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ACCELERATED AGEING OF A PULTRUDED FRP COMPOSITES PA6/GF

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Abstract: Nowadays, mobility is experiencing numerous transformations driven by the need to reduce carbon footprint. The INFRAlight project aims to develop an environmentally friendly composite railway infrastructure to reduce the carbon footprint in economic development. Rails are subjected to severe natural and mechanical weather conditions such as temperature variations, relative humidity, UV radiation. Therefore, the study of durability under severe service conditions is essential to the industrial exploitation of these materials. One of the materials considered for this application is a pultruded fibre-reinforced plastic (FRP) made of polyamide 6 (PA6) and glass fibres (GF). Literature shows that the durability of pultruded composite materials is still an understudied topic. However, several studies have shown that PA6 polymers are sensitive to moisture, leading to changes in their physicochemical properties and a decrease in their mechanical properties. In this study, accelerated hygrothermal ageing at 70 °C and 80 %RH was applied to the PA6/GF pultruded composites. The results show a decrease in mechanical properties during water absorption, followed by a recovery upon drying, highlighting the reversibility of the ageing process. Viscoelastic characterisation from vibration analysis complement these results to understand the effect of moisture on the material.

1 Introduction

Polyamide 6 (PA6) reinforced with glass fibres (GF) is widely used in many industrial sectors due to its mechanical performance and chemical properties. Pultrusion is a continuous process for producing composite profiles with uniform cross-sectional areas. However, several studies have shown that PA6 intensively absorbs water due to the presence of amide groups (-HN) in the amorphous part of the polymer. Initially, water occupies the available space (free volume) and then forms hydrogen bonds. As more molecules accumulate, the polymer's chain mobility is activated, reducing the attraction between molecules and increasing flexibility. This phenomenon explains the plasticization of PA6 after the absorption of water. This sensitivity to hygrothermal conditions has a significant impact on its mechanical and physicochemical properties. This effect has been extensively studied in the literature [1,2]. For example, Taktak et al. [4] observed a loss of approximately 60% in tensile strength and 74% in Young's modulus for PA6 specimens subjected to hydrothermal ageing at temperatures between 70°C and 90°C, while Pivdiablyk et al. [3] showed a decrease of the shear modulus, shear stress at yield and shield stress at rupture for woven PA6/GF composites after hygrothermal ageing (-40°C < T < 80°C) and (0 < RH < 85%).

This paper aims to study the effect of water absorption at 70°C and 80% RH on the mechanical and physicochemical properties of a PA6/GF pultruded composite to assess the suitability of such materials for outdoor use on rails. To evaluate this effect, mechanical tests, vibration analysis and dynamic mechanical analysis were performed before, during and after ageing.

2 Materials and methods

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The material used in this study is a pultruded PA6/GF composite 100% UD. This pultruded material is made up of two types of rovings the first is a 2400 tex roving with 17 μm filaments and the second is a 4800 tex roving with 24 μm filaments. On the outer layers are found the 2400 roving and in the core the 4800 roving. This led to a fibre volume fraction of 68 %. The pultruded profiles were cut, using water jet cutting, into specimens of different sizes in three orientations 0°, 45° and 90° relative to the fibre orientation. All cut specimens were then conditioned in a regulated room at 22 °C and 50 %RH to ensure that the specimens were in the same initial state. Table 1 shows the dimensions of the different samples.

Samples	Length (mm)/length between stubs (mm)	Width(mm)	Thickness(mm)
Fibre orientation 0°	250/150	25	2
Fibre orientation 45°	100/50	20	2
Fibre orientation 90°	90/50	20	2

Table 1: Dimensions of samples in the different orientations

2.1 Sorption

Moisture absorption tests were conducted by placing the specimens in climatic chambers at 70 °C and 80 %RH. The percentage of water absorbed was periodically measured by weighting the specimen with a scale of 0.1 mg accuracy (Sartorius Secura225D-1S) according to ASTM D5229/D 5229M-92 standard specifications [5]. The absorption curves were then obtained by the gravimetric method by averaging the percentage of water absorbed on five samples. The moisture content of a sample at a given duration, M_t was determined as follows:

$$M_t(\%) = \left(\frac{W_t - W_0}{W_0} \right) \times 100 \quad (1)$$

Where W_t and W_0 are the weights of the sample at a given time and before ageing, respectively.

