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Chemical behaviour of water absorption in a carbon/epoxy 3D woven composite

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Abstract. In this paper, moisture absorption of carbon/epoxy-amine 3D woven composite materials is studied by immersion in distilled water at 70°C. If the moisture uptake measured by gravimetry is slow and weak over time, various antagonistic phenomena appear. Desorption highlights mass losses due to chemical changes in the material that mask the true water content of the aged samples. The X-ray photoelectron spectrometry (XPS) reveals a decrease in the C and N proportions and an increase in the O proportions after ageing, allowing to observe surface erosion and oxidation of the matrix. Finally, the increase of Si is a sign of an extraction of the silica fillers exuded to the surface. This presence is confirmed by Fourier transform infrared spectroscopy (FTIR).

Keywords: 3D woven composite, epoxy-amine, silica, water absorption

INTRODUCTION

For more than fifty years, fibre-reinforced composite materials have demonstrated their importance in the aeronautics field through their excellent mechanical properties while allowing considerable structure mass saving compared to metals.

Whereas they were traditionally manufactured from prepreg fabrics, the design of 3D woven preforms, where the fibers are placed in the three main directions, makes it possible to facilitate the implementation of high thickness parts at low cost. From a mechanical point of view, the main advantage of 3D woven fabrics is their excellent resistance to out-of-plane stresses, especially delamination, as the cohesion of the material is ensured by the changes in plane of the weft rovings. Thus, they benefit from a better resistance to impacts and shocks compared to UD and 2D laminates. They also have good strength in all three directions due to their three-dimensional architecture. This architecture gives them a better tolerance to manufacturing defects¹⁻³.

Like all fibre-reinforced composites, 3D woven fabrics are sensitive to moisture and, therefore, to hygrothermal ageing. The matrix absorbs water molecules that will diffuse in all three directions. Depending on the polymer's nature, this water absorption can reversibly or irreversibly alter the properties of the composites. The literature has many reported the consequences of hygrothermal ageing: solvent absorption, additive migration, plasticization, hydrolysis and leaching, oxidation, differential swelling, depolymerization, etc. These phenomena can cause embrittlement and cracking of the material, leading to loss of mechanical properties that may be irreversible and adhesion alteration of the bonds to be made⁴⁻⁷. The moisture diffusion behavior in 3D woven composites has rarely been studied. For thick parts, saturation is difficult to achieve, even in accelerated ageing⁸. On the other hand, physico-chemical modifications can still take place on surface.

The present study deals with analyzing the surface modifications of a 3D woven composite material induced by hygrothermal ageing to understand its low mass gain and know its surface state in view of a bonded repair.

EXPERIMENTAL

The 3D woven composite material is composed of carbon reinforcement and an aeronautical epoxy/amine matrix. These samples have the following dimensions $50 \times 50 \times 9.5 \text{ mm}^3$. Neat resin samples are also studied and have the following dimensions: $10 \times 10 \times 3 \text{ mm}^3$.

Hygrothermal ageing has been carried out on these materials in distilled water immersion at 70°C in a Climats VRT Extreme 320 climatic chamber. The immersion temperature is quite lower than the glass transition temperature. After 230 days of immersion, some samples are placed in an oven at 70°C for desorption. The samples are periodically weighted using a 0.1 mg resolution Mettler AE 200 electronic balance.

Sorption curves obtained by gravimetry in distilled water immersion at 70°C for the two materials followed by desorption and their diffusion parameters are gathered in FIGURE 1 and TABLE 1. Carbon fibers being impermeable, the composite mass variations are reduced to the matrix mass fraction.

