Polyvinyl alcohol yarns long term properties characterization and assessments. Part II: Chemical durability

Y.Bian & X.Colin Arts et Métiers ParisTech, PIMM (UMR CNRS 8006), France

M.Aressy *Terre Armée Internationale, France*

ABSTRACT: For more than a decade now, High Tenacity Polyvinyl Alcohol (HT-PVAl) yarns have been attracting a lot of interest in the geosynthetic community, particularly for the reinforcement of stabilized ground structures in civil engineering. PVAl interest principally lies in its excellent resistance to strongly alkaline or acidic environments combined with a high stiffness that makes it a serious reinforcement material. Today, several products manufactured with HT-PVAl 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 in extreme pH conditions. Despite this rising attraction for PVAl, 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 second part of this study, we will focus on the chemical degradation mechanism and kinetics of HT-PVAl yarns. This study will be based on a series of aging tests carried out in laboratory at various temperatures and pH values. Physico-chemical and mechanical characterization methods will be proposed in order to define aging tracers allowing the evaluation of the long-term performance of HT-PVAl yarns.

Keywords: Poly(vinyl alcohol), PVAl, yarns, geosynthetics, durability, oxidation

1 INTRODUCTION

Mechanically stabilized ground structures are composite masses made of three main components: the fill, the reinforcement and the facing. For several years now, reduced access to desirable fill sources have been noticed. There are various reasons for this trend such as the cost or environmental issues. This leads to favor the use of fill material found on site, but this one is often of lower quality. To improve its performance, treatments such as lime or cement binders are generally used. The consequence of these treatments are mainly an increase of the soil pH above 11, which remains stable in time (Detry, J. et al. 2005). Such an increase of pH eliminates the possibility of using PET material for reinforcement as its degradation mechanisms change when the pH value exceeds 9 and are considerably accelerated when it approaches 11 (Van Schoors, L. 2009). For these reasons, the use of PVAl material has been promoted over the years. High Tenacity Polyvinyl alcohol (HT-PVAl) yarns are particularly interesting for reinforcement function in civil engineering applications because of their excellent resistance to strongly alkaline and acidic environments combined with their high stiffness.

However, the long-term durability of HT-PVAl yarns has never been fully demonstrated. Some studies have shown that PVAl fully preserves its properties upon highly aggressive conditions (Nai-Ali, L.K. et al. 2014), whereas other studies shown that it will lose some of its properties (Nishiyama, M. et al. 2006). However, no clear mechanism allowing for an accurate lifetime estimation has been carried out. The work described in this paper aims at improving the knowledge of PVAl degradation path under different pH conditions. At the time of writing, the aging tests are still being carried out and then, we will only discuss here our first experimental observations. The final objective of this work is to come up with a clear degradation mechanism and kinetic analysis of HT-PVAl yarns and ultimately, to provide a physico-chemical or mechanical tracer enabling to assess properly their lifetime.

2 MATERIAL AND PROTOCOL

2.1 Sample preparation

HT-PVAl yarns stored in an air-conditioned room at nominal temperature (50%RH, 22°C) were wound on glass test tubes with the end of the yarn blocked in the wound yarns. Each tube carries about 4 meters of yarns to ensure the quantity of sample needed for further experimental characterization after aging, especially for uniaxial tensile tests. The physico-chemical characteristics of conditioned unaged HT-PVAl samples are shown in Table 1.

Table 1. 1 hysico-chemical characteristics of unaged 111-1 VAI yarns						
Glass transition	Melting	Crystallinity ratio $X_c (\%)^{(1)}$	Water	Degree of	Linear	Fiber
temperature	temperature T _m		content	Hydrolysis	density	diameter
$T_{g}(^{\circ}C)^{(1)}$	(°C) ⁽¹⁾		$(_{\rm wt}\%)^{(1)}$	$(\%)^{(2)}$	$(dtex)^{(2)}$	(µm) ⁽³⁾
53	239±1	70±2	1.8±0.2	> 98	2000	20±4

Table 1: Physico-chemical characteristics of unaged HT-PVAl yarns

(1): measured by MDSC, at 3°C.min⁻¹ with a modulation of \pm 2°C/60s under nitrogen.

