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Long-term performance and durability of polycarbonate/carbon nanotube nanocomposites

Leonid V. Pastukhova, Frans P. M. Merckx, Ton Peijs and Leon E. Govaert

1. Introduction

Polymer-based materials are being used in a variety of load bearing applications where structural integrity and long-term durability is of great importance. Examples of such systems can be found in a wide range of industrial applications in the transport, electrical, leisure, and medical industry. In many applications, severe loading conditions (e.g. creep and fatigue) and environmental conditions (e.g. temperature and humidity) have put an increased demand on material performance [1]. In all of these areas, endeavours to achieve performance increases together with weight reductions has intensified attempts to improve physical properties of polymeric systems, which among others have led to the usage of nanoreinforcements. In this context, the addition of nanoreinforcements is of particular interest as it can have a significant effect on both short-term mechanical performance and long-term properties such as the resistance to static (creep) and cyclic (fatigue) loadings.

Due to their good mechanical properties, low density, and ease of processing polymer nanocomposites are of interest for a multitude of applications in the automotive, electronics, and leisure industry. Besides having an impact on short-term mechanical performance of polymers, the addition of nanoreinforcements can have also a significant effect on long-term properties such as the resistance to static (creep) and cyclic (fatigue) loadings. However, despite its significance there is a shortage of long-term mechanical performance data for thermoplastic-based polymer nanocomposites. Reason being that existing characterization methods for long-term performance and durability are time consuming and limited in their applicability. Here, an engineering approach to predict long-term time-to-failure of polycarbonate/carbon nanotube (PC/CNT) nanocomposites is presented based on short-term experimentation with an application to both creep and fatigue. Results showed that the addition of CNTs had an opposite effect on two important long-term failure mechanisms. Addition of CNTs lead to improvements in durability in the plasticity-controlled failure regime, whereas it had an adverse effect in the slow crack growth-controlled regime, meaning that in the latter regime nanocomposite performance was significantly less than that of the neat polymer matrix.
development of engineering composites. Traditional polymer composites are multiphase materials made by combining polymer matrices with various reinforcements. Aim of the reinforcement is to improve mechanical properties of the polymer matrix by utilising key properties of the filler such as high stiffness and high strength. Traditional reinforcements have dimensions at the micron scale ($10^{-6}$ m). Examples of such fillers are glass, carbon, and aramid fibres [2]. Typically, a large amount of fibers is needed to substantially improve the overall properties of a composite material (tens of weight percent) often leading to loss of processability [3].

In recent years, advances in nanotechnology have promoted the development of reinforcements with dimensions at the nano-scale ($10^{-9}$ m). This dimensional shift has opened new possibilities for altering physical properties of polymer matrices (mechanical, electrical, thermal, etc.) by incorporating relatively small amounts of nanofillers (several weight percent or less) [3, 4]. Nanocomposites are being considered as a potential replacement of traditional composites or when combined with traditional reinforcements as a means to add other functionalities (electrical, thermal, sensing, etc.) or further improve the mechanical performance of traditional composites by creating hybrid or hierarchical composites [5–10]. Among potential materials that can be used as a matrix for composite materials, thermoplastic polymers offer advantages such as low density, high specific strength and toughness, together with ease of processing. In order to achieve good dispersion of nanofillers in the thermoplastic matrix, several methods are reported in literature including solution mixing, melt blending, and in-situ polymerization [3, 11]. Some of the most common thermoplastic materials used are acrylonitrile butadiene styrene (ABS), polyethylene (PE), polypropylene (PP), polyamides (PA), polystyrene (PS), poly(methyl methacrylate) (PMMA), polycarbonate (PC), etc. The most common nanofillers are carbon nanotubes (CNTs), nanoclays, and graphene based nanoplatelets (GNPs). CNTs can be considered as one atom thick carbon layers rolled in small cylinders. Most common types of CNT are: (i) single wall carbon nanotubes (SWCNT) and (ii) multi-wall carbon nanotubes (MWCNT). CNTs have often been used to improve the stiffness of polymer matrices. The Young’s modulus of a thermoplastic matrix varies from 2000 MPa to 4000 MPa for amorphous polymers and from 300 to 6000 MPa for semi-crystalline polymers. Addition of CNTs which have superior mechanical properties (Young’s moduli up to 1 TPa and tensile strengths up to 100 GPa [12]) can not only greatly improve the mechanical properties of polymer matrices but will also affect other physical properties (electrical conductivity, thermal conductivity, fire retardancy, air and liquid permeability, fatigue resistance etc.). These multi-functionalities have opened new possibilities for potential industrial applications of polymer nanocomposites. It has been well-documented that the addition of CNTs significantly affects short-term properties of thermoplastic polymers and an increase in elastic modulus and yield stress has been reported for a wide range of thermoplastic matrices including PE [13–17], PS [18–20], PMMA [21–24], PP [25–28], PA [29–31], PC [32–35], and many more.

