A simple model to fit and interpret creep curves-behaviour of modified micro-cellulose particulate composites

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Abstract

Microcrystalline cellulose is largely used to improve thermos-mechanical properties of composites. This study aims to evaluate the creep behaviour of micro-cellulose epoxy-based composites, and the effect of reinforcements’ silanization treatment. A new viscoelastic model, based on the generalized logistic function was successfully tested. The results were directly associated with the material’s structure-property relationships. Rigid particles restricted the molecular chain’s motion, mainly on the amorphous segments. This difference achieved the needing of more energy, to achieve creep deformation. Then, MCC improved the structural integrity, when incorporated into an epoxy matrix. On one hand, the incorporation of silanized-MCC increased the mechanical behavior of the composite, due to the stiffer structure. Furthermore, the chemical modification provided an increment in the glassy plateau, associated with higher thermal energy required to initiate strain of the amorphous polymeric chains. This behaviour conducted in an abrupt decrease of load-bearing capability for the composites. Finally, the proposed model is suitable to be employed in creep curves, aiming to easily interpret the structure-property relationships of this test.

Introduction

Particulate polymeric-based composites are the most used composites in the worldwide, due to their wide availability and cheapness, compared to fiber-reinforced ones (Rajak et al. 2019; Kerche et al. 2021b). These materials are characterized as being composed of particles suspended in a matrix. Depending on the particle’s size, the reinforcement mechanisms may differ. For instance, nano-composites, present strengthening mechanism at the atomic/molecular level. However, particulate composites are designed to produce unusual combinations of properties and, then, the reinforcement mechanism is a bit complex (Randall M. German 2016).

In particular, due to its versatility, cellulose (nano-cellulose, micro-cellulose and derivatives) is one of the most promising particle to manufacture composites and has been employed in different sectors (Trache et al. 2016; Kargarzadeh et al. 2017; Motta Neves et al. 2022). Microcrystalline cellulose (MCC) is an example of this reinforcement’s configuration. It can be obtained from innumerous biomass sources, such as bleached pulps and vegetable fibers, like ramie, jute, curauá, and kenaf (Neves et al. 2019b, a, 2021a; Kerche et al. 2021a). Moreover, different isolation processes (radiation-enzymatic, extrusion) and treatments (steam explosion, alkali hydrolysis) may be used to extract the crystals. (Abdul Khalil et al. 2012; Neves et al. 2021a).

MCC has many advantages over other particles, such as ceramics, glasses and metals, as lower cost and weight, chemical inertness, easy processing, independence of petrochemical resources, sustainability, among others. Moreover, when incorporated into a polymeric matrix, MCC can improve the mechanical performance of the matrix, leading to a green and sustainable product (depending on the matrix), with a high-added value (Gan et al. 2020; Low et al. 2021). Additionally, an extra improvement of properties can
be achieved by functionalizing MCC with silanes, prior to matrix incorporation, once MCC is not fully compatible with polymers, such as epoxy resin (Wang et al. 2020; Neves et al. 2021b).

Creep is a time-dependent mechanical property in which the stress is applied and monitored in the function of time (Reis et al. 2020). The polymer viscoelastic nature is directly dependent on temperature and the applied stress. Hence, the changes in creep can be directly attributed to the particle ability to restrain the molecular motion of the amorphous chain segments.

At a given stress level, and above the glass transition temperature ($T_g$), the free volume increases, and the polymer amorphous chain segments can statistically occupy several spaces, due to the higher internal energy. This causes a loss of dimensional stability and load-bearing capability, decreasing the mechanical response. There is lower internal energy, below $T_g$, and the molecular restriction, imposed by the particles, on the amorphous chain segments, can lead to a higher mechanical property (Marrucci 2003; Ornaghi et al. 2020b). Hence, the improvement in mechanical properties is directly dependent on the particle capacity to restrain the polymer chain segment motion, in different experimental conditions. This restriction depends on the composite system (i.e., matrix and reinforcement) and the viscoelastic region studied.

