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NUMERIC-EXPERIMENTAL STUDY OF THERMOPLASTICS SUBJECT TO DIFFERENT WATER ABSORPTION RATIOS, DIFFERENT TEMPERATURES AND ITS EFFECTS ON VISCOELASTIC BEHAVIOR

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Abstract. *Polymers are being used in many structural applications, and therefore, it is important to understand the effects of environmental factors, such as water and temperature. Offshore applications, like bend stiffeners, can be subject to non-standard environmental conditions, bringing more difficulties to the analysis. Due to the complex mechanical behavior of these materials, it is necessary to use appropriate numerical models that can reproduce these inelastic effects. Water absorption and temperature can play an essential role in the mechanical response of thermoplastics. In this work, a thermoplastic polymer is subject to different water absorption ratios and temperatures, and a numerical-experimental characterization of their viscoelastic behavior is presented. The material was characterized experimentally through dynamic-mechanical analysis for three different water absorption ratios (dry, saturated, and an intermediary condition of water absorption) and two different temperatures. Different material models are studied, including classic viscoelastic models. In these material models, a superposition principle is used considering temperature and water absorption analogously to the time-temperature shift factor. With this approach, it is possible to obtain a good representation of thermoplastic mechanical behavior considering different water absorption ratios and different temperatures.*

Keywords: *Viscoelastic, water absorption, thermoplastics, dynamic-mechanical analysis.*

1. INTRODUCTION

It is always a challenge to characterize the mechanical response of thermoplastics. They can present non-linear elastic behavior, plasticity, damage, and sensibility to deformation rate and temperature. These behaviors are already complicated enough to be solved in a numeric-experimental way, and it can get even more complex. The water absorbed by the polymeric structure, and the environment's temperature, can play an important role in the mechanical behavior of these materials. In a dry thermoplastic (not considering temperature variation), the response can be a lot different (CALLISTER, 1991). Offshore applications are a good example where these materials are exposed to the influence of water and temperature. Bend restrictors and polymeric barriers of flexible pipes are good examples.

Therefore, the knowledge of how humidity, water absorption and temperature can change the material behavior and also the influence of dimensions, temperature, relative humidity of the sample are crucial when time dependence in taken into account (NÚÑEZ *et al.*, 1999).

As there is not much reference about how water absorption and temperature variation influence the mechanical behavior of thermoplastics, the main objective of this work is to present a numeric-experimental study of the effects of water absorption and temperature variation in the mechanical response polymeric thermoplastics. For this, the inclusion of water absorption and temperature sensibility into the classic viscoelastic model is proposed. Thus, from dynamic-mechanical experimental observations of polyamide samples (PA6), the model representativeness is evaluated in the time domain.

2. CONSTITUTIVE MODEL

2.1 General

There are different material models to represent viscoelastic behavior. One of the most known is the generalized Maxwell model. Analogously, this model can be represented by the rheological model in Figure *1*, where there is an association of elastic mechanical components, the springs, and dissipative mechanical components, the viscous dampers.

Mechanically, the generalized Maxwell model has a spring of stiffness E_∞ in parallel with N Maxwell elements (spring and viscous damper in series), where the spring stiffness is represented by E_i and η_i represents each damper.
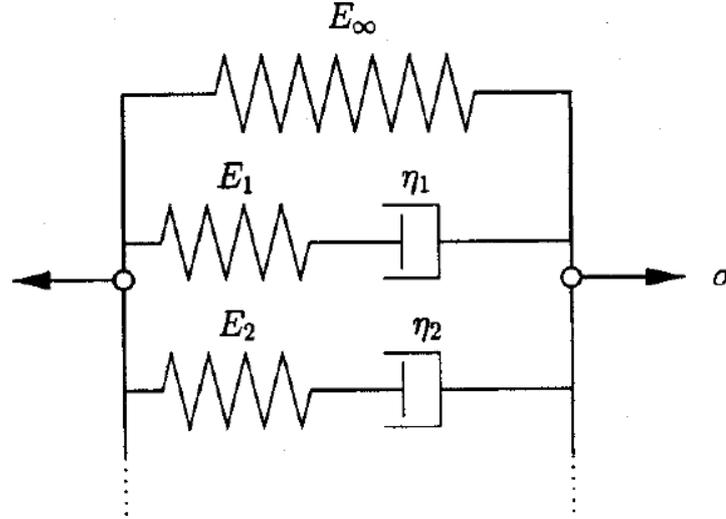

