

Polyvinyl alcohol yarns long term properties characterization and assessments. Part I: Physical behavior – consequences of water affinity

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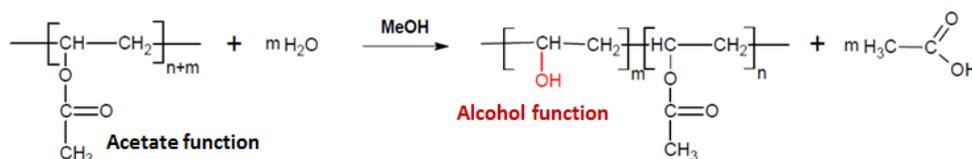
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ABSTRACT: For more than a decade now, High Tenacity Polyvinyl Alcohol (HT-PVAI) yarns have been attracting a lot of interest in the geosynthetic community, particularly for reinforcement functions. PVAI interest principally lies in its excellent resistance to strongly alkaline or acidic environments combine with a high stiffness that makes it a great alternative material to classical reinforcement products. Today, several products manufactured with HT-PVAI yarns can be found on the market and their demand is boosted by the increasing use of soil treatments, recycled materials or low-quality fills with extreme pH conditions. Despite this rising attraction for PVAI, its characterization remains an open issue for the scientific community, as well as a challenge for the standardization organization that faces difficulties in specifying this material and assessing its long-term durability. In the first part of this study, we will focus our investigation on the physical behavior of HT-PVAI yarns particularly when exposed to water. Indeed, geosynthetic characterization are generally carried out in alkaline or acidic solution. Because of its chemical nature, PVAI has a strong affinity for water. Consequently, it is necessary to fully understand the mechanism of water sorption as well as its consequences on the physical structure and mechanical properties to correctly assess the durability of HT-PVAI yarns. Here, we will present a series of physicochemical and mechanical analyses aimed to determine the kinetics of water sorption, the plasticization effect of water, and its impact on mechanical properties (i.e tensile properties and creep). The authors will conclude this paper with the specific guidelines that should be respected when testing HT-PVAI yarns durability with regards of their water affinity.

Keywords: Poly(vinyl alcohol), yarns, geosynthetics, water, sorption, plasticization.

1 INTRODUCTION

PVAI is obtained by hydrolysis of Polyvinyl Acetate (PVAc) and is known for its water affinity due to its chemical structure composed of highly polar functions.



The water affinity of PVAI is tied to the amount of alcohol functions (*m*) versus acetate functions (*n*) in the polymer chain. When *m* reaches values above 98 mol%, the intermolecular hydrogen bonding prevails that limits the access of water to the main polymer chain and thus, leads to a so called non-soluble PVAI (Sakurada, I.). This non-solubility is temperature dependent. When reaching temperatures above 80°C, the mobility of the main chain will facilitate the access of water to the alcohol function and thus, lead to a full dissolution of the material. In fact, this singular behavior is what allows the use of HT-PVAI yarns for reinforcement applications in all environmental conditions.

Yet, even though PVAL with high saponification degree can be considered as non-soluble, this does not mean that it does not entirely interact with cold water. Below 80°C, a small amount of water sorption will take place principally in free volume or where there exists some chain irregularities (i.e remaining acetate function, head to head irregularities) (Sakurada, I.). Looking in the literature, a phenomenon of swelling is used to explain the consequences of water sorption (Nait Ali, L.K et al.) which, in other words, means that dissolution is initiated to a small extent of structural modifications when exposing PVAL to water.

In this paper, we will focus our investigation on characterizing this water sorption; defining its kinetics and evaluating its impact on the mechanical properties to discuss the best way to handle this material for assessing its durability.

2 CHARACTERIZATION OF HT-PVAL YARNS

2.1 Sample preparation and pre-treatment

HT-PVAL yarns with a saponification degree of 98 mol% and a linear density of 2000 Dtex were used in this study. Four different types of conditionings were considered and are detailed below.

Dry yarns. Yarns were dried under primary vacuum at 130°C for 5 hours and then stored in a desiccator for more than two days. The determination of the drying conditions will be described later in this paper.

