Influence of water on the short and long term mechanical behaviour of polyamide 6 (nylon) fibres and yarns

Humeau Corentin [1], Davies Peter [1, *], Le Gac Pierre Yves [1], Jacquemin Frédéric [2]

[1] Marine Structures Laboratory, IFREMER Centre Bretagne, 29280 Plouzané, France
[2] GeM, UMR CNRS 6183, Université de Nantes, 44606 Saint-Nazaire Cedex, France

* Corresponding author : Peter Davies, email address : peter.davies@ifremer.fr

Abstract :

Polyamide fibres are known to be sensitive to water, and this has limited their marine applications. However, their low stiffness and high strength could be attractive for shallow water mooring line ropes, particularly for floating wind turbines. Such applications require the influence of water on mechanical behaviour to be fully understood, and this paper presents results describing how water affects static and creep response of polyamide 6 fibre yarns. First, the effect of water on fibre Tg is quantified, then tensile behaviour is examined. Finally, a model based on Schapery's non-linear creep analysis is identified for different humidity conditions. The results show that while moisture has a small effect on short-term tensile behaviour, long term response is strongly affected and this must be considered in any marine application.

Keywords : Aging, Moisture, Fibre, Creep, Viscoelastic model

1. Introduction

Polyamide fibres are used very extensively in a range of industrial applications from textile fabrics to climbing ropes, tire cords and architectural structures. They were first marketed in the 1930's so there is considerable experience available; recent overviews of their chemistry, manufacture and properties can be found in [1], [2]. There is also an increasing interest in these fibres for marine applications. Nylon fishing nets and single point offshore moorings are well established, but the former involve intermittent immersion while the latter are usually replaced after one or two years. Today nylon ropes are being considered for station keeping of ocean energy structures, and in particular for floating wind platforms [3], [4]. This is an application where long term durability is critical, and the combination of high loads and continuous immersion is encouraging new developments in fibre coatings and improved rope constructions. There is therefore renewed interest in the influence of water on nylon properties, particularly those of polyamide 6 fibres.

If we first consider the microstructure of nylon fibres and their influence on tensile behaviour; Marcellan et al. have provided a detailed description of the micro-mechanisms which contribute to nylon 66 fibre deformation, and which produce a non-linear stress-strain response [5]. Initially isotropic amorphous regions are loaded but as load is increased the oriented amorphous and crystalline regions are progressively elongated, leading to progressive stiffening. In the final stage of loading, which can be considered as viscoplastic, macrofibril sliding results in damage.

Various authors have examined the influence of water on bulk nylon properties. For example, Arhant et al presented a water diffusion model which accounted for the change in water uptake due to the passage from the glassy to the rubbery state during wet aging [6]. Experimental examination of the

rates of transport of liquid water along a wide variety of yarns supports the view that water travel occurs essentially by capillary action [7].

Hunt & Darlington studied the creep behaviour of bulk nylon 6.6 and quantified the influence of moisture [8]–[10]. They found the creep behaviour under varying humidity could be estimated using creep data at constant stress and humidity.

There have been various attempts to represent the mechanical response of polymer fibres. Militky proposes the following four categories [11]: Continuum, Micromechanical constitutive, Structural, and Multi-phase models. These differ in the way in which the fibre microstructure is accounted for. The continuum models ignore the molecular aspects of polymers and include elastic and viscoelastic behaviour of a homogeneous body. One example of this type of approach was proposed by Chailleux and Davies, who represented the time dependent strain in polyester fibres [12]. A certain number of identification steps, based on creep and recovery curves and specific load-unload sequences, are required to predict strain as a function of loading history. Once these have been performed the response to more complex loading sequences can be predicted. The use of this type of model to quantify moisture effects is discussed further below. Various spring and dashpot representations have been applied in other studies to account for the time dependent response. Micromechanical constitutive models can also use springs and dashpots, but these are associated with physical elements of the fibre such as molecular entanglements and crystallites. An example is the work of Fotheringham and Cherry to predict yield stresses [13], with an Eyring activation energy model to account for simultaneous cooperative movement of polymer chain segments. Structural models are based on calculation of the macroscopic mechanical behaviour based on the responses of the structural elements. Many consider the fibre as a composite material, including polymer fibrils in a less ordered matrix, such as the series model of Northolt and colleagues [14]. Finally, the multiphase models assume that the different phases of a fibre are continuous; the Takaynagi model is the best known [15]. This is based on combining the contributions of the amorphous phase, the crystalline phase and a tie chain phase. The behaviour of each of these phases can be defined in terms of degree of crystallinity and orientation, but they provide a very simplified approach to properties.

This paper will focus on the physical influence of water on mechanical properties of polyamide 6 fibre yarns; hydrolysis is not considered here. First, materials and methods specially developed for the study will be exposed. Second, the water ingress and the mechanical properties of dry fibres will be examined in order to define reference behaviour. Finally, the mechanical properties will be defined in different humid environments in order to quantify the influence of the amount of water in the fibre material.

2. Material and methods

In this section we present the material used in the present study and its general physical properties. In addition, the methods used for the investgation are reported. Some of these techniques have been specially developed for this study, so in these cases, experimental tests and identification methods are described in specific sub-sections.

Material

The study is focused on polyamide fibres, one of the most widely-used polymers on account of its ductility and high strength. Nylon fibres (polyamide) are produced from amide groups (-CONH-); there are several different types of nylon fibres: polyamide 6.6 / 6.12 / 4.6 / 6 / 12 (the number refers to the carbon atoms around the amide group in the monomer), which have found a wide range of

applications. The fibre used in the present study is a Nylon 6, grade 371 manufactured by Nexis™ fibres, and has the reference 1880 f 280, with a linear weight of 190.5 tex (g/km).

