

## Research Article

# Estimation of Long-Term Stiffness of Storage Aged GFRP Composite Samples Immersed in HCl Acid by TTSP Method

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The 15-year storage aged GFRP composite dumbbell-shaped specimens were immersed in concentrated HCl at different temperatures and times. The Young modulus, which is a yardstick of stiffness of the samples, was measured. The long-term stiffness at any time and temperature was predicted by using the master curve of stiffness obtained based on our accelerated testing results. In the first, second, third, and fourth years of the prediction the stiffness was 6800, 6400, 5550, and 5150 MPa, respectively. SEM micrographs of typical samples showed failure mode at the interface. The strength showed reduction due to degradation of fiber/matrix interfacial bond. The best match of our prediction obtained by using error function was between the first and the third years.

## 1. Introduction

Glass fiber reinforced polymer (GFRP) composites are the alternatives for the steel, metal, and wood materials in many applications. GFRPs have high specific tensile and compressive strength, good fatigue, and corrosion resistance. They are suitable for production of complex shape components with reduced manufacturing costs compared to conventional materials [1]. Unsaturated polyester resins and E-glass fiber are the most applicable materials as matrix and reinforcement of the composite, respectively [2].

A design life of 10–50 years is required for important areas of GFRP applications such as automotive and aerospace industry, bridge structures, water, acids, and waste disposals, offshore, and oil exploration. The use of GFRPs in hostile environments like acidic, alkaline, water, and moisture environments at high or low temperatures leads to physical and chemical ageing which leads to mechanical and chemical degradation [3]. Since it is difficult to perform tests on GFRPs for very long periods to cover their designed lifetime, the accelerated aging tests which can predict stiffness of the GFRPs are usually used [4]. During the last 40 years, several

lifetime models for viscoelastic materials have been proposed [5, 6]. The time temperature superposition principle (TTSP) is used vastly for determining the residual stiffness of GFRPs during aging in various environments. For this purpose, the environmental exposure can be intensified by using a higher temperature and higher concentration of the acid or using some amount of acid fog. Then, the prediction of long-term stiffness is feasible based on short-term measurements of modulus of elasticity at various temperatures in hostile environment and making superposition curves of modulus of elasticity from different temperatures [7].

The aim of this study is to estimate the long-term stiffness of the storage aged GFRP samples in various temperatures and concentrated HCl as a hostile environment. Time and temperature superposition method is applied. For this purpose the stiffness of the aged samples was measured.

## 2. Experimental

**2.1. Samples Preparation and Measurements.** The glass fiber reinforced polyester composite sheets were manufactured by N.S.Guassero Co., Italy, and stored for 15 years out of direct

TABLE 1: Times and temperatures of acid immersion before tensile tests.

	Environment	Times (week)	Tests
Samples in 35°C	33% HCl	1	Tensile
		2	
		3	
Samples in 50°C	33% HCl	1	Tensile
		2	
		3	
Samples in 75°C	33% HCl	1	Tensile
		2	
		3	

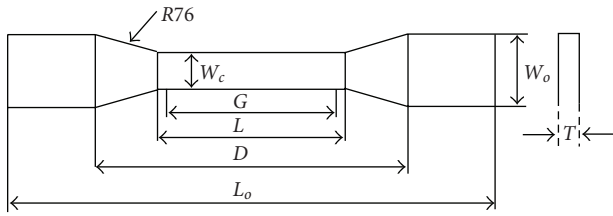


FIGURE 1: Specification of samples for tensile measurements.

reach of sun light at temperature between  $-3$  and  $48^\circ\text{C}$ . The matrix is Bisphenol-A polyester resin (code 53-G7D11), and short E-glass fibers are used as reinforcement.

Table 1 shows the times and temperatures of the samples immersed in acidic environment. Dumbbell-shaped samples were prepared by Milling (Hekert Universal 600) according to ASTM D638-03 standard. The specification and dimension of the samples are shown in Figure 1 and Table 2, respectively. Tensile tests were carried out by Multi-Purpose Instron Tester (model 4486). The crosshead speed was  $5\text{ mm/min}$ . The low crosshead speed led to the sufficient time for load transfer needed for growing cracks without blunting. The tensile tests were carried out 30 minutes after withdrawal from the acid bath. Each sample was tested in triplicate at a specific time and temperature.

