A COMPARATIVE STUDY ON THE EFFECT OF HOT/WET AND HOT/DRY AGING ENVIRONMENTS ON THE DEGRADATION OF FILAMENT WINDED COMPOSITES

C. Srivastava[a], A. Strandlie[a], B. Alcock[b], and S. A. Grammatikos[a]

a: Laboratory for Advanced and Sustainable Engineering Materials (ASEMlab), Department of Manufacturing and Civil Engineering, Norwegian University of Science and Technology, Gjøvik 2815, Norway
b: SINTEF Industry, Forskningsveien 1, Oslo 0373, Norway
chaman.srivastava@ntnu.no

Abstract: *Predicting the long-term response of polymer composite materials is a continuous challenge to the composite industry. The service aging of structural composites has different effects on composites' physicochemical behavior manifested as changes in the mechanical properties. This work presents the effects of hot/wet and hot/dry accelerated aging conditions on the interlaminar shear properties of vinyl-ester glass fiber coupons made with filament winding. The test coupons were aged for 224 days, removed and tested after every 28, 56, 112, and 224 days. It was observed that the response of composite coupons is different for the hot/wet and hot/dry aging environments for same duration of aging. This is attributed to the time-temperature-environment coupling during the aging regime. The overall response of the composite behavior is then represented via retention curves and degradation maps that can help correlate the results for both hot/wet and hot/dry aging environment as a function of exposure times and temperatures. The findings of the study thus provide an insight on the dependence of matrix-dominated properties of composite. The results can be taken into account when designing structure made from vinyl-ester glass fiber filament winded composite which foresee aging in hot/wet and hot/dry conditions.*

Keywords: Aging; Filament winded composites; Degradation Maps; Retention Curves

1. Introduction

The service life of composite materials can be approximated using lab-scale accelerated aging methods, where specimens are artificially aged for a defined period and then tested to determine the influence of artificial aging and its correlation with natural weathering. This characterization of the long-term response of the material and its associated structure towards a complex environment presents a continuous challenge to the industries [1]. The understanding behind the aging process is of extreme importance as it can help to prevent catastrophic failure of the structure.

A composite material is composed of reinforcement with a matrix surrounding it. Understanding the aging of structures made of composite materials is complex due to the combined matrix and fiber responses to aging. In this work, a testing regime comprising different aging environments and mechanical tests was formulated to segregate the effects of aging at fiber, matrix, and interface levels. The two most crucial service environments faced by composites are hot/dry and hot/wet conditions. Thermo-oxidation of the matrix, hazing, and formation of microcracks have been reported to severely affect the service life in hot/dry environments [2, 3], whereas hydrolysis, interfacial failure, and selective leaching of the matrix have been reported to degrade the composite severely [4]. This paper presents mechanical performance results on vinyl-ester glass fiber filament winded composite coupons subjected to hot/dry and hot/wet environments, for a period of 224 days. The study will focus on matrix degradation through interlaminar shear strength testing.

2. Mechanical testing

Interlaminar shear testing (ILSS) was carried out following the ASTM D2344 test standard using a short beam shear specimen (SBS), where the specimen geometry and the dimensions are shown in Figure *1*. The composite coupon is a bi-layered structure where the top layer is made from unreinforced polyethylene (PE) polymeric layer, which has a thickness of 1.2 mm, and the remainder of the composite coupon is composed of glass fiber reinforced vinyl ester composite produced by filament winding. The fiber volume fraction of the composite was calculated to be 56% using the calcination method [5] and 52% using micro-Computed Tomography (CT-scanning). The glass transition temperature of the unaged vinyl ester matrix is 98-100°C, measured using Differential Scanning Calorimetry (DSC).