Figure 1. Generalized Maxwell Model. [4]

2.2 Time Domain

For viscoelastic materials and according to the generalized Maxwell model, the relation between stress and strain in the time domain is given by the convolution integral as following in Eq. (1) (SIMO; HUGHES, 2006):

$$\sigma(t) = \int_{-\infty}^{t} G(t-s)\,\dot{\varepsilon}(s)\,ds \tag{1}$$

In this case, G (t) is the relaxation function, and it is defined by the Eq. (2):

$$G(t) = E_\infty + \sum_i^N E_i \, exp \frac{-t}{\tau_i} \tag{2}$$

In Eq. (2), the relaxation time is defined as $\tau_i = \frac{\eta_i}{E_i}$.

Also, the superposition principle for time-temperature defined in (FERRY, 1980) can be incorporated into the mathematical model to take into account temperature effects on the viscoelastic response. Therefore, it is necessary to multiplicate the relaxations time by a shift factor $A(T)$, as shown in Eq. (3):

$$\bar{\tau}_i = A(T)\,\tau_i \tag{3}$$

There are several models for obtaining the translation factor (shift factor). The most common is the Williams-Landel-Ferry model. Its equation is given by Eq. (4):

$$log(A(T)) = \frac{-C_1\,(T-C_3)}{(C_2 + T - C_3)} \tag{4}$$

Thus, with the modifications in the relaxation time, the new relaxation function can be obtained as shown in Eq. (5):

$$G(t) = E_\infty + \sum_i^N E_i \, exp \frac{-t}{A(T)\,\tau_i} \tag{5}$$

This superposition principle was initially proposed for time-temperature superposition (FERRY, 1980). However, according to (MARKOVITZ, 1974), it can also be generalized for other factors that can influence the viscoelastic behavior, such as temperature and water absorption, just by changing the expression that defines the shift factor $A(T)$.

Then, in order to incorporate scenarios with more than one effect (for example, different water absorption ratios and different temperatures), the equation shown in Eq.(4) can be used for each factor, such as $\bar{\tau}_i = A(T)\,A(\alpha)\,\tau_i$, where α could represente the water absorption. Finally, it is important to mention that previous studies (CASAGRANDA, 2020) have

already studied the influence of water absorption considering two different water absorption ratios, and this model was proven to be assertive when only water absorption is taken into account.

3. METHODOLOGY

This work first presents the experimental characterization of the polymer of interest, and then a numerical characterization of a modified viscoelastic model.

3.1 Experimental procedure

From a polyamide 6 sheet, 10 rectangular samples were obtained for the dynamic-mechanical test, with approximately 7 mm thick, 13 mm wide, and 35 mm long (7 x 13 x 35 mm). The samples were dried following the ASTM D570 standard, where they were conditioned in an oven at 50°C for 24h, and then cooled in a vacuum dissector. All samples were weighed with a analytical Balance with a resolution of 0.1 mg, and then five samples were immersed in demineralized water at an ambient temperature of 23 ° C. The other five were kept dry in the vacuum desiccator. Periodically, the samples immersed in demineralized water were removed, dried with paper, immediately weighed, and returned to immersion. The procedure was repeated until the samples reached saturation.

Finally, with TA ElectroForce® 3200 Serie III dynamic testing machice, a dynamic-mechanical stress test of the five submerged samples in the saturation condition (submerged for a long period) and five samples in the reference condition (dry) was performed. Thus, data were obtained to obtain the storage and loss modules, at room temperature (23° C), as a function of three frequencies: 0.1 Hz, 1 Hz, and 10 Hz.

3.2 Numeric-experimental characterization

With all experimental data in hands (stress and strain history obtained in the dynamic-mechanical test), it was evaluated the capacity of the proposed model with the modified shift factor to represent the mechanical behavior of the material. Three scenarios were evaluated according to Table *1*.

Table 1. Description of all scenarios evaluated.

Scenario	Description
I	Three frequencies for each of the three water absorption ratios without taking temperature into account in the model
II	Three frequencies for each of the three water absorption ratios, taking different temperatures into account. In this scenario, the model is not water-absorption-sensitive.
III	Combining scenario I and scenario II. The model became temperature and water absorption sensitive.