The effect of the MCC concentration and its functionalization on the epoxy resin was already studied (Luo et al. 2016; Wang et al. 2020; Neves et al. 2021b). However, the discussion on the creep curves was not found in previous literature, evidencing this work's contribution. This study has as the main novelty, to study creep behavior of epoxy/MCC composites at 5 wt.% of reinforcement. The effect of silanization was also studied. A novel proposed model, based on a generalized logistic function, is presented to correlate the instantaneous elastic deformation, in function of temperature, with creep response. The creep curves were studied from 30°C to 190°C, aiming to englobes all viscoelastic regions and a deep discussion about the viscoelastic response, creep and structure-property relationships are addressed.

**Materials And Methods**

**Materials**

MCC functionalization: Powder microcrystalline cellulose (MCC, width ~ 20 µm, Sigma Aldrich), 3-aminopropyltriethoxysilane (APTES, Sigma Aldrich), ethanol, 99.5% (Química Moderna) and glacial acetic acid (Química Moderna).

Composites: Diglycidyl-ether of bisphenol-A (DGEBA, epoxy resin, Araldite LY1564, Advanced Vacuum), hardener (amine-based, Ren HY150, Advanced Vacuum) and acetone (Zeon). All reactants were used as-received.

**Composite’s manufacturing**
MCC was functionalized with APTES, producing amino-functionalized cellulose (MCC-Si) and deeply reported in a previous paper (Neves et al. 2021b; Motta Neves et al. 2022). Briefly, the functionalization was performed by hydrolysis, condensation and grafting of the amine functional groups, onto the MCC surface.

The composites were manufactured using the following steps: 5g of MCC or MCC-Si were added to 50 ml of acetone and sonicated for 1 hour, using an amplitude of 40% and 500 W in an ice bath. Then, this suspension was added to 50 g of epoxy resin, homogenized and sonicated, using the same aforementioned parameters. The mixture was magnetically stirred at 80°C for 3 h and placed in an oven at 80°C for 12 h. After cooling, the hardener was added to the composite (15:100 hardener:resin, by weight, according to the manufacturer), mixed manually, and by magnetic stirring for 10 min. Three cycles (10 min) of degassing were carried out in a vacuum oven at −0.8 bar. Finally, the mixture was cast into silicone rubber molds, cured in situ for 48 hours, at room temperature, and post-cured (2 h at 70°C, 2 h at 90°C, 2 h at 120°C, and 15 h at 150°C, according to the manufacturer). It is important to stress that the content of 5 wt.% of reinforcement (for the pristine MCC or the modified one) was chosen based on the best results for mechanical and thermal stability, previous reported (Neves et al. 2021b; Motta Neves et al. 2022).

Characterization

Dynamic-mechanical properties were obtained using a single cantilever clamp, according to ASTM D4065-12 with a specimen size of 35×10×4 mm in a TA Instruments Q800 AT DMA equipment. The tests were performed from 30 to 200°C temperature range, 3°C.min⁻¹ rate, 0.1% deformation amplitude and 1Hz frequency.

Creep tests were performed using a temperature range from 40°C to 250°C, varying steps of 20°C, totalizing 12 different temperatures, for each composite. Each composite was tested at a 5 MPa creep load. The tests were performed using a three-point bend clamp and with a specimen size of 35×10×4 mm in the same aforementioned DMA equipment.

Time-temperature superposition (TTS) is a short-term analysis that allows the prediction and evolution of the relaxation process, in inaccessible experimental time (John D. Ferry 1980; Reis et al. 2020). One of the most successful methodologies is based on Williams-Landel-Ferry (WLF) model, given by Eq. 1:

\[
\log a_T = \left( -\frac{C_1(T-T_0)}{C_2 + (T-T_0)} \right) \quad (1)
\]

Where \(a_T\) is the shift factor, used to shift the curves, under different isotherms, \(C_1\) and \(C_2\) are constants, \(T_0\) is the reference temperature (usually \(T_g\)) and \(T\) is the current test temperature.
Instantaneous strain vs. temperature curves were fitted using the sigmoidal Gompertz function, given in Eq. 2. Briefly, it describes growth as slowest, at the start and end of a given period. For particulate composites, a generalized logistic function is used, where the right-hand value function asymptote is approached much more gradually, by the curve than the left-hand. It contrast to the simple logistic function, in which both asymptotes are approached by the curve symmetrically (Marrucci 2003).

\[ f(t) = a e^{-e^{bct}} \]  

where \(a\) is an asymptote, \(b\) sets the displacement along the x-axis, \(c\) is the growth rate and \(e\) is the Euler’s number.