Morphology

To study the morphology of the fibres with high resolution, SEM (Scanning Electron Microscopy) imaging was employed using FEI Quanta 200 equipment. This provides information on the surface aspects (kink bands, micro fibrils, etc) and the diameters of each fibre, Figure 1. The average diameter obtained with this technique was 28.3 μm with a standard deviation of 0.6μm. Moreover, the surface aspect of the fibres was smooth, with no major defects.
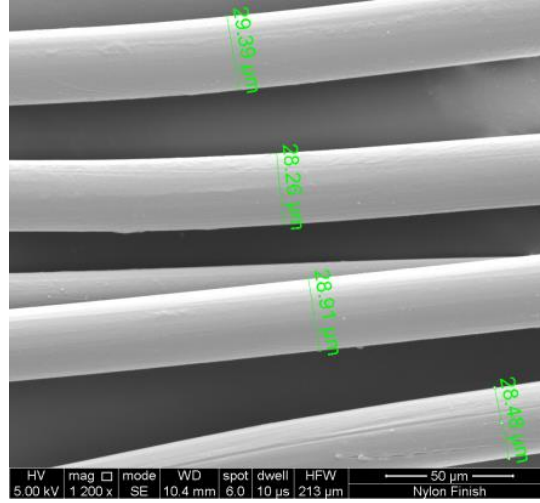

Figure 1. SEM image with diameter measurement on fibres in a Nylon 6 yarn

Crystallinity

Polyamide 6 is a semi-crystalline polymer and its mechanical behaviour is strongly dependent on the degree of crystallinity (X_c). In this study, this value was established by DSC (Differential Scanning Calorimetry) tests on Q200 equipment from TA Instruments™ at a heating rate of 10°C/min from room temperature to 300°C under nitrogen flux. Then X_c was calculated from the enthalpy of fusion of the polymer, ΔH_f, and a theoretical 100% crystalline material value, ΔH_f^0, (Eq. 1).

$$X_c = \frac{\Delta H_f}{\Delta H_f{}^0}$$

Eq. 1

The theoretical enthalpy of fusion of 100% crystalline polyamide 6 was taken as 188 J/g (value from [6]). Using this value and the ΔH_f obtained by DSC, a degree of crystallinity of 40.1% was determined.

Glass transition temperature measurements

There is no standard technique to determine the glass transition temperature (Tg) of polymer fibres. Therefore, a special clamping method was developed to test fibres in a Metravib™ 150N DMA+ (Dynamic Mechanical Analysis) device. The details of the device are shown in Figure 2. Before the test, initial sample length between the loading pins, Lo, was measured after a dynamic pre-loading (Lo between 20 and 30 mm).
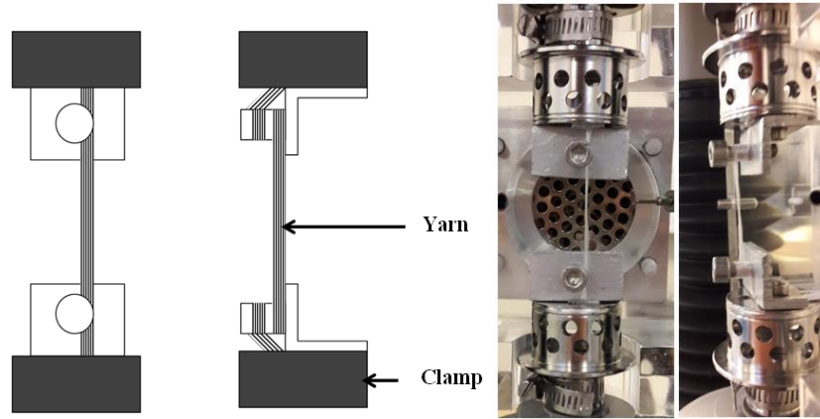
Figure 2. Clamp used for DMA testing of fibres.

Then tests were performed under different environmental conditions inside a temperature and humidity controlled chamber. This was filled with silica gel to get the properties at 0%RH and then different humidity conditions were used to characterize the influence of water content on the properties. Specimens were tested at a frequency of 1 Hz and a dynamic strain of 5.10^{-3}. The tests were conducted from 25°C to 150°C at 2°C/min in the oven. The humidity chamber can only regulate with accuracy at a constant humidity and temperature; therefore, the modulus was determined at 5°C temperature steps from 25°C to 60°C and at 10% relative humidity steps from 10%RH to 80%RH.

Water content measurements in immersed fibres

Water conditioning of bulk polymers is a well-studied subject but polymer fibres are quite different from bulk samples. When studying polymer fibres and their dependence on relative humidity one can use Dynamic Vapor Sorption (DVS) equipment. However, there is no existing method to determine water uptake in immersed filaments of polyamide 6 and dissociate the water within the material from the water on the surfaces and in between the fibres. This quantity was therefore determined with DSC analysis on a filament bundle after immersion. The technique is based on the free/bonded water theory [16], but to avoid confusion the terms internal and external will be used here; the moisture inside the fibres is considered as internal ($C_{i,\infty}$) while molecules within the yarn structure on and between fibre surfaces are noted as external ($C_{e,\infty}$). The expressions Eq. 2 to Eq. 4 allow the different water quantities to be determined by analysis of fusion, ΔH_f, and vaporisation, ΔH_v, enthalpies during a cooling and heating sequence. A DSC recording is shown in Figure 3.
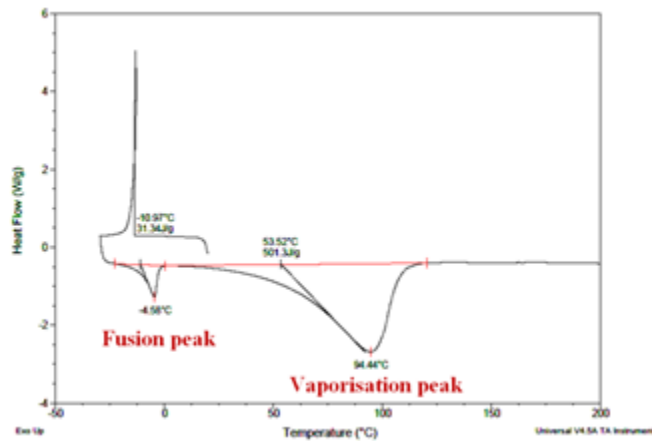