The first and second scenarios use the superposition principle mentioned. For the first case, water absorption was considered using the shift factor. For the second case, the temperature was also considered using the shift factor. So, the first two cases were analyzed to set a reference showing how the model can represent both effects separately, and also it was noticeable that temperature and water absorption are relevant when evaluating a polymeric mechanical response. It should be noted that in the first scenario it was take into account the water absorption instead of the temperature, analogous to a "time-water absorption" superposition principle. The Prony and WLF parameters were obtained using all the responses of the three frequencies of the DMA tests, dry with absorption $\alpha = 0$, saturated with absorption $\alpha = 1$ and an intermediary ratio with absorption $\alpha = 0.5$.

Then, in the third scenario, both effects were combined simultaneously through the expression $\bar{\tau}_i = A(T) \, A(\alpha) \, \tau_i$, which introduces temperature and water absorption dependence.

4. RESULTS

4.1 Scenario 1: superposition principle time-water absorption ratio

For the first scenario, in the viscoelastic law, a "time-water absorption" superposition principle was considered to capture the effect of water absorption on the mechanical response of the material. The generalized Maxwell model parameters and the parameters of the Williams-Landel-Ferry equation are presented in Table 3.

In this scenario, using "time-water absorption" superposition principle as an analogy, Eq. (4) became Eq. (6), being α the water absorption ratio as mentioned before:

$$log(A(\alpha)) = \frac{-C_1 \, (\alpha - C_3)}{(C_2 + \alpha - C_3)} \tag{6}$$

Table 2. Generalized Maxwell Model parameters for Scenario 1

E_1	108.9932 MPa	τ_1	0.0012 s	C_1	7.4505e5
E_2	906.0129 MPa	τ_2	2.0680e-7 s	C_2	9.5555e4
E_3	354.7183 MPa	τ_3	5.1395e3 s	C_3	0.9613
E_∞	70.9080 MPa				

Figure 2 shows a comparison between the experimentally measured stress and the numerically calculated stress, through the generalized Maxwell model, for the three frequencies analyzed in the dry condition. Figure *3* shows the comparison using the same parameters for the three frequencies analyzed in the intermediary condition. Figure *4* shows the comparison using the same parameters for the three frequencies analyzed in the saturated condition.
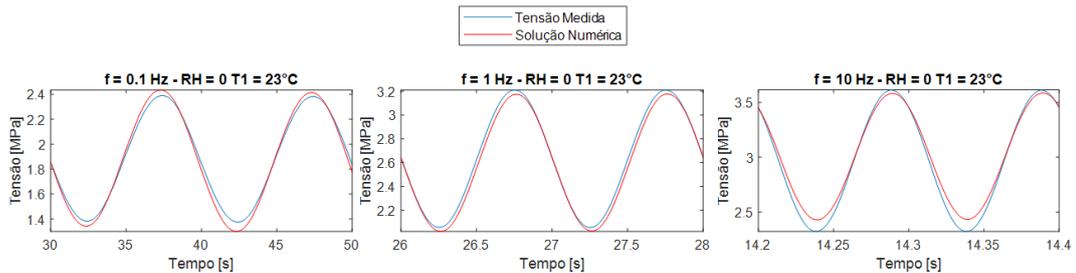
Figure 2. Scenario 1: comparison between numerical and experimental stress as a function of time for dry samples at T=296K.
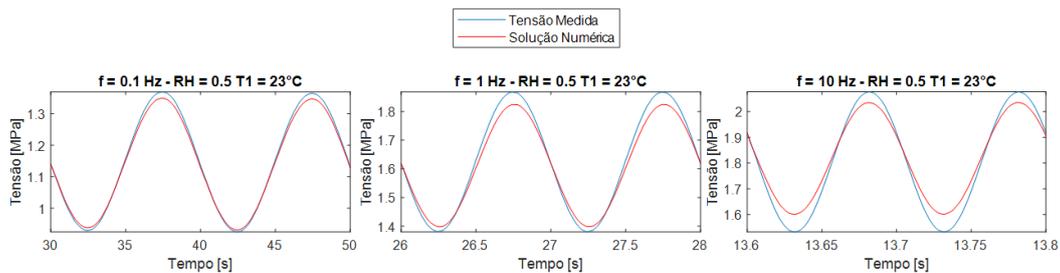
Figure 3. Scenario 1: comparison between numerical and experimental stress as a function of time for intermediary water absorption ratio samples at T=296K.
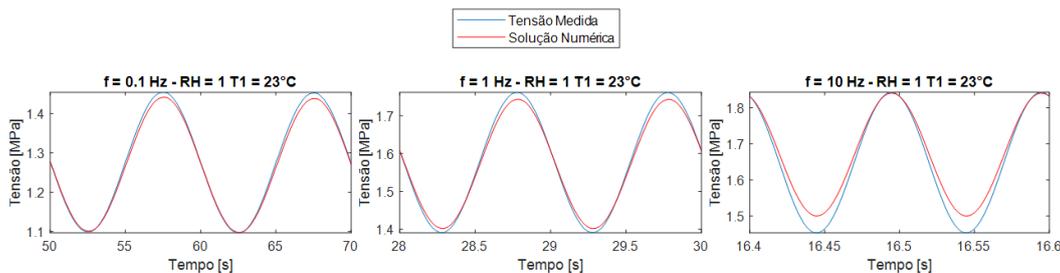
Figure 4. Scenario 1: comparison between numerical and experimental stress as a function of time for saturated samples at T=296K.