**Results And Discussion**

**Dynamic mechanical behavior**

The dynamic mechanical behavior of the epoxy resin and the nanocomposites are presented in Fig. 1a-b. Figure 1a represents the storage modulus (\(E'\)) of the epoxy and the reinforced materials. It is evidenced that the incorporation of MCC shift to higher temperatures the load-bearing capacity, of the composites. This improvement was \(\approx 60^\circ\text{C}\) for both MCC and MCC-Si composites, compared to neat cured resin. This is because the rigid particles restrict the molecular motion of the amorphous chain segments, requiring more energy (higher temperature) to decrease the composite's load-bearing capability.

MCC also improves the structural integrity, when incorporated into an epoxy matrix, independently of surface chemical modification. Hence, the initial plateau decreasing (glassy region) is related to the beginning of the glass transition temperature, where a considerable improvement of free volume is achieved and a loss of structural integrity is obtained.

\(E'\) values at both glassy and rubbery regions (below \(T_g\)) were not altered for both composites, stating that the particle reinforcement enhances the local stiffness and increases the free volume. Then, the surface modification does not affect the dynamical mechanical behavior, contrasting previous literature (Lavoratti et al. 2018; Kerche et al. 2021b).

After \(T_g\), the storage modulus decreases to the elastomeric region, for both samples. However, an abruptly drop for epoxy, compared to MCC composites, is reported, which represents that the reinforcement effect (the same that extends the glassy plateau) is also observed, in the elastomeric region. An increase in the free volume allows the molecules to obtain different spatial conformations, leading to a considerable decrease in the capacity to store the received energy.

Without restriction, imposed by particles, polymer segments can move freely, due to the cooperatively action of all neighboring chains, for the same energy state. In this sense, MCC acts as a particle, situated
among the polymeric chains, that imposes an additional restriction, avoiding further molecular motion and maintains the modulus – as in the case of crystallites for semicrystalline polymers. On the other hand, differently from semicrystalline polymers, it can be said that the particles act as “non-thermally labile crystallites”.

MCC chemical modification does not significantly alter the storage modulus by seeming to “homogenize” the dissipation of energy in the glass transition region, as observed in the loss modulus peak (E”, Fig. 1a). In other words, the maximum energy dissipation occurs at higher temperatures, where the polymer matrix has low restriction in molecular motion, then, glass region is extended at higher temperatures and the molecular restriction is more evidenced. Furthermore, usually, the shoulder represents an additional relaxation event related to the material (John D. Ferry 1980; Kerche et al. 2021b). In this sense, relaxation process does not seem to be altered by the MCC incorporation, because the main peak and a shoulder can be observed with distinct magnitudes. Chemical modification does not alter, significantly, load-bearing capability to change the energy dissipation.

When loss modulus is divided by storage modulus, tan \( \delta \) (Fig. 1b) represents the viscoelastic behavior, considering the elastic and viscous components. In the glass transition, higher dissipation of energy is obtained for MCC-Si composites, which is an indicative of a poorer interface, if compared to pristine MCC composite. Since the energy is transmitted to the particles by the interface, and as the low the tan delta values as strong the interface, lower energy is dissipated as heat in this transition.

Differently of fiber reinforced polymers, the interface, for particulate composites, is local, and the amorphous chains’ molecular restriction is most dependent on the particle characteristic than the interface. Figure 2 schematically represents the molecular polymer restriction, caused by MCC using, in function of temperature, for epoxy and its composites. Epoxy chain segments’ molecular motion is restricted by MCC particles, which extends the load-bearing capability to higher temperatures. Moreover, due to the lower deformation, imposed into the polymeric chains, by MCC, with temperature increasing, the particle percolation network promotes the deformation of amorphous chain.