(2): supplier data

(3): measured by optical microscopy

2.2 Aging protocol

Tubes of wound HT-PVAl yarns were exposed to sulfuric acid (pH = 2.4), distilled water (pH = 7) and sodium hydroxide (pH = 12) at 50, 60 and 70°C. For each solution and temperature, twelve samples (i.e. twelve tubes of wound yarns) were disposed in a sealed glass container with enough spaces (distance > 1cm) between each other to ensure a uniform exposure throughout the length of the tubes. The containers were kept in three bain-maries (one for each aging temperature) filled with water and protected from UV exposure. Samples from each solution and temperature were collected every one or two months for physico-chemical and mechanical characterizations. Samples were rinsed with running water for 5 minutes and wiped with Joseph paper to eliminate the surface moisture. After that, samples were stored in an air-conditioned room (50%RH, 22°C) for at least two weeks before testing their physico-chemical and mechanical properties. As a reference, we have used a tube of wound unaged HT-PVAl yarns immerged in distilled water at 22°C for 24h, then rinsed and stored in the same conditions as the aged samples. In this paper, we will mainly discuss the results obtained at 70°C since the aging protocol is still ongoing.

3 CHARACTERIZATION METHOD

3.1 *Thermogravimetric analysis (TGA)*

The thermal decomposition of unaged and aged PVAl yarns was performed by a TGA-Q500 from TA Instruments, with a 10°C/min constant heating rate from 22 to 900°C under nitrogen. The weights of the samples as a function of time and temperature were monitored to reveal the different steps of thermal decomposition of PVAl yarns.

3.2 Modulated differential scanning calorimetry (MDSC)

DSC analysis with modulated temperature ($\pm 2^{\circ}C/60s$) was performed under nitrogen on unaged and aged yarns to measure their thermal and morphological characteristics (T_g , T_m , X_c and water content) at different aging times. The analysis was carried out using a DSC-Q1000 calorimeter from TA instrument, with a 3°C/min constant heating rate from -60 to 350°C. The measurement and calculation of each parameter were detailed in a previous paper by the authors (Bian, Y. et al. 2018).

3.3 Fourier-transform infrared spectroscopy (FTIR)

FTIR analysis in transmission mode was performed on PVAl films elaborated from aged and unaged HT-PVAl yarns in order to detect the potential chemical modifications of the material upon aging. The films were obtained using 50 mg of yarns cut into small pieces and mixed with 4 ml of dimethyl sulfoxide (DMSO) in a glass container. Indeed, DMSO is known to be a good solvent for PVAl (Sakurada, I., 1985). The mixture was shaken at 120°C for 16 hours to give a transparent solution in which PVAl yarns were totally dissolved. After cooling the PVAl solution at ambient temperature, 30 drops of the solution were disposed on a flat glass sheet to form a large drop of PVAl solution which is then dried at 80°C for 24h under vacuum to give a dry PVAl film. The films were kept in a desiccator containing silica gel to avoid moisture regain before FTIR analysis. The analyses were carried out using a Frontier FT-IR spectrometer from Perkin Elmer in a spectral range extending from 500 to 4000 cm⁻¹ with a minimum resolution of 4 cm⁻¹.

3.4 Ultraviolet-visible spectroscopy (UV-Vis)

UV-Vis analysis was performed on PVAl films elaborated from aged and unaged HT-PVAl yarns to detect the evolution of the carbon-carbon double bonds and the carbonyl groups in PVAl. The film fabrication is the same as that for FTIR analysis, but using 100mg of yarns in 4 ml of DMSO to obtain a thicker film necessary for the UV-Vis analysis. The analyses were carried out using a Lambda 35 UV/VIS spectrometer from Perkin Elmer.

3.5 Uniaxial tensile testing

Uniaxial tensile tests were performed on unaged and aged yarns following ASTM D2256 standard to determine the retained strength at break, strain at break and modulus after each exposure time. Each sample was tested 5 times to give an average value of each measurement.

