Experimental Study and Modeling of the Relaxation Behavior of the Injected Polypropylene Composites Reinforced with Short Glass Fibers

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Abstract—We present a study of the viscoelastic behavior of thermoplastic composites of polypropylene reinforced with short glass fibres. We clarify the effect of the mould temperature and the volume of fibers, on the stress relaxation. We modeled this behavior starting from the experimental data obtained after several tests of relaxation at various temperatures. A phenomenological approach is used by coupling the rheological model of Maxwell generalized with the principle of time-temperature superposition (PTTS) to evaluate behavior in relaxation long-term. That gives a better prediction of the durability of the thermoplastic composites, reliable with the real conditions of use.

Keywords—Model of Maxwell generalized, Relaxation test, Short glass fibres, Thermoplastic composites, Viscoelastic behaviour.

I. INTRODUCTION

The organic matrix composites reinforced with short glass fibres have more applications in the implementation of structural parts of various sizes in many industries such as the automotive and aerospace and electrical. These sectors have turned to this alternative view that these materials offer a better extension of their structure with equal or superior mechanical properties of metallic materials [20]. The long-term behavior of these materials affects their shelf life and their functioning.

Viscoelasticity is an important concept to identify and analyze the behavior of long-term structures [9]. It allows us to describe the behavior of materials showing the effects of strain rate under applied loads. These effects are illustrated by the phenomenon of creep under certain loads or stress relaxation. For most composite materials, the viscoelastic behavior is mainly due to the matrix [21-22].

Obtaining reliable results for the prediction of long-term behavior of these composite materials usually requires the use of long and expensive trials. Many studies have focused on the definition of characterization methods for the description of the viscoelastic behavior [1-3-5].

The linear viscoelastic behavior can be represented by a set of models based on two elements, a spring which has a linear elastic behavior and a damper which has a pure viscous behavior. Different combinations are possible from both.

The most commonly used models are those of Maxwell, Kelvin-Voigt, Zener and Oldroyd [12]. Generally, the equation of the linear viscoelastic model is defined by a relationship between stress and strain and their derivatives with respect to time [13,14].


Moreover, the principles of superposition based on the equivalence of time and stress conditions. These principles are based on the fact that the temperature and the applied strain in the elastic range, have a direct effect on the relaxation phenomenon. The Principle of Time-Temperature Superposition allows with a limited numbers of isothermal tests at different temperatures a description of the material viscoelastic behavior over a wide range of time [4]. The relaxation tests conducted at elevated temperatures may be used for the prediction of long term behavior at ambient temperature. These accelerated techniques, coupled with analytical models of stress relaxation are frequently served [19,24] for the description of the viscoelastic behavior of organic matrix composites.
II. EXPERIMENTAL PROCEDURES

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A. Materials

The reinforced polypropylene is used, with different rates of short glass fibers, sized or not. The Polypropylene reference is 3120MN 1. It is presented in the form of granules colorless, translucent, density $\rho = 905 \text{ kg/m}^3$, melt index 12gr/10min and melting temperature of 166 °C. The glass fibers used are "E" type, average length of 4 mm before processing, and 10µm diameter. For the preparation of the different samples, we used an injection molding machine industrial type ARBURG 350 C 500. This machine has a clamping force of 500kN. The samples were injected at two different mold temperatures (Tm = 30 °C and Tm = 100 °C).

B. The relaxation tests

Relaxation tests were carried out using the device type LLOYD LR50K on specimens such ISO 527-2. This machine is equipped with a thermostatic chamber cooled by a flow of nitrogen and optionally heated by an electric resistance and air ventilation. During each relaxation test, the deformation constant is measured by high accuracy gauges and the temporal evolution of the stress is recorded with an acquisition of 1 point/second. Relaxation tests have been made at controlled temperatures (21°C-40°C-60°C-80°C).

III. EXPERIMENTAL RESULTS

A. Study of rate fibers incidence

We studied the evolution of relaxation during the time of polypropylene with different rates of short glass fibers. Figure 1 shows the evolution of the stress relaxation over time.

The increase in fibers rate promotes a significant improvement in stress relaxation. Note that the initial stress is greater in the case where the rate is higher.

B. Effect of mold temperature

In this section we treat the case of two of parts, molded at Tm = 30°C and Tm = 100°C, we studied the evolution of the stress relaxation over time.