**Creep behavior**

The creep behavior of epoxy and its composites, in different MCC concentrations, is presented in Fig. 3a-c). The following trend is noted among all curves: (i) after the initial instantaneous elastic deformation (\( \varepsilon_0 \)), the curvature, corresponding to the viscoelastic behavior, is more pronounced at the glass transition temperature and follows a steady deformation (after curvature). (ii) the temperature increases the initial deformation (increasing \( \varepsilon_i \)) for all samples, in different magnitudes. For instance, MCC 5%-Si, presented \( \varepsilon_i \) lower than epoxy and MCC 5%. The same behavior was observed by increasing the reinforcement content.

Relaxation of amorphous chain segments is more challenging to be achieved, if the particle imposes any restraints. Hence, by increasing the number of particles, more restraining is imposed and more energy is
required to achieve the deformation. Considering the particle/matrix interphase improvement, the energy required to deform the amorphous chain would increase, as for silanized samples.

The effect of the MCC and silanization can be better visualized if the curve of instantaneous creep strain vs. temperature is plotted (Fig. 4a). Linearity of the strain can be noted in the glassy and elastomeric regions. Higher $\varepsilon_i$ is observed at $T_g$ for all samples, but in lower magnitude for reinforced samples. A higher difference in the values in the elastomeric region is observed, compared to the glassy region. Besides, a less abrupt increase, showing that the particle mainly reinforces the matrix at higher temperatures.

Mechanical response is very similar for both composites and neat epoxy. Hence, tensile or flexural tests tend to give similar values, when tested in the glassy region, when MCC is used as particle. Moreover, the magnitude of deformation is too similar, to the dynamic mechanical runs. For instance, those neat epoxy presented an increase in deformation four times, comparing the values in 20°C to those in 170°C. The, since our interest is the initial plateau and not the values, Gompertz function seems to be adequate for this system, since it was considered that the deformation converges to zero, as proposed by the Gompertz function (see Eq. 2).

From Gompertz function “a”, “b” and “c” parameters are taken and they are presented at Table 1. For polymers, these parameters can be associated with some physical features: i) “b” (i.e., the displacement along the x-axis extension) can be associated with the polymer ability to maintain the dimensional stability (maintaining the load-bearing capacity) in the glassy region. The higher the value, the higher the times that the polymer maintains the structural integrity, without significant losses in the creep test.

According to Table 1, higher values are obtained for silanized samples, indicating that the chemical modification, at the MCC surface, gives an increment in the glassy plateau. It is important to remember that the reinforcement effect depends of many factors and it can be visualized in different viscoelastic regions, depending on the composite system (Ormaghi et al. 2020a, b). Phenomenologically, higher values mean that higher thermal energy is necessary to the system, before the amorphous polymeric chains increase the free volume, in a significant way. Then, there is an abrupt decrease of the load-bearing capability, i.e., beginning of the glass transition region.

<table>
<thead>
<tr>
<th>Sample</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>$r^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy</td>
<td>4.05</td>
<td>0.008</td>
<td>117.68</td>
<td>0.934</td>
</tr>
<tr>
<td>MCC 5%</td>
<td>3.09</td>
<td>0.0057</td>
<td>124.03</td>
<td>0.954</td>
</tr>
<tr>
<td>MCC 5%-Si</td>
<td>1.69</td>
<td>0.08</td>
<td>120.07</td>
<td>0.967</td>
</tr>
</tbody>
</table>
On one hand, “a” parameter is the amplitude, i.e., the difference among the initial and final plateaus (see Fig. 4). The lower “a” value was obtained for MCC 5%-Si, compared to both epoxy and MCC 5%. It means that the reinforcement effect restricts the molecular motion of the polymeric epoxy chain, from \( T_g \). A more abrupt increase, in the free volume at \( T_g \), means that the polymeric chains are far, apart from each other, and more availability in occupying different spaces is possible, increasing the viscous component and the dissipation of energy, as heat.

MCC composites also play an important role in this stage, since they allowed lower differences between two plateaus, which means that higher energy is maintained at the interface of the particles and lower energy is dissipated as heat. Finally, the growth rate (“c” parameter) is higher for those MCC composites than neat epoxy. The growth rate is the curvature between two plateaus, and the higher the values, obtained for the composites, mean that the major portions of the polymeric chains, that deform between the glassy and elastomeric states, deform faster, due to the higher thermal energy, accumulated at the glassy region.

