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Effects of Accelerated Ageing in a PTFE Matrix Polymer Composite

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Summary: The objective of this work is to present a comparative study of the behaviour of a polymer composite before and after accelerated ageing with exposure to UVB radiation and water vapour. The goal is to propose a methodology to characterise material ageing by observing its phenomenological behaviour without taking into account chemical or physical changes that result from ageing. With this objective, tensile and creep tests were performed and the experimental results were used in an inverse approach to identify the material parameters in a three-parameter rheological model. A silica-polytetrafluoroethylene (PTFE) matrix reinforced composite was investigated. It was verified that significant differences in the composite behaviour only occurred after a long time. In particular, the strength of the composite increased significantly.

Keywords: ageing; composites; mechanical properties; parameter identification; viscoelastic properties

Introduction

The need to improve the performance of structures and equipment during their use requires better knowledge of materials and their behaviour, which may lead to the development of new technologies. One advantageous manifestation of this process is the development of composite materials, particularly composites that consist of a polymer matrix reinforced with fibres or particles. The increasing use of polymers demands deeper knowledge of not only their elastic properties but also their energy dissipation characteristics, as well as the influence of time and temperature on these properties.

The typical polymer response consists of an initial instantaneous elastic deformation followed by a time-dependent deformation that results from a combination of elastic and viscous effects.[1]

The objective of this work is to study the influence of accelerated ageing on the behaviour of a polymeric composite by observing how ageing affects the model parameters. Ageing can cause material properties and integrity to deteriorate, which leads to an undesirable loss of functionality. The proposed methodology fits to the model up-date, which seeks to match experimental results to analytical modelling. Initially, the composite is submitted to standard creep and tensile tests. Next, the obtained experimental results are compared with their theoretical counterparts obtained from analytical rheological models. An optimisation algorithm is used to fit the experimental results to the analytical models to identify the desired viscoelastic constants.[2] The effects of ageing on the strength, stiffness and viscosity of the material are analysed.

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Experimental Part

A polytetrafluoroethylene (PTFE) matrix reinforced by 42% volume of silica particles that are homogenously distributed in the matrix was used as the benchmark for the proposed methodology. The particular composite analysed here is a commercial product furnished as laminated plates by the manufacturer.[3]

The PTFE has several advantages, including exceptional resistance to high temperatures, chemical stability and low-friction properties.[4] Silica particles are usually incorporated into PTFE to increase stiffness at both ambient and high temperatures. The particular composite analysed here is manufactured in the form of laminated plates from which gaskets to the oil and gas industry are machined.[3]

To evaluate the mechanical behaviour of this composite, tensile and creep tests were performed before and after the material was exposed to accelerated ageing. The mechanical tests were performed at room temperature in a universal testing machine, the Instron Model 5567, with a capacity of 30 kN. All specimens had the standard size specified by the ASTM D638-03: 2 mm thick, 4 mm wide and a gage length of 25 mm. The width and thickness of the samples were measured at room temperature with a calliper with a precision of 0.01 mm.

The tensile tests were repeated five times and the creep tests were repeated three times for the original as-received material. For the aged material, the tensile tests were repeated three times, and the creep tests were repeated two times. The presented results are the average values for each test.

Tensile Test

The tests were performed using a rate of 5 mm/min according to the ASTM D638-03 recommendations for samples cut in the two orthogonal lamination directions: longitudinal (L) and transversal (T). The test was performed on the samples as-received (without ageing) and after ageing for 794, 964 and 2643 hours.

Creep Test

The creep test was performed according to the recommendations of ASTM D2990-01. The tests required application of a constant stress of 3 MPa. The data obtained in this test are necessary to forecast the creep modulus and the strength of the material and to provide long-term predictions of dimensional changes that may occur as a result of such loading. The creep modulus J(t), as presented by Christensen[5] and Wineman and. Rajagopal,[1] is defined as the relationship between applied stress and the resulting strain. That is, $J(t) = \varepsilon(t) / \sigma_0$, where $\varepsilon(t)$ is the creep deformation when the specimen is submitted to a constant stress σ_0.