After reaching the saturation point, quasi-static mechanical tests were conducted on half of the specimens and the rest were placed for 50 days in a desiccator which in turn was placed in an oven for drying at 70 °C and 0 %RH. Desorption was monitored through gravimetric analysis until an equilibrium state was reached. The mechanical properties were also examined to evaluate the reversibility of the ageing process.

2.2 Quasi-static mechanical analysis

All tensile tests were conducted according to ISO 527-4 on an MTS Criterion C45.105 tensile machine equipped with a 100 kN load cell at a speed of 3 mm/min for specimens with a 0° fibre orientation, and 1 mm/min for specimens with a 45° or 90° fibre orientation. This difference in the loading speed aims to match the same strain rate for all the tested samples (0.0003 s^{-1}). These different tests were instrumented by a digital image correlation (DIC) technique to evaluate the in-plane strain tensor. Young's modulus was calculated using linear regression between 0.05 % and 0.25 % strain on five samples in each case and the shear modulus G_{LT} was calculated from tensile test results for each sample as follows:

$$\frac{1}{G_{LT}} = \frac{4}{E_{45}} - \frac{1}{E_L} - \frac{1}{E_T} + 2 \frac{\nu_{LT}}{E_L} \quad (2)$$

Where E_L , and E_T are Young's moduli measured from tensile tests in the longitudinal and transverse directions, E_{45} is the apparent modulus measured from the off-axis test, and ν_{LT} is the Poisson's ratio measured from tensile tests in the transverse direction.

2.3 Vibration analysis

The viscoelastic parameters (elastic modulus and damping factor) of the composite specimens were determined using impulse modal analysis. The principle of this non-destructive method is to study the dynamic behaviour of a coupon through its natural vibration modes. In practice, the samples were suspended with elastic bands to simulate free-free boundary conditions. The samples were subjected to

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a longitudinal or transverse mechanical impulse using an impact hammer. An accelerometer positioned on the sample captured its transient vibratory response (in traction/compression and flexion). Through signal acquisition and Fast Fourier Transform (FFT) analysis, the frequency response function can be determined. Considering sample dimensions, the dynamic elastic modulus is calculated from beam theory as follows:

$$E_t = 4 \times \rho \times L^2 \times f_t^2 \quad (3)$$

$$E_f = 0.946 \times \rho \times \frac{L^4}{e^2} \times f_f^2 \quad (4)$$

Where E_t and E_f are the dynamic elastic modulus in traction/compression and flexion, respectively, ρ is the material density, L the sample length, e the sample thickness and f_t, f_f the resonance frequencies of the first tensile and first flexural vibration modes, respectively.

2.4 Dynamic mechanical analysis

This technique allows for the characterisation of the viscoelastic parameters of the material. The viscoelastic behaviour is evaluated through forced dynamic tension-compression testing as a function of temperature. After verifying the linear domain range, a displacement amplitude of 1 μm was imposed at a frequency of 10 Hz to the PA6/GF composites with fibre orientations of 90°. A heating rate of 2 °C/min was applied to identify the evolution of the glass transition temperature T_g . The dimensions of the specimens used for this test were 60 × 10 × 2 mm. The complex dynamic elastic modulus E^* and loss factor $\tan(\delta)$ can be written as:

$$E^* = E' + iE'' \quad (5)$$

$$\tan(\delta) = \frac{E''}{E'} \quad (6)$$

Where E' is the storage modulus (real part) related to the material elastic behaviour, and E'' is the loss modulus (imaginary part) related to the material viscous behaviour. The loss factor $\tan(\delta)$ represents the ratio of the viscous to elastic effects.