Figure 3. DSC results highlighting water located between and within fibres after immersion

$$C_{e,\infty} = \frac{\Delta H_f}{X_c . \Delta H_f{}^0}$$ **Eq. 2**

$$C_{t,\infty} = \frac{\Delta H_v}{X_c . \Delta H_v{}^0}$$ **Eq. 3**

$$C_{i,\infty} = C_{t,\infty} - C_{e,\infty}$$ **Eq. 4**

Tensile behaviour

Quasi-static tensile tests were carried out on yarn samples on a 10 kN capacity Instron™ test frame, at a loading rate of 50 mm/minute. Strain was measured using two digital cameras to measure the displacements of two markers fixed to the sample, separated by a known distance (typically 300mm).

Tensile creep tests were performed using the DMA equipment described above.

3. Nylon reference behaviour

To understand the relationship between water uptake and tensile behaviour, these aspects have to be studied separately first. Therefore, this section is devoted to the definition of glass transition temperature, water sorption and mechanical behaviour of dry fibres.

Glass transition temperature

The reference glass transition temperature was established in a 0%RH environment, Figure 4. These tests were performed in a standard oven chamber filled with silica gel dehydrate.

The results obtained show a typical polyamide response. The glass transition temperature value was determined by considering the drop in storage modulus E'. In the reference state (0%RH) the Tg value reaches 55°C on average, which is a little higher than for bulk polyamide 6 (around 50°C).
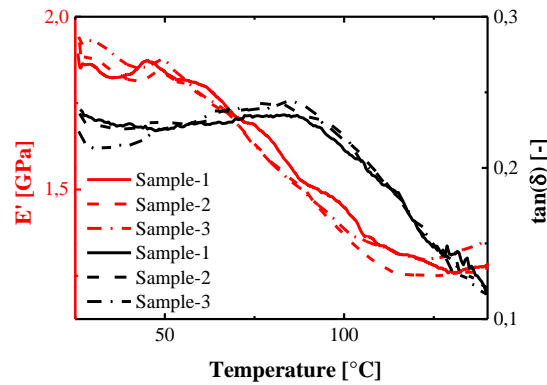

Figure 4. E' and tan(δ) thermal response of dry nylon 6 yarn while stressed at 1Hz under 0%RH atmosphere.

Water sorption

To establish water sorption kinetics in fibres surrounded by a humid environment rather than liquid water the DVS technique is used. This testing method records the weight variation with a constant time step during tests where the relative humidity is controlled and progressively increased by steps. These tests were performed on short lengths of yarns (5mm) of Nylon 6.

Water uptake in the Nylon 6 appears to follow Henry's law for low water activity (below a=0.5), for higher activity water quantities deviate from this law. Similar results were observed in previous studies of bulk polyamide [6], [17]. These studies showed that the deviation is due to cluster creation inside the material, and it appears to be controlled by the Eq. 5, with $C_\infty(a)$ and a the water activity. It has been shown that H can be represented by an Arrhenius law characterised by a pre-exponential factor H_0 and activation energy E_a [6], [17]

$$C_\infty(a) = H.a + b.a^m = H_0.exp\left(\frac{-E_a}{R.T}\right).a + b.a^m \qquad \text{Eq. 5}$$

To establish these parameters, we use a two-step identification. First, we consider that ($H.a$) is predominant compared to the power term and we identify H_0 and E_a from the curve of $ln(H)$ vs. $1/T$. Then, we subtract the linear term from the initial maximal moisture content and identify b and m over the second part of the curve. These parameters appear to be independent of the temperature as previously shown in [6], [17]. In the case of Nylon 6 fibres we obtain the following parameters: $H_0 = 1.39$; $E_a = -7kJ.mol^{-1}$; $b = 3$; $m = 7$. If we refer to the published values on bulk polyamide 6 materials in [6] we can note that the values of activation energy (E_a) and b are very similar to the published parameters. Nevertheless, in the case of PA6 fibre materials the pre-exponential factor (H_0) and m both differ from the parameters of bulk specimens. The polymer chains in fibre materials are usually more oriented and their crystallinity ratio is higher, this affects the maximal water uptake (m and H_0) significantly.

The model curve obtained (Equation 5, solid line in Figure 5) shows a good correlation with experimental points at 25°.
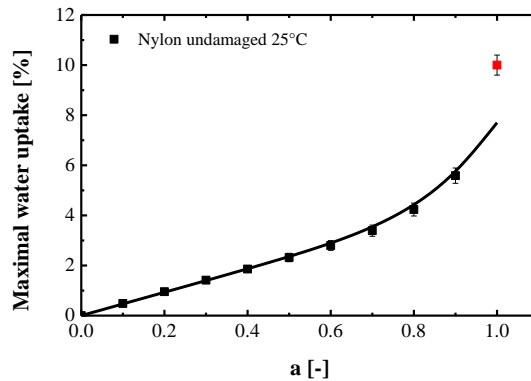

Figure 5. Maximal water uptake in humid environment [black points] and immersed [red point] compared to the identified model [black line].

Contrary to the case of water diffusion in a humid environment, when the samples are immersed there is no standard device that can record the weight variation with the same accuracy as DVS. Therefore, the DSC method described in the Materials & Methods section above was used to identify the different water quantities: inside filaments, between fibres and in total.

The samples were pre immersed in deionised water at 25°C for different times and then analyzed by DSC.

All the results obtained with this technique are reported in Figure 6. First, the water uptakes, between fibres and in the entire sample, show a similar shape and large standard deviations (results

from 3 tests for each point). The scatter in results may be caused by the variation in handling between each specimen, or due to drying differences. Nevertheless, the water content within the filaments remains constant for all the measurements and shows low scatter for a given immersion time. This can be explained by a handling time that remains low compared to the diffusion kinetics.