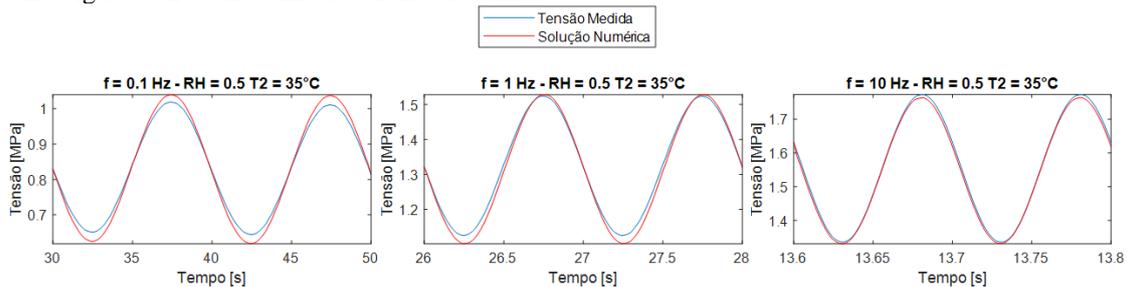Figure 7 and Figure 8 show the same situation at T=308K.

Figure 5. Scenario 1: comparison between numerical and experimental stress as a function of time for intermediary water absorption ratio samples at T=308K.
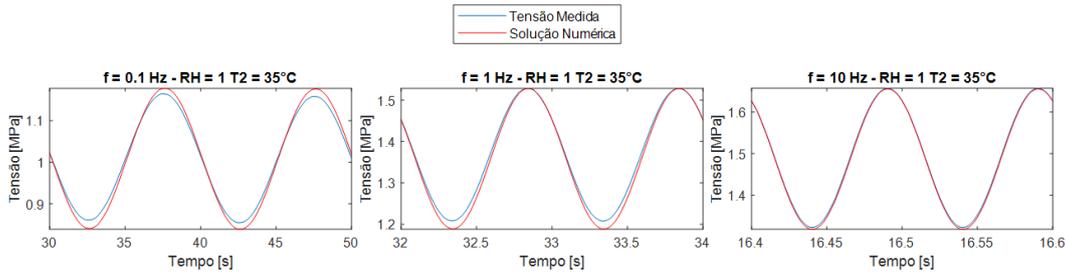
Figure 6. Scenario 1: comparison between numerical and experimental stress as a function of time for saturated samples at T=308K.

It is evident that the numerical solution for this scenario presents a better solution when comparting with experimental data measured in the DMA test, as it is possible to see that the curves are closer to each other in Figure 7 and Figure 8. Also, it is possible to verify that for the cases at T = 296K with higher frequency the error is higher.

4.2 Scenario 2: superposition principle time-temperature

For the second scenario, in the viscoelastic law, a "time-temperature" superposition principle was considered to capture the effect of temperature on the mechanical response of the material. The generalized Maxwell model parameters as well as the parameters of the Williams-Landel-Ferry equation are presented in Table 3.

Table 3. Generalized Maxwell Model parameters for Scenario 2.

