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Moisture Absorption and Degradation of Glass Fiber/Vinylester Composites

P. Mannberg, K. Giannadakis, A. Jakovics, J. Varna

Abstract

Vacuum Infusion is a closed mould manufacturing process that can replace open mould processes. To improve resin flow it is common to add flow enhancement layers to the reinforcement stack. This paper is aimed to analyze water uptake in these materials and its effect on mechanical performance. Ageing data for 3000 h in 90ºC water are presented for GF NCF/VE composite without flow layer and three composites with it. Tensile tests demonstrate degradation of mechanical properties and increasing viscoelastic and viscoplastic strains in wet composites.

Introduction

Manufacturing process that has developed significantly and has resulted in a number of successful applications is Vacuum Infusion [1]. For Vacuum Infusion of large surface area components it is necessary to use either internal or external flow layers that promote rapid resin flow. Today several commercial reinforcements that have internal flow layers exist and the basic principle for all of them is a coarse microstructure with regions of low fiber content that create easy flow paths for the resin. The question of interest here is how well laminates based on such reinforcements resist environmental ageing in general and water ageing in particular.

Moisture uptake and subsequent degradation of mechanical properties due to environmental loading is very important and therefore extensively studied e.g. [2-5]. Comparison of mechanical properties between aged and dry specimens shows that the reduction of the mechanical properties may be substantial. The mechanisms behind the reduction are degradation of all phases; resin, interphase and fiber. All the work has been done on materials without internal flow layer and fibers in thickness direction.

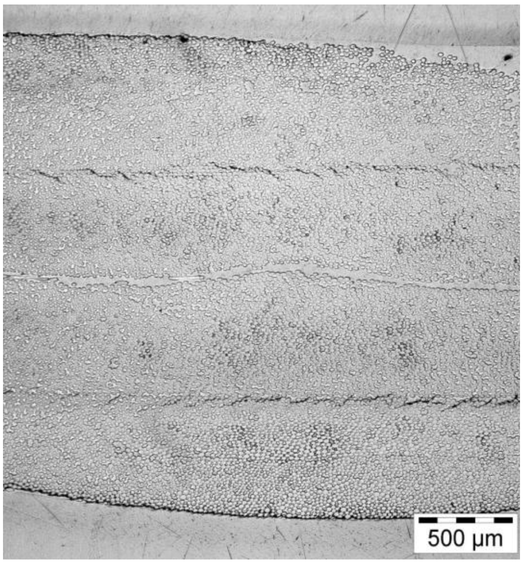
The present investigation is aimed to demonstrate the differences in moisture uptake and properties related to flow layers and to identify the origin of properties change for composites without flow layers. Virgin and aged samples have been investigated and differences in water uptake and degradation are analyzed.

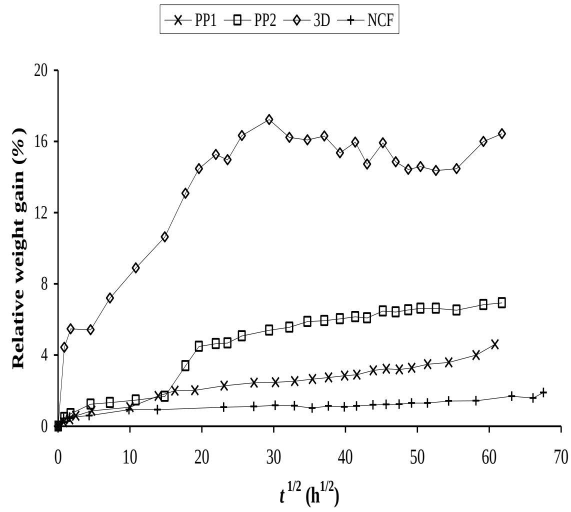
1. Materials and Sample Preparation

Knitted biaxial E-glass [45,-45], non-crimp fabric (NCF) composite was analyzed in this study. The reinforcement was laid in two layers to achieve symmetry and a suitable thickness.

The surface weight of the fabric was 2 x 1800 g/m^2. Three different commercially available materials with internal flow layers were also included in the study (called PP1, PP2 and 3D). All three contain a central flow layer of chopped strand mat (CSM) of E-glass placed between surface layers. All composites were made with the same bisphenol-A epoxy-vinylester, Dow Derakane 411-C50. The recipe used is, 0.3% Akzo NL-51P, 0.1% Akzo NL-63-100, 0.1% Akzo NLC-10 and 1.5% Akzo Butanox M50.