In the case of immersion we cannot describe the transient part of the diffusion curve since the exposure time would be too close to the diffusion characteristic time. Therefore, the handling time becomes critical, and has an impact on the water uptake values obtained within the filaments.
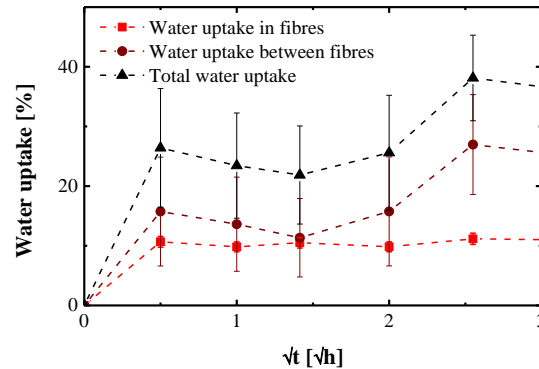

Figure 6. Water uptake in filaments after immersion, both within and between fibres in the yarn, versus square root of time

Finally, the maximum moisture content in immersed filaments (10%) is compared with the values from humid environment exposure and the model results shown previously for a humid environment, Figure 5. This comparison highlights a clear difference between the diffusion behaviour immersed and in humid environment. The model established for relative humidity diffusion cannot therefore accurately predict the value in the case of immersion. It would be interesting to perform additional tests in humid environments closer to 100%RH, in order to compare these experimental values both to Henry's law and to the results for immersed fibres.

Mechanical behavior

Quasi-static tension
In the case of polyamide fibres, the stress-strain curve follows a typical S-shaped profile, Figure 7. This behaviour is common for many melt-spun fibres. Similar curves have been noted previously [5] for Nylon 6-6 fibres. The same four domains can be identified here:

- From 0 % to 3.5 % strain, the curve reflects an alignment of the amorphous regions, the crystalline domain remaining unloaded. As a consequence, amorphous regions are partly decreased, by the crystallisation induced by mechanical stress, the crystallinity ratio increases significantly [5].
- From 3.5 to 10 % strain, the characteristic shape of the end of the amorphous domain orientation appears. In this part, the crystallinity ratio increases more slowly [5].
- From 10 to 15 % strain, enthalpy mechanisms are activated: C-C bonds form crystals and oriented regions are elongated. The chains from crystalline regions start to be affected by the loading and then break.
- Above 15% strain, the visco-plastic deformation mechanism is related to macro-fibrils sliding.

These micro and macro-damage mechanisms result in a ductile failure of the polyamide fibre.
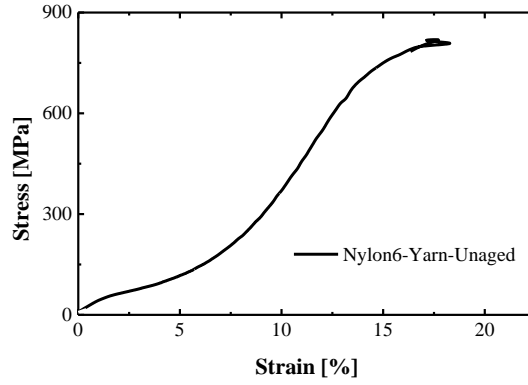
Figure 7. Quasi-static tensile behaviour of unaged Nylon 6 yarns

Tensile creep

In service, mechanical loads are rarely quasi-static. For example, a mooring line may be subjected to a constant mean load with cyclic amplitude variations due to waves. In this section the creep behaviour of these fibres will be characterized, as a first step towards investigating their long term response.

Nylon polymer shows a logarithmic viscoelastic/viscoplastic creep behaviour [8]–[10]. To model this type of mechanical response under creep loading a thermodynamic model is used, based on Schapery's theory [18].

In this study we use the model identification developed previously and detailed in [12], [19]. This technique is based on multiple creep/recovery cycles with different stress levels (Figure 8) for which the different elastic, viscoelastic and viscoplastic parameters (g_0D_0, g_2D_1, m, D_p) are identified by minimising the differences between the model equations, Eq. 6, and the experimental data for each cycle.

$$\begin{cases} \varepsilon_c = g_0D_0\sigma_c + g_2D_1\sigma_c log_{10}(t+1) + \sigma_c\left(m + D_plog_{10}(t+1)\right) \\ \varepsilon_r = g_2D_1\sigma_c log_{10}\left(\dfrac{t}{t-t_1}\right) + \sigma_c\left(m + D_plog_{10}(t_1+1)\right) \end{cases}$$

Eq. 6

In this set of equations σ_c is the stress applied on the specimen from 0 to t_1 seconds and the parameters g_0D_0, g_2D_1, m, D_p are the identified viscoelastic/viscoplastic parameters. They respectively correspond to the instantaneous compliance (g_0D_0), the creep rate (g_2D_1), the instantaneous plasticity (m) and the plastic rate (D_p).

After identification of these parameters (detailed in [12], [19]) at different loading levels, interpolations were made on each parameter in order to predict their value for any applied stress (with polynomial functions).

In the study, we performed seven creep/recovery cycles from 10 to 70N, which corresponds to a range from 58 to 409 MPa (Figure 8). These stresses correspond to the usual range of application of nylon ropes (below 50% of their ultimate stress).
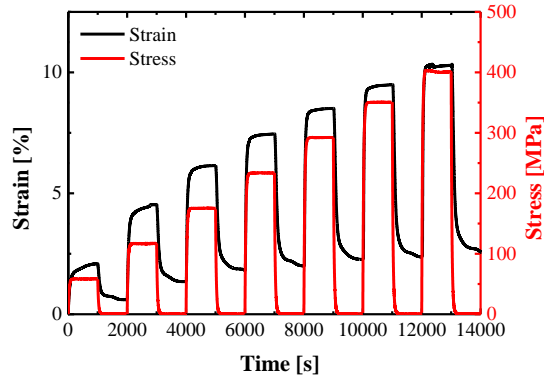
8

Figure 8. Creep/recovery behaviour of dry, unaged Nylon 6 yarn at 0%RH and 25°C

An example of the results obtained for Nylon 6 at 25°C and 0%RH is shown in Figure 8. This gives information on the creep/recovery behaviour of dry Nylon 6. It is clear that there is a significant residual deformation after unloading.