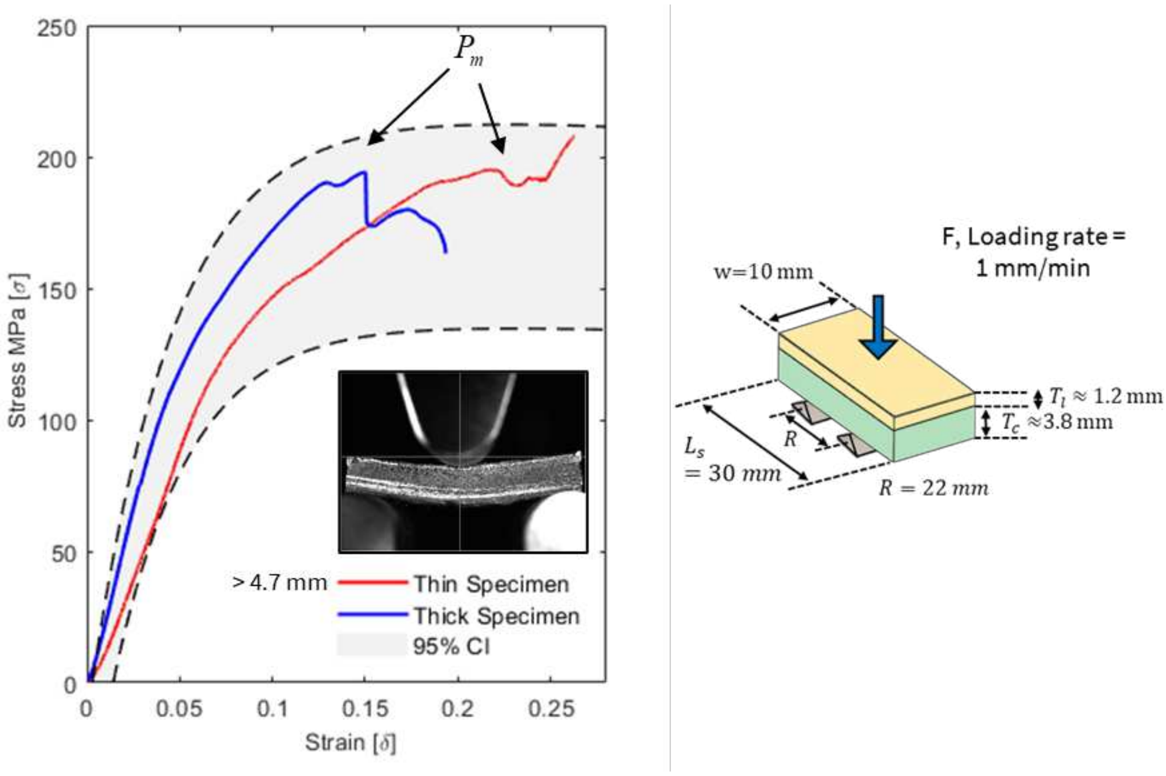

Figure 1: (a) Stress-strain curve for interlaminar shear testing (b) Interlaminar shear strength coupon prepared as per ASTM D2344 standard.

The mechanical tests were performed on the Instron 5966 UTS machine, where the loading pin and support pin diameter is 5 mm. The roller separation is set to 22 mm, 4 times the thickness of the total composite coupon. The loading rate is quasi-static at 1mm/min. A representative stress-strain curve for composite coupons is also presented in Figure *1*. The point of the first load drop in the stress-strain curve is taken to be the P_{max} value, and the interlaminar shear stress is calculated using Equation (*1*).

$$\tau = \frac{0.75 \times P_{max}}{b \times h} \tag{1}$$

2.1 Hot/Dry Aging

Before aging, the ILSS coupons were dried at 30°C in a vacuum oven for 48 h to remove residual humidity absorbed during storage. After drying, the specimens are removed and allowed to cool overnight in a vacuum desiccator. Termaks laboratory drying oven with fan-controlled airflow was used to create hot/dry conditions where the coupons are aged isothermally at room temperature (23°C), 40°C, 60°C, and 80°C, for a total period of 224 days. The maximum temperature is lower than the glass transition temperature (Tg) of the vinyl-ester matrix of the composite to avoid activating unwanted and unrealistic aging mechanisms above Tg.