3 Results and discussion

3.1 Water sorption

Around 30 specimens were aged in a climate chamber at 70 °C and 80 %RH. The absorption curves of PA6/GF in different orientations are shown in Figure 1. It's apparent that the water uptake of PA6/GF follows a two-stage process: an initial stage leading to maximum moisture absorption where the absorption phase appears to be linear with the square root of time. However, in the second stage, the diffusion behaviour shows a decreasing trend after reaching maximum moisture absorption. A similar behaviour was already observed by Lin Sang [6] where the moisture diffusion was investigated for woven carbon fabric reinforced PA6 after hydrothermal ageing. This loss was attributed by the authors to the cleavage reactions of macromolecular chains during ageing, known as leaching. Both phenomena start at the same time when the composite to hygrothermal ageing. The phenomenon of sorption is predominant at short times and becomes less and less important (Fickian behaviour), while leaching is initially very slight and then becomes more pronounced and predominant.

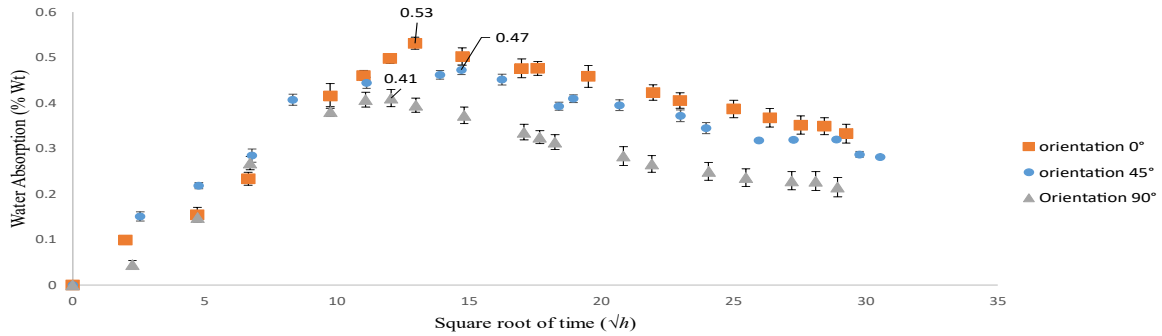


Figure 1 : Moisture uptake curves of PA6/GF specimens in three orientations 0°, 45°, 90°.

3.2 Water desorption

To examine the reversibility of ageing mechanisms, the PA6/GF specimens were dried at 70 °C and 0 % RH. The desorption curves show that the amount desorbed at equilibrium is 0.81 % for the specimens with a 0° fibre orientation, 0.92 % with a 45° fibre orientation, and 0.86 % with a 90° fibre orientation, different from the saturation values reached during the absorption phase. This saturation is confirmed by the vibrational analysis data that shows that dynamic moduli in bending and tension reach constant values at these points.

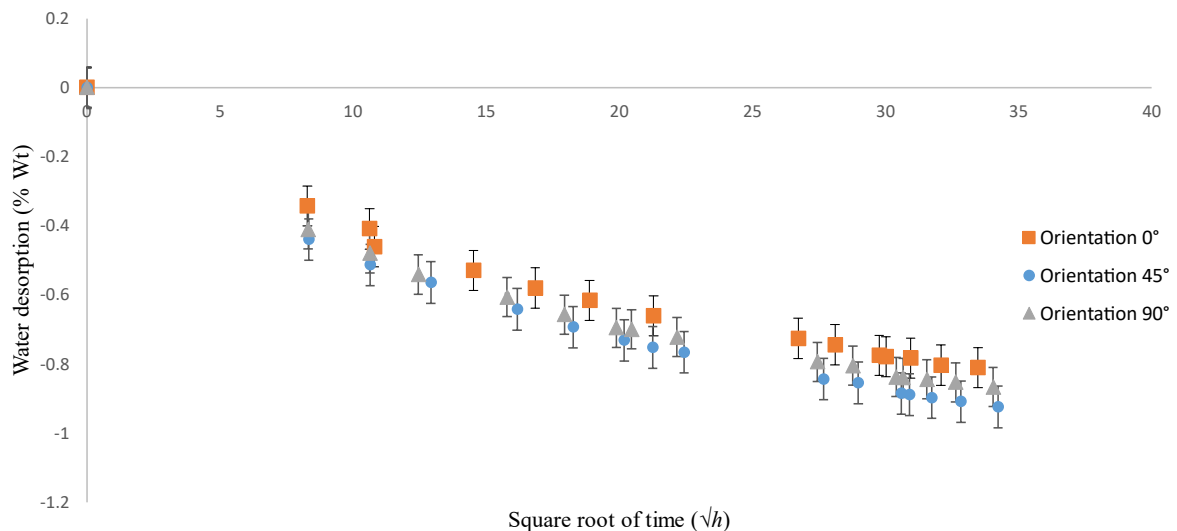


Figure 2. Desorption curves of PA6/GF after drying.