Being a relatively novel material, polymer nanocomposites have attracted a lot of attention; however, due to the lack of long-term mechanical performance data for polymer nanocomposites, the use of these materials in industrial applications has been limited. Therefore, development of material characterisation methods and reliable long-term performance estimation tools is of utmost importance for this class of materials. Since the long-term mechanical performance of polymer composites reinforced with nanofillers is matrix dominated [36], it is very likely that, similar to unfilled polymer systems, under some applied stress different failure mechanisms can be encountered. On this account, it seems reasonable to investigate the time- and stress-dependence of polymer matrices and the influence of nanoreinforcements on time-dependent failure of such polymer matrices.

There are well-established methodologies for the characterisation of time-dependent failure of various polymer systems. These methods are often based on characterising creep rupture (plasticity-controlled failure) [37, 38] and fatigue rupture (slow crack growth-controlled failure) [39–41]. From these approaches for a large selection of polymers (unfilled and with traditional reinforcements), it has been shown [42] that there is a clear distinction in response under static (creep) and cyclic (fatigue) loading for the same maximum applied stress as shown in Figure 1. At higher applied stresses and shorter times, the dominant failure mechanism is plasticity-controlled failure. Here, the applied stress leads to plastic flow within the material and these plastic deformations accumulate over time until they reach a critical deformation level, leading to material failure. At lower applied stresses (and longer times) another process is active: slow crack growth. Imperfections within a polymeric material act as precursors for cracks and under an applied load these cracks will grow until they reach a critical size resulting in failure [43–46]. By plotting in a double logarithmic graph, the maximum applied stress versus time-to-failure for both static and cyclic loadings (Figure 1b), an important observation can be made: cyclic loading leads to an increase in resistance to
plastically-controlled failure but a decrease in resistance to crack growth. Hence, cyclic loading has an opposite effect on both failure mechanism [42]; therefore, providing a powerful characterisation tool for failure mechanism identification.

In this study, we will investigate how the addition of CNTs affects plasticity-controlled failure and slow crack growth-controlled failure of a polycarbonate (PC) matrix under both static and cyclic loadings along with the basic principles of phenomenological models that can be used to estimate the lifetime of polymer nanocomposites.

2. Background

2.1. Plasticity-controlled failure

Under an applied load, a polymer flows due to increased polymer chain mobility [47]. During constant strain rate experiments (tensile tests) plastic flow is increasing with time until at some point (the yield point) plastic flow within the material exactly matches the experimentally applied strain rate (condition of steady state plastic flow). As has been demonstrated by Bauwens-Crowet et al. [48], steady state plastic flow at the yield point in a constant strain rate tensile test is identical to steady state flow during secondary creep when a polymer is subjected to a constant load. Therefore, stress and temperature dependence of plastic flow under creep loading can be measured by means of tensile tests at different applied strain rates. This dependence can be described using Eyring’s activated flow theory [49]. For instance, in a simple case where a single process governs the deformation (as is the case for PC at room temperature and above), the magnitude of plastic flow is defined by:

\[
\dot{e}_{pl}(\sigma, T) = \dot{e}_0 \cdot \exp\left(\frac{\Delta U}{RT}\right) \cdot \sinh\left(\frac{\sigma V^*}{kT}\right) \tag{1}
\]

where part I, \(\dot{e}_0\) is a rate factor, which is a parameter that depends on the thermodynamic state of the material (age of the amorphous phase). In part II of the equation, the Arrhenius type exponent, \(\Delta U\) is the activation energy, \(R\) is the universal gas constant, and \(T\) is the absolute temperature. These factors cover the temperature dependency of the plastic flow rate. In part III, the hyperbolic sine, \(\sigma\) is the applied stress, \(V^*\) is the activation volume, and \(k\) is the Boltzmann’s constant. This part captures the stress dependency of the flow rate. However, polymers cannot flow indefinitely, and eventually plastic deformations will localise and failure will occur. Therefore, time-to-failure in the plasticity-controlled region can be estimated by calculating the total accumulated strain. Once this reaches its critical value \(e_{cr}\), failure will occur:

\[
e_{pl}(t) = \int_0^t \dot{e}_{pl}(\sigma, T, t') \, dt \text{ with failure if } \dot{e}_{pl} = \dot{e}_{cr} \tag{2}
\]

where \(e_{pl}\) is the plastic strain at a certain time, \(\dot{e}_{pl}\) is the plastic flow rate according to Equation 1, and \(\dot{e}_{cr}\) is the plastic strain at failure. Note, that although \(e_{cr}\) is usually smaller than the actual strain-at-break, this phenomenological measure has been shown to be a reliable measure for predicting time-to-failure of polymers [42, 48, 50]. Under a constant load assuming constant plastic flow rate during a creep test, Equation 2 can be simplified to:

\[
t_f = \frac{e_{cr}}{\dot{e}_{pl}} \tag{3}
\]

Thus, knowing the deformation kinetics which can be determined by performing tensile tests at different strain rates, consequent time-to-failure predictions can be made using the critical strain concept based on Equation 3.