2.2 Hot/Wet Aging

Hot/wet aging was conducted in Grant Sub Aqua water baths with a temperature stability of ±0.2°C. Before being placed in heated water baths, the coupons are dried in a vacuum oven at 30°C for 48 h to remove any residual moisture absorbed from the environment during storage. The dried specimens are then placed in water baths at 20°C, 40°C, 60°C, and 80°C. Distilled water is used as a hot/wet aging medium. The maximum temperature is again selected to be below the Tg of the vinyl ester matrix of the composite. The specimens are aged for a total period of 224 days. The specimens are kept in a refrigerator for storage at 4°C and kept to condition overnight before testing.

3. Experimental Results and Discussion

Retention curves and degradation maps are created to study the evolution of interlaminar shear strength as a function of aging time and temperature. The stress vs. the midspan deflection of each composite coupon at each aging interval is plotted to visualize the behavior of composite coupon. From Figure 1, it is observed that the behavior of the composite coupon is linear at the beginning of the mechanical test, but due to the presence of the polyethylene layer, the initial behavior alters after 1-3% strain. The coupon failure is observed as a sharp drop in the stress-strain curve. The point of the first deflection, which drops more than 15%, is considered the maximum load (Pm) for calculating the short beam strength using Equation (1).

Then, interlaminar shear strength retention curves are plotted as a ratio of the interlaminar shear strength at time (t) divided by the interlaminar shear strength of unaged composite coupon. The value 1 is thus chosen as a reference which is also presented as a red dashed line in degradation maps. The absicca represents the test intervals of 0, 28, 56, 112, and 224 days. The average of the retention values at each ageing time and temperature interval and their corresponding standard deviation for 5 specimen replicates under hot/wet aging is tabulated in Table *1*.

Table 1: Interlaminar shear strength retention for composite coupons aged in hot/wet aging environment.

	20°C	40°C	60°C	80°C
	Ret.	Ret.	Ret.	Ret.

28	1.186 ± 0.18	1.136 ± 0.19	1.108 ± 0.26	0.954 ± 0.24
56	1.086 ± 0.29	1.057 ± 0.32	1.134 ± 0.10	0.779 ± 0.04
112	1.088 ± 0.13	1.074 ± 0.23	0.885 ± 0.27	0.716 ± 0.13
224	1.095 ± 0.18	0.948 ± 0.45	0.843 ± 0.05	0.651 ± 0.08

Figure *2* (a) and (b) presents the ILSS retention curves and degradation map for hot/wet aging condition. It is observed that for lower temperatures (20°C, 40°C, 60°C) well below the Tg of the vinyl-ester matrix of composite coupons, the coupons exhibit an initial strengthening of ILSS value for 28 days. This strengthening effect can be attributed to additional crosslinking of vinyl ester at lower temperatures, and hence the interlaminar shear strength, which is a matrix-dominated property increases. Similar results have also been reported by Sousa et. al. [6]. A slight strengthening of ILSS which can be masked by an early onset of degradation is observed for 28 days of aging at 80°C. This temperature is close to the glass transition temperature of the vinyl ester matrix and has a higher kinetics of reaction. Thus the degradation of the polymer superimposes the post-curing effect and no appreciable change is observed.

