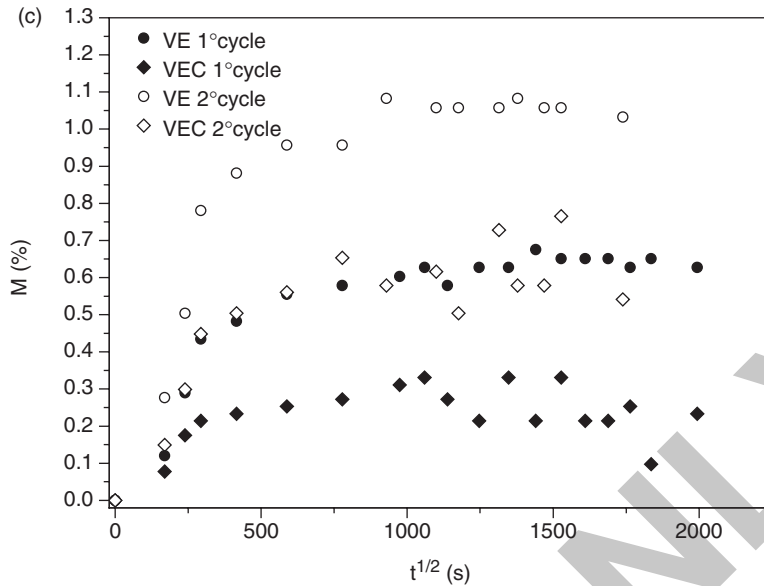


Figure 1. Continued.

**Table 1. Water equilibrium concentration,  $M_{\infty}$  for matrix and composites, in the first and second cycles at different temperatures.**

Bath temperature (°C)	$M_{\infty}$ (%)	
	1° cycle	2° cycle
20		
Matrix	0.463	0.825
Composite	0.206 (E)	0.415 (E)
	0.185 (C)	0.330 (C)
40		
Matrix	0.579	0.955
Composite	0.476 (E)	0.740 (E)
	0.232 (C)	0.382 (C)
60		
Matrix	0.656	1.105
Composite	0.264 (E)	0.997 (E)
	0.262 (C)	0.442 (C)

E, experimental; C, calculated.

But we consider that if this calculation is made, the effect of the fiber and fiber–matrix interface is not taken into account.

The matrix absorbed more water content than composite materials. In all cases, the experimental values were higher than the calculated ones, hence, we can conclude that, although the matrix is the most important in water absorption process, the interface, voids content, and imperfect adhesion between fiber and matrix play a role in the composites water uptake. The main differences were observed in the second cycle.

**Table 2. Changes in the glass transition temperature after immersion.**

Material	Initial	$T_g$ (°C)					
		1° cycle			2° cycle		
		20°C	40°C	60°C	20°C	40°C	60°C
Matrix	103.4	103.3	103.2	103.1	102.9	102.7	102.5
Composite	122.4	122.4	124.0	118.1	120.7	114.0	114.0

As expected, the fibers act as inert on the VE matrix water absorption. The saturation value for the matrix was higher than that of the composites, for both the cycles and all studied temperatures. On the other hand, the maximum water absorption increased with both the cycle and the temperature.

An important effect that should be taken into account is the immersion temperature in relation to the  $T_g$  of the sample. The absorbed water due to plasticization effect lowers the  $T_g$ . The  $T_g$  of the neat matrix and composites was obtained by means of the  $\tan \delta$  peak in the DMA measurements. The initial  $T_g$  of the VE matrix was close to 103°C. As a consequence, the determination of the water absorption measurements for the all temperatures was taken in the glass state for the initial samples.

Table 2 shows the  $T_g$  for the materials before and after immersion on the water at different temperatures and on dried specimens. In case of the matrix, the change in the  $T_g$  after immersion was not significant because this material did not degrade by water sorption.

The  $T_g$  of composite materials was higher than that of the matrix. This effect can be explained by the impediment of fibers to the polymer chain movement.