Figure 2 illustrates the evolution of the stress relaxation over time, for a composite with polypropylene reinforced 30% short glass fibers and injected at mold temperatures Tm = 30 °C and Tm = 100 °C. We note a very large increase in stress relaxation depending on the mold temperature. This is explained by the effect of mold temperature on the kinetics of crystallization of our material.
C. Study of the impact of fibers treatment

To study the effect of fibers treatment on the stress relaxation, we studied the effect of fiber/matrix interfacial behavior in relaxation state. Figure 3 shows the evolution of the stress relaxation of polypropylene reinforced with 10% short glass fibers with and without sizing, the mold temperature is 30°C.

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This figure shows that the fibers treatment produces an increase in the stress relaxation. This result allows us to conclude that the size plays an important role in improving the adhesion between the matrix and fibers. Figure 3 shows the evolution of the stress relaxation of polypropylene reinforced with 10% short glass fibers with and without sizing, the mold temperature is 30°C.

Figure 3: Evolution of the stress relaxation of polypropylene reinforced with 10% short glass fibers, mold temperature is 30°C.

D. Modeling from relaxation tests at different temperatures

Different methods have been used to determine the sufficient number of elements Maxwell to represent the behavior of the stress relaxation of materials. One of the methods most commonly used is the successive residual method.

The experimental data obtained from tests of relaxation were used to calculate the parameters of the Maxwell model. Two criteria were used to determine the number of elements in the Maxwell model. The first criterion is the maximum relative difference (MRD maximum relative difference) between the measured experimental data and model values. It is defined by the following equation:

$$MRD = \max\{\frac{\text{value measured} - \text{value calculated}}{\text{measured value}}\} \times 100$$ (1)

The model with the number of elements corresponding to a Maxwell MRD value ≤ 5% was selected as the model which gave a good fit. Statistical analysis of the model is the main step of the analysis. It is based in some cases on the mathematical analysis of the data as to the application of the method of Daniel [15] or Lenth [16]. Its objective is to identify statistically influential factors on the response (s) observed (s).

The second criterion is the quality of fit of the experimental curve from an equation with more parameters can be understood from the calculation of adjusted coefficient $R^2_{adj}$ defined by the following equation:

$$R^2_{adj} = 1 - \frac{(1-n)(1-R^2)}{n-p-1}$$ (2)

Or $R^2$ is the coefficient of determination, n-1 is the number of degrees of freedom and p is the number of independent variables. The determination coefficients of is defined by the equation:

$$R^2 = 1 - \frac{\text{sum of squared residuals}}{\text{sum of total square}}$$ (3)

More the value of the coefficient of determination $R_{adj}$ is near 1, more responses calculated by the model are close to those measured during the experiment.
The obtained values of MRD and the adjustments made on relaxation tests of composites reinforced with short glass fibers are shown in the following table:

**Table 1**

**Comparison of the Maxwell Model with One and Two and Three Components of the Composite Reinforced with Different Rates of Short Glass Fibers and at Different Mould Temperatures**

<table>
<thead>
<tr>
<th>Composite type</th>
<th>Model with 1 element</th>
<th>Model with 2 element</th>
<th>Model with 3 element</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% Fibres</td>
<td>Treatment</td>
<td>Mold Temperature °C</td>
</tr>
<tr>
<td>0</td>
<td>--</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>--</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Treated</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>Treated</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>N Treated</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>N Treated</td>
<td>30</td>
<td></td>
</tr>
</tbody>
</table>

Experimental data are adapted to a Maxwell model with two or three elements. The MRD values decreased with an increase in the number of components (Table 1). For the model of a single element, the MRD values vary between 18.6 and 27.4% for the model with two elements, the MRD values ranged from 8.03 to 15.5%. For the model of a single component, the MRD values vary between 18.6 and 27.4%, for the model with two components, MRD values ranged between 8.3 and 15.5%.

In case of three-term model, MRD values are usually less than 2%, with a maximum value 1.78%.

Furthermore, a comparison based on the values R²Adj revealed that the three components Maxwell model gives a better fit. Therefore, the model of the three-element Maxwell which satisfies both criteria (MRD ≤ 5% and greater than 0.990 R²Adj) was chosen as the best fit equation for relaxation data.

Generalized Maxwell model is chosen to describe the viscoelastic behavior of the composite [17]. It involves combining different parallel Maxwell models and a simple spring (Figure 5).