2.2. Crack growth-controlled failure

Crack growth-controlled failure manifests itself as a propagation and growth of cracks under an applied stress inside the material. Cracks are initiated within

![Figure 1. (a) Static vs cyclic loading. (b) Schematic illustration of the effects of cyclic loading on plasticity-controlled and crack growth-controlled failure mechanisms in a thermoplastic polymer matrix.](image-url)
the material due to the presence of flaws and imperfections that result in local stress concentrations. The stress state around a crack tip can be described using linear elastic fracture mechanics (LEFM) [51]. Considering Mode I loading (crack opening), the stress state at the crack tip is defined by a stress intensity factor as $K_I$:

$$K_I = Y \sigma \sqrt{\pi a}$$  \hspace{1cm} (4)

where $\sigma$ is the applied remote stress, $a$ is the crack length, and $Y$ is a geometry factor. The evolution of crack length with time or, in other words, crack propagation rate, $\dot{a}$ is related to the stress intensity factor by a power law; this relation is known as the Paris’ law [52]:

$$\dot{a} = AK_{I}^{m}$$  \hspace{1cm} (5)

It has been shown by Gray et al. [53], that, by knowing the crack propagation kinetics (parameters $A$ and $m$ in the Paris’ law), time-to-failure can be predicted, assuming some initial crack length and neglecting the time of crack initiation by means of the following equation:

$$t_f = \left( \frac{\sigma}{\sigma_f} \right)^{-m}$$  \hspace{1cm} (6)

where $\sigma_f$ is a scaling factor, which can be understood as the level of stress leading to a failure time of 1 s. Therefore, according to Equation 5, a log-log plot of time-to-failure versus applied stress results in a straight line. Dependence of the time-to-failure versus applied stress is also a straight line in a double logarithmic plot with a slope $-1/m$ according to Equation 6.

3. Experimental

3.1. Materials

The following materials were selected for this study: polycarbonate (PC) and polycarbonate reinforced with carbon nanotubes (PC + CNT). The grade of polycarbonate for both unfilled and nanocomposite samples was - LEXAN™ resin 141 R, a bisphenol-A based thermoplastic from SABIC (Bergen op Zoom, Netherlands), while multiwalled carbon nanotubes (MWCNT) were obtained from Hyperion. The PC/CNT nanocomposites were in-house compounded at SABIC by diluting a 10 wt.% PC/CNT masterbatch using twin-screw extrusion (Coperion ZSK25, L/D = 32, 300 rpm, 20 kg/hr throughput, melt temperature 300°C) to compounds with 1 wt.% and 3 wt.% CNT loading. Subsequently these nanocomposites were injection molded (Engel 45, melt temperature 300°C, mold temperature 80°C) into tensile bars with a geometry according to ISO 527 Type 1A. In order to avoid effects of moisture, samples were stored in a sealed bag with silicone gel moisture absorbent.

3.2. Heat treatment

Annealing was performed in an air circulated oven at a temperature of 120°C (i.e. below the glass transition temperature, $T_g$). Initial equilibration of the sample temperature was measured to take approximately 10 min. After a predefined ageing time, the samples were removed from the oven and allowed to cool to room temperature in air before being tested.

3.3. Mechanical testing

All uniaxial tensile and creep measurements at room temperature were carried out using an Instron 5566 universal tensile machine equipped with a 10 kN load cell. The temperature in the lab was held constant at 24°C throughout all tensile and creep experiments. Engineering stresses were calculated using the average of the cross-sectional surface area as measured at three locations in the gauge section. Tensile experiments were carried out at a constant crosshead speed, resulting in constant engineering strain rates ranging from $10^{-5}$ s$^{-1}$ to 0.05 s$^{-1}$. Creep tests were performed at constant load and, therefore, constant engineering stress. To avoid overshoot effects, the load was slowly applied within 10 s. Clamps were carefully aligned to ensure that torsional stresses did not affect the results. The creep rupture tests were performed in uniaxial extension over a wide range of stresses. These ranges were carefully chosen for each material and temperature in order to obtain failure within a time-scale ranging from $10^2$ s to $10^3$ s (longest experimental time-scale is approximately 2 days). Time-to-failure was determined by the time of fracture. For unfilled PC and PC + 3 wt.% CNT two sets of experiments were carried out at different temperatures (40°C and 60°C). These tests were performed on an Instron 8801 universal tensile machine equipped with an environmental chamber. The samples were placed in the chamber and once the temperature had reached a set value, the tests were started after 10 min (once the temperature inside the chamber equilibrated). Cyclic tests were carried out on an Instron 8872 servohydraulic fatigue testing system. For each set of samples, the stiffness was determined first in order to ensure the correct tuning of the measured signal. Load ratio and frequencies were changed according to the test requirements. For all tests, a sinusoidal cyclic load was applied, while for each test the load amplitude, maximum load, and frequency were kept constant. Temperature in the lab was at a constant 20°C throughout all cyclic fatigue experiments.
3.4 Scanning electron microscopy