Equilibrated yarns at 50%RH/22°C. Yarns were kept in an atmospheric controlled room for at least four days at 22°C and 50% of relative humidity. This corresponds to the manufacturer bobbin.

Equilibrated constrained yarns at 100%RH/22°C. Yarns were tightly rolled over a borosilicate test tube then immersed in distilled water at 22°C for at least one day.

Equilibrated un-constrained yarns at 100%RH/22°C. Yarns were freely immersed in distilled water at 22°C for at least one day.

2.2 Determination of drying conditions

To determine the best drying conditions, a series of thermogravimetric analysis (TGA) were performed under nitrogen using a TGA-Q500 apparatus from TA Instruments. The protocol applied consists of a 50°C/min constant heating ramp from 25°C to various temperatures: 110°C, 120°C, 130°C, 140°C and 180°C followed by a 1000 minutes isotherm. At these temperatures, the weight changes of the samples as a function of time are presented in Figure 1. The resulting curves show that up to 130°C, a certain amount of water was evaporated during the ramp and the initial stage of the isotherm, followed by a quick stabilization of the sample weight. From 140°C, the samples lost weight continuously suggesting that a thermal degradation took place.

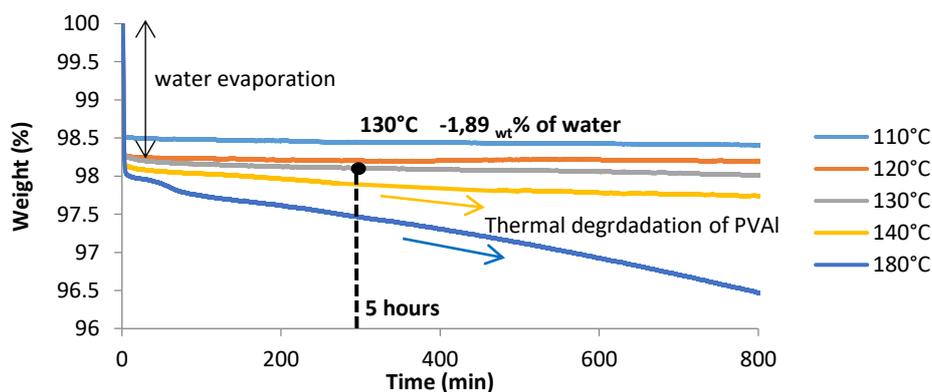


Figure 1. TGA thermographs of equilibrated yarns at 50%RH/22°C under nitrogen at different temperatures for 800 min

As a result, the best drying conditions were considered to be 130°C for 5h. To further improve the drying process a primary vacuum oven was used for the preparation of dry samples.

2.3 Determination of the water content and glass transition temperature

The determination of the water content was done using two different analytic methods. First, we used the drying protocol previously presented, that is to say TGA analysis under nitrogen with a ramp of 50°C/min followed by a 5h isothermal at 130°C in order to determine the quantity of absorbed water. Then, we used

a method based on Modulated Differential Scanning Calorimetry (MDSC). In other words, DSC analysis was performed with modulated temperature ($\pm 2^\circ\text{C}/60\text{s}$) under nitrogen using a DSC-Q1000 apparatus from TA Instruments. The protocol was a $3^\circ\text{C}/\text{min}$ constant heating ramp from -60°C to 350°C . The main advantage of MDSC over DSC is that the sinusoidal modulation applied on the heating ramp allows dividing the heat flow measurement in two components: the Reversing Heat Flow (heat capacity component) and the Non-reversing Heat Flow (kinetic component). Consequently, phenomena which are heat capacity related, such as the glass transition, and phenomena which are kinetics dependent, such as the water evaporation, can be separated into two heat flow curves and thus, measured separately (Figure 2). This is of great interest as it was reported before that T_g and water evaporation may be overlapped for PVAI samples (Nait Ali, L.K.).