In order to investigate the effect of aging on fracture mode of GFRP, the fracture surfaces of storage aged and nonaged samples were studied by SEM (Philips XL 30), The Netherlands.

**2.2. TTSP Procedure.** According to the time-temperature equivalency in this test, the acceleration is accomplished by immersing the specimens in a concentrated HCl acid bath at temperatures of  $35$ ,  $50$ , and  $75^\circ\text{C}$  for one, two, and three weeks.

By using modulus of elasticity ( $E$ ) in those temperatures, the time-temperature curves were depicted on a logarithmic scale (Figure 2). The lowest temperature curve (at  $35^\circ\text{C}$ ) was selected as the reference curve, and then the two other curves at  $50^\circ\text{C}$  and  $75^\circ\text{C}$  were shifted, respectively, to the right side to be superimposed on the reference to obtain the preliminary master curve (Figure 3). The horizontal shift

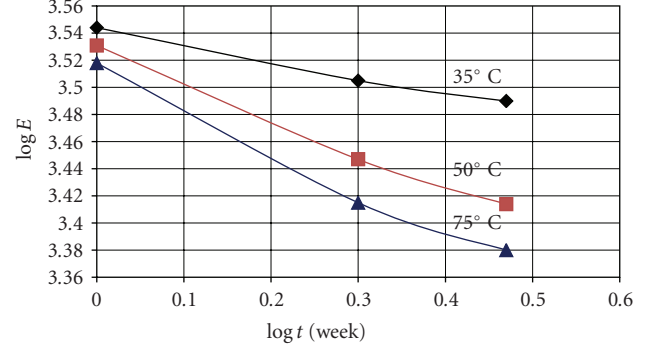


FIGURE 2: Modulus of elasticity versus time of acid immersion of the samples at three different temperatures.

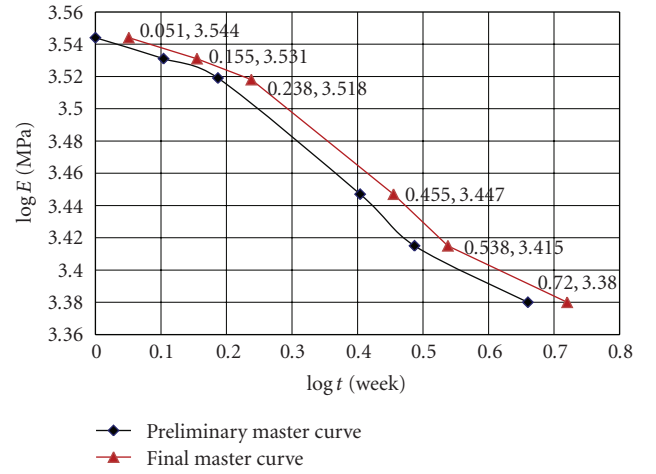


FIGURE 3: Preliminary master curve in comparison with final one after applying the shift factor.

required for each curve to be superimposed on the master curve is called the shift factor for that temperature ( $a_T$ ). The aim of applying the shift factor is to determine the shift of the master curve for compensating the effect of time at room temperature. Calculated shift factors are plotted as a function of the absolute temperature (Figure 4). The Arrhenius relationship is used to calculate the shift factor trend [8]. The absolute value of  $a_{300}$  is used to shift the master curve to the right side on the horizontal axis to obtain final master curve (Figure 3).

The relationship between the decay of the accelerated experimental results and long-term life of the samples is correlated with the  $K$  factor.  $K$  factor is the modulus of elasticity ratio at natural long time exposures ( $E_l$ ) to the accelerated aging time ( $E_a$ ) for obtaining the similar decay [8].

For estimating the modulus of elasticity at various times, the following equation is used [8]:

$$E_l = E_0 + \frac{1}{k} \int_0^t \left( \frac{dE_a}{dt} \right) dt, \quad (1)$$

TABLE 2: Dimension of specimen for tensile tests (mm).

$T$	$W_c$	$W_o$	$G$	$L$	$D$	$L_o$
$3.2 \pm 0.4$	$6 \pm 0.5$	$19 \pm 6.4$	$50 \pm 0.25$	$57 \pm 0.5$	$135 \pm 5$	183

TABLE 3: Experimental modulus of elasticity of the samples after immersion in acid.