In brief, if higher energy is required to deform the polymer amorphous chain segments, prior to \( T_g \), in the glassy region, higher energy is accumulated so far, leading to higher “b” values. If the interface promotes an additional restriction, at the polymeric chains’ molecular motion, lower energy is dissipated between two plateaus, leading to lower “a” value. The rate that this dissipation occurs (“c” parameter) is directly related to the energy storage, at the glassy rate, and how this energy is dissipated from \( T_g \). If more chains segments act cooperatively to maintain the structural integrity and this energy is released at once, the higher the growth rate.

TTS curves for the epoxy resin and its MCC 5%-Si composite are presented in Fig. 4, following the WLF model, presented in Eq. 1. Only both curves are presented (TTS for MCC 5% was not done), aiming to compare the results with higher and lower creep resistance over time. It is plausible to assume that those MCC 5% behavior is intermediate related to both, then it was not plotted.

The deformation with time, for the reinforced composites, is lower and reached a maximum at the \( T_g \) (\( \sim 10^1 \) s), in which the values are similar, when compared to the epoxy resin (\( \sim 10^2 \) s). This behavior is expected, due to the aforementioned effects of increasing in void content with the increase in deformation, for the particulate reinforced composites (see Fig. 2). Nonetheless, the curve slope seems close for both samples, at \( T_g \), which is related to close values for the deformation magnitude, a behavior also reported on the dynamic mechanical runs (see Fig. 1 and the discussion of Fig. 4)

**Conclusions**

In this study, the importance of micro-crystalline cellulose reinforcement and the effect of silanization, applied in polymer composite is demonstrated, in which a complete study of creep behavior was carried out, involving all viscoelastic regions. Rigid particles restrict the amorphous chain segments’ molecular motion. Then, more energy, to conduct creep deformation was required. On the other hand, MCC improves
the structural integrity, when incorporated into an epoxy matrix, regardless the surface modification with silane.

The curves were fitted using the sigmoidal Gompertz function, which describes growth as slowest, at the start and end of a given period, with high reliability ($r^2 > 0.93$). In addition, the proposed model based on a generalized logistic function presented a linear correlation to the instantaneous elastic deformation, as a function of temperature, with creep response.

The Gompertz function's parameters, obtained for silanized specimens, indicate that the chemical modification, at the surface of MCC, gives an increment in the glassy plateau. Thus, higher values are associated with higher thermal energy, required by the system, before the amorphous polymeric chains increase the free volume significantly. Then, these results are related to the abrupt decrease of the load-bearing capability, i.e., the beginning of the glass transition region. Concluding, the addition of MCC-Si can increase the mechanical behavior of the composite, as a result of a stiffer structure.

**Declarations**

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**Conflicts of interest/Competing interests**

The authors declare that there is no conflict or competing of interest.

**Availability of data and material**

The authors declare that all data used are transparent and available.

**Code availability**

The authors declare that all code or software used are available.

**Authors’ contributions**

Heitor Luiz Ornaghi Jr: conceptualization, methodology, samples’ characterization, results analysis, writing-original draft. Roberta Motta Neves: samples’ manufacturing, preparation and testing, results discussion. Eduardo F. Kerche: conceptualization, methodology, review and editing. Francisco Maciel Monticeli: results analysis and discussion, data treatment, review and editing. Ademir José Zattera: review, editing, supervision, funding.

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References


**Figures**

**Figure 1**

Dynamic mechanical curves for the samples studied. A) storage modulus and loss moduli, and b) tan delta.
Figure 2

Schematic representation of the molecular restriction, imposed by MCC particles: a) and b) represents the epoxy resin in the glassy and glass transition/elastomeric regions, while c) and d) represent the same regions with the influence of MCC particles.
Figure 3

Experimental creep curves for: a) Epoxy, b) MCC 5% and c) MCC-Si 5%. Different scales were used, aiming to visualize the curves better.
Figure 4

Dependency of the instantaneous creep strain vs. temperature, for epoxy and its composites, studied using Gompertz function (a) and detailed parameters (b).
Figure 5

Time-temperature superposition curves, for epoxy and MCC 5%-Si composites.

Supplementary Files

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