Composites were manufactured using vacuum infusion with one stiff and one flexible mould half. A polyamide film was used as the flexible side. After completed infusion the plates were in-mould cured at ambient temperature over night. The coupons were subjected to a post cure at 80°C for 9 hours to ensure full cure. To prevent moisture from entering the laminate through defects on the edges and interphases a thin layer of resin was painted to the edges. After complete preparation the samples were put in sealed containers together with silica gel and dried at 50°C for 60 h. The dry weight of the samples (zero moisture content) was determined by recording the weight loss during the 50°C dry conditioning until the weight stabilized. The thickness of the plate was 2.6 mm, the fiber volume fraction of NCF plate was 54% and the void content close to zero. Fig.1 shows the microstructure of the reference NCF material which has high and quite homogeneous fiber content and no visible voids. The fiber content in composites with flow layer was lower, between 27-36%





a) b)

Fig. 1. NCF composite: a) Optical micrograph of the cross-section showing high fiber content and low void content; b) moisture absorption curves for NCF composite and three composites made using resin flow layer

2. Experiments

Experiments were performed to investigate the influence of sorption and ageing on mechanical performance. Ageing was performed by immersion of samples in hot dematerialized water. The water absorption tests were performed according to ISO 62 with exception of the geometry that was adjusted to the size of tensile test specimens. Dematerialized water was used for the immersion ageing to get a controlled environment and to avoid influences from minerals and unknown contaminants. Ten samples were randomly selected and then immersed in water at temperature of 90°C for 3000 h. Before immersion the dry samples were weighed and during the test they were removed from the water and weighed at increasingly long intervals. The scale used was a Mettler-Toledo PM4600 with precision

0.01 g. Water uptake is defined by the relative moisture weight content M as a function of time, t.

Tensile tests (quasi-static monotonic loading and creep) were used to characterize the degradation in mechanical properties of the aged materials. The equipment used was an Instron servo hydraulic universal test machine equipped with a 10 kN load cell. Strain was recorded with a 25 mm gauge extensometer.

3. Results and Discussion

3.1. Water Uptake

The weight gain over time was recorded for ten coupons immersed in water. An average of the relative weight gain was then calculated, Fig. 1b presents the results. For comparison three different composites produced with the same technique but with flow layers resulting in lower fiber content and higher porosity are also shown. There is a large difference in the maximum relative weight gain and the time to reach maximum value. The 3D material with flow layer which has a different microstructure than PP1 and PP2 demonstrates clear non-Fickean behavior reaching plateau region quite early. It also appears as if the saturation levels for other composites never are reached, since even after more than 3000 h conditioning the materials still gain weight. Material 3D shows a completely different behavior with a much higher rate of weight gain and with much higher saturation level. Part of the difference can be explained by the difference in void content. A comparison between NCF and PP1, see Tab. 1, which both have low void content but differ much in fiber architecture and fiber content, shows that the effective diffusion coefficient is higher and the saturation level lower for the material with high fiber content. This may be due to poor bonding between the fiber and the matrix which may lead to a path for the moisture transport.

For polymer composites it is common to use the simplest model for the moisture sorption behavior i.e. Fickian diffusion. Fickian diffusion assumes that the moisture transport is proportional to the moisture gradient. In the literature typical values for the diffusion coefficient of thermoset composites at room temperature is in the range 10^{-12} - 10^{-14} m^2/s [6] and a value reported for vinyl-ester composites is 4.3×10^{-11} m^2/s [7]. In several studies the Fickian model has given an accurate description of observed moisture sorption behavior but deviations from the Fickian behavior can also be found [7].
According to [8] the moisture content increases with time as,

$$\frac{M - M_0}{M_m - M_0} = 1 - \frac{8}{\pi^2}\sum_{i=0}^{\infty}\frac{1}{(2i+1)^2}\exp\left(-\frac{(2i+1)^2\pi^2 D}{h^2}t\right), \qquad (1)$$

where M_0 is the initial moisture content and M_m is the saturation level.

The effective diffusion coefficient, D, is found by fitting the theoretical solution (1) to experimental data. In the present paper fitting is made by the least squares method that is finding the value of D that minimizes

$$S = S\left(D\right) = \sum_{i}^{n}(M_{\text{experiment}}(t_i) - M_{\text{calculated}}(t_i))^2 . \qquad (2)$$

In (2) t_i is the time instant for each measurement, n is the numbers of measurements included in the fitting procedure, $M_{\text{experiment}}(t_i)$ is the experimentally determined concentration and $M_{\text{calculated}}$ is the predicted concentration at time t_i. Diffusion coefficients, as calculated by the least square method Eq. (2), for the four materials are presented in Ta. 1. The magnitude of the diffusion coefficient is in good agreement with results from literature [7].