Time (week)	Temperature ( $^{\circ}\text{C}$ )	$E$ (MPa)
1	35	3500
	50	3400
	75	3100
2	35	3200
	50	2800
	75	2600
3	35	3100
	50	2600
	75	2400

TABLE 4: Experimental modulus of elasticity of the nonacid immersed samples.

Storage aged samples	$E$ (MPa)
15-year aged ( $E_0$ )	8130
15.5-year aged	7200
16-year aged	6800
16.5-year aged	6250
17-year aged	6400
17.5-year aged	5950
18-year aged	5550
18.5-year aged	5400
19-year aged	5150

where  $K$  is a constant,  $E_0$  is the modulus of elasticity of reference sample before immersion in the acid, and  $E_a$  is calculated from the final master curve.

### 3. Results and Discussions

Tables 3 and 4 show the experimental results of the modulus of elasticity ( $E$ ) of acid-immersed and non-acid-immersed samples, respectively. Immersion of the samples in the acid at specific times and temperatures caused a decrease in the modulus of elasticity. This is due to the physical and chemical degradation of the samples. The more the increase in the time and temperature of immersion, the more the decrease in the modulus of elasticity [2]. The degradation of the samples proceeds not only by acid immersion but also by ageing during their storage. As an evidence to show, the modulus of elasticity of a typical 15-year storage aged sample is 1470 MPa less than an ASTM standard specimen [9].

Figure 2 illustrates the modulus of elasticity versus time of acid immersion of the samples at three different temperatures with logarithmic scale. It is seen that the modulus of elasticity has a descending manner as the time and temperature of immersion are increased. It is observed that the rate of degradation is decreased by increasing the time or temperature of the acid immersion. This decreasing manner could be explained by the high resistance of the network part of the resin containing fiber glass. Similar behavior has been observed by Caceres et al. [8] and Aldajah et al. [10] during ageing of GFRPs samples in alkaline and sea water environments.

Figure 3 shows the TTSP curves made from the data in Figure 2. Initially, a preliminary superposition curve is made, followed by the final master curve. The curve at  $35^{\circ}\text{C}$  is selected as reference curve, and the 50 and  $75^{\circ}\text{C}$  curves were shifted to the right to be imposed on the reference in order to make the preliminary master curve. The time of long-term

TABLE 5: Calculation of acceleration factor.

	Log $t$ (week)	week
Time of degradation in ambient temperature (new master curve)	0.72	5.25
Time of degradation in acceleration process	0.44	3
Acceleration factor (k)	$5.25/3 = 1.73$	

degradation is estimated from the scale time on the master curve. Since the preliminary master curve does not estimate the long-term degradation, this curve must be shifted to the right through considering the value of shift factor to make the final master curve. The following equation is obtained from the final master curve:

$$E_a = 3642.6 - 778.4 \ln t. \quad (2)$$

The length of time of the final master curve on the scale of time is representative of long-term degradation. This time is used to obtain the acceleration factor.

Table 5 indicates how the acceleration factor is calculated. Regarding the concept of acceleration factor, by dividing the real time of degradation from the master curve to the time of degradation in our experiments, the value of  $K$  factor is obtained. The acceleration factor calculated in this work is low which may be due to the storage aging of samples before accelerated experiments [11].

Figure 4 shows the variation of the shift factors versus temperature. The effect of the long-term room temperature on aging is considered by the aid of the shift factor. The curves in Figure 2 at 35, 50, and  $75^{\circ}\text{C}$  were shifted to 0, 0.104, and 0.187, respectively, to make the final master curve.

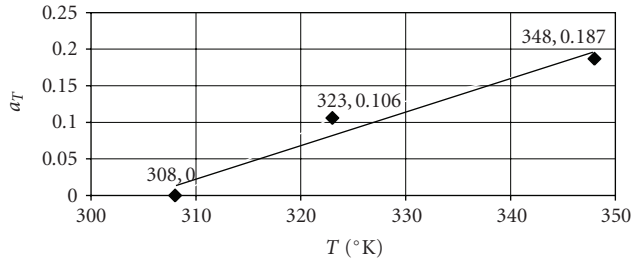


FIGURE 4: Variation of the shift factor versus temperature.