3.3 Quasi-static mechanical properties

Uniaxial tensile tests were conducted on unaged (reference condition), aged and dried states. Figures 3 and 4 summarise the mean values and standard deviation of the quasi-static mechanical properties.

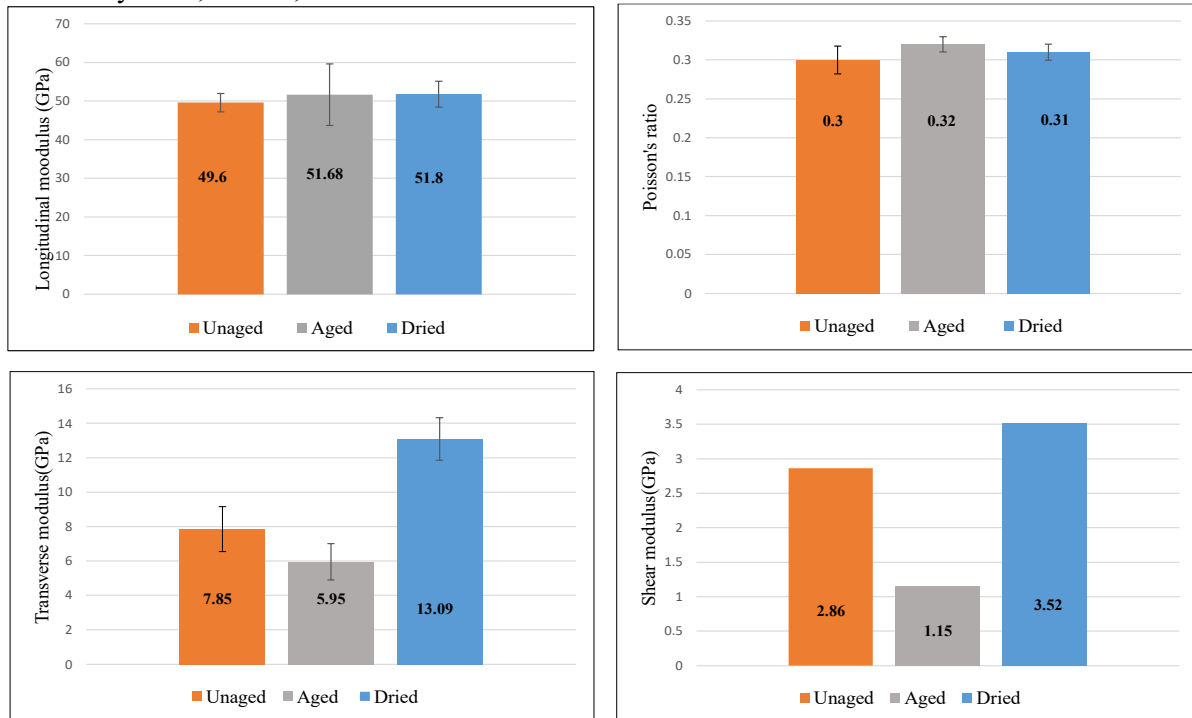


Figure 3: Comparison of elastic properties between unaged, aged, and dried samples.