Ageing Test

The variation of properties with time is usually slow at room temperature and becomes faster with increasing temperature. Intentional ageing above ambient temperature is a procedure that allows proper simulation of long-term effects that can affect the properties of the material. Thus, in just a few days or weeks, the damage that can occur after months or years of exposure to the sun is reproduced. In fact, UV radiation causes virtually all of the photo-degradation of materials exposed to sunlight. Thus, this test was conducted to verify the occurrence and effects of ageing in these composites.[6]

A chamber with controlled humidity and temperature was used, and 30 samples, 15 cut in the transverse direction (T) and 15 in the longitudinal direction (L), were tested. A standard cycle, with 4 h of UVB incidence at 60 °C (TL12RS Philips fluorescent lamps) and 4 h of exposure to moisture (water vapour) at 50 °C, was used. As previously mentioned, the samples were exposed to different amounts of exposure: 794 h, 964 h and 2643 h.[6] Table 1 shows the total ageing time and the time of exposure to UVB for the samples.

The accelerated ageing tests were conducted on polymers and polymer

Table 1.
Ageing in hours.

Total test time	UVB incidence
794	406
964	494
2643	1335

composites at the Federal University of Campina Grande according to the usual practice.

Results and Discussion

The as-received material showed unexpected non-isotropic behaviour; the specimens machined in the L direction were tougher than those machined in the T direction. This behaviour was not expected based on the manufacturing procedure and the microstrucural analysis.

After 964 h of ageing, the toughness anisotropic behaviour disappeared; however, it reappeared after 2643 h of ageing. This behaviour is clearly observed in the graphs shown in Figure 1. By comparing the graphs in Figures 2 and 3 it is possible to observe in greater detail the initial anisotropy decreasing. This effect results from an increase in the strength in the transverse direction rather than deterioration of the material due to the UVB exposure.

Figure 2 also presents error bars [7,8] and it can be observed that, when the material is tested under tension, the experimental results from the different specimens were very similar. The percent error varied between 1.5% and 4.0% when the material tested in the L-direction is considered and between 1.4% and 5.0% for the material tested in the T-direction.

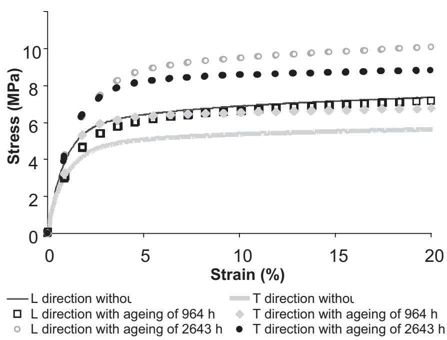

Figure 1.
Stress-strain curve for the material with and without ageing in two orthogonal directions (L and T).

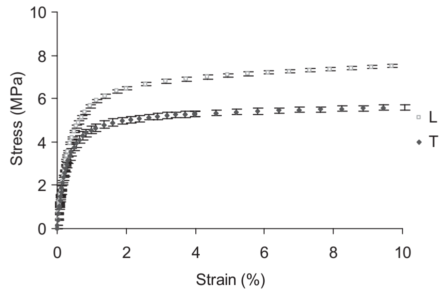

Figure 2.
Stress-strain curve with error bars for as-received material.

Additionally, as depicted in Figure 4, the strength of the composites increases as the exposure time increases.

In Figure 4, one can also see that the difference in the tensile behaviour after ageing for 794 h and 964 h was small; however, after 2643 h, a strong increase was observed in the material mechanical strength. This fact shows that ageing produces structural changes in the composite. In addition, ageing becomes more apparent for stresses greater than 4 MPa, which is the yield stress determined for the as-received material.