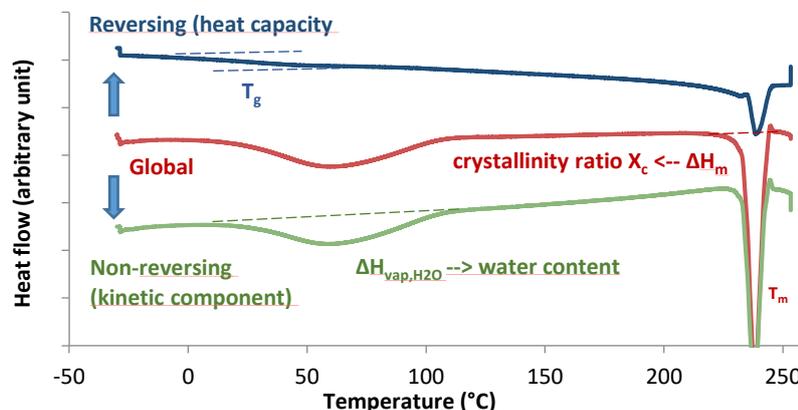


Figure 2. Example of MDSC thermogram for equilibrated yarns at 50%RH/22°C.

The melting temperature T_m and enthalpy ΔH_m were directly measured from the Global Heat Flow graph. ΔH_m was used to calculate the crystallinity ratio (X_c):

$$X_c(\%) = \frac{\Delta H_m}{\Delta H_m^\circ} \times 100$$

where ΔH_m° is the melting enthalpy of the PVAI crystal with $\Delta H_m^\circ = 161 \text{ J/g}$.

The T_g and the enthalpy of water evaporation $\Delta H_{\text{vap,H}_2\text{O}}$ were obtained from the Reversing Heat Flow and Non-reversing Heat Flow graphs respectively. $\Delta H_{\text{vap,H}_2\text{O}}$ was used to calculate the water content as follows:

$$\text{water content}(\%) = \frac{\Delta H_{\text{vap,H}_2\text{O}}}{\Delta H_{\text{latent,H}_2\text{O}}} \times 100$$

where $\Delta H_{\text{latent,H}_2\text{O}}$ is the latent heat of water vaporization with $\Delta H_{\text{latent,H}_2\text{O}} = 2265 \text{ J/g}$.

2.4 Tensile properties

The tensile properties of the different samples were measured following the test procedure described under ASTM D2256 standard. The results obtained are illustrated in Figure 3. In order to compare the evolution of the mechanical behavior between the various samples, the authors have chosen to work with a secant modulus at 2% of deformation.