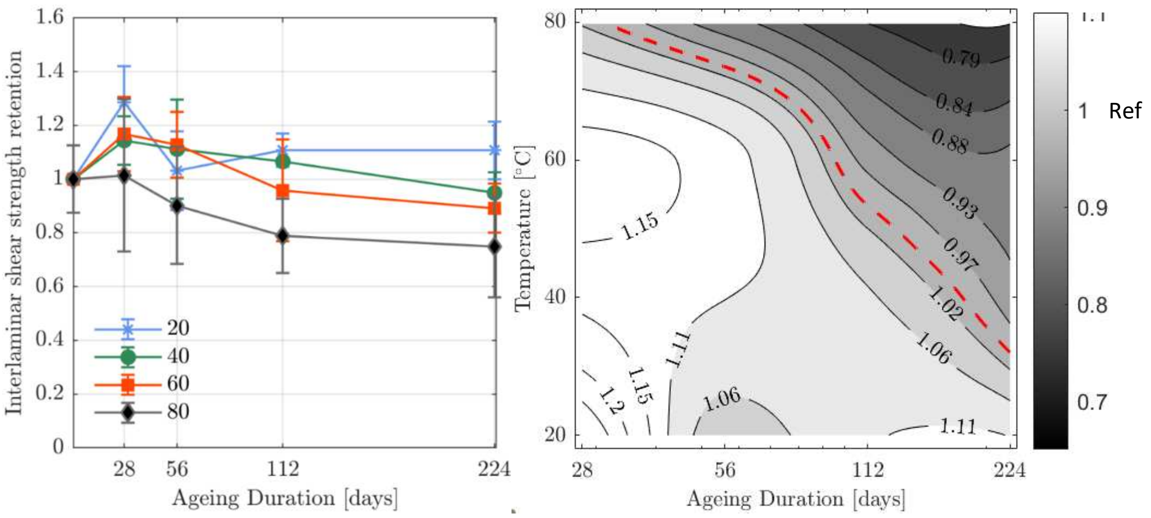

Figure 2: (a) ILSS retention curves (b) degradation map for filament-winded composite coupon aged in hot/wet conditions for 28, 56, 112 and 224 days at 20°C, 40°C, 60°C and 80°C.

For 56, 112, and 224 days, the observed inter-laminar shear strength values starts to fall for temperature ranges of 40°C, 60°C, and 80°C, also reported in [7]. This effect is attributed to the plasticization of the matrix [8, 9] and differential swelling between the fiber and matrix [10] thus leading to an easier fiber/matrix seperation and pull out. Hydrolytic leaching of the silane sizing on the fiber/matrix interface has also been reported to cause eventual degradation within the laminate, which can be visible as swelled up pitted regions on the fiber surface[7, 11]. Interestingly, the competing effect of strengthening and degradation at 20°C leads to a slight increase in the retention values at 224 days. This anomalous behavior can be attributed to possible secondary bonds created between the free radicals of polymer and the hydroxyl molecules at low temperatures as reported also in [12]. At a duration of 224 days, it was observed that the maximum reduction of -3%, -11%, and -23 % was observed for 40°C, 60°C and 80°C at 224 days, respectively.

Figure *3* (a) and (b) presents the interlaminar shear strength retention curves and degradation map for hot/dry aging over the aging period of 224 days. The general trend for hot/dry aging of filament winded composite varies again for both the aging duration and temperature. The average of the retention values at each ageing time and temperature interval for hot/dry aging and their corresponding standard deviation for 5 specimen replicates is tabulated in Table *2*.

It is observed for 28 days, ILSS retention values for all aging regimes, increases where the maximum strengthening effect is visible for temperatures close to the Tg of the vinyl-ester matrix (60°C and 80°C). This strengthening effect can be again attributed to additional crosslinking of vinyl ester and hence the interlaminar shear strength which is a matrix dominated property increases. The initial strengthening is often due to time-temperature coupling, where higher temperature (but below Tg) and longer exposure duration cause a higher increase in the matrix-dominated properties for vinyl ester-based composites [13]