As in Figure 2, Figure 4 also presents error bars that demonstrate the good reproducibility of the results. For the L-direction (Figure 4a), the errors vary from 2.3% to 5.5% for the material aged for 794 h, from 1.0% to 10.0% for the material aged for 964 h and from 2.0% to 10.0% for the material aged for 2643 h. Figure 4b

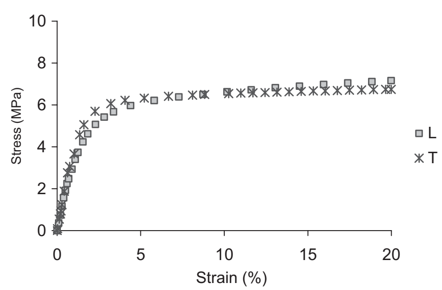

Figure 3.
Stress-strain curves for the material after ageing for 794 h.

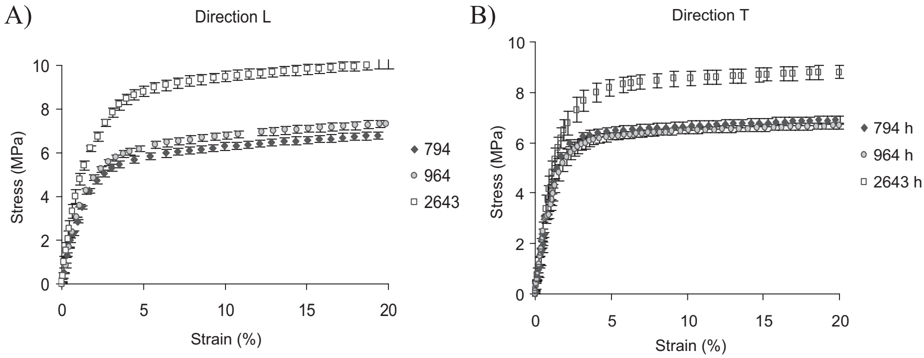

Figure 4.
Aged stress-strain curves with error bars for the composites: A) L-direction; B) T-direction.

shows the results for the T-direction; the error bars are also presented and show that the errors vary from 1.0% to 6.0% for the material without ageing, from 2.0% to 4.0% for the material with 794 h of ageing and from 3.0% to 9.0% for the material with 2643 h of ageing.

The results of the creep tests are shown in Figures 5 and 6 for the L- and T-directions, respectively. Comparing the results before and after ageing, it can be seen that there is a decrease in deformation as the exposure time to UV increases, which confirms the results of the tensile tests. Moreover, as highlighted in Figure 7, when comparing the deformations after the material was aged, the specimens have a higher transverse strain relative to the longitudinal strain. This behaviour is opposite to that observed before ageing, which is shown in Figures 5 and 6. This behaviour must be better understood; no microstructural or dimensional differences were observed that could justify these results.

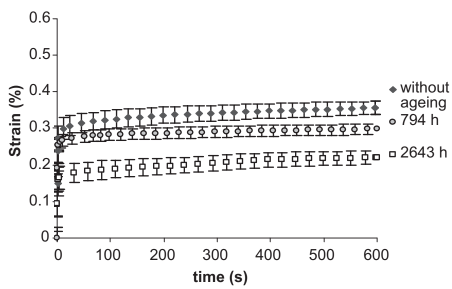

Figure 6.
T-Direction Creep-Strain-Time curves of the as-received material and the material after 794 h and 2643 h of ageing.

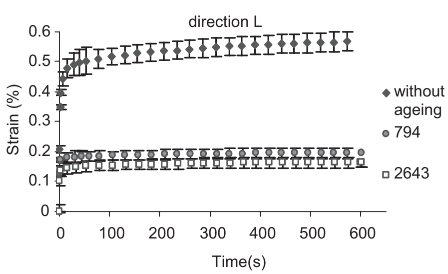

Figure 5.
L-Direction Creep-Strain-Time curves of the as-received material and the material after 794 h and 2643 h of ageing.