Dispersion of CNTs in the PC matrix was evaluated using a FEI Inspect F scanning electron microscope (SEM). For this, injection molded tensile bars (untested) were cold fractured in liquid nitrogen. Samples were coated with a thin layer of gold before imaging.

3.5 Dynamic mechanical thermal analysis

Dynamic mechanical analysis (DMTA) was performed on a TA Instruments Q800. Rectangular samples of PC and PC + CNT nanocomposites were prepared with dimensions of $1 \times 4.5 \times 30$ mm$^3$. A frequency of 1 Hz was used in a strain-controlled experiment. The storage and loss modulus were measured in a temperature window ranging from $-80^\circ C$ to $200^\circ C$.

4. Results and discussion

4.1 Plasticity-controlled failure

4.1.1 Unfilled PC

Applied stress leads to increased polymer mobility and stimulates molecular rearrangements [54], resulting in a constant rate of plastic flow [49]. The magnitude of this plastic flow rate depends on strain rate (time) and temperature. Consequently, if the applied strain rate and temperature changes, the yield stress of the polymeric material will change accordingly in order to find an equilibrium between applied strain rate and intrinsic plastic flow rate. The accumulated critical strain [50], connecting deformational kinetics of plastic flow rate to time-to-failure predictions, can be used to make life-time predictions based on constant strain-rate test data. Figure 2 shows results of this type of modelling for unfilled PC at different temperatures, proving that accurate predictions for different temperatures can be made using the concept of critical strain. Corresponding Eyring parameters for the stress and temperature dependency for unfilled PC are listed in Table 1.

![Figure 2](image)

Figure 2. (a) Strain rate dependence of the yield stress of PC at various temperatures. The solid lines represent the best-fit using Equation 1. (b) Stress dependence of the time-to-failure of PC in uniaxial loading. The solid lines represent predictions using Equation 3.

<table>
<thead>
<tr>
<th>Material</th>
<th>V$^*$ [nm$^3$]</th>
<th>$\Delta U$ [kJ/mol]</th>
<th>$\dot{\varepsilon}_0$ [s$^{-1}$]</th>
<th>$\varepsilon_c$ [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unfilled PC (as-moulded)</td>
<td>3.4</td>
<td>315</td>
<td>$1.53 \times 10^{21}$</td>
<td>0.014</td>
</tr>
<tr>
<td>Unfilled PC (annealed)</td>
<td>3.4</td>
<td>315</td>
<td>$1.09 \times 10^{28}$</td>
<td>0.014</td>
</tr>
</tbody>
</table>

4.1.2 PC/CNT nanocomposites

In order to understand the effect of CNTs on short- and long-term performance of the PC matrix, first tensile tests at a constant strain rate of $10^{-3}$ s$^{-1}$ and creep tests at different levels of applied stress at room temperature have been performed. Results of these initial tensile tests are shown in Figure 4a and reveal that the addition of nanotubes leads to an increase in yield stress ($\sim$10% at 3 wt.% CNT) and Young’s modulus ($\sim$40% at 3 wt.% CNT) compared to unfilled PC.
The evolution of plastic strain rate during creep experiments can be visualized in a so-called Sherby-Dorn plot [57] (Figure 4b). A Sherby-Dorn plot for PC + 3 wt.% CNT at four different creep stresses shows that three distinct regions of creep can be recognized: (i) a region of decreasing strain rate (primary creep), (ii) a region where plastic flow rate remains approximately constant (secondary creep), followed by (iii) a region with increasing strain rate (tertiary creep) accompanied by strain localization in the form of necking. These observations indicate that the influence of the addition of CNTs in the polymer matrix can be captured using the same concept as used for describing deformation kinetics and time-to-failure prediction of unfilled PC.