E_1	205.7587 MPa	τ_1	0.2017 s	C_4	7.4666e6
E_2	92.7884 MPa	τ_2	0.039 s	C_5	2.5418e7
E_3	308.8958 MPa	τ_3	2.7966e4 s	C_6	301.5891
E_∞	127.4197 MPa				

Figure 7 presents the comparison between the numerical and experimental solution for the dry samples at 296K. In Figure 8, it is possible to observe the comparison between the numerical and experimental solution of the intermediary water absorption ratio at 296K.
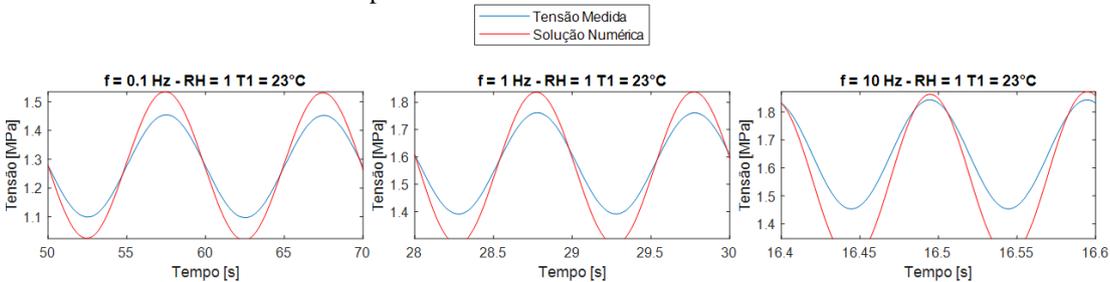

Figure 9 presents the last case, with water-saturated samples at T=296K. It is important to remember that scenario 2 does not take into account water absorption. On the other hand, the temperature effect is considered by the same expression used in scenario 1.
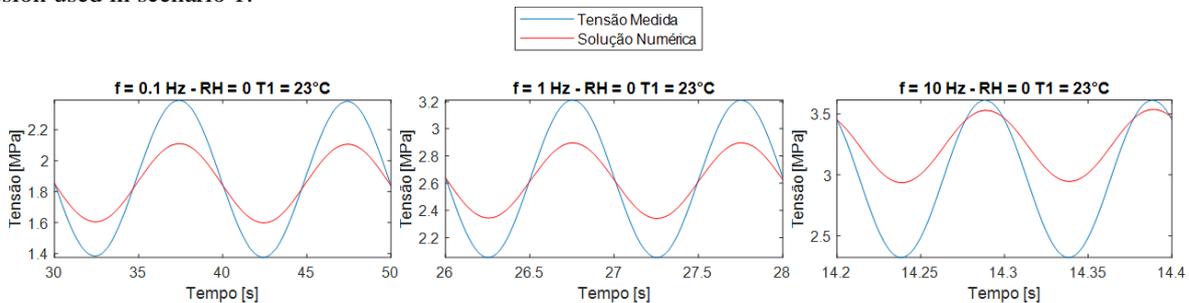

Figure 7. Scenario 2: comparison between numerical and experimental stress as a function of time for dry samples at T=296K.
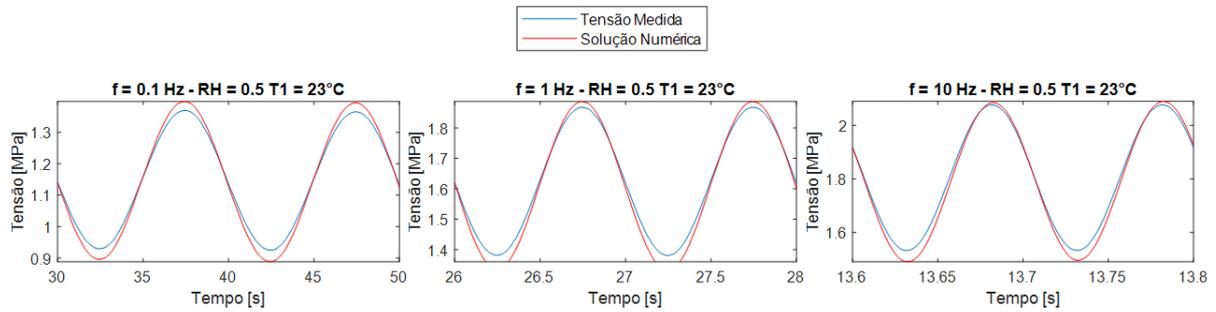
Figure 8. Scenario 2: comparison between numerical and experimental stress as a function of time for intermediary water absorption ratio samples at T=296K.
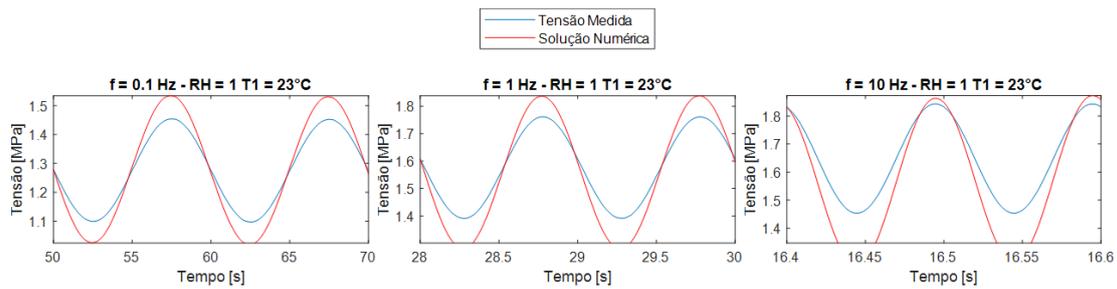