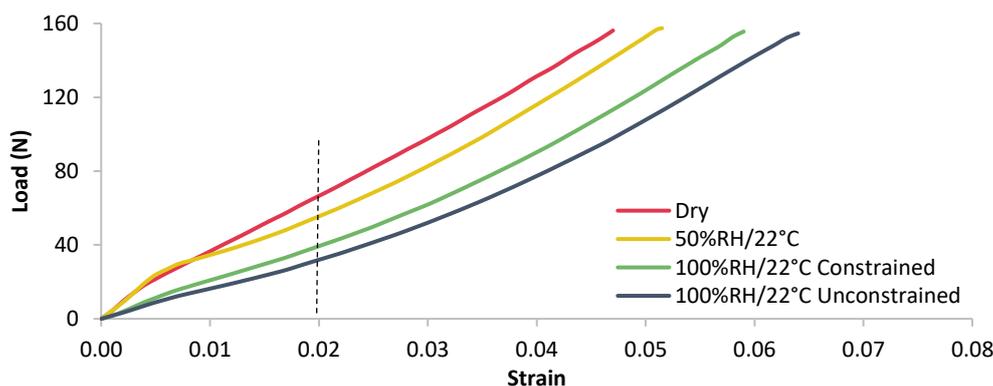


Figure 3. Typical tensile curves of the different samples

2.5 Compilation of results

The TGA, MDSC and tensile test results are shown for each yarn sample in Table 1. The two methods to measure the water content give comparable results. Dry yarns contain no water while equilibrated yarns at 50%RH and 100%RH shows approximately 2 wt% and 5.2-5.5 wt% of water respectively, independent of exposure conditions. It should be noted that the unconstrained sample exhibits a measured 2% of shrinkage upon water exposure. The T_g of dry yarns (83°C) decreases with the raising of water content up to 53°C for 50%RH and then, up to 30-27°C for 100%RH, implying a plasticizing effect of water on PVAI yarns. The decrease of the secant modulus is also observed as the water content increases and T_g decreases. The results also highlight a significant gap in stiffness between the constrained and unconstrained samples. It is assumed that this behavior is the consequence of a swelling effect which led to the shrinkage observed in unconstrained sample due to water sorption.

Finally, the values of T_m and X_c remain almost unchanged whatever the water content. As these two parameters characterize the crystalline phase of PVAI, it seems that water sorption occurs only in the amorphous phase of PVAI yarns and does not modify its crystalline phase.

Table 1. Physical and mechanical characteristics of HT-PVAI yarn samples for different conditionings

	Dry	Equilibrated yarns at 50%RH/22°C	Equilibrated constrained yarns at 100%RH/22°C	Equilibrated unconstrained yarns at 100%RH/22°C
T_m (°C)	238-240			
Crystallinity ratio X_c (%)	75	70	-	72
T_g (°C)	83	53	30	27
Water content (wt%) by MDSC	0	1.8	5.2	5.5
Water content (wt%) by TGA	0	1.9	-	5.5
Strength (N)	156.2 ± 2.3	157.4 ± 1.8	155.6 ± 4.1	154.6 ± 6.2
Elongation (%)	4.7	5.2	5.9	6.4
Secant modulus at 2% (N)	33.3	27.8	19.7	16

3 KINETICS OF WATER SORPTION

3.1 Water sorption in distilled water

Water sorption tests were performed by total immersion of unconstrained and constrained yarns in distilled water at 22°C. Samples were taken after different immersion times, wiped with paper to eliminate the surface moisture, and then tested by MDSC, TGA and in some cases, tensile tests were also performed.

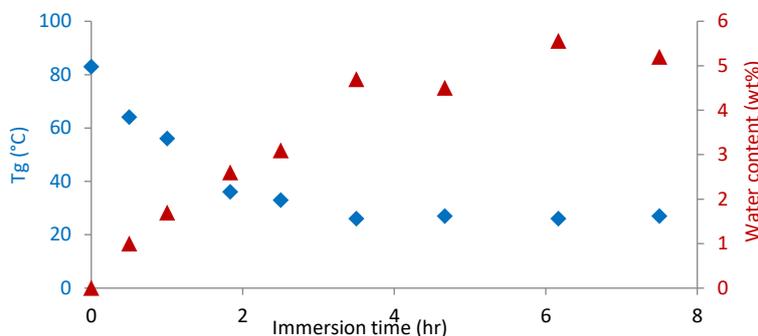


Figure 4. T_g and water content as a function of immersion time for initially sample

Figure 4 shows the evolution of T_g and water content of yarns as a function of immersion time. As expected, the water content increases with immersion time and tends towards a final asymptotic value around 5.5%, while T_g decreases with immersion time and reaches a final constant value around 27°C for unconstrained sample. The sorption curves show that saturation is obtained after about 6h of exposure at 100%RH and 22°C. The decrease of T_g is seen to stop after about 2.5h while the water content continues to rise. This behavior suggests that the water sorption may follow two different mechanisms. In Figure 5, we have plotted the evolution of T_g and secant modulus at 2% for the constrained and unconstrained

samples versus water content. This plot highlights the impact of water sorption on T_g and demonstrates that the mechanism of sorption does not seem to be influenced by the method of exposure: constrained or unconstrained, as the T_g values are equivalent for a given wt% of water. It also shows that the secant modulus decreases in two steps: A first decrease with a stabilization up to the T_g equilibrium for about 3.5 wt% of water content followed by a second substantial decrease which could be attributed to the transition between the glassy and rubbery states, as the T_g reaches values close to ambient temperature. A gap can be noted at the end of the process between the plateau values of the constrained and unconstrained sample. This gap could be the consequence of the swelling/shrinkage effect observed for unconstrained samples which seems to be associated to the second sorption process when high content is reached (see Figure 7).