In practice, most applications induce some relative humidity or immersion in water, therefore the results from the same identifications on Nylon in humid environments are detailed in the next section.

4. Influence of water on Nylon 6 fibres.

First, the influence of water on the glass transition behaviour will be discussed, then effects on mechanical response in tension and creep will be presented.

Glass transition temperature

The glass transition temperature is a physical parameter that is very sensitive to water uptake.

Measurements and identification

To investigate changes in the Tg with water content in the fibres, DMA was performed at a fixed temperature while the relative humidity was increased in steps (Figure 9). Then, the average E' value was recorded at each step and this corresponds to the value for a particular temperature and relative humidity.
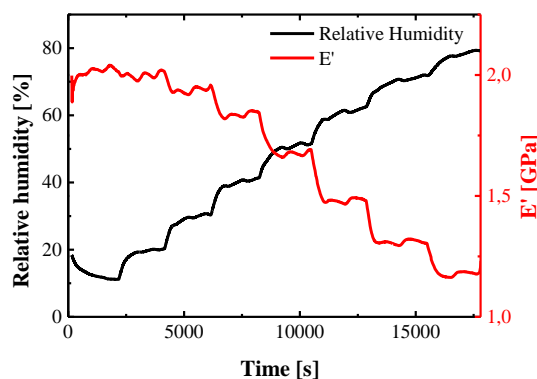

Figure 9. Example of a DMA test at 25°C under different humidity conditions.

The range of temperatures that can be studied is smaller than in the 0%RH case; tests were performed from 25 to 50 °C.

9

Figure 10a shows all the data from tests at different conditions. In a second step (Figure 10 b.), the Tg was established for each conditions by optimising its value to superpose each curve (E' as a function of T-Tg) on the master curve based on the results in dry air (Figure 4).
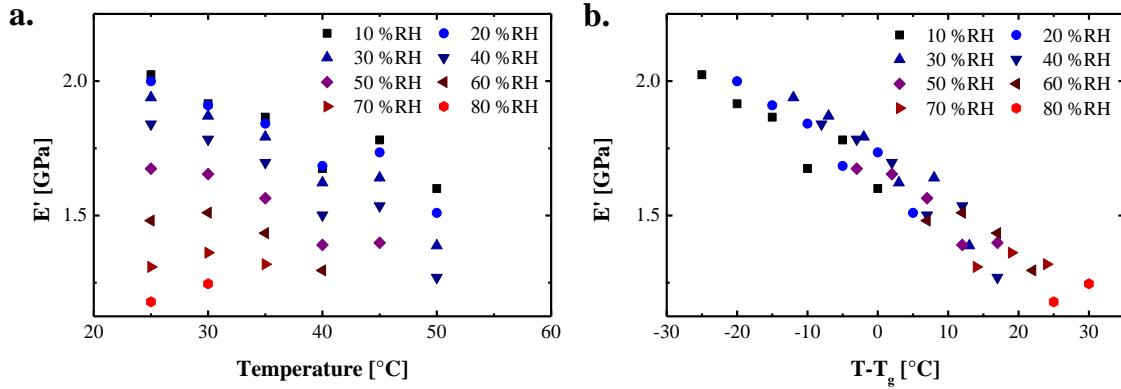

Figure 10. E' thermal response of nylon6 yarns under different temperature and humidity conditions.

Finally, the results of the Tg variation with the relative humidity are reported in Figure 11 (black points).

1.1.1. Tg prediction

Some previous studies have established models which predict the Tg variation of a material as a function of water uptake [20], [21]. Among them the Simha-Boyer expression [21] appears to be in good agreement with experimental results for polyamide material [6] and was examined here. This approach predicts the variation in T_g as a function of glass transition temperature of the polymer in the dry state: T_{gp}, of the solvent (water), T_{gs} , and the relative volume of water in the amorphous phase of the polymer $v_{w,a}$. In this case, T_{gp} and T_{gs} are respectively taken equal to 328K (Figure 4) and 110K [22], $v_{w,a}$ is defined by the equations Eq. 7 and Eq. 9

$$T_g = \frac{T_{gp}.T_{gs}}{T_{gs} + v_{w,a}.(T_{gp} - T_{gs})}$$

Eq. 7

$$C_a(t) = \frac{C(t)}{C(t) + (1 - X_c)}$$

Eq. 8

$$v_{w,a} = \frac{C_a \rho_a}{C_a \rho_a + (1 - C_a)\rho_w}$$

Eq. 9

To summarise, combining the equations Eq. 7, Eq. 8 and Eq. 9 provides the relationship between the glass transition temperature of the polymer (T_g) and water uptake in the polymer (*C(t)*). Moreover, in 3.2 we related the moisture water uptake in the polymer to the water activity (*a*) (**Erreur ! Source du renvoi introuvable.**5). Therefore, by replacing *C(t)* in Eq. 8 by $C_\infty(a)$ for each temperature and relative humidity, we can predict the variation of T_g with relative humidity according to Simha-Boyer theory (red line).
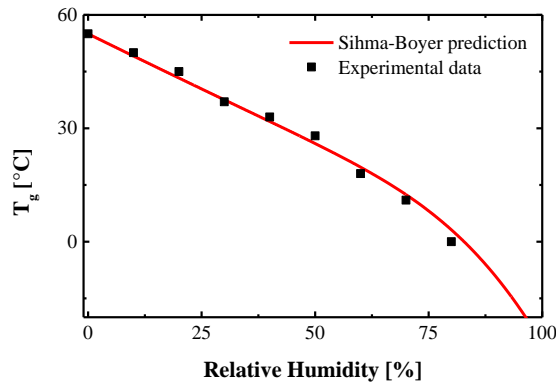
Figure 11. Glass transition temperature variation as a function of the relative humidity.