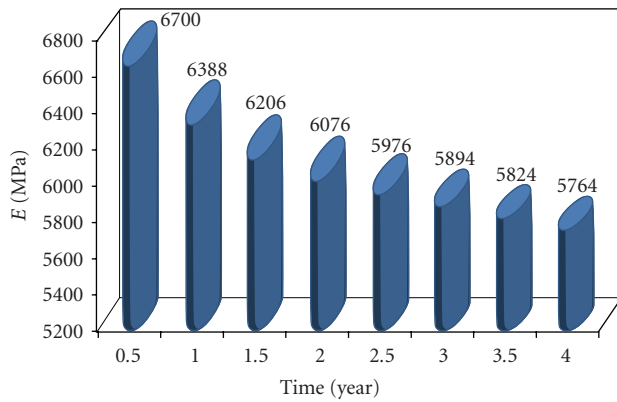


FIGURE 5: Predicting long term modulus of elasticity by (2).

By considering the shifted value in each curve, the shift factor equation is achieved:

$$a_T = 1.4921 \ln T - 8.5366. \quad (3)$$

As it was mentioned in a previous section the absolute  $a_{300}$  obtained from (4) is such that the preliminary master curve must be shifted to the right to make the final master curve.

Figure 5 shows the results of calculated prediction of the modulus of elasticity for some years. The long-term modulus of elasticity is calculated by (2). Since the scale of time of accelerated experiments is a week, the limits of the integral are weeks too (the lower limit is selected to be 1 instead of zero). As it is expected the results of the prediction show a descending manner that is due to the physical, chemical, and mechanical degradations of the GFRP. The following equation which shows the trend of long-term modulus of elasticity prediction is obtained by the data in Figure 5, the time is in year:

$$E_1^{ca} = 6388 - 450 \ln t. \quad (4)$$

A similar life time prediction of GFRPs by using TTSP method and making master curve is shown by other workers [12, 13].

Figure 6(a) shows micrograph of fracture section of the GFRP sample before acid immersion at ambient temperature. From this figure, one may notice the close adherence of fibers. A few fibers are pulled out from matrix when tensile stress was applied. This is due to storage aging of the

composite. Although the samples are aged for 15 years, there are still a reasonable interfacial bond and adherence between fibers and the matrix.

Figure 6(b) shows micrograph of fracture section of the GFRP sample after 21 days of acid immersion at 35°C temperature. It is clear that, when tension was applied, all the fibers were pulled out of matrix. This figure confirms the destructive effect of the acid on the GFRP composite structure and shows how acid penetration deteriorates fibers/matrix interfacial bond. During the acid absorption of the interphase, acid solution penetrated into the free space of polymer which induced more new cavities and cracks, thus the interphase gradually is damaged [14]. In addition to the destructive effect of acid, aging of the specimens intensified the amount of damage imposed on the samples.

Figure 6(c) shows micrograph of fracture section of fresh GFRP sample without acid immersion. By comparing Figures 6(a), 6(b), and 6(c), one may notice that fresh sample shows more significant matrix resin adhering to fiber surfaces than aged samples. In Figures 2(a) and 2(b) smooth fiber surfaces of aged samples with much less residue indicate degraded interfacial bonding by environmental aging. Similar observation was also given by Watanabe and Tsai [15], Sekine et al. [16], and Komai et al. [17].

When the GFRP samples are in contact with the mineral acid solution environment, acid diffuses into the macromolecule of the polymer, degrades the matrix, reinforcements, and interfaces. The absorption of acid at different times and temperatures accelerated the rate of aging. Thus reduction of mechanical properties such as tensile strength, modulus of elasticity, and elongation at break occurred. The effect of this highly destructive process is evidenced by swelling, discoloration, and decrease in the mechanical properties of the samples. Chemical attack of polymer matrix by the acid solution environment led to hydrolysis of ester groups of the matrix. Since these groups are located in the chain backbone of the polymer, chain scission occurs. The decrease in molecular weight due to this scission can lead to the reduction in the mechanical properties [11]. While acid solution penetrates into the composite, the uptake of acid happens by the capillarity, conducted along the network of fibers, voids, and cracks [15]. Thus the ionic exchange occurs between the metallic cations (e.g., Na<sup>+</sup> ions) at the glass surface and the hydrogen ions in the acid solution, resulting in leaching of metallic cations from the outer layer of the fibers [16]. The difference in the size of hydrogen ions and the replaced cations results in tensile stresses in the glass fibers. These stresses cause the crack propagation at the interphase resulting in failure of the samples. After the leaching process, the Cl<sup>-</sup> ions have been released and diffused quickly into the voids of the matrix. They transfer into the interphase and weaken the bonds strength. Washing of fibers surfaces and releasing of Cl<sup>-</sup> ions affect the matrix and fiber/matrix interfacial bond and gradually decrease the mechanical properties of the GFRP samples [17].