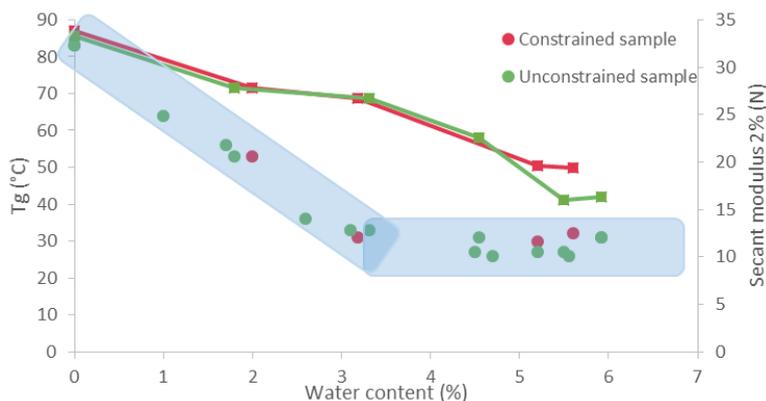


Figure 5. T_g and secant modulus versus water content for the constrained and unconstrained samples

3.2 Water sorption in different RH

Water sorption tests were performed on initially dried and unconstrained yarns at different temperatures (22, 30, 40°C) and relative humidities (30, 50, 70, 90%RH) in a DVS-1000 climatic chamber from Surface Measurement System. The sample weight was followed as a function of time during the water sorption process, from which the water content at each time was calculated to draw the sorption curves. The immersion test data presented previously were used for the 100%RH data.

To better understand the water diffusion mechanism in PVAI yarns, normalized water content is drawn as a function of the square root of immersion time to be compared with a data fitting by the Fick's second law of diffusion (Figure 6). Here, the saturated water content for each %RH-Temperature couple is normalized to 1 and the Fick's law is written in cylindrical coordinates since PVAI fibers can be considered as infinitely long cylinders and the diffusion of water only occurs in the radial direction:

Fick's second law of diffusion in cylindrical coordinates:
$$\frac{\partial C}{\partial t} = \frac{D}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C}{\partial r} \right)$$

Equation of the data fitting by Fick's law:
$$\frac{M_t}{M_\infty} = \frac{C_t}{C_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(\frac{-D\pi^2 n^2 t}{r^2}\right)$$

where C is the concentration of water in the radial direction, t is the immersion time, D is the diffusion coefficient, r is the average radius of PVAI fibers, M_t is the water content at time t, M_∞ is the water content at saturation.

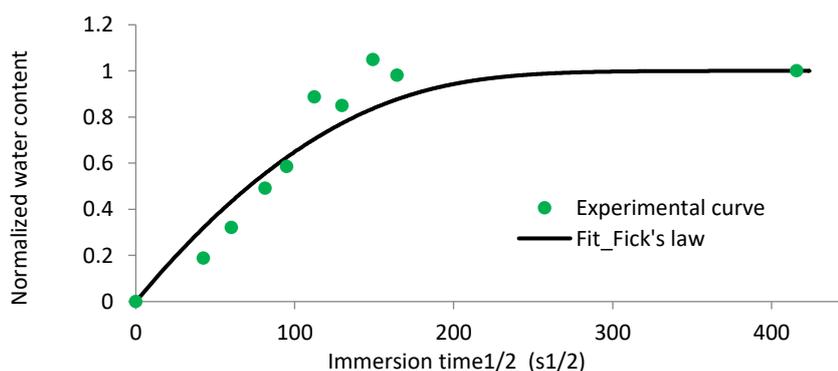


Figure 6. Fitting of the sorption data by the Fick's second law

Each sorption curve is then fitted by the Fick's second law of diffusion and the coefficient D of water diffusion in PVAI yarns is calculated and given in Table 2 for the different sorption conditions.