Water uptake has been modeled by Fick's second law for several materials. Fick's law is not applied to inhomogeneous materials, so when no chemical interaction exists between the material and water, diffusion is the only mechanism for sorption and the material structure change is negligible. These composite materials do not fill some of these assumptions: (a) composite materials are inhomogeneous in nature, (b) hydrophilic resins can interact with water, (c) capillarity could be another sorption mechanism due to the fiber-matrix interface, and (d) the dimensions of the materials can be changed during immersion.

An effective diffusion coefficient,  $D_{\text{eff}}$  can be estimated taking into account only the increase weight during immersion, and defining a maximum increase of weight in the specimen ( $M_{\text{max}}$ ) instead of an equilibrium value ( $M_{\infty}$ ). This coefficient considers all the mechanisms involved in water absorption process like a diffusion process.

Fick's second law can be expressed in terms of time ( $t$ ) and water concentration ( $c$ ) by the following equation [14]:

$$\frac{dc}{dt} = D_{\text{eff}} \frac{d^2c}{dx^2} \quad (3)$$

where  $x$  is the direction transverse to the flow direction.

**Table 3. Effective diffusion coefficient,  $D_{\text{eff}}$ , for matrix and composites, in the first and second cycles at different temperatures.**

Bath temperature (°C)	$D_{\text{eff}}$ (mm <sup>2</sup> /s)	
	1° cycle	2° cycle
20		
Matrix	$1.91 \times 10^{-6} \pm 3.4 \times 10^{-7}$	$8.61 \times 10^{-6} \pm 2.1 \times 10^{-6}$
Composite	$1.56 \times 10^{-6} \pm 6.7 \times 10^{-7}$	$6.62 \times 10^{-6} \pm 7.2 \times 10^{-7}$
40		
Matrix	$5.32 \times 10^{-6} \pm 6.6 \times 10^{-7}$	$9.48 \times 10^{-6} \pm 8.6 \times 10^{-6}$
Composite	$5.53 \times 10^{-6} \pm 6.4 \times 10^{-7}$	$1.02 \times 10^{-5} \pm 1.2 \times 10^{-6}$
60		
Matrix	$1.12 \times 10^{-5} \pm 2.4 \times 10^{-6}$	$9.16 \times 10^{-6} \pm 2.4 \times 10^{-6}$
Composite	$1.04 \times 10^{-5} \pm 4.4 \times 10^{-7}$	$9.89 \times 10^{-6} \pm 7.4 \times 10^{-7}$

Experimentally,  $D_{\text{eff}}$  can be obtained from the initial slope of  $M\%$  (water absorption percent) versus  $t^{1/2}$  (square root of immersion time) curve as follows [13]:

$$D_{\text{eff}} = \pi \left( \frac{h}{4M_{\text{max}}} \right)^2 \left( \frac{dM}{dt} \right)^2 \quad (4)$$

where  $h$  is the specimen thickness and  $M_{\text{max}}$  is the maximum relative water uptake.

Table 3 shows the  $D_{\text{eff}}$  obtained for these materials at different temperatures and times.

For the first cycle, the maximum water content or the relative water uptake and effective diffusion coefficient increase with the water temperature because water acts as plasticizer which decreases the  $T_g$  value and increases the flexibility of the matrix.

The composite material is affected by the voids and the presence of the fibers but fibers act inert for water absorption. At lower temperature (20°C), the unidirectional glass fibers produce a decrease in the diffusion coefficient compared to the matrix.

An exponential equation can be used to model the diffusion coefficients obtained from Equation 3 as a function of the bath temperature.

$$D_{\text{eff}} = D_{\text{eff0}} \times \exp\left(-\frac{E_a}{RT}\right) \quad (5)$$

where  $D_{\text{eff0}}$  is the pre-exponential factor,  $T$  is the test temperature in absolute scale (K),  $R$  is the universal gas constant and  $E_a$  is the 'apparent' activation energy for the diffusion process.