![Figure 5: Generalized Maxwell model with 4 branches](image)

In this study, we proposed the generalized Maxwell model with three terms to represent the stress relaxation.

\[ \sigma(t) = \sigma_\infty + \sigma_0 \varepsilon_1^{(t/\tau_1)} + \sigma_0 \varepsilon_2^{(t/\tau_2)} + \sigma_0 \varepsilon_3^{(t/\tau_3)} \]

with \( \sigma_\infty = \sigma_4 = E_4 \varepsilon_0 \)
Generally, considering $E_i = E_\infty$; the tank being cannot be relaxed. With $\sigma_i = \text{constant characteristic}$ and $\tau_i = \text{characteristic time during an interval } i$.

The fit of the experimental points obtained is performed using Equation 4. This adjustment requires fixing the time number characteristic of the constitutive law used. The various adjustments made using the identification by the analysis of variance ANOVA using a calculation software, show that it is necessary to choose a number of sufficient maxwell reaching $R^2_{\text{Adj}}$ near 1 and MRP less than 5%.

A smaller elements number does not correlate with the experimental results.

A greater number does not allow adjustment of superior quality. In our study, the number of items chosen to give a good fit is of order 3.

This result explains the existence of three time intervals, and thus three distinct relaxation time. The existence of these three slots can be attributed to different molecular rearrangements, which characterize the viscoelastic process. So we distinguish the behavior in the short and medium and long term. The short-term behavior may be related to rapid movements of the segments along the chains (Rouse movements). In a second step, the chains tend to organize themselves to oppose the local deformations imposed by the applied stress. Finally, the system tends to a steady state (long-term) where the length of the chain reaches its equilibrium value (motion stability of these channels).

The results are used to trace the evolution of the parameters of our rheological model based on characteristic times for different composites presented in Table 2.

### Table 2

<table>
<thead>
<tr>
<th>% Fibers</th>
<th>Treatment</th>
<th>Mold temperature</th>
<th>Test temperature</th>
<th>Rheological model</th>
<th>$R^2_{\text{Adj}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>30</td>
<td>21</td>
<td>$\sigma(t) = 10.95 + 3.82e^{-0.01t} + 3.22e^{-0.51t} + 3.52e^{-0.16t}$</td>
<td>0.9878</td>
</tr>
<tr>
<td>10</td>
<td>Treated</td>
<td>30</td>
<td>21</td>
<td>$\sigma(t) = 16.5 + 3.81e^{-0.01t} + 3.32e^{-0.009t} + 4.5e^{-0.03t}$</td>
<td>0.9859</td>
</tr>
<tr>
<td>30</td>
<td>Treated</td>
<td>30</td>
<td>21</td>
<td>$\sigma(t) = 22.23 + 4.43e^{-0.01t} + 3.68e^{-0.03t} + 4.89e^{-0.01t}$</td>
<td>0.9923</td>
</tr>
<tr>
<td>10</td>
<td>N Treated</td>
<td>30</td>
<td>21</td>
<td>$\sigma(t) = 13.01 + 2.62e^{-0.05} + 2.43e^{-0.01t} + 3.52e^{-0.02t}$</td>
<td>0.9918</td>
</tr>
<tr>
<td>30</td>
<td>N Treated</td>
<td>30</td>
<td>21</td>
<td>$\sigma(t) = 22.12 + 3.56e^{-0.03t} + 2.96e^{-0.05t} + 3.01e^{-0.02t}$</td>
<td>0.9726</td>
</tr>
<tr>
<td>10</td>
<td>Treated</td>
<td>100</td>
<td>21</td>
<td>$\sigma(t) = 16.2 + 4.8e^{-0.03t} + 3.09e^{-0.14t} + 4.3e^{-0.28t}$</td>
<td>0.9986</td>
</tr>
</tbody>
</table>

The application of the rheological Maxwell model generalized with three elements on thermoplastic composites reinforced with short glass fibers at different test temperatures showed very interesting results (Figure 6).

**Figure 6:** Comparison between the rheological model and the measured stress relaxation of the composite reinforced with 10% short glass fibers sized fibers at different test temperatures.
The time-temperature equivalence defined by WLF permits from several tests at different temperatures, to describe the stress relaxation for a wide spectrum of time. Indeed, for a given reference temperature, a translation factor a_T for each temperature test allows the offset of each curve and thus the construction of the viscoelastic behavior master curve of each composite.