When RH is lower than or equals to 50%, D increases when raising the temperature, and RH has almost no influence on the value of D. These agree with the Fick's law where D depends only on temperature. In contrast, when RH is higher than or equals to 70%, D increases with the raising of both temperature and RH, implying a non-Fickian diffusion process.

This observation is complementary to the previous results suggesting a two step sorption mechanism which would explain a variation in the diffusion process.

Table 2. Diffusion coefficient D (m².s⁻¹) of water in PVAI yarns under different sorption conditions

Temperature	Relative humidity				
	100%RH	90%RH	70%RH	50%RH	30%RH
40°C	--	4.6 E-9	1.3 E-9	7.8 E-10	7.3 E-10
30°C	--	8 E-10	4.5 E-10	2.8 E-10	2.7 E-10
22°C	7.0 E-10	3.0 E-10	1.7 E-10	1.3 E-10	--

3.3 Sorption mechanism

To illustrate the water sorption of HT-PVAI yarns, the water content at saturation and at different temperatures has been drawn as a function of RH in Figure 7. The saturated water content increases when raising the RH following a non-linear relationship which does not entirely follow the Henry's law.

Henry's law generally shows a linear relationship between saturated water content and RH when Fickian diffusion is confirmed (Colin, X. et al.). Considering, the diffusion coefficient calculated above, it can be assumed that for a RH up to 50-60%, the water diffusion is Fickian and consequently the sorption at saturation follows Henry's law. In contrast, when RH is higher than or equals to 50-60%, the water diffusion is non-Fickian and the sorption does not follow Henry's law. The extra water absorbed at higher RH compared to the theoretical value extrapolated from the Henry's law demonstrates a change in the mechanism of water sorption. Finally, the temperature seems to have no influence on the saturated water content of HT-PVAI yarns, implying that PVAI can be classified among the moderately polar polymers (Colin, X. et al.).

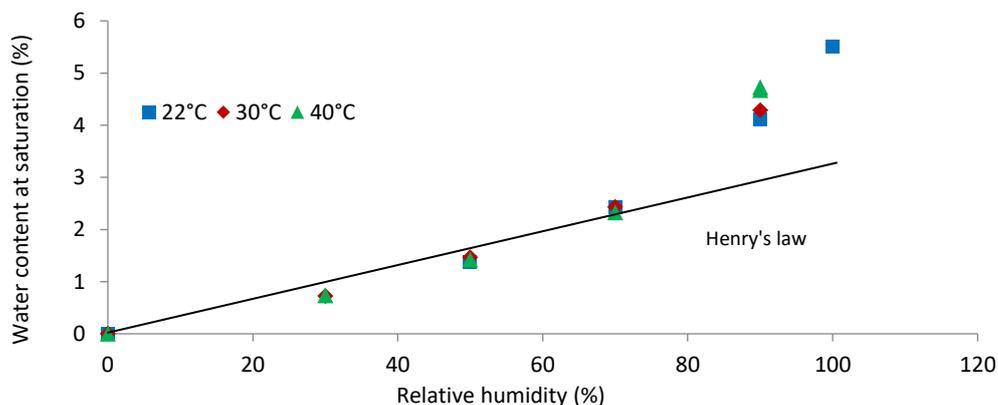


Figure 7. Water content at saturation as a function of relative humidity

Based on all our observations we can suggest a two-step mechanism:

- A first phase, up to about 3-3.5% of water content, where water diffuses solely in the amorphous region of the polymer, leading to a decrease of T_g and consequently, some variations in the stiffness. This behavior can be attributed to a pure plasticization effect.
- A second phase, above 3-3.5 wt% of water content, where the polymer continues to absorb water and the stiffness continues to decrease, but the T_g remains constant. In this phase, the stiffness decrease would be more drastic whether the sample is constrained or not and undergoes shrinkage. At this stage of investigation, it is difficult to decide among several possible mechanisms.