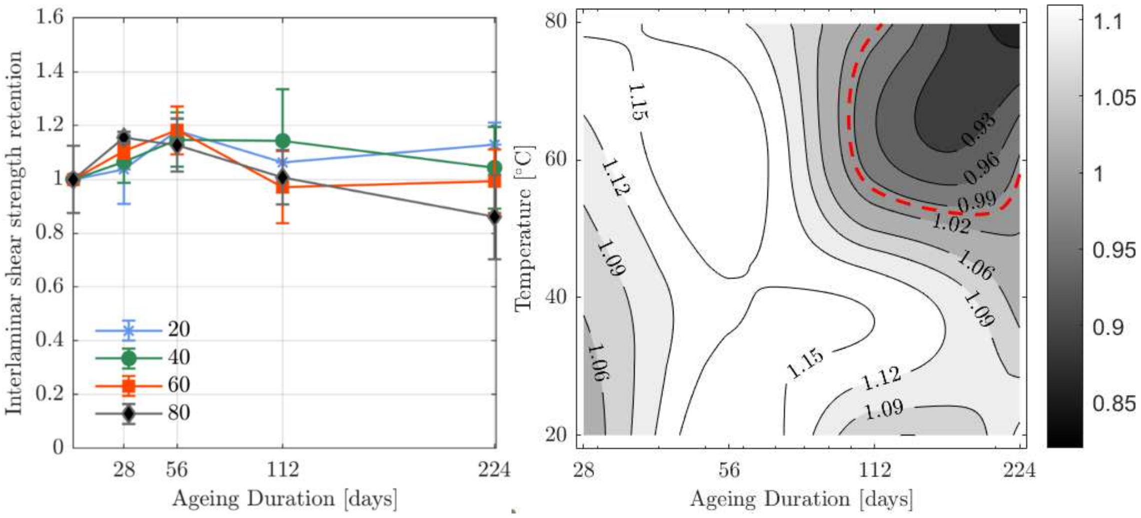

Figure 3: (a) ILSS retention curves (b) degradation map for filament-winded composite coupon aged in hot/dry conditions for 28, 56, 112 and 224 days at 20°C, 40°C, 60°C and 80°C.

For aging duration of 56, 112, and 224 days, the interlaminar shear strength values of the coupons start to fall, but are above the reference unaged value of 1. Hence, no particular degradation is observed at 20°C, 40°C, 60°C for a total ageing duration of 224 days. The onset of degradation in the interlaminar shear strength is observed at a higher aging temperature of 80°C between 112 and 224 days. This degradation zone is visible in the upper right quadrant of the degradation map where the retention values fall sharply below 1 signifying apparent degradation from the unaged interlaminar shear strength values. At a duration of 224 days, it was observed that an increase of +4%, +1%, and +0.2 % was observed for 20°C, 40°C and 60°C respectively, whereas a degradation of -10% was observed at 80°C.

It is also reported that the presence of any micro-cracks [3] during the aging helps to create crevices where the oxygen can percolate and create an oxide layer and thus aids in the oxidation of the whole polymer. However, for filament winded composites, it is observed that due to the presence of fibers in the hoop layer, which is parallel to the surface of the composite, the oxide layer is arrested and hence the diffusion of the oxygen is arrested, which protects the bulk of the coupon to remain unaffected [14]. This barrier towards the diffusion of oxygen can be destroyed close the Tg of the material as the physico-chemical characteristics of the material changes and thus allowing more percolation and overall thermo-oxidation of the composite coupon. [15]

Table 2: Interlaminar shear strength retention for composite coupon aged in hot/dry aging environment.

	20°C	40°C	60°C	80°C
	Ret.	Ret.	Ret.	Ret.
28	1.034 ± 0.28	1.025 ± 0.12	1.09 ± 0.02	1.161 ± 0.04
56	1.181 ± 0.05	1.104 ± 0.08	1.172 ± 0.19	1.029± 0.17
112	1.098 ± 0.08	1.258 ± 0.11	1.151 ± 0.23	1.009 ± 0.19
224	1.091 ± 0.11	0.965 ± 0.26	1.058 ± 0.14	0.862 ± 0.35