Strain rate dependence of the yield stress and time-to-failure dependence of PC/CNT nanocomposites has been compared with results of unfilled PC. This comparison is shown in Figure 5. A notable observation from this comparison is that the addition of CNTs does not affect the activation volume \( V^* \), i.e. the slopes of the lines remain the same with only a parallel shift. To further elaborate on this idea PC/CNT nanocomposites were tested at different temperatures. By performing tests at different temperatures similar to the tests on unfilled polycarbonate and subsequently using Eyring modeling, deformation kinetics of PC/CNT nanocomposites can be accurately described as can be seen in Figure 6a and c for PC + 1 wt.% CNT and PC + 3 wt.% CNT, respectively. Eyring parameters for PC/CNT nanocomposite materials are presented in Table 2.

Time-to-failure predictions using the critical strain concept are shown in Figure 6b and d for PC + 1 wt.% CNT and PC + 3 wt.% CNT, respectively. In creep predictions for nanocomposites, values of the critical strain were found to be slightly less than those for unfilled PC as shown in Figure 7. At the same time, it was observed that the strain-at-break in tensile tests was lower for the nanocomposite samples. Neat PC matrix typically has an elongation at break of around 100%, while PC + 3 wt.% CNT showed a significantly reduced elongation at break of approximately 15% as a result of an embrittlement effect by the nanofiller. Some deviation of experimental data from predictions at higher temperatures and longer times can be explained by stress and temperature induced physical ageing during the long-term creep measurements (for instance as in the case of the longest measurement at 60 °C.

![Figure 3](image-url)  
**Figure 3.** (a) Strain rate dependence of the yield stress of PC for as-moulded and annealed samples. The solid lines represent a best-fit using Equation 1. (b) Stress dependence of the time-to-failure of PC in uniaxial loading. The solid lines represent predictions using Equation 3.

![Figure 4](image-url)  
**Figure 4.** (a) Stress versus strain for unfilled PC and PC/CNT nanocomposite with 1 wt.% and 3 wt.% CNT. Markers indicate the yield stress. (b) Sherby-Dorn plot for several applied stresses.
in Figure 6b). Interestingly, the values of activation volume and activation energy are similar for both unfilled PC and PC/CNT nanocomposites. The only parameter that has to be changed to capture the deformation kinetics of the nanocomposites is the preexponential factor $\alpha_0$. This is similar to the case of annealed PC and therefore, interestingly, the addition of CNTs has the same effect on yield stress and deformation kinetics as changing the thermodynamic state of the unfilled matrix. To further elaborate on this observation, two sets of unfilled PCs were annealed at 120 °C for two different periods of time (20 min and 2 hrs, respectively). A temperature of 120 °C was chosen in order to observe effects of annealing at shorter times based on the time-temperature superposition principle (annealing at higher temperature allows one to achieve the same increase in yield stress at a shorter time). Annealing times were chosen in such a way that the resulting yield stresses were close to those of the nanocomposite materials. Ageing kinetics of PC at different temperatures was extensively studied by Klompen et al. and

Figure 5. (a) Strain rate dependence of the yield stress of unfilled PC and PC/CNT nanocomposites with 1 wt.% and 3 wt.% CNT. The solid lines are guides to the eye. (b) Stress dependence of the time-to-failure of unfilled PC and PC/CNT nanocomposites in uniaxial loading. The solid lines are guides to the eye.

Figure 6. Strain rate dependence of the yield stress of PC + 1 wt.% CNT (a) and (c) PC + 3 wt.% CNT. The solid lines represent the best-fit using Equation 1. Stress dependence of the time-to-failure of PC + 1 wt.% CNT (b) and PC + 3 wt.% CNT (d) in uniaxial loading. The solid lines represent predictions using Equation 3.
Engels et al. [58–60], providing all the necessary information regarding the time required to obtain a certain level of yield stress at different temperatures. Having annealed unfilled PC samples for a pre-defined time, yield stresses were measured at different strain rates and results are presented in Figure 8 for both 1 wt.% and 3 wt.% nanocomposites.

Experimental observations in plasticity-controlled failure have shown that the addition of CNTs in the PC matrix leads to an increase of the yield stress by ~10%, which results in a 100-fold lifetime improvement compared to unfilled PC. Clearly, in the plasticity-controlled failure regime the addition of CNTs is highly beneficial with respect to long-term mechanical behaviour. Moreover, the deformation kinetics of the PC/CNT nanocomposite systems can be described by the same set of values of activation volume and activation energy in the Eyring equation, with the only parameter that changes being the value of $e_0$, similarly to that of aged (annealed) samples. Therefore, the increase in yield stress and elastic modulus and subsequent improvement in lifetime for PC/CNT nanocomposites under a constant load are similar to those of annealed unfilled PC samples. An increased yield stress (either due to annealing or the addition of nanofiller) results in an increased resistance to plastic deformations. Consequently, at the same applied stress it will take longer time to reach the critical amount of plastic strain, thus leading to a marked increase in creep lifetime at the same applied stress.