Indeed to explain the second phase, we are investigating at least two options. First, is there a mesophase or a highly orientated phase in which the water starts diffusing when the amorphous region reaches its saturated water content? If the yarn is not constrained the water will impact more dramatically the structure of this phase and lead to the shrinkage of the yarn (which can be considered irreversible).

The second option is based on the work done by Ishikawa, K. et al., who suggested that the PVA crystals can absorb a certain amount of water leading to consequent and irreversible deformation of the lattice which could explain the observed behavior. In our initial testing, we have not noticed any variations of the melting point or crystallinity ratio with DSC, which leads us to believe that the crystalline region was not impacted by water. However, complementary testing is currently running in order to check this assumption.

4 IMPACT OF WATER ON YARN UNDER MECHANICAL LOADING

The authors saw previously that if constrained and unconstrained samples exhibit similar water sorption behavior, the consequences on their mechanical properties are different. Indeed, unconstrained samples exhibit a swelling behavior which leads to about 2% of shrinkage and impacts their final stiffness.

In a reinforcement application, HT-PVAI yarns are constantly under a minimal load when exposed to moisture. Their behavior should correspond to the one of *Equilibrated constrained yarns at 100%RH/22°C*. Here the authors tried to check whether there is a minimal loading that should be applied to block shrinkage and be able to assess properly the durability of HT-PVAI yarns in conditions that match the application. In other words, the authors tried to measure the impact of loading on the mechanical properties upon water sorption. This was done using a Dry/Wet creep protocol, which was initially proposed by Nait-Ali et al. to determine the reduction factor for water affinity that should be used for HT-PVAI yarns. In their work, these last authors follow the increase of elongation after various Wet/Dry cycles at a given loading (30% UTS). In our case, we have launched a creep test on a sample at a given loading under 50%RH and 22°C in a container. Once a relative stabilization was obtained, water was added and the creep test was pursued at 100%RH and 22°C leading to an increase of elongation as illustrated in Figure 8.

Tests were done at 1% UTS, 3% UTS, 5% UTS, 10% UTS and 30% UTS and the differential elongation was followed. At the end of each test, a tensile test was launched without releasing the loading to determine the residual properties of the yarn after water exposure.

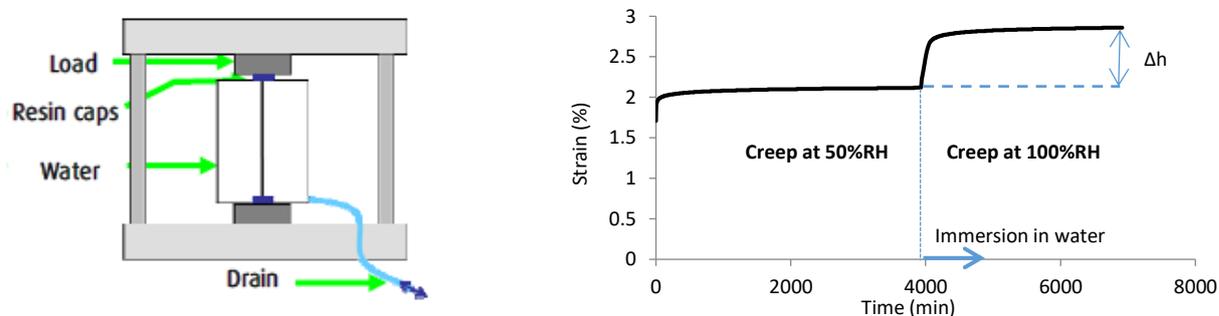


Figure 8. Illustration of the Dry/Wet creep test

First, we observe that the increase in elongation due to water exposure follows a linear relationship which intercept at 0 with the loading applied (Figure 7), which means that as long as the yarn is held in its position, it will only undergo creep upon water exposure. In other words, shrinkage is limited to unconstrained samples.