In the case of composite materials, the diffusion coefficient value depends on the several factors such as: (1) temperature, (2) voids content, (3) free volume, (4) network formed, (5) fiber–matrix interface, etc. Using the Arrhenius equation and separating the effect of the temperature in the value of the activation energy, the other factors are included in  $D_{\text{eff0}}$  value.

Figure 2 shows the relationship between  $D_{\text{eff}}$  and temperature, pre-exponential factor, and activation energy which was obtained from this figure for

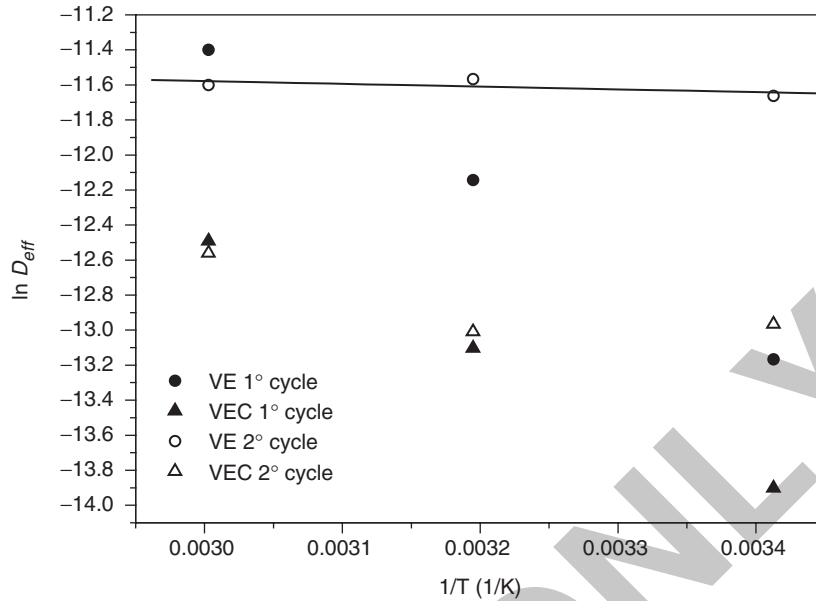


Figure 2. Arrhenius plot of the effective diffusion coefficient vs inverse of temperature for different specimens.

Table 4. Parameters of Arrhenius model obtained for studied materials.

Material	$M_{\infty}$ (%)					
	1° cycle			2° cycle		
	$D_{\text{eff}0}$ (mm <sup>2</sup> /s)	$E_{\text{act}}$ (kJ/mol)	$r$	$D_{\text{eff}0}$ (mm <sup>2</sup> /s)	$E_{\text{act}}$ (kJ/mol)	$r$
Matrix	4.936	35.9	0.9986	$1.5 \times 10^{-6}$	1.3	0.664
Composite	0.120	28.7	0.9920	$5.76 \times 10^{-5}$	6.0	0.790