4 RESULTS AND DISCUSSION

4.1 Visual inspection

Upon aging, a first observation can be done visually. Comparing the unaged and aged yarns under various conditions, a clear change in color is noticed. In Figure 1, we are presenting the pictures of several aged samples at 70°C in the different solutions in comparison to an unaged sample. It is shown that samples aged in hot water and sodium hydroxide change from a white to yellowish color, while the samples aged in sulfuric acid change from a white to light brown color. For polymers, the change in color is a sign of chemical modification (chemical aging) particularly when yellow to brown colors are observed. They generally result from the formation of double bonds in the main chain (Colin, X. et al., 2011).



Figure 1. Visual comparison of samples aged at 70°C between 1 and 9 months in the different solutions

4.2 Thermal analysis

We have carried out a series of thermal characterizations using TGA and MDSC analyses to observe the impact of aging on thermal properties. In Figure 2 (a), we are presenting the TGA results of the thermal decomposition of a sample aged at 70°C. Based on a literature review, the decomposition of PVAl in inert atmosphere is a two-step mechanism consisting in an elimination of the chemically bonded water (removal of the hydroxyl side groups on the main chain) followed by the pyrolysis of the residue (Thomas, P.S. et al. 2001). This behavior is confirmed for the unaged sample as seen in Figure 2 (a). Regarding the aged samples, it appears that the elimination of the chemically bonded water is affected by the type of aging solution, even after short time of exposure. We can observe two well-defined behaviors for samples aged in water and in sodium hydroxide, where the water elimination step seems initiated at lower temperature. Besides, for samples aged in sulfuric acid, the water elimination step seems to be happening at a much higher temperature. The distribution of the curves can lead to believe that the most acidic is the aging medium, the more thermally stable is the sample.



Figure 2. (a) TGA thermograms of thermal decomposition of unaged and aged samples. (b) DSC thermograms of unaged and aged samples.

This behavior is also confirmed by DSC (see Figure 2 (b)) showing that a degradation step attributed to the elimination of the chemically bonded water occurs at the melting of samples aged in water and sodium hydroxide, while it is not observed for samples aged in sulfuric acid (in fact, it should be expected at a much higher temperature).

Additionally, the T_g and water content were measured using MDSC after conditioning the sample at 22°C and 50%RH using the method described previously (Bian, Y. et al. 2018). The results are presented in Figure 3 and show no significant influence of chemical aging on the T_g and water content.



Finally, the T_f and X_c of aged samples were monitored using DSC. If no significant difference is observed for samples aged in water and sodium hydroxide (not shown here), a slight drop of the T_f (from 239 to 236°C) can be detected for samples aged in sulfuric acid, while X_c remains constant (78 ± 2%) (see Figure 4).



Figure 5 illustrate the evolution of the melting peak over 14 months. On the thermogram, we can see that after 243 days of exposure, a new peak appears around 236°C and overlaps with the initial melting peak at 239°C. The contribution of the new melting peak at lower temperature increases with time of exposure while the initial melting peak tends to disappear.



Figure 5. Evolution of the DSC melting peaks of samples aged in sulfuric acid at 70°C

4.3 UV-VIS spectroscopy

UV-VIS spectra presented in Figure 6 show differences between unaged and aged sample at 70°C after 14 months of exposure. We are presenting the spectra after subtraction of the initial spectrum, which provides a better view of the emerging absorption bands. In our wavelength range of measurement, there is no change in water and sodium hydroxide even after 14 months of exposure. In contrast, in sulfuric acid, we observed three new growing absorption bands at 230, 284 and 333nm. In Figure 7, we are presenting the evolution of their absorbance as a function of exposure time and a table where we have listed their probable attribution based on a literature review (Simirnov, L.V. et al. 1968; Yamaguchi, T. et al. 1959; Maruyama, K. et al. 1985). Polyene -(CH=CH)_n- or polyenone -(CH=CH)_n-CO- structures with different level of conjugation are generally reported. The bands observed at 230nm could correspond to polyene or polyenone structures with two conjugated double bonds. Similarly, the band observed at 284 and 333nm could correspond to a polyene or polyenone structures with three and four conjugated double bonds respectively. Another possible polyenone structure can be aldehyde, ketone, carboxylic acid and ester.