Figure 9. Scenario 2: comparison between numerical and experimental stress as a function of time for saturated samples at T=296K.
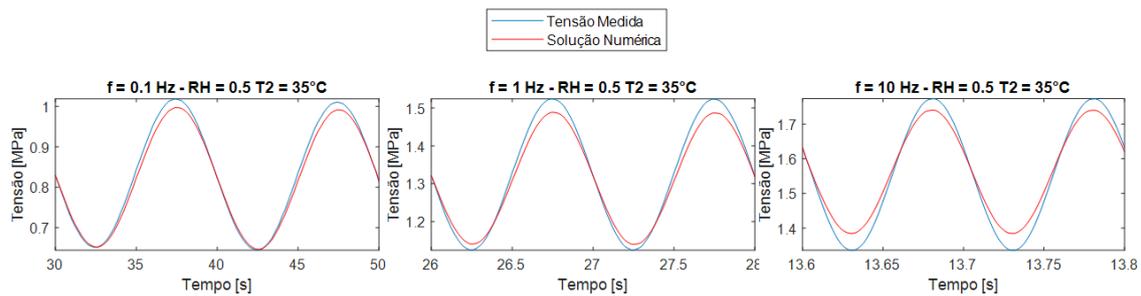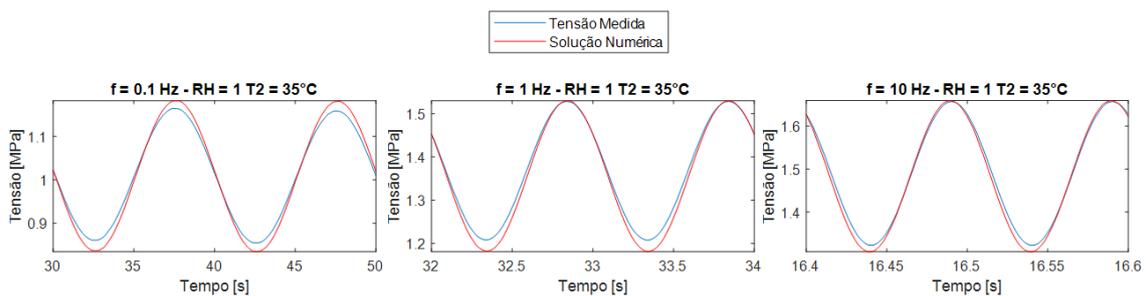

Figure 10. Scenario 2: comparison between numerical and experimental stress as a function of time for intermediary water absorption ratio samples at T=308K.

Figure 11. Scenario 2: comparison between numerical and experimental stress as a function of time for saturated samples at T=308K.