The reduction in the mechanical properties of the original samples is explained by weathering and thermal degradation. Although the specimens were not affected by direct exposure of sun light, UV light exists in the



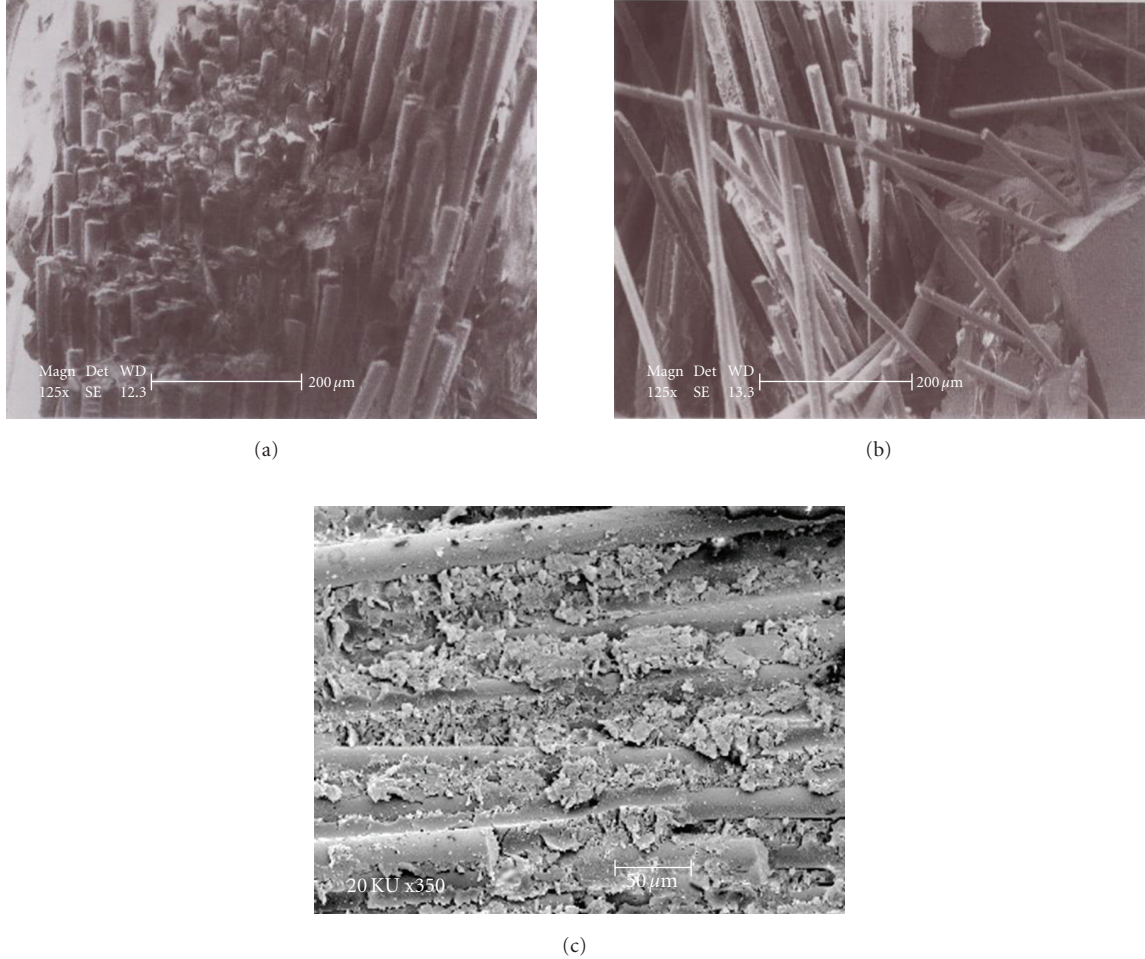


FIGURE 6: Fracture section of the aged GFRP sample (a) before acid immersion, (b) after 21 days acid immersion at 35°C temperature and (c) fresh GFRP sample without acid immersion.