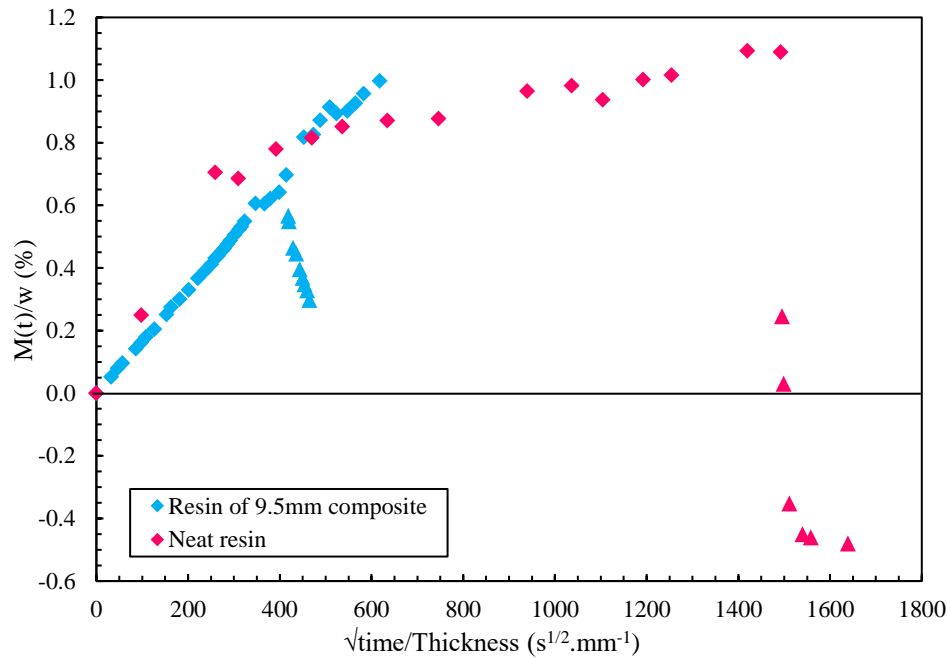


FIGURE 1. Water sorption curves in immersion at 70°C followed by water desorption curve in an oven at 70°C , reduced to the matrix mass fraction.

TABLE 1. Sorption and desorption curves' diffusion parameters of the neat resin and the 3D woven composite resin.

Diffusion parameters	Neat resin	Resin of composite
$D_{\text{sorption}} \text{ (mm}^2/\text{s)}$	7.85×10^{-7}	3.17×10^{-7}
Mass uptake – 300 days (%)	1.09	0.99
$D_{\text{desorption}} \text{ (mm}^2/\text{s)}$	5.52×10^{-6}	3.42×10^{-7}
Mass loss – 30 days (%)	1.51	0.40

After 300 days of ageing, saturation is not reached, and a slow rise continues to occur. Masse uptake of the neat resin and composite samples is respectively 1.09 and 0.99 %. The water diffusion in the resin neat has already slowed down. It has reached the second diffusion stage, while the matrix composite diffusion, although lower, is still on the first diffusion stage and seems to reach a higher water uptake eventually.

Some samples are desorbed at 70°C in an oven. On desorption curves, the neat resin curve falls and reaches saturation after about 30 days. The samples do not regain their initial mass but reach a much lower value of -0.48% from the initial state, i.e., -1.51% compared to the 300-day aged state, which reflects irreversible mass losses during

moisture absorption. Then several reversible or irreversible processes take place at the same time and may be opposed⁹. Indeed, an extraction of particles from the samples is noticeable in the water of the immersion beakers, which suggests mass losses.

An analysis by Fourier transform infrared spectroscopy (FTIR) in attenuated total reflectance (ATR) allows determining that these extracted particles are silica fillers from the epoxy resin (FIGURE 2). They alter the aged composite spectra at 3600cm^{-1} peak associated with isolated silanol vibration and 990cm^{-1} peak linked with Si-O bond¹⁰. Moisture absorption is apparent by the increase of the $3650\text{-}3150\text{cm}^{-1}$ band, related to O-H bonds, during diffusion of H₂O molecules, and by the attenuation of the $3150\text{-}2750\text{cm}^{-1}$ band, corresponding to N-H bonds, by hydrolysis. Oxidation is also perceptible on the 1650cm^{-1} peak where the ketone functions (C=O) are grafted.