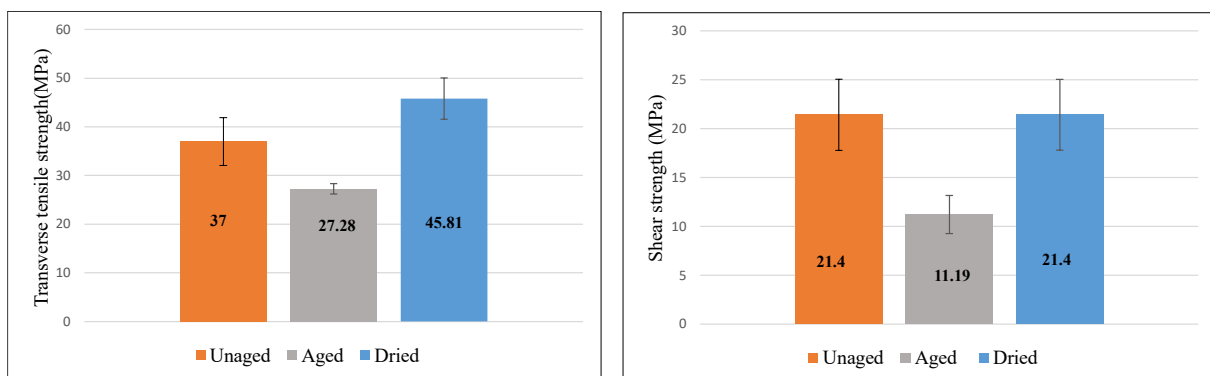


Figure 4: Comparison of ultimate properties between unaged, aged, and dried samples.

First, tests carried out on the materials along fibre directions allow to obtain the longitudinal modulus and the Poisson's ratio. No difference is observed for these parameters between the unaged, aged, and dried state. This result confirms that the mechanical performance PA6/GF along the fibre direction is dominated by the glass fibre which is unaffected by the absorption of water.

The second test is the transverse tensile test. A decrease in transverse modulus from 7.85 GPa to 5.95 GPa (24.2% loss) is observed as well as a decrease of transverse tensile strength from 37 MPa to 27.28 MPa (27% loss). Then this value increases respectively to 13.09 GPa and 45.81 MPa after drying.

The third test shows the same trend where the shear modulus decreased from 2.86 GPa to 1.15 GPa (60% loss) and the shear strength from 21.4 MPa to 11.19 MPa (48% loss). After drying, these values increase respectively to 3.52 GPa and 21.4 MPa.

During ageing, water diffuses into the composite mainly through the resin, even though diffusion may also occur at the resin/fibre interfaces. Water absorption in the resin leads to a decrease in its inherent rigidity due to plasticization (increased mobility of macromolecular chains). After drying PA6 polymer gains a certain rigidity leading to an increase in the mechanical properties of the PA6/glass fibre in the directions 90° dominated by the matrix behaviour. This gain of properties after drying is due to an additional water loss related to the difference between storage conditions (22°C, 50% RH) and drying conditions.

3.4 Vibration analysis

To gain a deeper understanding of how hygrothermal ageing impacts the mechanical properties of PA6/GF, non-destructive testing by impulse modal analysis was conducted. Figures 4 and 5 display the evolution of the dynamic elastic modulus during ageing and drying, respectively in tensile and flexural mode. Each point reflects the average of five measurements. For specimens with fibre orientations at 0°, it can be observed that the longitudinal modulus did not vary during ageing and drying, confirming that glass fibres, which are not affected by water absorption dominate the mechanical properties in this orientation. But for the other orientations, Young's modulus decreases with ageing, due to a plasticisation of the matrix. Once saturation is reached and samples dried, an increase in this modulus is observed, confirming the gain of rigidity of the material as observed with the quasi-static tests.