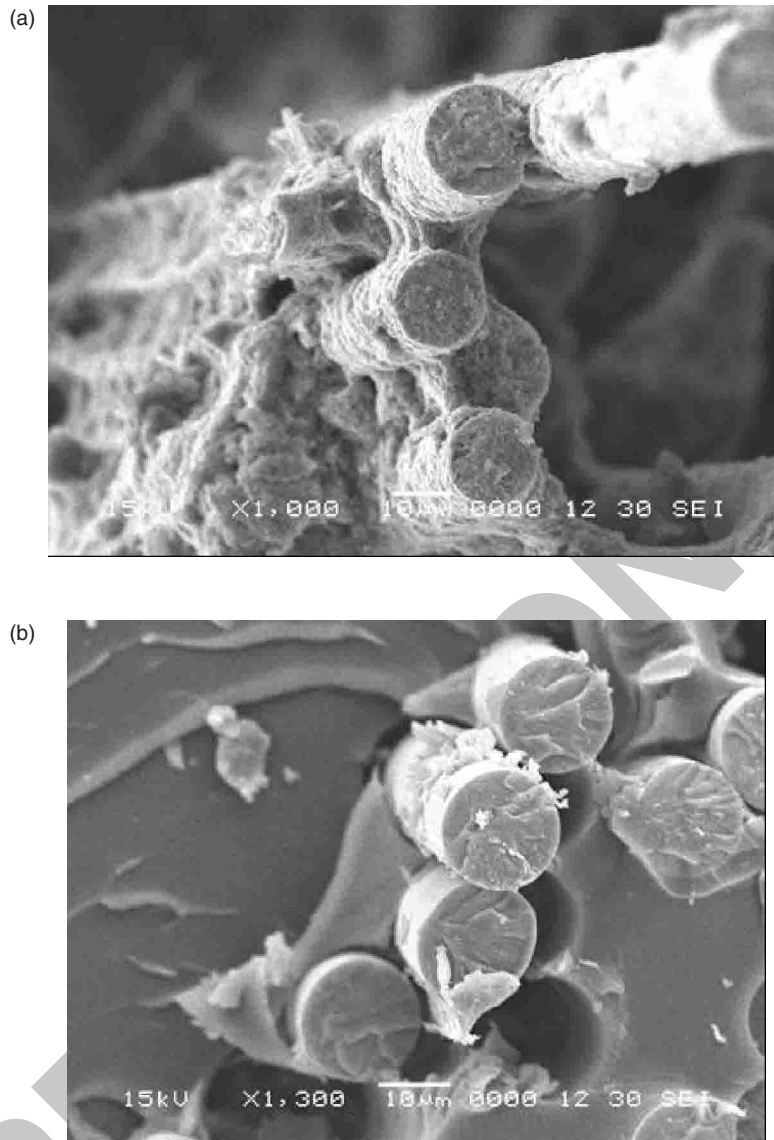
different materials. The resulting pre-exponential factors and activation energy values are shown in Table 4.

In the case of the first cycle, it is clear that, nevertheless the material, the effective diffusion coefficient increased when temperature increased because diffusion is a thermally activated process. In the second absorption process, the parameter seems to be independent of the test temperature and this behavior may be due to the effect that hot water produces on the material: voids creation, extraction of soluble materials, and postcuring. Such effect is not important in the second cycle because the samples are at their final state.

The activation energy values show that unidirectional glass fiber composites are less affected by temperature expressed by the lower activation energy value in the first cycle as a consequence of the fiber quantity or matrix dilution effect.

For the second cycle, the fiber–matrix interface and voids could be the main cause of the activation energy and pre-exponential factor decrease.