The observation that both moisture saturation level and diffusion constant change with void content has been earlier explained in [9] assuming that the equilibrium moisture level in matrix and voids are different. Assumptions made to obtain a quantitative expression are: a) assuming that fibers do not absorb any moisture; b) the equilibrium moisture level in void free matrix material is independent of the reinforcement type and architecture; c) moisture can be stored in voids as a mix of water vapor and liquid.

Tab. 1. Moisture uptake and diffusion coefficient data

Materia l	**Average relative weight gain, M_c** (%)	**Average weight gain** (*g*)	**Diffusion coefficient** (10^{-7} mm^2/s)
NCF	0.48	0.17	3.1
PP1	2.5	0.45	1.3
PP2	4.0	0.81	2.5
3D	5.7	0.79	3.4

3.2. Effect of Moisture on Mechanical Properties

Typical stress-strain curves are presented in Fig. 2. The reference NCF composite is presented in a separate figure because it exhibits a different failure mode: shear yielding in the polymer matrix instead of fiber fracture.

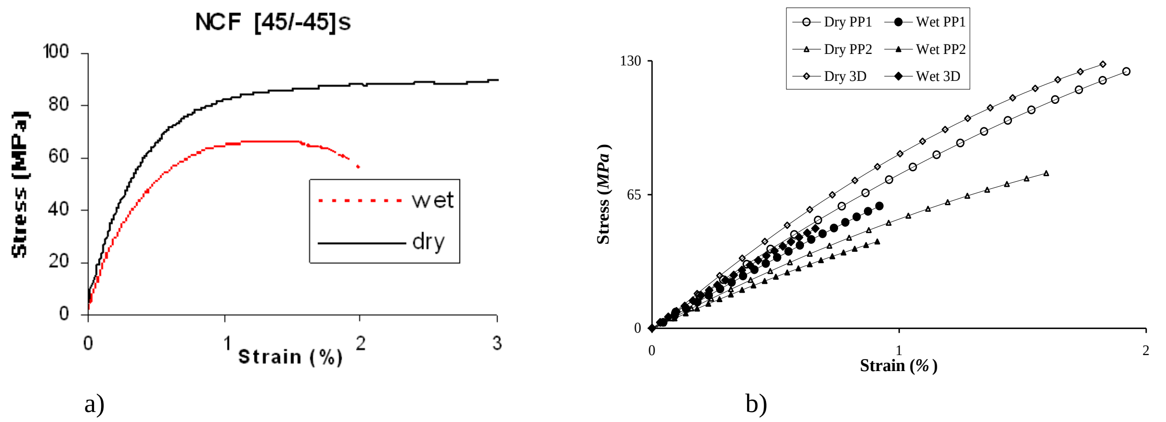


Fig. 2. Moisture effect on stress-strain curves of a) NCF; b) PP1, PP2 and 3D composites

Test results show a decrease in initial slope, tensile strength and failure strain for the immersion aged material. The reduction is not as severe for the reference NCF composite as for the other three materials. For materials PP1, PP2 and 3D the decrease in tensile strength and failure strain is in the range of 50-70 percent as compared to virgin material. There is no linear region in the stress strain curve for the [45/-45]s NCF composite. Therefore an apparent elastic modulus was determined as a trend line in strain region between 0.05 and 0.20%. Average values based on three specimens are 16.7 GPa for dry composite and 12.7 for wet. The maximum stress values are 87.5 and 63.6 MPa respectively.

The NCF composite was subjected to more detailed analysis. It was found, comparing initial elastic properties with values after loading to high stress, that the elastic constants are almost not changing thus indicating that microdamage in the composite is rather limited.

Creep and strain recovery tests were performed in order to understand the origins of the nonlinear behavior and the observed differences between wet and dry material. In these tests, following the methodology described in [10], the viscoplastic part of the strain can be separated from the viscoelastic part.