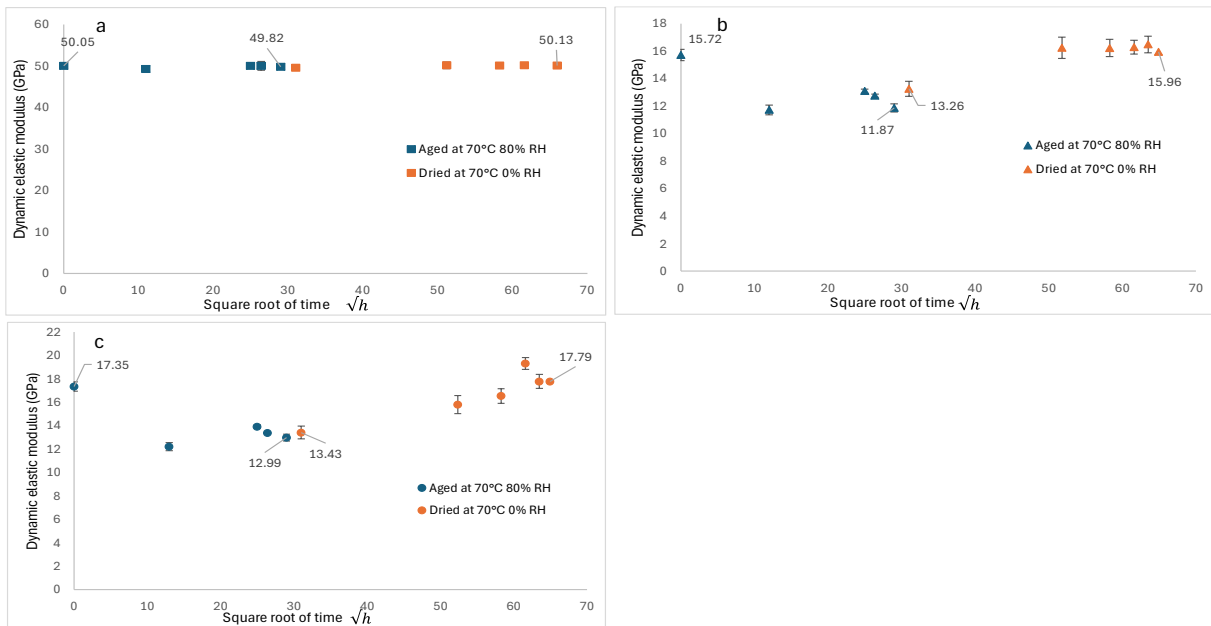


Figure 5: Evolution of dynamic elastic modulus in traction mode during ageing and drying for samples with a) 0° fibre orientations b) 90° fibre orientations c) 45° fibre orientations.

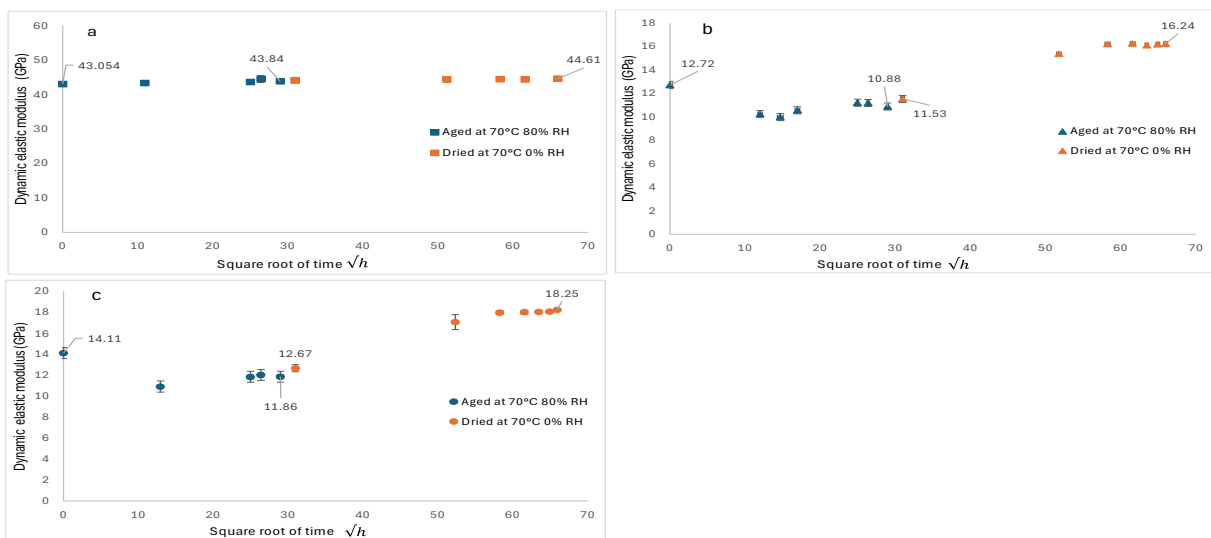


Figure 6: Evolution of dynamic elastic modulus in flexion mode during ageing and drying for samples with a) 0° fibre orientations b) 90° fibre orientations c) 45° fibre orientations.