### 4.2. Crack growth-controlled failure

In order to fully characterise the long-term performance of polymer systems, one needs to be aware that there are two stress dependent failure mechanisms. As previously discussed, there is plasticity-controlled failure, which is typically observed during basic mechanical characterisation or tensile testing. To observe crack growth-controlled failure under a static load, long-term measurements are required with the more durable materials requiring longer times to observe and identify slow crack growth-controlled failure. One of the ways to accelerate crack propagation, and consequently, reduce the experimental time-scale required to observe crack growth, is to apply a high amplitude tension-tension cyclic (fatigue) load thus increasing the crack propagation rate [61]. In unreinforced polymers, typically the change in failure kinetics can be observed macroscopically by looking at the way the material has failed: in case of plasticity-controlled failure clear strain localisation (necking) is visible, whereas in crack growth-controlled failure, failure occurs in a brittle manner with some cracks being visible (as in a transparent material such as PC) [42].

In the current study, first a cyclic load with two different $R$-values ($R = \frac{r_{	ext{min}}}{r_{	ext{max}}}$) of 0.1 and 0.25 was applied to unfilled PC to demonstrate the effect of cyclic load on both plasticity-controlled and crack growth-controlled failure. Results are shown in Figure 9a. Under high amplitude cyclic loading both failure mechanisms can be identified with distinct differences in macroscopic failure as shown in Figure 9b. Plasticity-controlled failure was accompanied with large plastic deformations and strain localisation (necking), whereas under lower applied stress less plastic deformation has been accumulated, and clear brittle fracture can be observed. Moreover, a clear transition from one mechanism to the other is visible when plotting the data in a log-log plot.

Similar to unfilled PC, static and cyclic tests were performed for PC/CNT nanocomposite systems. Results are shown in Figure 10 for both PC + 1 wt.% CNT and PC + 3 wt.% CNT (Figure 10a and b, respectively). In Figure 11, nanocomposite

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### Table 2. Eyring parameters and the average critical strain for PC/CNT nanocomposites.

<table>
<thead>
<tr>
<th>Material</th>
<th>$V^*$ [nm$^3$]</th>
<th>$\Delta U$ [kJ/mol]</th>
<th>$\dot{e}_0$ [s$^{-1}$]</th>
<th>$e_{cr}$ [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC + 1 wt.% CNT</td>
<td>3.4</td>
<td>315</td>
<td>$1.5 \times 10^{10}$</td>
<td>0.012</td>
</tr>
<tr>
<td>PC + 3 wt.% CNT</td>
<td>3.4</td>
<td>315</td>
<td>$9.25 \times 10^{10}$</td>
<td>0.07</td>
</tr>
</tbody>
</table>

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**Figure 7.** (a) Plastic flow rate during secondary creep versus time-to-failure for unfilled PC, PC + 1 wt.% CNT, and PC + 3 wt.% CNT. (b) Critical strain dependence on CNT loading. Dotted line is a guide for the eye.
samples after failure are illustrated having similar macroscopic failure features as unfilled PC. With regards to plasticity-controlled failure, as expected, nanocomposite samples show superior behaviour compared to unfilled PC (for PC + 3 wt.% CNT improvements in time-to-failure are in the order of two decades). However, a very noteworthy observation is that in the crack growth-controlled failure region the addition of CNTs has reduced the lifetime under cyclic loading (for PC + 3 wt.% CNT the shift in time-to-failure is in the order of one decade). Having seen that in the plasticity-controlled failure region behaviour of annealed unfilled PC and PC nanocomposites were similar, the same two sets of annealed unfilled PC samples have been prepared and were subsequently tested under a cyclic load at R = 0.1.

Remarkably, the nanocomposite samples did not only show similar behaviour in the plasticity-controlled failure region but showed similar behaviour in the crack growth region as well. Results of such comparison are shown in Figure 12 for both PC + 1 wt.% CNT and PC + 3 wt.% CNT (Figure 12a and b, respectively).

The reason for these similarities might be due to the fact that the incorporation of CNTs in a polymer matrix can lead to the local reduction of mobility of polymer chains due to a decrease in free volume, which in turn can explain the apparent increase in yield stress and elastic modulus. As can be seen from the SEM images in Figure 13, the CNTs are well and homogeneously dispersed in the PC matrix. Many nanotubes are visible owing to the high contrast between them and the polymer matrix, with the PC/CNT nanocomposites demonstrating a relatively uniform filler distribution across the cold fractured surface. Immobilization of polymer chains near the CNT surface has been observed to lead to an increase in $T_g$, and, hence, a decrease in molecular mobility [62].