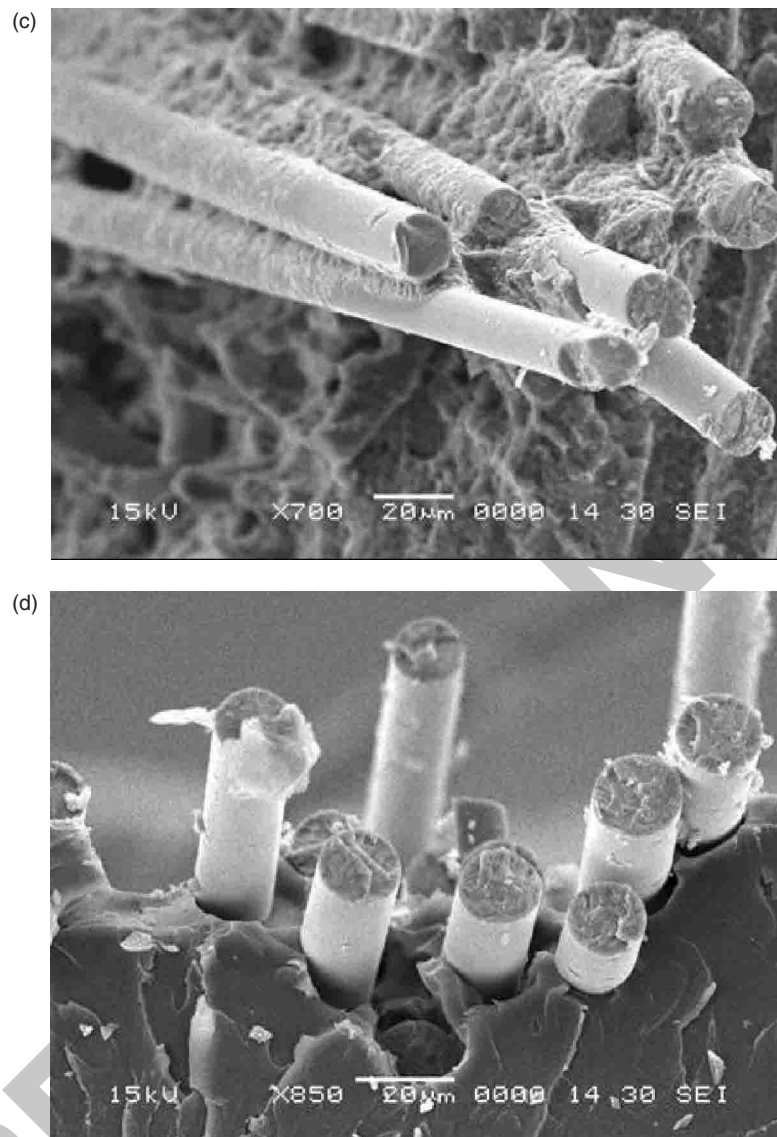




**Figure 3.** SEM micrographs of composite materials after water exposure at different temperatures and both cycles: (a) 1<sup>o</sup> cycle – 20°C; (b) 1<sup>o</sup> cycle – 60°C; (c) 2<sup>o</sup> cycle – 20°C; and (d) 2<sup>o</sup> cycle – 60°C.

Figure 3 shows the SEM micrographs of the fracture composite surface obtained from flexural tests. Figure 4 shows the SEM micrographs of matrix and composites before flexural tests. For unidirectional glass fiber composites, the fiber–matrix interface presented good adhesion at low temperature for both cycles. The main changes occur in the neat matrix and in the surrounding matrix in the case of composite materials. The interface is less affected by the water.

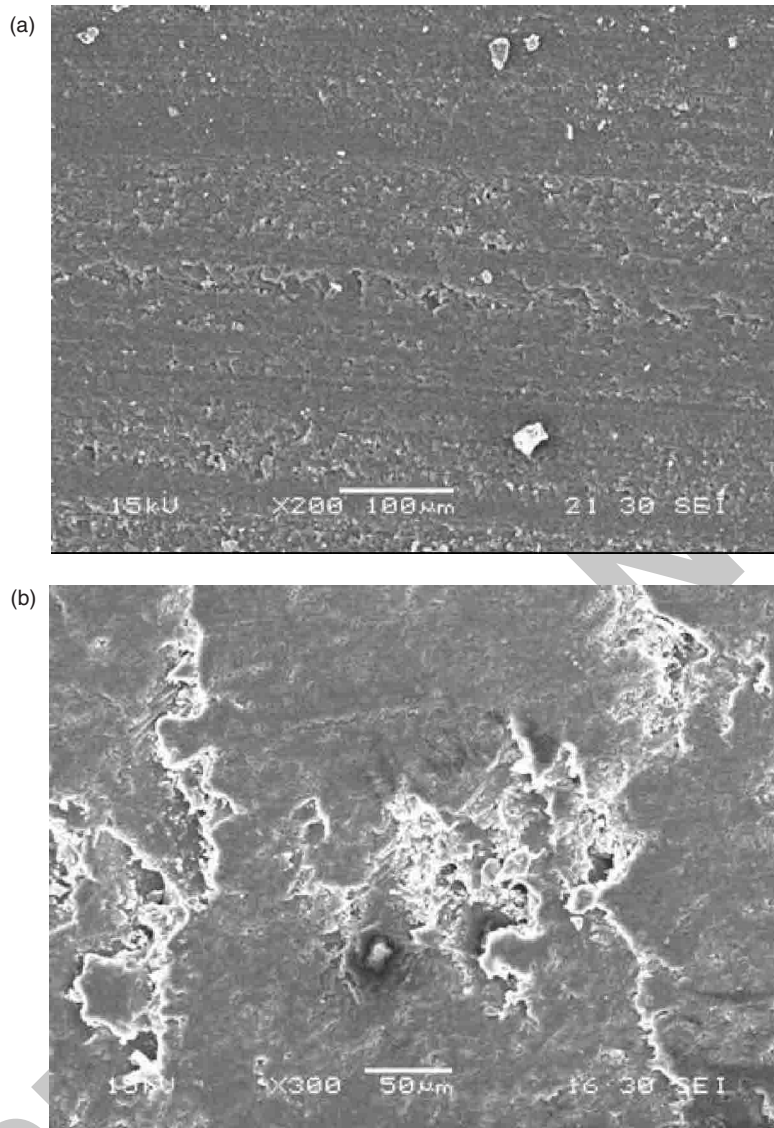
We assumed that degradation of the matrix occurs during fast drying. For example (a) during water absorption, the sample skin is solicited in a compression