Figure 6. UV-VIS spectra of unaged and aged samples after subtraction of the initial spectrum



Figure 7. Absorbance of the new UV bands as a function of exposure time for the samples aged in sulfuric acid at 70°C and their attributions from literature (Simirnov, L.V. et al. 1968; Yamaguchi, T. et al. 1959; Maruyama, K. et al. 1985)

4.4 FTIR spectroscopy

The FTIR spectra of samples aged in water and sodium hydroxide at 70°C show no significant sign of aging at the current exposure time, thus they are not shown here. However, in the case of sulfuric acid, the absorbance of the IR band at 3340 cm⁻¹ assigned to hydroxyl groups -OH of PVAl decreases as compared to unaged sample (see Figure 8). It implies the consumption of hydroxyl groups during the aging process in sulfuric acid.



Figure 8. FTIR spectra of unaged and aged samples in sulfuric acid at 70°C in transmission mode. Attribution of the main absorption bands (v: stretching vibration, δ : bending vibration, w: wagging vibration)

A magnification of the FTIR spectra between 1600 and 1800 cm⁻¹ (see Figure 9 (a)) shows the growth of a new broad and composite band between 1800 and 1600 cm⁻¹. A deconvolution of this composite band (see Figure 9 (b)) using Gaussian functions shows four elementary bands at 1757, 1711, 1665 and 1630 cm⁻¹. Based on a literature review (Carlsson, D.J. et al. 1969; Tireau, J. 2011), the bands at 1757, 1665 and 1630 cm⁻¹ can be attributed to esters, carbon-carbon double bonds and conjugated carbon-carbon double bonds respectively. The band at 1711 cm⁻¹ can be attributed to ketones and carboxylic acids. These observations confirm the existence of polyene or polyenone structures in aged PVAI samples, as mentioned previously in UV-VIS analyses.



Figure 9. (a) FTIR spectra between 1600 and 1800 cm⁻¹ of unaged and aged samples in sulfuric acid at 70°C. (b) Deconvolution of FTIR spectrum of the sample aged in sulfuric acid at 70°C for 14 months.

4.5 Uniaxial tensile testing

Figure 10 shows the evolution of the retained stress at break for aged yarns as a function of exposure time. So far, no significant changes have been observed in the mechanical behavior of the yarns aged in water and sodium hydroxide. However, in the case of sulfuric acid, we observe a slight drop in the retained stress after 337 days of exposure which seems to decrease linearly, announcing a drop in mechanical properties.



4.6 Compilation of the results

The results presented above show that, no sign of aging is seen after 14 months in water and sodium hydroxide at 70°C, while in sulfuric acid, a clear sign of aging starts appearing after only 8 months (243 days) of exposure at 70°C.

First, we have seen modifications of the chemical structure of HT-PVAl yarns. We have observed a growth of three new UV absorption bands at 232, 284 and 333nm, which are characteristics of polyene or polyenone structures with different number of conjugated carbon-carbon double bonds. The appearance of these bands seems to grow slowly up to 331 days and then, more rapidly from 377 days. Additionally, FTIR analysis showed the emergence of new IR absorption bands between 1800 and 1600 cm⁻¹ after 377 days of exposure. They are attributed to esters and carbon-carbon double bonds. Further analysis, particularly chemical treatment (such as reaction with an ammoniac gas), will be necessary in order to clearly identify the different chemical functions observed and to better understand the aging mechanism. However, the presence of ester functions suggest that a crosslinking process is operating, which has been confirmed with the observation of a gel-like structure when trying to dissolve the aged material in DMSO.

Then, thermal analysis showed that so far, aging has no impact on the glass transition temperature or the water uptake in any of the solution tested. However, in sulfuric acid, a shift of the melting temperature from 239 to 236°C takes place between 243 and 331 days of exposure, then it seems to continue to decrease with the time of exposure.

Interestingly, the shift of the melting temperature seems to be correlated with the decrease in mechanical properties observed for samples aged in sulfuric acid. This behavior was also observed in the case of thermal aging but these results remain to be published.