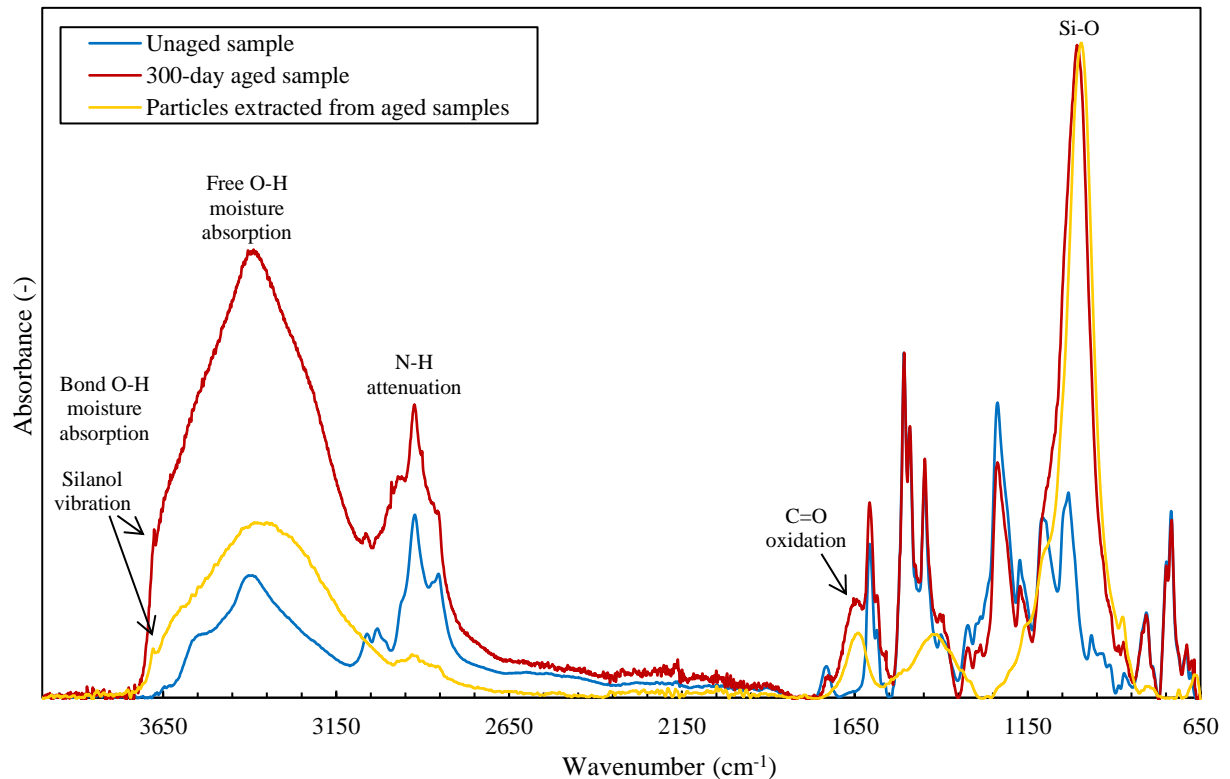