**Figure 3.** *Continued.*

mode, (b) the sorption curves present a classical Fickian shape from which the coefficients of water diffusion can be easily determined in their initial linear part, (c) the diffusion coefficient values determined by Equation (3) are realistic and in good agreement with the orders of magnitude currently reported in the literature, and (d) the coefficients of water diffusion obey really an Arrhenius law, shows that no matrix degradation occurs during the first immersion.

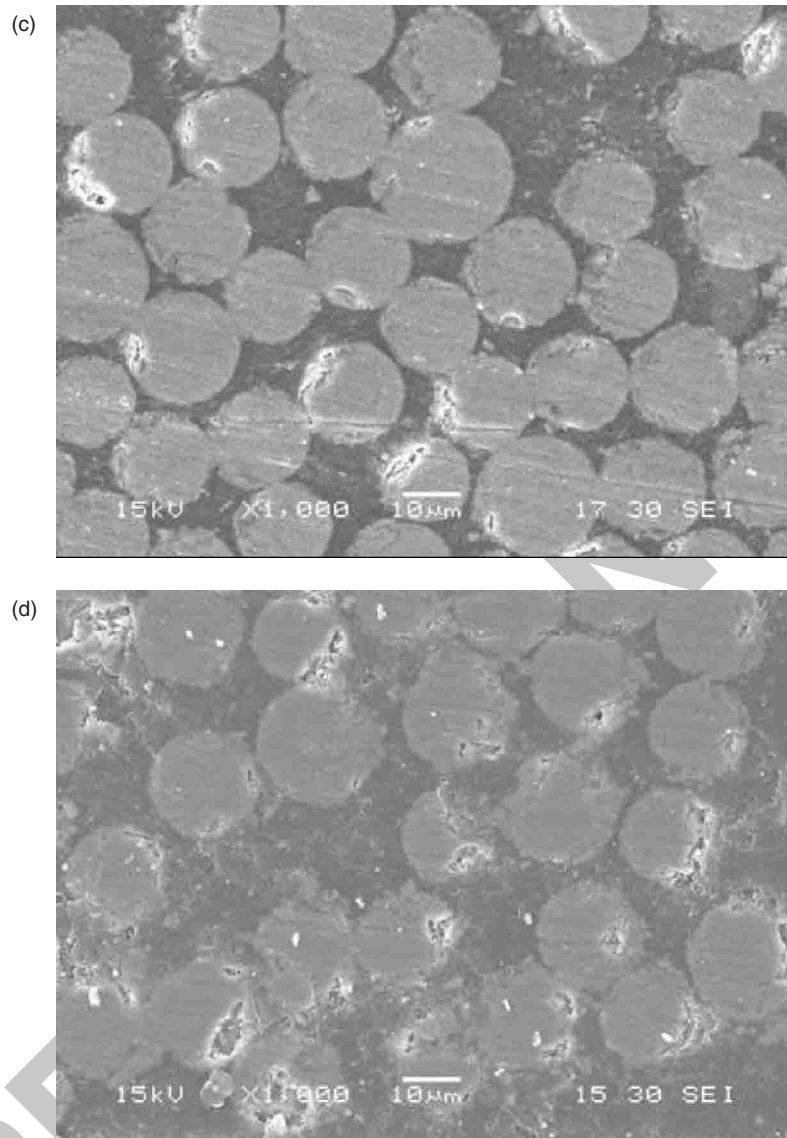
It is important to note that the diffusion coefficient values would be totally different (higher) in a damaged material (as evidenced for the second immersion (Table 3)). In this case, water diffusion would be a combination of a Fickian mechanism and a complex