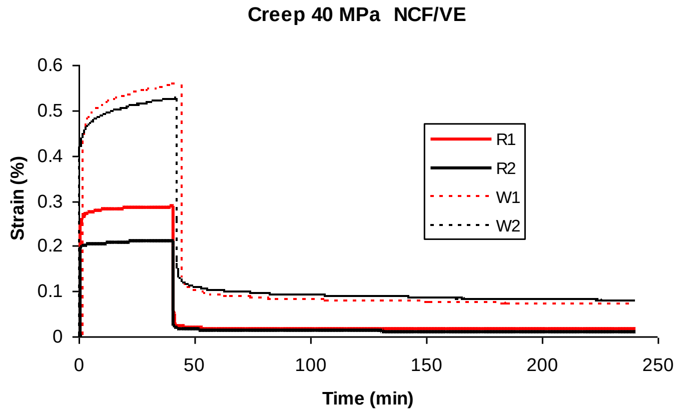
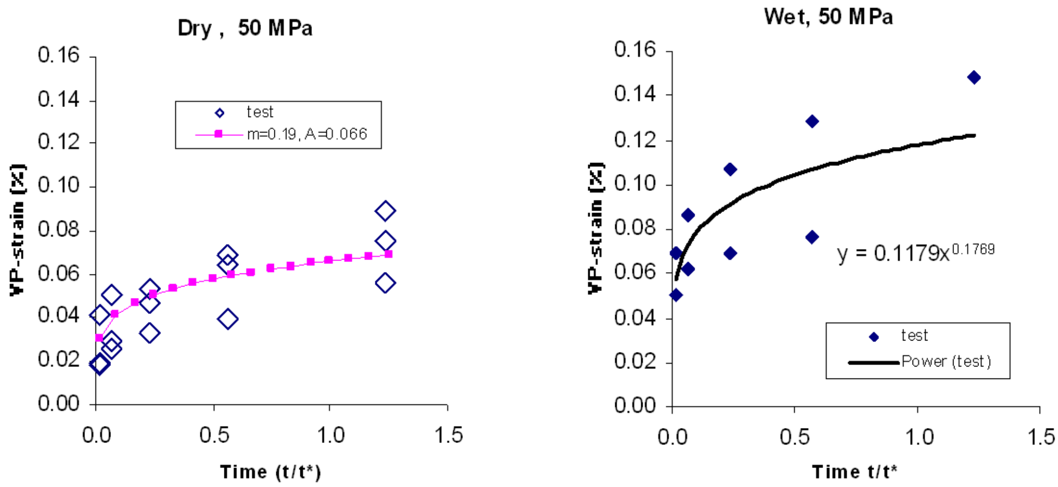


Fig. 3. Creep curves at 40 MPa applied stress for reference(dry) and wet NCF composite. W is notation for wet specimen, R –for dry reference specimen



a) b)

Fig. 4. Viscoplastic strain accumulation in NCF composite during creep test at 50 Mpa: a) dry specimens; b) wet specimens. Fit to data is shown as solid line. Characteristic time t*=3600 sec

Typical creep curves at 40 MPa and strain recovery curves are shown in Fig. 3 showing significant differences in time dependent behavior of wet and dry material. The creep strain in the wet material is about two times higher. Only a part of it can be explained with larger viscoplastic strain development because of plasticizing usually observed in wet polymers. The viscoplastic strain which is almost zero for dry specimens reaches values close to 0.1% in wet specimens (final irreversible strain at the end of recovery). Obviously the viscoelastic strain has also increased significantly and is, generally speaking, nonlinear. More detailed analysis of viscoplastic strain development in constant stress loading shows, see Fig. 4, that in wet composite viscoplastic strains develop much faster. They follow a power law with time as previously demonstrated for several composites and polymers [10,11].

Conclusions

The moisture sorption in composites with resin flow layer and without it was analyzed considering NCF reference composite without flow layer and three composites with it, showing large difference in diffusion coefficient and levels of moisture content.

The effect of moisture in these materials on mechanical performance in tension is analyzed showing large reduction in initial modulus, strength and strain to failure in wet materials. More detailed analysis of sources of nonlinearity and the effect of moisture is analyzed in series of creep tests separating the viscoelasticity and the viscoplasticity. It is shown that at given stress level both strain constituents are significantly higher in wet specimens.

Acknowledgement

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Authors

Mr. Mannberg, Peter
Swerea-SICOMP,
Box 271, SE-941 26 Piteå
Sweden
E- mail: Peter.Mannberg@sicomp.se

Mr. Giannadakis, Konstantinos
Prof. Varna, Janis
Lulea University of Technology
SE 97187 Lulea, Sweden
E- mail: Janis.Varna@LTU.SE
E- mail: Konstantinos.Giannadakis@LTU.SE

Prof. Dr. Phys. Jakovics, Andris
University of Latvia
Faculty of Physics and Mathematics
Zellu str. 8
LV-1002, Riga, Latvia
E- mail: Andris.Jakovics@lu.lv