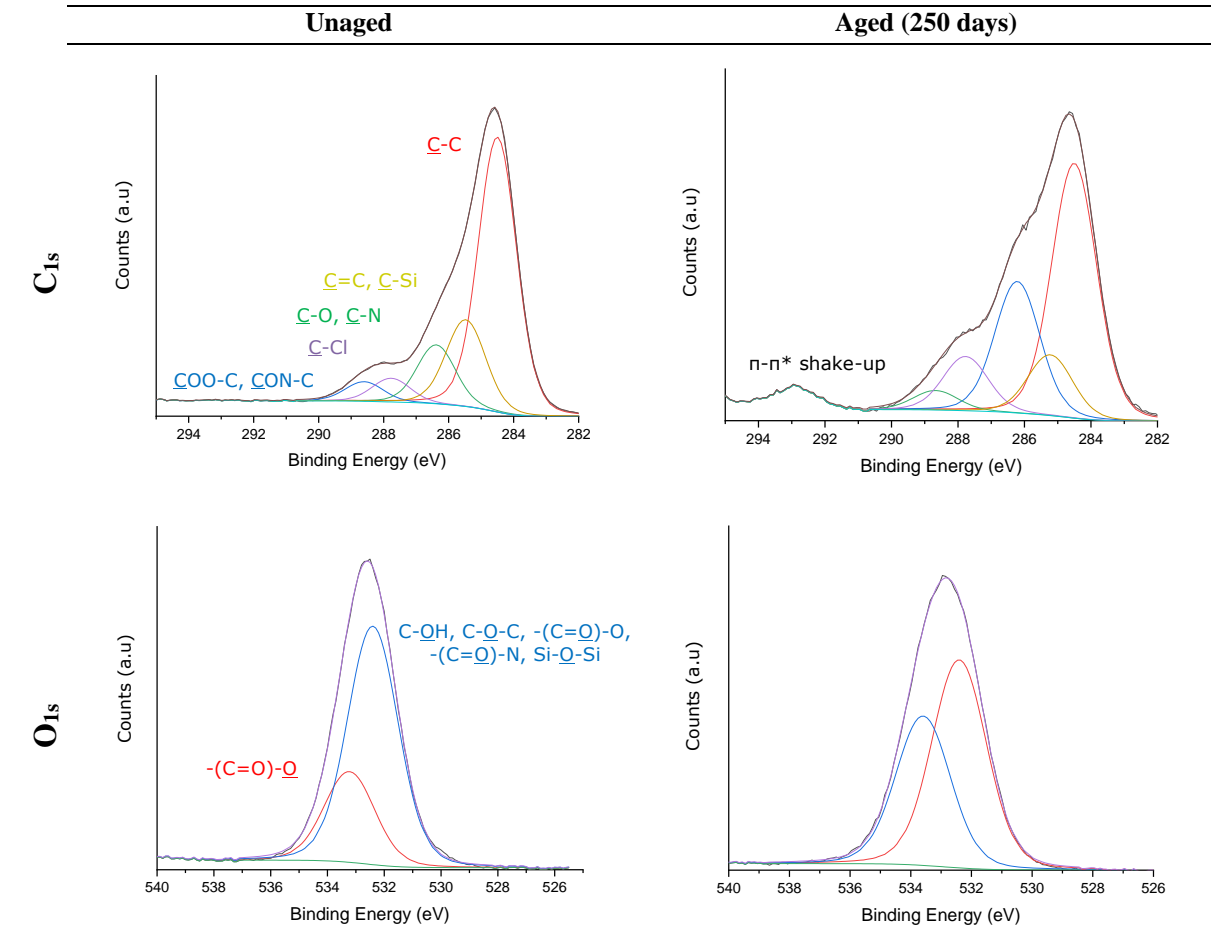