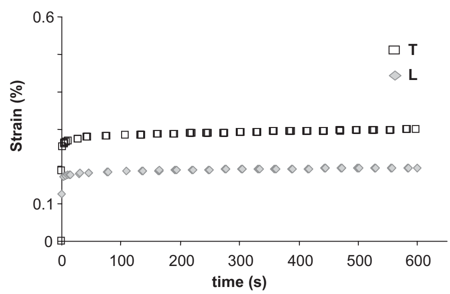

Figure 7.
Creep curve for material aged for 794 h in the L- and T-directions.

Figures 5 and 6 show the experimental error bars for the creep tests. For the L-direction, the experimental errors range from 2.0% to 9.0% for the as-received material, from 2.5% to 11.0% for the material with 794 h of ageing and from 10.0% to 13.0% for the material with 2643 h of ageing. For the T direction, the error bars show that the error varies between 5.0% and 11.0% for the as-received material, between 2.8% and 10.5% for the material with 794 h of ageing and between 5.3% and 10.0% for the material with 2643 h of ageing. Lower errors are observed in the tensile test results than in the creep tests.

The graphs in Figures 8 and 9 show the results of the creep modulus in the L- and T-directions, respectively. The creep moduli decrease with ageing for both directions: approximately 40% in the T-direction and 67% in the L-direction.

From the experimental results, it is possible to suppose that the ageing process increases the number of cross-linked structures,[9,10] which is reflected by the increase in stiffness with ageing. To better characterise the crosslinks structures, it would be interesting to carry out a swelling test[11] or determine the variation of the crosslink density indirectly by measuring the elastic and the viscoelastic responses of the material with dynamic mechanical analysis (DMA).[12]

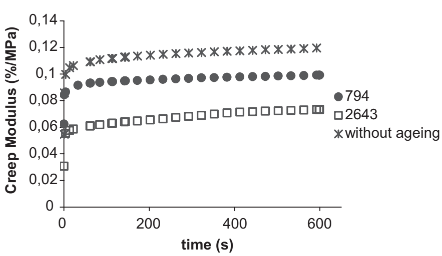

Figure 8.
T- Direction - Creep modulus of the material without ageing and aged for 794 h and 2643 h.

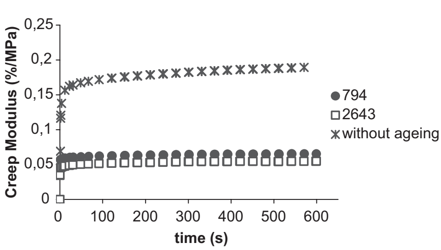

Figure 9.
L - Direction - Creep modulus of the material without ageing and aged for 794 h and 2643 h.

The values of the material parameters obtained from an inverse methodology are now presented. The approach is a numerical-experimental technique in which the experimental results are fitted to an analytical model using an optimisation procedure.[2,13,14]

The theoretical viscoelastic model adopted as the analytical counterpart in the identification step is sketched in Figure 10. With this model the behaviour of materials subjected to tensile stress or creep can be simulated using springs for the elastic behaviour and dashpot for the viscous behaviour.[1,4,15]

In this model, E and E_M are the elastic moduli, $\varepsilon1$ and $\varepsilon2$ are the strains and η is the viscosity coefficient. Moreover, it can be shown that the viscous behaviour of polymers can always be represented by the following function:[1]

$$J(t) = J_\infty + (J_0 - J_\infty)e^{-t/\tau_C} \qquad (1)$$

where $J(t)$ is the creep modulus as previously defined, J_0 is the creep modulus at the initial time ($t=0$), and J_∞ is the creep modulus as time tends to infinity. J_∞ can also be called the *Balance Creep modulus*. τ_c is the delay time. The parameters J_0 , J_∞, and τ_c are correlated with the elastic modulus, *E,* and E_M is correlated with the viscosity coefficient η, as shown in Table 2.