**Figure 4.** SEM micrographs of matrix and composites after water exposure at different temperatures for the second cycle: (a) matrix before immersion; (b) matrix after immersion 2° cycle – 60°C; (c) composite before immersion; (d) composite after immersion 2° cycle – 40°C; and (e) composite after immersion 2° cycle – 60°C.

transport in a porous (microcracked) material. On the other hand, during the rapid water drying, sample skin is solicited in a tensile mode, hence drying is more penalising than absorption.

The fiber–matrix adhesion decreased as temperature increased. The cycle (1° or 2°) affects more the composites exposed at higher temperature. At high temperature, matrix voids could be observed. Similar results can be observed for mat glass-fiber composites.



**Figure 4.** Continued.

Dynamical mechanical properties of the samples were determined by using a DMA in three-point bending mode. In order to determine the aging produced by water immersion, the samples were dried before testing.

Table 5 shows the results of the storage modulus,  $E'$  and loss modulus,  $E''$  at room temperature and  $E'_{150^{\circ}\text{C}}$ , i.e.,  $E'$  in the rubbery state of studied composites before and after immersion. Retention modulus, calculated as  $E'_{150^{\circ}\text{C}}/E'_{25^{\circ}\text{C}}$  was also included to show that the modulus decrease during the glass–rubber transition. It is shown that composite modulus decreases after immersion but the differences are negligible at 20 and 40°C because matrix content is only about 40 wt% and water has no effect on fiber properties.

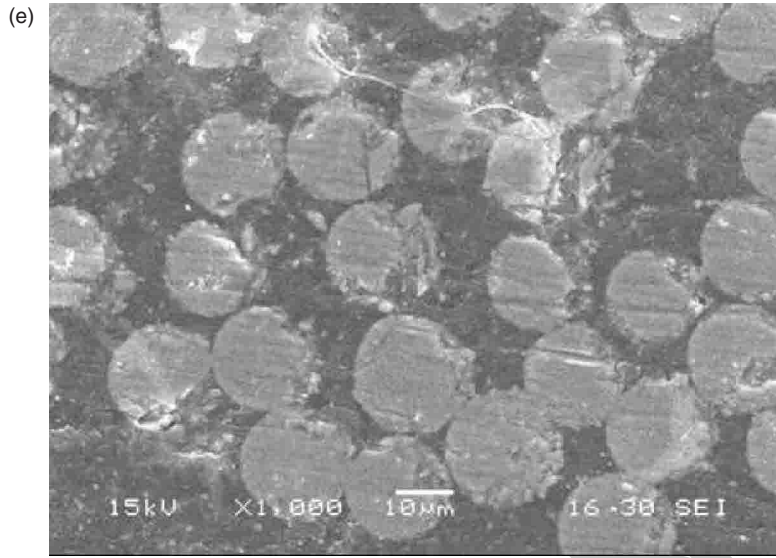


Figure 4. Continued.

Table 5. Dynamical-mechanical properties of composite materials.