3.5 Dynamic mechanical properties

Many studies confirm that hygrothermal ageing induces physical and chemical degradation which can affect the mechanical response of the composite material. A DMA test was conducted to identify changes of storage modulus (E') and loss factor $\tan(\delta)$ between the unaged and the aged states.

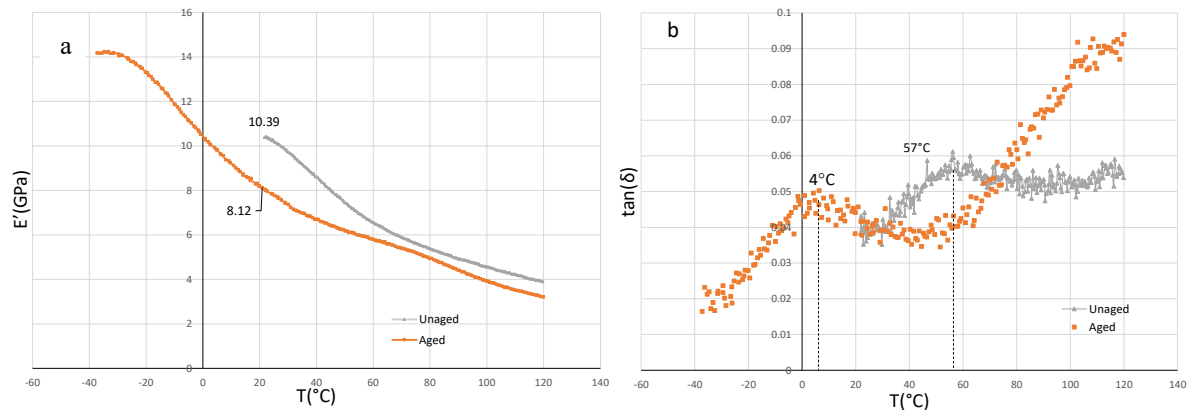


Figure 7: DMA (a) storage modulus and (b) loss factor results of unaged and aged PA6/GF fibres.

Figure 7 shows a 22 % decrease in the storage modulus at 20 °C from 10.4 GPa to 8.1 GPa due to ageing. The results indicate a pattern like that observed in quasi-static experiments and vibrational analysis, with a 24.2% (Figure 3) and a 25.5% (Figure 5) decrease respectively in the quasi-static and dynamic transverse modulus. This decline is attributed to the influence of water, caused by the plasticizing impact of molecules within the polyamide [7]. Besides, there is a significant decrease in T_g (i.e. the temperature corresponding to the peak of the loss factor) from 57°C to 4°C after ageing. The decrease of T_g can be related to the increase in the mobility of the PA6 polymer chains due to the formation of hydrogen bonds between the amide groups and water [8][9].

The results obtained from this article show that the absorption curve of PA6/GF at 70°C and RH=80% shows two stages: the first is a rapid water uptake and the second is a mass loss due to polymer degradation. This water uptake leads to a decrease in mechanical properties especially for samples with fibre orientations of 90° and 45° due to a plasticization effect. Then DMA test shows a decrease in the T_g , this effect is widely shown in the literature where the water absorbed breaks the secondary bond between the polar groups leading to a decrease in the T_g .

4 Conclusion

In this study, hygrothermal ageing of pultruded PA6/GF in the different orientations at 70°C and 80% RH were investigated. The absorption curves exhibit two distinct phases: an initial stage in which water absorption rises until it reaches a peak, followed by a subsequent phase characterized by a steady decline in mass relative to the square root of time.

To study the effect of water molecules on the mechanical properties of pultruded PA6/GF, tensile tests, and vibrational analysis were evaluated. A decrease in the mechanical properties for the specimens with 90° and 45° of fibre orientations is observed, while these properties are not affected for the specimens with 0° of fibre orientations. DMA analysis shows a significant decrease in the T_g due to an increase in the mobility of PA6 chains. This study will be complemented by a numerical model to predict the response of the material after other hygrothermal conditions.

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