FIGURE 2. FTIR spectra of unaged and aged 3D woven composites samples and their extracted particles.

Moisture absorption is possibly greater than the gravimetrically measured mass absorption, but it is hidden by fillers losses. During desorption, the composites have not yet reached saturation. However, the results show a difference in diffusion kinetics. Desorption diffusivity D is significantly faster than absorption, as shown in TABLE 1 for each sample. The diffusivity in sorption is slowed down by the mass losses caused by silica extraction by the water. On the other hand, during desorption, there doesn't seem to be any phenomenon slowing down the exit of water. New sorptions will be conducted to observe if they are accelerated or even intensified by desorption.

Surface modifications after 250 days ageing are then observed by X-ray photoelectron spectrometry (XPS) on 9.5 mm 3D woven composite materials. TABLE 2 gathers the high-resolution spectra related to carbon (C_{1s}) and oxygen (O_{1s}) before and after ageing. They represent the different chemical bonds of the functional groups constituting the material and their respective intensities. They are used to determine the elementary compositions and the associated ratios by observation of the shift of binding energy relative to the main component (aromatic C).

TABLE 2. C_{1s} and O_{1s} XPS spectra of the 3D woven composite unaged and after 250 days of hygrothermal ageing.



The compositions of chemical elements and functional groups before and after 250 days of ageing are respectively indicated in TABLES 3 and 4. While the proportions of C, N and Cl decrease with hygrothermal ageing, O and Si increase. The decrease in the proportions of C and N indicates matrix degradation and fibre erosion. Disappearance of the epoxy-hardener bonds is noticeable by the fall of the proportions in bonds (-COH-CH_x-NH-) and in N/C and Cl/C ratios confirming the hydrolysis of resin. Ageing reveals the π - π^* satellite shake-up band, representative of aromatic or graphitic structures. As this band is not or weakly detectable on pure epoxy resins, it is likely the signature of the fibers¹¹. Therefore, its appearance on aged samples means that the carbon fibers are exposed.

The appearance of silica fillers, which rise to the surface, is marked by a strong increase in the Si proportions and Si/C ratio. The proportions of O also increases, suggesting significant oxidation of the surface.

Finally, the decrease of the proportions of C-C and the increase of C-O and C-H illustrate the absorption of H₂O molecules by the matrix, and thus a water uptake, or even oxidation.

TABLE 3. Surface element proportions for the unaged and aged composite material.

Samples	Element composition (%)						Ratios			
	C _{1s}	O _{1s}	N _{1s}	Cl _{2p}	Si _{2s}	Si _{2p}	O/C	N/C	Cl/C	Si/C
Position (eV)	285	533	400	285	169	103				
Unaged	68.9 ± 3.9	18.2 ± 0.9	4.3 ± 0.2	0.91 ± 0.05	1.0 ± 0.05	5.9 ± 0.3	0.26	0.06	0.013	0.08
Aged (250 days)	58.2 ± 2.90	26.2 ± 1.3	2.1 ± 0.1	0.11 ± 0.01	1.4 ± 0.05	9.5 ± 0.5	0.45	0.04	0.002	0.16

TABLE 4. Surface functional group proportions for the unaged and aged composite material.

Samples	Functional group composition (%)					
	$\underline{\text{C}}=\text{C}$, $\underline{\text{C}}-\text{Si}$	$\underline{\text{C}}-\text{C}$	$\underline{\text{C}}-\text{O}$, $\underline{\text{C}}-\text{N}$	$\pi-\pi^*$	$-(\text{C}=\underline{\text{O}})-\text{O}$, $\text{C}-\underline{\text{O}}-\text{C}$, $\text{C}-\underline{\text{O}}\text{H}$, $-(\text{C}=\underline{\text{O}})-\text{N}$, $\text{Si}-\underline{\text{O}}-\text{Si}$	$-(\text{C}=\text{O})-\underline{\text{O}}$
Position (eV)	284.5	285.4	286.4	292.8	532.4	533.4
Unaged	58.9	19.2	12.6	-	72.4	27.6
Aged (250 days)	48.9	11.7	13.2	1.89	58.2	41.8

CONCLUSION

A simple gravimetric monitoring would suggest that the 3D woven composite seems to be subjected to hydrothermal ageing. Due to its thickness, diffusion into the center of the sample is very slow. In reality, its behavior to moisture absorption is marked by various phenomena. It has been observed by desorption, Fourier transform infrared spectroscopy, and X-ray photoelectron spectrometry that water uptake is present but is counterbalanced by surface erosion of the matrix and extraction of silica fillers. In addition, oxidation is observable. Differences in diffusivities are also observed between sorption and desorption. Complementary analyses, in particular with the scanning electron microscope, are in progress to validate the first results and to observe the surface degradation. Further sorption and desorption cycling tests will be carried out to observe the behaviour of the materials. A quantification of fillers losses through time is undertaken.

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