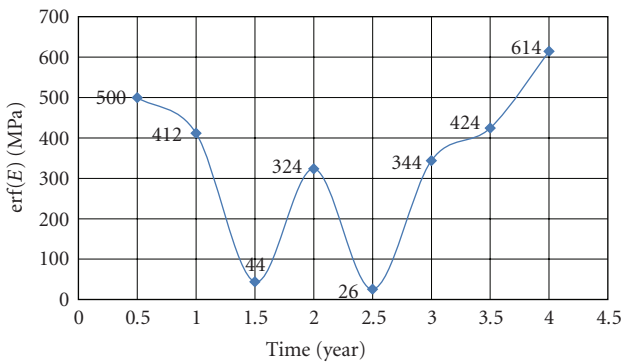


FIGURE 7: The result of error function prediction versus lifetime.

environment and could harm the matrix. Weathering is initiated by the absorption of UV radiation by chromophores and in the activation of excited states in the macromolecules. When a polymer composite is exposed to a source of energy (solar or thermal), the absorbed energy by the polymer

matrix results in the formation of free radicals. Once free radicals have been produced, reaction with oxygen generates hydroperoxides. These hydroperoxides can dissociate further to produce a series of decomposition products including aldehydes and ketones. The decrease of the mechanical properties is due to the formation of these products and scissoring of polymer macromolecules [18]. Regarding the storage period of specimens, heat, moisture, and air-borne pollution all influence the mechanism of degradation. The effect of moisture causes the hydrolytic breakdown of the fiber/matrix interface. It results in the reduction of efficiency in load transfer between the matrix and the fiber reinforcement [19]. The increase in the temperature accelerates the reaction of free radicals with oxygen. This leads to thermo-oxidation of the polymer matrix. Meanwhile the difference between thermal coefficient of matrix and reinforcements causes the dissociation of the phases and promotes mechanical properties reduction.

*Checking the Validity of the Master Curve.* In order to check the validity of the procedure for prediction of calculated stiffness, eight specimens were tested in the

interval of half year. Indeed, after plotting of master curve the stiffness of 15.5-, 16-, 16.5-, 17-, 17.5-, 18-, 18.5- and 19-year-old samples was measured (see Table 4). The concept of error function (erf) is applied to specify the validity of the master curve according to the following equation [20]:

$$\text{erf}(E) = |E_l^{\text{ex}}(t) - E_l^{\text{ca}}(t)|, \quad (5)$$

where  $E_l^{\text{ex}}(t)$  and  $E_l^{\text{ca}}(t)$  are, respectively, equations of experimental and calculated long-term stiffness. Equation (6) is obtained from the data in Table 4 which shows the experimental stiffness:

$$E_l^{\text{ex}}(t) = 6702.2 - 971.9 \ln t. \quad (6)$$

Figure 7 shows the variation of error function of modulus of elasticity versus lifetime of the samples. A close consideration of the data in Figure 7 shows that the 1.5 and 2.5 years of lifetime have the best match with our prediction.

## 4. Conclusions

The main results obtained from the present work are summarized as follows.

- (1) By considering linear viscoelastic behavior of polymer matrix and applying accelerated aging tests and TTSP method, the prediction of long-term stiffness of the samples has been accomplished.
- (2) The predicted stiffness for the first, second, and third years was 6800, 6400, and 5550 MPa, respectively. Our prediction in this period has less deviation from the experimental measurements.
- (3) The predicted modulus of elasticity has descending trend similar to the actual values.
- (4) The acceleration factor which is obtained in this work is to some extent low. This is due to the long term storage aging of the specimens.
- (5) The stiffness of aged GFRP samples decreases rapidly with increasing times and temperatures of the acid immersion.
- (6) SEM micrographs show that storage aging of the samples has deteriorating effects on the fiber/matrix interfacial bonds.

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