In order to verify this influence of CNT content on polymer mobility, the $T_g$ of unfilled PC and PC
+ 3 wt.% CNT were measured using DMTA (Figure 14). Based on the observed increase in yield stress an increase in T_g would be anticipated for these nanocomposite systems. However, similar to a previous study [35], only a very small increase in T_g was observed for the PC/CNT nanocomposites (159 °C for PC + 3 wt.% CNT compared to 158 °C for neat PC, determined by the maximum of the tan delta peak). This increase is by far not sufficient to explain the strong increase in yield stress observed in Figure 5. It has been suggested that the addition of nanofillers can lead to an anti-plasticization effect, which promotes a higher resistance to plastic deformation [63]. However, it should be noted that anti-plasticization is generally accompanied by a marked decrease in T_g, which is not observed in the PC/CNT nanocomposites. The fact that the response of the PC/CNT nanocomposites resembles that of an annealed PC closely, rather seems to suggest that the presence of CNTs influences the evolution of the physical ageing process. Once cooled below T_g, the polymer glass will no longer be in a thermodynamic equilibrium state and will display a continuous strive to regain it. Even during fast cooling, this leads to a considerable increase of the yield stress compared to unaged samples [59].

Figure 10. (a) Time-to-failure versus maximum applied load under static (creep) and cyclic (fatigue) loading for unfilled PC and PC + 1 wt.% CNT. (b) Time-to-failure versus maximum applied load under static and cyclic loading for unfilled PC and PC + 3 wt.% CNT. Both sets of experiments are performed at 3 Hz and 20 °C.

Figure 11. Samples after failure of PC + 3 wt.% CNT, corresponding to both failure regions; (bottom) plasticity-controlled failure (necking), and (top) crack growth-controlled failure (brittle fracture).

Figure 12. (a) Time-to-failure versus maximum applied load under static (creep) and cyclic (fatigue) loading for unfilled PC, PC + 1 wt.% CNT, and annealed PC (20 min at 120 °C). (b) Time-to-failure versus maximum applied load under static and cyclic loading for unfilled PC, PC + 3 wt.% CNT, and annealed PC (2 hrs at 120 °C). Both sets of experiments are performed at 3 Hz, R = 0.1, and 20 °C.
unfilled matrix, the physical ageing process involves localised, subtle changes in chain conformation that allows chain segments to rearrange with respect to each other and strengthen their interaction. Apparently, interactions between (segments of) polymer chains and nanofillers intensify markedly during physical aging, leading to a stronger increase of yield stress with time. Close to $T_g$, chain mobility is much higher due to thermal activation, and conformational changes occur over a much larger scale. This enhanced mobility will make that the stronger interactions between chain segments and nanoparticles, as created during ageing, will have disappeared close to $T_g$.

With regard to the observed differences in the crack growth region of failure: at the initial stage of deformation crack tip blunting occurs during a period of crack initiation. The stress state in such a case can be described by yielding of material in the vicinity of a crack tip, and the subsequent formation of a plastic zone. The size of this plastic zone is directly related to the value of the yield stress; a low yield stress will produce a large plastic deformation zone at the crack tip that will effectively lead to crack blunting which increases fracture toughness [64] and is hypothesized to decrease fatigue crack propagation. Vice versa, an increase in yield stress due to the incorporation of CNTs will reduce the size of the plastic zone and, therefore, lowers the effectiveness of this crack tip blunting mechanism which, in turn, leads to an increased crack propagation rate and a lowered failure resistance of the polymer nanocomposites. An increase in yield stress due to annealing has been shown to have a similar detrimental effect on PC’s ability to stabilise crack growth [65]. As mentioned earlier, nanocomposites showed also a more brittle failure behaviour in tensile tests, with PC + 3 wt.% CNT having an elongation at break of approximately 15% as compared to 100% for neat PC matrix.

Relatively large amounts of nanofiller reinforcement can lead to the formation of agglomerates and very significant embrittlement effects as a result of strain concentrations due to the stiffness mismatch between polymer and nanofiller [66]. The strength of the interphase can also be a factor affecting
overall fatigue resistance [67]. Moreover, it has been demonstrated that samples generally display reduced fracture toughness in the case of both annealing [68] and the addition of CNTs (for instance, in PMMA the reduction in Mode I fracture toughness with the addition of 1 vol.% MWCNTs is 47%) [69]. Lower fracture toughness will lead to a reduced critical crack length at the same applied stress level and, therefore a shorter time-to-failure.