To conclude, the Simha-Boyer prediction (red line) and experimental data (black points) in Figure 11 show a good correlation. This observation is true even for the highest relative humidity values (80%RH).

Hygroscopic expansion

The other major physical change induced by water in the polymer is hygroscopic expansion. This phenomenon is created by the insertion of the water molecules between the polymer chains, which generates swelling.

Here, the hygroscopic elongation was recorded on Nylon 6 yarn samples stressed at a negligible load (0.5MPa) in a relative humidity regulated environment from 20 to 80%RH at 25°C. These tests were performed in the DMA device with the same clamps as before (presented in 2.2). The results obtained are reported in Figure 12.

Some previous results are available on this subject for bulk [23] and fibre [24] polymers. A reasonably linear dependence of hygroscopic elongation on the water uptake was observed, with a threshold value. For the water content close to the saturation value, this relation does not appear to be verified, probably due to clustering effects in the polyamide [24]; for high water content the molecules start to gather in clusters and therefore the increase in water uptake will generate lower hygroscopic elongation than in the case of isolated molecules.
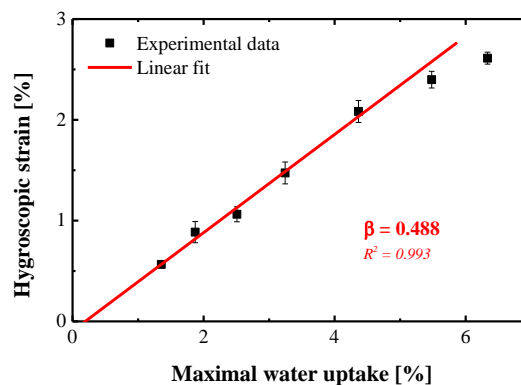

Figure 12. Hygroscopic elongation as a function of the water content in the Nylon 6 yarn.

The results of the present study highlight the same trend, with a hygroscopic coefficient (β) equal to 0.488. This linear law is verified up to a 5% water uptake in the fibres, nevertheless we do not have the threshold value since it appears to be reached for relative humidity lower than 20%RH.

Further studies should aim to determine the threshold value for polyamide 6, but this type of test will require the development of a special test device, which can maintain low relative humidities in the range from 0 to 20%RH.

Quasi-static tensile behaviour

After ageing, the Nylon 6 yarn samples show a slight deviation from the unaged reference behavior when tested under quasi-static tension, Figure 13. It should be noted that the exposure times considered here allow the effect of water absorption alone to be investigated, with no hydrolysis [25].
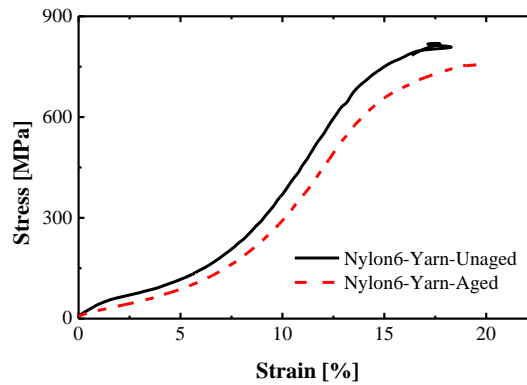

Figure 13. Quasi-static tensile behaviour of Nylon 6 yarns unaged and aged

The stiffness and break strength are reduced by water diffusion, which is due to reversible plasticization effects. Nevertheless, these changes are still small compared to results for bulk polyamide in the literature [26]–[29], for which very large changes have been noted. Short yarn samples are saturated with water after 15 minutes of exposure. However, the time required for sample preparation and performing tensile tests on yarns is approximately 5 minutes, and therefore the fibres will start to desorb significantly before testing. This suggests that the effects of water on the quasi-static mechanical response obtained for the aged yarns here may be underestimated.

Tensile creep behaviour

One of the aims of the present study is to get a better understanding of how nylon fibres will behave during long term exposure to a marine environment. For mooring line use ropes will be permanently stressed and either immersed in water or exposed to high relative humidity. Therefore, the next section is devoted to creep testing on wet fibres. Measurements were made using the same relative humidity device, clamps and DMA equipment as described previously. The tests were carried out at 25°C and with the same protocol as for the creep tests at 0%RH (3.3.2), in order to compare both cases. Three different humidity conditions were studied (20, 40 and 60% RH) and in each case samples were loaded at seven different load levels from 10 to 70 N, figure 14.
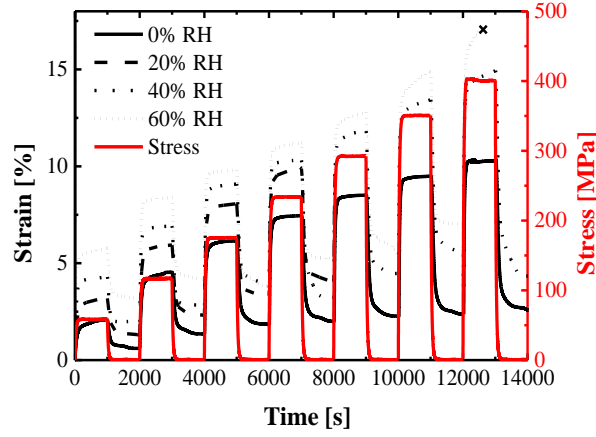
Figure 14. Creep tests performed under different humid conditions from 0 to 60%RH.

The creep strain results (Figure 14) obtained before identification show the large increase in the initial value and creep rate induced by water uptake. The recovery data show a permanent elongation increasing with the relative humidity. These results are not unexpected; as we observed previously, water uptake induces significant plasticization (reversible decrease in Tg) and therefore makes the material more ductile (for the conditions of this study). However, this increase in strain may have a large effect on the station-keeping ability of mooring lines as it will affect the apparent stiffness, and must be considered in rope design.