T_0 illustrate the curve displacement direction, either F_T_0 (t) relaxation function for the reference temperature T_0^0 and F_T (t) the relaxation function at temperature T. As proposed by several researchers [11], may write:

\[ F_{T_0} (\log t) = F_T [\log t + f (T)] \]  \hspace{1cm} (5)

Where T_0 is a reference temperature, and f(T) is the translation factor (logarithmic scale).

Assuming that f (T) = log_a_T to (t), then:

\[ F_{T_0} (\log t) = F_T [\log t + \log_a_T] = F_T [\log (t a_T)] \]  \hspace{1cm} (6)

As a result: \[ F_{T_0} (t) = F_T (t . a_T) \]  \hspace{1cm} (7)

t.a_T quantity is called the reduced time or pseudo time. Thus, it has been shown that time units t at the temperature T_0 are equivalent to t.a_T in time units at the temperature T. The translation factor a_T is an inherent property of a viscoelastic material and must be determined experimentally.

For T < T_0, a_T < 1; for T > T_0, a_T > 1 and T = T_0, a_T = 1.

By applying the procedure of the translational factor a_T as described above a series of curves made at different temperatures, a "master curve" can only be obtained. Thus, the stress relaxation at any temperature T can be represented by the stress relaxation at a reference temperature T_0, on time scale.

Predicting the long-term behavior of composites is the subject of an extensive literature [2,18]. These studies use numerical methods (finite element) proposing a complex mathematical formalism. However, we chose to focus our attention on the "phenomenological" models, easier to handle and giving a more "physical" than mathematical description of the behavior.

The functions of the translation factors are determined by non-linear regression according to the difference between the test temperature and the reference temperature (T - T_0) for each thermoplastic composite.

The function of translations factors for a polypropylene reinforced with 10% sized glass fibers molded at Tm = 30 °C is:

\[ \log 10a_T = 15.32 - 10.2(T - T_0) - 3.69 - 10.4(T - T_0)^2 \]

R^2_adj = 0.99 \hspace{1cm} (8)

The translations factor's function for the polypropylene reinforced with 30% sized glass fibers molded at Tm = 30 °C is:

\[ \log 10 a_T = 9.913 \times 10^{-2} (T - T_0) - 6.37 \times 10^{-4} (T - T_0)^2 = 0.97 \]

R^2_adj \hspace{1cm} (9)

Motivated by the representation of experimental phenomena observed in Figures (6-7-8). We have chosen to perform a phenomenological approach of stress relaxation with polynomial type (Equation 8 and 9). That can bind the stress relaxation by the translation factor for a given temperature.

For polypropylene reinforced with 10% sized glass fibers molded at Tm = 30 °C we obtain:

\[ \sigma(t) = 25.550 - 2.781 \log (t.a_T) + 9.3 \times 10^{-2}[\log (t.a_T)]^2 \]

R^2_adj = 0.99 \hspace{1cm} (10)

For polypropylene reinforced with 30% sized glass fibers molded at Tm = 30 °C we obtain:

\[ \sigma(t) = 30.684 - 2.565 \log (t.a_T) + 6.00410^{-2}[\log (t.a_T)]^2 \]

R^2_adj = 0.9873 \hspace{1cm} (11)

![Figure 7: Stress relaxation's master curve of polypropylene reinforced with 10% short and sized glass fibers, Tm = 30°C and a reference temperature is 21°C.](https://example.com/figure7.png)
IV. CONCLUSION

Viscoelastic phenomena reflect different molecular rearrangement process. Indeed, the molecular structure controls mechanical and viscoelastic properties. During injection of the thermoplastic composite, the mold temperature has a great influence on the cooling of the parts. This variation causes a change in the degree of polymer matrix crystallinity.

We studied the relaxation composite, polypropylene / short glass fibers, depending on the importance of processing parameters and fibers structure. An increase in the temperature of the mold, on one hand, and a sizing treatment on fibers surface, on the other hand, have led us to an improvement of the stress relaxation.

We have developed a methodology, based on two approaches especially in terms of reliability to determine element's number of generalized Maxwell model needed to describe our relaxation tests.

We have shown that three branches are sufficient to represent the relaxation time on the applied relaxation tests considered. Based on the principle of superposition and the generalized Maxwell model, we have modeled the long-term behavior of thermoplastic composites with phenomenological models. The validation of these models by comparing predictions with experimental results on "long" test is performed.

REFERENCES