4.3. Extrapolation to static loading in crack growth-controlled failure

Kanters et al. [70] proposed a phenomenological, crack-propagation based model which takes into account the influence of both frequency and load amplitude on the time-to-failure in cyclic tension-tension fatigue. The model is based on multiplicative decomposition of crack propagation rates by assuming two reference limit cases: one at $R = 0$ (cyclic) is assumed to scale with frequency and another at $R = 1$ (static) is frequency independent. Time-to-failure for any combination of R-value and frequency (for tension-tension fatigue) can be described using Equation 7 and parameters listed in the Table 3:

$$
\log(t_f(R, f)) = R^a \cdot \log \left( \frac{\sigma}{\sigma_{f, static}} \right)^{-m} + (1-R^2) \cdot \log \frac{1}{f} \left( \frac{\sigma}{\sigma_{f, cyclic}} \right)^{-m} 
$$

(7)

where $\alpha$ is the parameter to capture the non-linear dependency on R-value (load ratio), $\sigma$ is the maximum applied stress, $f$ is the frequency of the applied cyclic load, $\sigma_{f, cyclic}$ cyclic and $\sigma_{f, static}$ static are pre-factors for two reference loading cases ($R = 0$ and $R = 1$, respectively).

Table 3. Parameters to describe the time-to-failure as function of R-value and frequency using Equation 7 for PC + 3 wt.% CNT.

<table>
<thead>
<tr>
<th>Material</th>
<th>$\alpha$ [-]</th>
<th>$c_{f, static}$ [MPa s$^{1/m}$]</th>
<th>$c_{N_f, cyclic}$ [MPa]</th>
<th>$m$ [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC + 3 wt.% CNT</td>
<td>3.11</td>
<td>145690</td>
<td>2382</td>
<td>2.2</td>
</tr>
</tbody>
</table>

Figure 15. PC + 3 wt.% CNT: (a) Time-to-failure under cyclic fatigue loading versus maximum applied stress, for different load ratios at 3 Hz. Markers represent measurements, solid lines predictions using Equation 7. (b) Time-to-failure in cyclic fatigue for a maximum applied stress of 45 MPa versus load ratio. Lines represent the time-to-failure calculated using Equation 7.

Figure 16. PC + 3 wt.% CNT: (a) Time-to-failure under cyclic fatigue loading versus maximum applied stress for different load ratios at 1 Hz. Markers represent measurements, solid lines predictions using Equation 7. (b) Time-to-failure under cyclic fatigue loading versus maximum applied stress for different stress ratios at 10 Hz. Markers represent measurements, solid lines predictions using Equation 7.
The model has been validated for different frequencies and R-values as presented in Figure 15 and 16. It is shown that the model gives adequate predictions of time-to-failure for polymer nanocomposites. Extrapolation allows one to predict also static failure based on relatively short-term cyclic experiments. Thus, for the first time, the long-term mechanical performance of polymer nanocomposites was studied not only experimentally but was also described by physical models, giving new significant insights into the fundamentals of mechanical behaviour of polymer nanocomposites.

5. Conclusions

In this study an engineering approach for the evaluation of long-term performance of polymer nanocomposites has been introduced, with an application to both creep and fatigue. Cyclic loading has shown to be an effective technique for failure mechanism identification due to the strong acceleration of crack propagation. Deformation kinetics in the plasticity-controlled failure regime of polymer nanocomposites can be characterised by performing tensile tests at different strain rates and can be modelled by using the Eyring equation. Remarkably, the activation volume and activation energy of the nanocomposites were identical to those of the aged neat PC matrix. Therefore, it was hypothesised that the marked increase in yield stress and time-to-failure in the plasticity-controlled failure region is due to an increased resistance to plastic deformation mainly as a consequence of reduced chain mobility due to interactions between sections of the polymer chain and nanofillers. In the crack-growth controlled region of failure this influence persisted. The reduction in the size of the plastic zone behind a crack tip may lead to an increase in macroscopic crack propagation rate and/or decrease in fracture toughness, which in turn will result in embrittlement and a reduced durability of polymer nanocomposites. These observations confirm that a comparison of long-term mechanical performance between materials or the effect of the addition of nanoreinforcements to a polymer matrix cannot be justified simply by comparing short-term properties (yield stress, creep rate, etc.). In addition, it is important to understand the deformation and crack propagation kinetics and to identify underlying failure mechanisms in the polymer matrix under given conditions. This study showed that the addition of CNTs has an opposite effect on two important failure mechanisms in long-term mechanical behaviour, with CNTs having a positive effect in the plasticity-controlled regime, while having a negative effect in the crack growth controlled regime. These results also signify that overall long-term performance improvements of nanocomposites can be significantly less than those observed during typical short-term material characterisation tests.

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Disclosure statement

No potential conflict of interest was reported by the authors.
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