Identification of model parameters

In order to describe the influence of humidity more accurately, and to set up a framework to predict long term strain, a viscoplastic/viscoelastic model has to be identified. In this work we consider a modified Schapery model to define this viscous behaviour (see part 3). For each condition (stress and humidity) the different parameters of the law have been identified, following the same method as for the dry fibres in part 3.

The results obtained (detailed in Figure 15) highlight a clear influence of the relative humidity and stress on the different viscoelastic/viscoplastic parameters. First, the instantaneous compliance ($g_0 D_0$) increases with increasing stress and relative humidity. Second, the creep rate ($g_2 D_1$), decreases with stress rise while relative humidity has a small impact. Third, the instantaneous plasticity (m) is only slightly affected at high stresses, while for lower stresses it increases rapidly with the relative humidity rise. Finally, the plastic rate (D_p) is increasing with relative humidity ingress and only slightly decreasing with the stress.
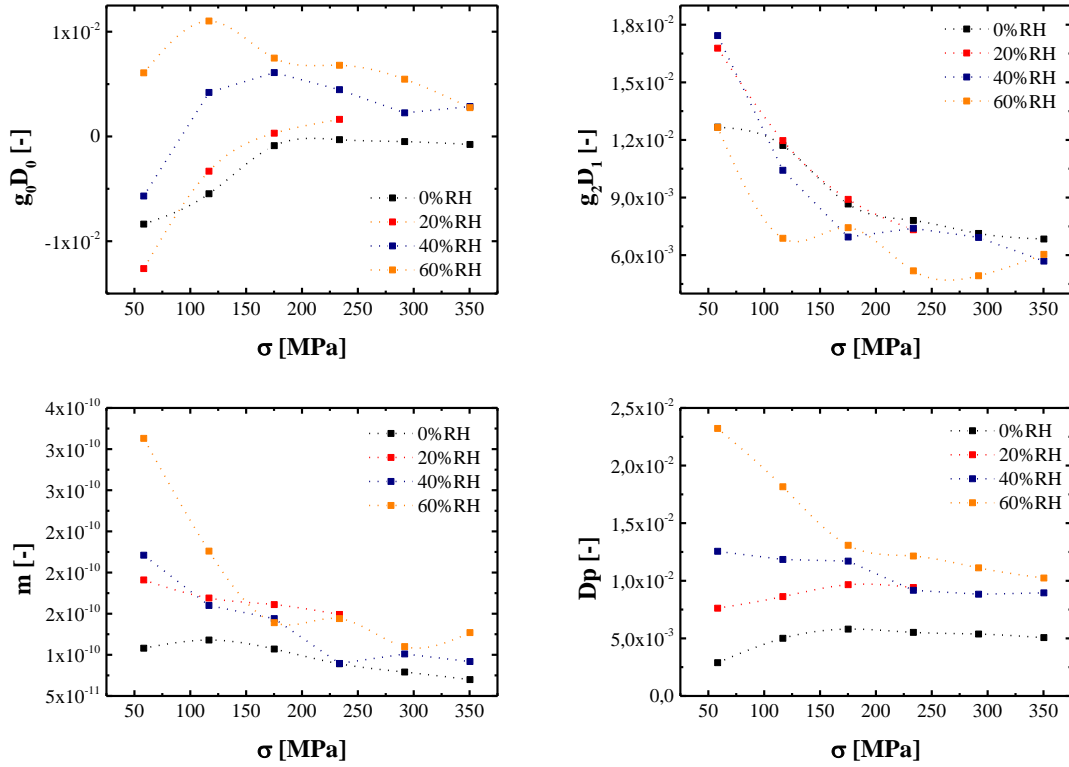
13

Figure 15. Identified model parameters

These plots show that the model parameters, elastic, viscoelastic and viscoplastic, are all affected by both applied stress and moisture in a complex manner. This indicates that in order to predict the response of a mooring line it will be necessary to perform a complete characterization. These variations in long term strain will affect the effective line stiffness, and will need to be included in any analysis. They are specific to nylon fibre ropes; most other fibres used for mooring lines are much less sensitive to moisture. The consequences for the line may be positive if they allow larger displacements to be absorbed, or negative if stiffness proves insufficient to keep the device on station.

Further tests are underway in order to develop and validate this modelling approach and to extend it to both fully immersed polyamide yarns and to rope samples. The latter undergo an additional constructional stretch due to the rope geometry, which must also be analysed and included in the model.

Conclusions

Nylon fibres are particularly sensitive to moisture, which reduces the Tg of the amorphous structure. This can be predicted, and has a small influence on the static tensile properties but a significant effect on the long term behaviour. It is therefore essential to quantify the influence of moisture on the creep response of nylon 6 fibres if they are to be used in long term marine applications such as mooring of floating wind turbines. A simple model summing elastic, viscoelastic and viscoplastic strain components, could prove useful in quantifying these effects.

Data Availability Statement.

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

References

[1]   B. L. Deopura, R. Alagirusamy, M. Joshi, et B. Gupta, *Polyesters and Polyamides*. Elsevier, 2008.

[2]   A. R. Bunsell, *Handbook of Tensile Properties of Textile and Technical Fibres*. Elsevier, 2009.

[3]   I. M. L. Ridge, S. J. Banfield, et J. Mackay, "Nylon fibre rope moorings for wave energy converters", in *OCEANS 2010*, 2010, p. 1-10.

[4]   S. D. Weller, L. Johanning, P. Davies, et S. J. Banfield, "Synthetic mooring ropes for marine renewable energy applications", *Renew. Energy*, vol. 83, p. 1268-1278, nov. 2015.