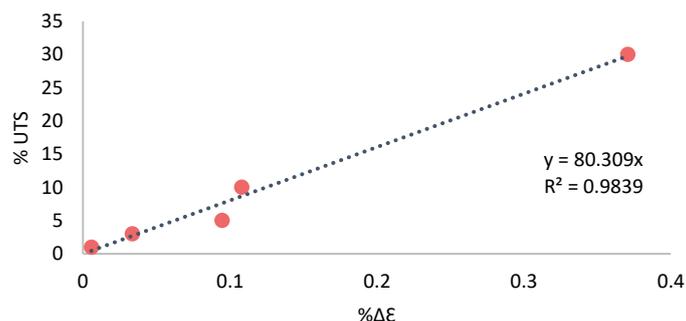


Figure 9. Differential elongation versus applied load

Then, the tensile test done after the Dry/Wet creep exposure shows that independently of the loading applied, the mechanical properties of the yarn after water exposure (Figure 10) are similar and exhibit the same properties as the *Equilibrated constrained yarns at 100%RH/22°C*.

It can be concluded that the loading applied has no influence on the properties of the yarn upon water exposure. Additionally, this confirms the Nait Ali et al. proposition regarding a reduction factor for water affinity in the range of 0.83 for geosynthetics made of HT-PVAL yarns. Indeed, the application of a mixing law between *Equilibrated yarns at 50%RH/22°C*, which are the manufacturer product in normal conditions, and *Equilibrated constrained yarns at 100%RH/22°C*, which shall be representative of yarns exposed to 100%HR in use conditions, leads to a reduction of the strength 15% (or a $R_{f_{wa}}$ of 0.85) based on the results of this study.

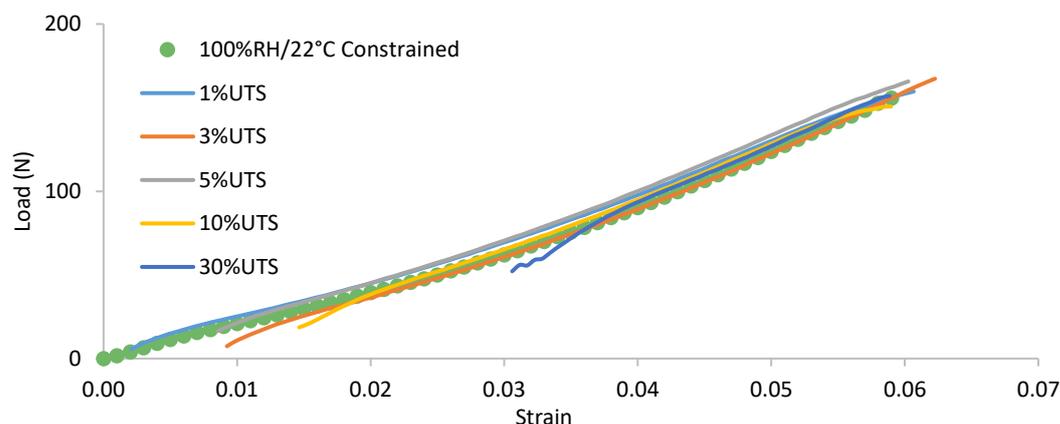


Figure 10. Comparison of the tensile curves after Dry/Wet creep test

5 CONCLUSION

In this work, we have proposed new methods of characterization of HT-PVAL yarns allowing to measure their water content and T_g . Using these methods, we have carried out a series of water sorption analyses allowing to suggest a two-step mechanism for water diffusion in HT-PVAL yarns used in civil engineering applications. The authors have shown that the mechanical behavior of the yarn varies whether it is constrained or not, but the water diffusion mechanism remains unchanged. Consequently, the authors intend and recommend using constrained yarn for durability study to avoid its shrinkage and to properly characterize its mechanical behavior after ageing, particularly its stiffness. Indeed, the fact that shrinkage happens upon water exposure may lead to modify the aging behavior in alkaline or acidic solution if samples are not constrained.

Finally, the authors propose to pursue investigations on the second phase of the sorption mechanism of HT-PVAL yarns by exploring the possibility of diffusion in a potential mesophase or in the crystalline regions of the polymer.

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