4. Conclusion

The effects of hot/wet and hot/dry aging of filament winded composites, on interlaminar shear strength are presented in this work. It is observed that the time-temperature-environment coupling plays a critical role in determining the extent of degradation in vinyl-ester glass fiber reinforced composites. It can be concluded that the composite coupons aged in hot/wet aging conditions show a higher degradation of the matrix-dominated properties when compared with hot/dry aging condition for the same duration and temperature aging regimes. The presence of water is shown to accelerate the degradation process as it can initiate secondary degradation mechanisms like hydrolysis and leaching of the matrix which are not present in hot/dry aging environment. The coupons aged in hot/dry aging environment are only prone to degradation through a thermo-oxidative aging which is found to be not aggressive as hot/wet aging and slight degradation was observed at 224 days. This degradation is manifested as reduction of -23% at 80°C in the interlaminar shear strength values in hot/wet aging when compared to -10% at 80°C in hot/dry aging environment. It is also evident from the degradation maps, that the degradation zone size and the onset for the hot/wet aging shifts towards lower temperatures and shorter ageing duration which is not the case in the hot/dry aging. Hence, these findings can be used to make structural application decisions when designing composites structure used in civil engineering applications and made from vinyl-ester glass fiber filament winding.

Acknowledgments

The work reported in this paper is based on activities within the center for research-based innovation, SFI Manufacturing in Norway, and is partially funded by the Research Council of Norway under contract number 237900.

5. References

1. Council, N.R., *Accelerated Aging of Materials and Structures: The Effects of Long-term Elevated-temperature Exposure (Publication NMAB; 479)*. 1996: National Academies Press.
2. de Souza Rios, A., et al., *Effects of accelerated aging on mechanical, thermal and morphological behavior of polyurethane/epoxy/fiberglass composites.* Polymer Testing, 2016. **50**: p. 152-163.
3. Hawileh, R.A., et al., *Temperature effect on the mechanical properties of carbon, glass and carbon–glass FRP laminates.* Construction and Building Materials, 2015. **75**: p. 342-348.
4. Sethi, S. and B.C. Ray, *Environmental effects on fibre reinforced polymeric composites: Evolving reasons and remarks on interfacial strength and stability.* Advances in colloid and interface science, 2015. **217**: p. 43-67.
5. ISO, E., *1172.* Textile-glass-reinforced plastics-Prepregs, moulding compounds and laminates-Determination of the textile-glass and mineral-filler content-Calcination methods (ISO 1172: 1996), 1996.
6. Sousa, J., et al., *Hygrothermal ageing of pultruded GFRP profiles: Comparative study of unsaturated polyester and vinyl ester resin matrices.* Composites Part A: Applied Science and Manufacturing, 2021. **140**: p. 106193.
7. Karbhari, V., *E-glass/vinylester composites in aqueous environments: Effects on short-beam shear strength.* Journal of Composites for Construction, 2004. **8**(2): p. 148-156.
8. Gautier, L., B. Mortaigne, and V. Bellenger, *Interface damage study of hydrothermally aged glass-fibre-reinforced polyester composites.* Composites Science and Technology, 1999. **59**(16): p. 2329-2337.
9. Zhou, J. and J.P. Lucas, *Hygrothermal effects of epoxy resin. Part I: the nature of water in epoxy.* Polymer, 1999. **40**(20): p. 5505-5512.
10. Joliff, Y., et al., *Study of the moisture/stress effects on glass fibre/epoxy composite and the impact of the interphase area.* Composite Structures, 2014. **108**: p. 876-885.
11. Salmon, L., et al., *Hydrolytic degradation of model networks simulating the interfacial layers in silanecoupled epoxy/glass composites.* Composites Science and Technology, 1997. **57**(8): p. 1119-1127.
12. Zhou, J. and J.P. Lucas, *Hygrothermal effects of epoxy resin. Part II: variations of glass transition temperature.* Polymer, 1999. **40**(20): p. 5513-5522.
13. Marouani, S., L. Curtil, and P. Hamelin, *Ageing of carbon/epoxy and carbon/vinylester composites used in the reinforcement and/or the repair of civil engineering structures.* Composites Part B: Engineering, 2012. **43**(4): p. 2020-2030.
14. Gong, J., et al., *A numerical study of thermal degradation of polymers: Surface and in-depth absorption.* Applied Thermal Engineering, 2016. **106**: p. 1366-1379.
15. Pochiraju, K.V., *Modeling thermo-oxidative aging and degradation of composites*, in *Long-term durability of polymeric matrix composites*. 2012, Springer. p. 383-425.