Based on the literature, the oxidation is the main degradation path expected for PVAl in acidic (Sakurada, I. et al. 1963) and alkaline (Shiraishi, M. et al. 1962) environments. In acidic solution, it is generally expected that oxidation promotes crosslinking by intermolecular acetalization and esterification while in alkaline solution, oxidation leads to enolization and cleavage of the main polymer chain by reverse aldol reaction.

So far, the results presented here seem to be in good agreement with the literature for acidic conditions. However, the absence of aging sign in alkaline conditions do not enable further discussion.

5 CONCLUSION

At this stage, we are not able to draw a clear conclusion on the degradation mechanism and kinetics of HT-PVAl yarns under various temperatures and pH conditions. However, the results show that there is a real difference between the agings in acidic and alkaline solutions, and that they most probably do not follow the same chemical degradation mechanism. As aging continues, we are expecting to be able to provide more justifications and finally fulfill the research objectives.

REFERENCES

- Bian Y., Colin X., Aressy M., 2018, Polyvinyl Alcohol Yarns Long Term Properties Characterization and Assessments. Part I: Physical behavior Consequences of water affinity, 11th IGS Conference Seoul.
- Carlsson, D.J., Wiles, D. M., 1969, The photodegradation of polypropylene films. II. Photolysis of ketonic oxidation products, *Macromolecules*, Vol.2 n°6 pp 587-597.
 Colin, X., Teyssèdre, G. & Fois, M. 2011. Ageing and degradation of multiphase polymer systems, in: Handbook
- Colin, X., Teyssèdre, G. & Fois, M. 2011. Ageing and degradation of multiphase polymer systems, in: Handbook of Multiphase Polymer Systems, volume 2/2, Boudenne, A., Ibos, L., Candau, Y. & Thomas, S. ed., John Wiley & Sons Ltd, Chichester, Chap. 21, pp. 797-841.
- Detry, J., Van Den Bergh, H., Bollens, Q., 2005, Study of a 30 years old lime treated silt area, TREMTI 2005, Communication C15.
- Maruyama, K., Akahoshi, H., Kobayashi, M., Tanizaki, Y., 1985, Assignement of conjugate double bond systems produced in heated PVA film by absorption and excitation spectra, Bull.Chem.Soc.Jpn, 58, pp 2923-2928.
- Nait Ali, L.K., Thomas, R. & Freitag, N. 2014, Polyvinyl Alcohol Physical Behaviour and Chemical Durability, 10th IGS Conference Germany.
- Nishiyama, M., Yamamoto, R., Hoshiro, H. 2006, Long term durability of Kuralon (PVA fiber) in alkaline condition. 10th IIBCC, Brazil, pp. 120-134.
- Sakurada, I. 1985, Polyvinyl alcohol fibers, International Science and Technology Series 6, New York
- Sakurada, I. & Matsuzawa, S. 1963, Degradation of Poly(vinyl alcohol) by Hydrochloric Acid, Kobunshi Kagaku, Vol.1 n°16 pp 349-352.
- Shiraishi, M., Matsumoto, M. 1962, On the Degradation of Polyvinyl alcohol in Hot Aqueous Alkali Solution, Kobunshi Kagaku, Vol.9 n°21 pp 722-727.
- Thomas, P.S., Guerbois, J.P, Russell, G.F., Briscoe, B.J. 2001, FTIR study of thermal degradation of poly(vinyl alcohol), Thermal analysis and Calorimetry, 64, pp. 501-508.
- Tireau, J., 2011, PhD-Propriétés à long terme des gaines de polyéthylène haute densité utilisées pour les ponts à haubans, Ecole Nationale Supérieure d'Arts et Métiers.
- Yamaguchi, T., Amagasa, M., Kinumaki, S., Takahashi, T., 1959, Studies on Colorization Mechanism of PVA at Heat Treatment by Ultraviolet Absorption Spectra, Kobunshi Kagaku, Vol.4 n°20 pp 571-578.
- Smirnov, L.V., Platonova, N.V., kulikova, N.P., 1968, Electronic Absorption Spectra of Polyvinyl Alcohol, Journal of Applied Spectroscopy.
- Van Schoors, L., Lavaud S., Duragrin D., Barberis N., 2009, Durabilité des geotectiles polyester en milieu modérement alcalin, Rencontres Géosynthétiques.