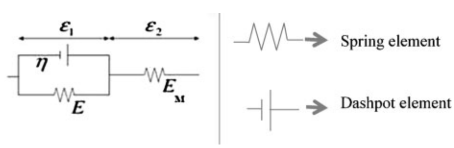

Figure 10.
Three-parameter model: Kelvin-Voight combined with free spring (KVM).[1,10]

Table 2.
Correlation Parameters of the viscoelastic model (Kelvin-Voight + spring).[1,10,14]

J_0	J_∞	τ_C
$\frac{1}{E_M}$	$\frac{E_M+E}{E_M E}$	$\frac{\eta}{E}$

By fitting the creep experimental curves (Figures 8 and 9) obtained by adjusting the experimental points to a theoretical curve, the parameters defined in equation (1) can be determined.[1,2,15] Table 3 shows the parameters from equation (1) for both directions of the test.

After identifying the parameters from equation (1) and their correlation with Table 2, the elastic moduli (E and E_M), the viscosity coefficient (η) and the delay time (τ_c) before and after the accelerated ageing process were obtained. Table 4 shows the results obtained for both directions for the as-received material and the material after 2643 h of ageing.

Analysing the experimental results, the three-element model properly describes the viscoelastic behaviour of the material. Moreover, it allows the value of the main parameters that characterise the composite, i.e., J_0, J_∞ and τ_c, to be estimated.

Comparing the experimental values and the parameters inferred from the modelling approach that are presented in Table 4, it is possible to verify that the results are compatible. The ageing effect is manifested in the stiffness of the composites, which increases both the moduli (E and E_M) and the coefficient of viscosity (η). However, the delay time (τ_c) increases in the L-direction but decreases in the T-direction.

It is important to observe Figure 10 to understand that the elastic instantaneous deformation is guided by the free spring with stiffness modulus E_M, and the viscous response is defined by the combination of E and η or, equivalently, by the delay time (τ_c). Then, the values shown in Table 4 indicate that, the instantaneous elastic response is less affected by ageing than the viscous response in both directions.

On the other hand, the creep modulus varies with the delay time. As the delay time increases, the gradient of the modulus curve also increases. Therefore, after ageing, the creep modulus curve for T (Figure 8) has a bigger slope than the curve of the creep modulus for L (Figure 9). This fact is also reflected in the results presented in Table 4. Ageing increases the delay time for the T-direction and decreases the delay time in the L- direction. Furthermore, after ageing, the creep modulus was almost constant over time.

Conclusion

It can be concluded that the proposed phenomenological methodology was able

Table 3.
Identified Parameters for the creep module[1,15]

Material	L			T		
	J_o (%/MPa)	J_∞ (%/MPa)	τ_C (s)	J_o (%/MPa)	J_∞ (%/MPa)	τ_C (s)
Without ageing	0.19	0.33	103.31	0.09	0.11	120.96
With ageing (2643 h)	0.13	0.16	51.86	0.06	0.07	231.89

Table 4.
Identified material parameters: E, E_M, η and τ_c.

Material	L				T			
	E (GPa)	EM (GPa)	η (MPa•s)	τ_c (s)	E (GPa)	EM(GPa)	η (MPa•s)	τ_c (s)
Without ageing	0.71	0.53	7.35×10^4	103.52	3.81	1.14	4.06×10^5	106,56
With ageing (2643 h)	2.92	0.78	1.51×10^5	51.71	5.09	1.82	1.18×10^6	213.89

to identify the influence of ageing in respect to mechanical behaviour of this PTFE composite. The changes in the observed experimental results were reflected consistently in the variation of the model parameters.

The identified parameters, presented in Tables 3 and 4, show that the creep modulus decreased after ageing in both the L- and T-directions, which is reflected in the J_∞ parameter. Because the ageing mostly affects the stiffness of the composite, a minor reduction in J_0 was expected.

Additionally, it was also observed that the elastic modulus and the viscosity coefficient increased. On the other hand, the delay time decreased in the L-direction and increased in the T-direction, which indicates that ageing for 2643 h greatly influenced the response of the viscous behaviour of the material.

The next step in this work is to perform the relaxation test and a complete microstructural characterization of the composite to correlate microstructural changes and the observed phenomenological behaviour.

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