[5]   A. Marcellan, A. R. Bunsell, L. Laiarinandrasana, et R. Piques, "A multi-scale analysis of the microstructure and the tensile mechanical behaviour of polyamide 66 fibre", *Polymer*, vol. 47, n° 1, p. 367-378, Jan. 2006.

[6]   M. Arhant, P.-Y. Le Gac, M. Le Gall, C. Burtin, C. Briançon, et P. Davies, "Modelling the non Fickian water absorption in polyamide 6", *Polym. Degrad. Stab.*, vol. 133, p. 404-412, Nov. 2016.

[7]   N. R. S. Hollies, M. M. Kaessinger, B. S. Watson, et H. Bogaty, "Water Transport Mechanisms in Textile Materials: Part II: Capillary-Type Penetration in Yarns and Fabrics. Part II: Capillary-Type Penetration in Yarns and Fabrics", *Text. Res. J.*, vol. 27, n° 1, p. 8-13, Jan. 1957.

[8]   D. G. Hunt et M. W. Darlington, "Accurate measurement of creep of nylon-6,6 at constant temperature and humidity", *Polymer*, vol. 19, n° 8, p. 977‑983, août 1978.

[9]   D. G. Hunt et M. W. Darlington, "Prediction of creep of nylon-6,6 at constant stress, temperature and moisture content", *Polymer*, vol. 20, n° 2, p. 241-246, févr. 1979.

[10]   D. G. Hunt et M. W. Darlington, "Creep of nylon-6,6 during concurrent moisture changes", *Polymer*, vol. 21, n° 5, p. 502-508, mai 1980.

[11]   J. Militky, "9 - The chemistry, manufacture and tensile behaviour of polyester fibers", in *Handbook of Tensile Properties of Textile and Technical Fibres*, A. R. Bunsell, Éd. Woodhead Publishing, 2009, p. 223-314.

[12]   E. Chailleux et P. Davies, "A Non-Linear Viscoelastic Viscoplastic Model for the Behaviour of Polyester Fibres", *Mech. Time-Depend. Mater.*, vol. 9, n° 2-3, p. 147-160.

[13]   D. G. Fotheringham et B. W. Cherry, "The role of recovery forces in the deformation of linear polyethylene", *J. Mater. Sci.*, vol. 13, n° 5, p. 951-964, May 1978.

[14]   M. G. Northolt, J. J. M. Baltussen, et B. Schaffers-Korff, "Yielding and hysteresis of polymer fibres", *Polymer*, vol. 36, n° 18, p. 3485-3492, Jan. 1995.

[15]   M. Takayanagi, K. Imada, et T. Kajiyama, "Mechanical properties and fine structure of drawn polymers", *J. Polym. Sci. Part C Polym. Symp.*, vol. 15, n° 1, p. 263-281.

[16]   P. Y. Le Gac, G. Roux, P. Davies, B. Fayolle, et J. Verdu, "Water clustering in polychloroprene", *Polymer*, vol. 55, n° 12, p. 2861-2866, June 2014.

[17]   M. Broudin *et al.*, "Moisture sorption in polyamide 6.6: Experimental investigation and comparison to four physical-based models", *Polym. Test.*, vol. 43, p. 10-20, May 2015.

[18]   R. A. Schapery, "On the characterization of nonlinear viscoelastic materials", *Polym. Eng. Sci.*, vol. 9, n° 4, p. 295-310, July. 1969.

[19]   E. Chailleux et P. Davies, "Modelling the Non-Linear Viscoelastic and Viscoplastic Behaviour of Aramid Fibre Yarns", *Mech. Time-Depend. Mater.*, vol. 7, n° 3-4, p. 291-303, Sept. 2003.

[20]   F. N. Kelley et F. Bueche, "Viscosity and glass temperature relations for polymer-diluent systems", *J. Polym. Sci.*, vol. 50, n° 154, p. 549-556, April 1961.

[21]   H. K. Reimschuessel, "Relationships on the effect of water on glass transition temperature and young's modulus of nylon 6 ", *J. Polym. Sci. Polym. Chem. Ed.*, vol. 16, n° 6, p. 1229-1236, June 1978.

[22]   M. Broudin *et al.*, "Water diffusivity in PA66: Experimental characterization and modeling based on free volume theory", *Eur. Polym. J.*, vol. 67, p. 326-334, June 2015.

[23] M. J. Adamson, "Thermal expansion and swelling of cured epoxy resin used in graphite/epoxy composite materials", *J. Mater. Sci.*, vol. 15, n° 7, p. 1736-1745, July 1980.

[24] K. Kawasaki, Y. Sekita, et K. Kanou, "The extension of nylon 6 as a function of the extent and nature of sorbed water", *J. Colloid Sci.*, vol. 17, n° 9, p. 865-871, Dec. 1962.

[25] R. Bernstein, D. K. Derzon, et K. T. Gillen, "Nylon 6.6 accelerated aging studies: thermal–oxidative degradation and its interaction with hydrolysis", *Polym. Degrad. Stab.*, vol. 88, n° 3, p. 480-488, June 2005.

[26] L. Silva, S. Tognana, et W. Salgueiro, "Study of the water absorption and its influence on the Young's modulus in a commercial polyamide", *Polym. Test.*, vol. 32, n° 1, p. 158-164, Feb. 2013.

[27] A. Launay, Y. Marco, M. H. Maitournam, et I. Raoult, "Modelling the influence of temperature and relative humidity on the time-dependent mechanical behaviour of a short glass fibre reinforced polyamide", *Mech. Mater.*, vol. 56, p. 1-10, Jan. 2013.

[28] V. Miri, O. Persyn, J.-M. Lefebvre, et R. Seguela, "Effect of water absorption on the plastic deformation behavior of nylon 6", *Eur. Polym. J.*, vol. 45, n° 3, p. 757-762, March 2009.

[29] I. Boukal, "Effect of water on the mechanism of deformation of nylon 6", *J. Appl. Polym. Sci.*, vol. 11, n° 8, p. 1483-1494, Aug 1967.