Clearly, from Figure 7 to Figure 11 and comparing to the previous figures, it is possible to observe that adding temperature influence to the model bring even more difficulties to the material behavior representation. Therefore, trying to model DMA data only with one of the effects it is not enough when the objective is to represent the behaviour in a

more accurate way. This can be particularly identified comparing Figure 7 and
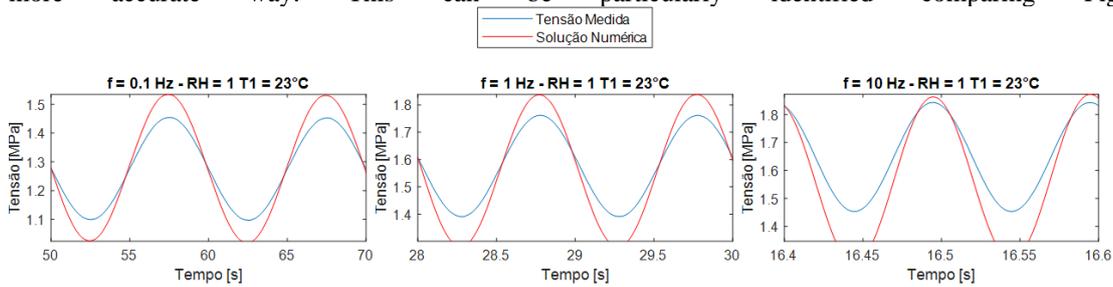

Figure *9*, where for different frequencies and water absorption radios, the numerical data can not get closer to the experimental data. Then, it is necessary to add the influence of water absorption ratios to the model to get a proper response.

4.3 Scenario 3: Combining temperature and water absorption effects to the model

In this third scenario, "time-temperature" and "time-water absorption" superposition principles were considered in the viscoelastic law in order to capture both effects on the mechanical response of the material. For this, two equations of Williams-Landel-Ferry were used to result into a new modified shift factor. Thus, the generalized Maxwell model parameters and the parameters of the Williams-Landel-Ferry equation are presented in Table 4.

Table 4. Generalized Maxwell Model parameters for Scenario 3.

E_1	853.5639 MPa	τ_1	1.7309e-5 s	C_1	20.8595	C_4	0.0463
E_2	150.8506 MPa	τ_2	0.07713 s	C_2	3.2957	C_5	23.9329
E_3	421.0074 MPa	τ_3	1.1063e6 s	C_3	0.5267	C_6	319.256
E_∞	14.9760 MPa						

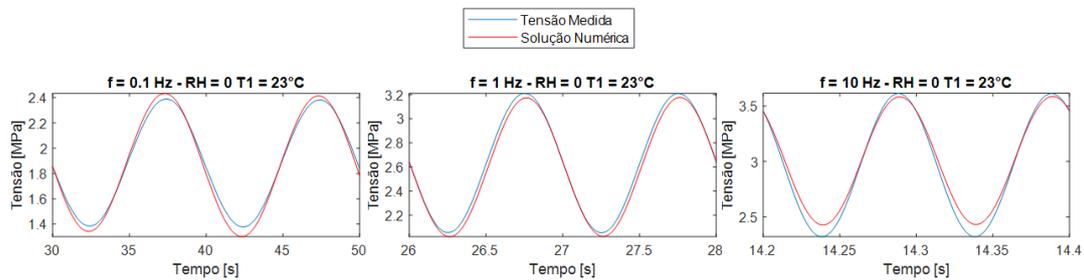

Figure 12. Scenario 3: comparison between numerical and experimental stress as a function of time for dry samples at T=296K.
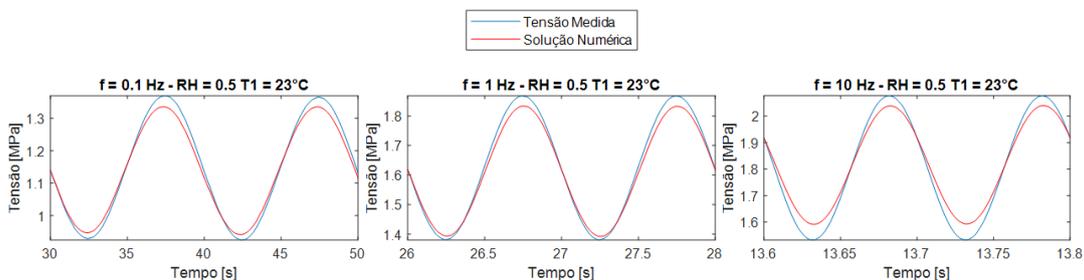