Property	Initial	1° cycle			2° cycle		
		20°C	40°C	60°C	20°C	40°C	60°C
$E'_{25^\circ\text{C}}$ (GPa)	19.8	19.0	15.9	18.9	19.1	18.5	19.9
$E''_{25^\circ\text{C}}$ (GPa)	1.02	0.708	0.887	0.993	0.505	0.670	0.928
$E'_{150^\circ\text{C}}$ (GPa)	2.65	2.30	1.92	1.66	2.64	1.85	1.69
Modulus retention (%)	13.4	12.1	12.1	8.8	13.8	10.0	8.5

On the other hand, the loss modulus  $E''$  shifts towards lower temperatures. Since  $E'$  is related to the network density, there is no significant loss of network structure after water exposure.

Figure 5 shows the stress–displacement curves obtained from 3PB tests for matrix and composites before immersion and after the second immersion cycle at 60°C. It was possible to observe from this figure, that fibers act as reinforcement of VE matrix because the resistance, the slope, and the curve are higher for composites than for matrix. On the other hand, the effect of water is clearly shown by the low values in these curves. The results of mechanical properties ( $E$ , flexural modulus and  $\sigma$ , flexural strength) obtained from these tests are summarized on Table 6. Although the modulus did not significantly change after both cycles, the strength is already reduced specially at a high temperature, probably because of the detriment to fiber–matrix interface.

## CONCLUSIONS

In this work, the cycling diffusion behavior of glass-fiber/VE matrix composites was studied.

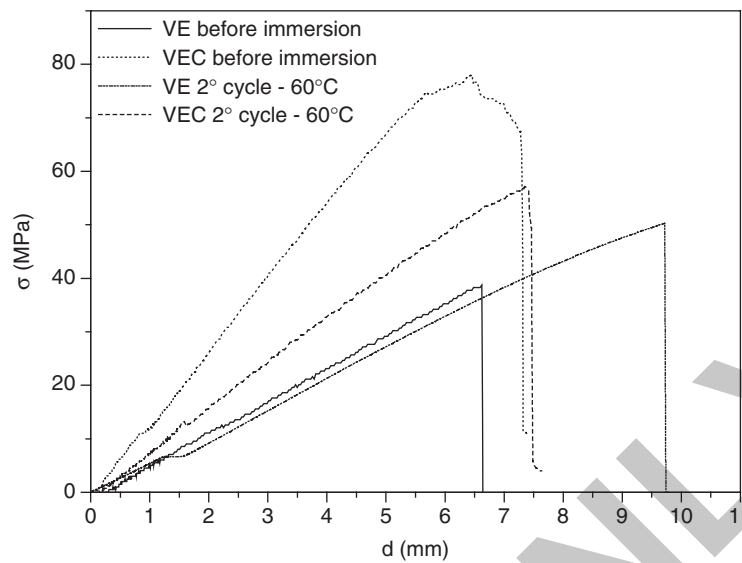


Figure 5. Stress–displacement curves obtained for matrix and composites from 3PB tests.

Table 6. Mechanical properties (3PB) of composite materials before and after immersion.

Property	Initial	1° cycle			2° cycle		
		20°C	40°C	60°C	20°C	40°C	60°C
$E$ (GPa)	8.3	7.3	7.5	7.4	8.0	7.4	6.6
$\sigma$ (MPa)	79.2	61.7	54.1	52.1	68.9	58.1	48.2

It was shown that glass fibers act as inert in the water absorption process of VE matrix and their main effect is the loss of interface adhesion. Composites absorb less water than matrix and, for both, the amount of water increased with the temperature increase and cycle. On the other hand, diffusion coefficients were similar for composites and matrix.

Temperature affects the diffusion coefficient values and the obtained values were fitted by an exponential equation.

It was possible to observe, from SEM micrographs, that the adhesion in the fiber–matrix interface decreased as temperature increased. The cycle affects the composites exposed at a high temperature more when loss of adhesion was observed at the fiber–matrix interface.

The flexural modulus did not change after water exposure, but the loss of strength was related to the poorer interface.

The storage modulus measured at room temperature did not change after exposure to water at 20 and 40°C but some differences were found at 60°C.

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