Figure 13. Scenario 3: comparison between numerical and experimental stress as a function of time for intermediary water absorption ratio samples at T=296K.
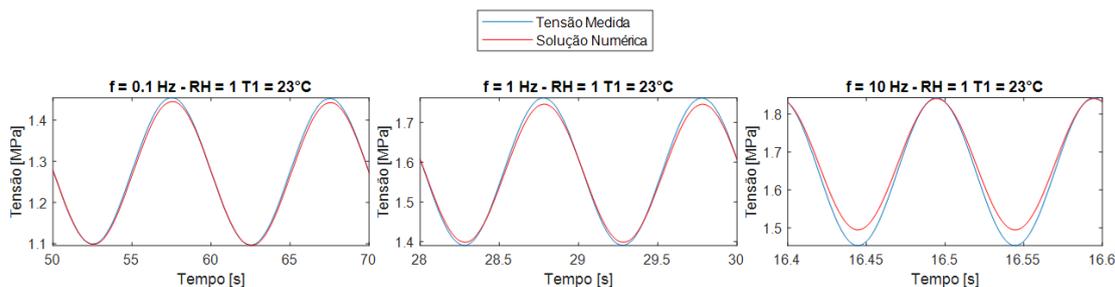
Figure 14. Scenario 3: comparison between numerical and experimental stress as a function of time for saturated samples at T=296K.
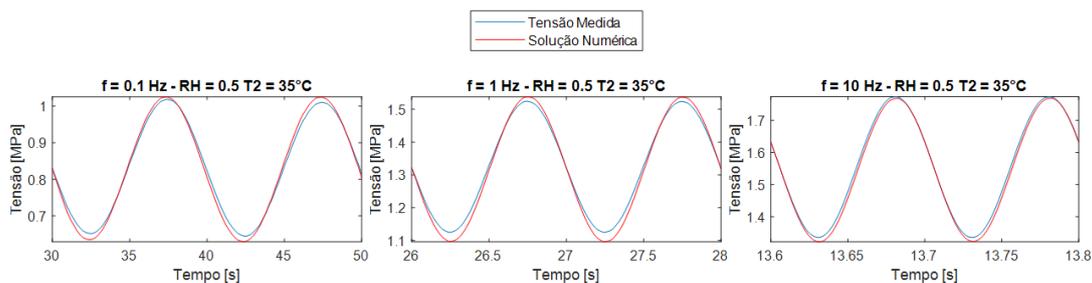
Figure 15. Scenario 3: comparison between numerical and experimental stress as a function of time for intermediary water absorption ratio samples at T=308K.
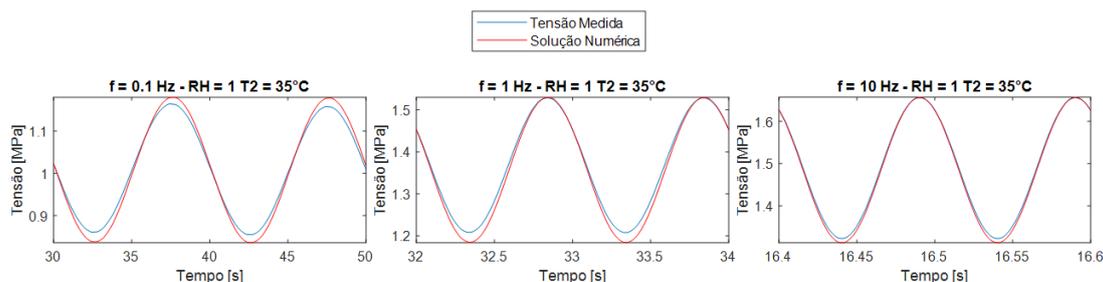
Figure 16. Scenario 3: comparison between numerical and experimental stress as a function of time for saturated samples at T=308K.

5. CONCLUSION

With the present methodology, this study was able to combine sensitivity to water absorption and temperature in the mechanical response of the thermoplastic polymer Polyamide 6 using a hypothesis to the "time-temperature" superposition principle. Through Scenario 1 and 2, it was observed that although water absorptions play an important role in the modeling of the mechanical behavior of Polyamide 6. Temperature also brings significant influence and needs to be evaluated when trying to model this material. The inclusion of only water absorption or temperature in the model can lead to errors in predicting the mechanical behavior of polymeric materials subject to different water absorption ratios and temperatures. These observations showed the relevance and contribution of this study to the topic addressed in this paper. Finally, with the modified WLF shift factor, it was possible to obtain a model capable of taking into account water absorption and temperature influence in the mechanical behavior of the material from DMA experimental data.

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