Original Article

Physical background of the endurance limit in poly(ether ether ketone)

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Abstract

In this study, it is demonstrated that the apparent endurance (fatigue) limit for plasticity-controlled failure in poly(ether ether ketone) is related to an evolution of the yield stress. The increase of the yield stress has two separate causes: (a) stress- and temperature-accelerated physical aging of the amorphous phase and (b) strain hardening as a result of texture development. Yield stress evolution is monitored using thermomechanical treatments during which the material is exposed to temperature and load. The combined contributions of both temperature and applied stress to yield stress evolution (below $T_g$) can be effectively modeled using an effective time approach employing an Arrhenius temperature-activation as well as Eyring stress activation. Combination of the yield stress evolution with a previously developed model for plasticity-controlled failure allows prediction of time-to-failure under both static and cyclic load, quantitatively capturing the observed apparent endurance limit.

Keywords

creep, endurance limit, fatigue, PEEK, plasticity-controlled failure, stress accelerated physical aging, yield stress evolution

1 | INTRODUCTION

High-performance thermoplastic materials are gaining increasing interest to potentially replace metal in an endeavor to optimize strength-to-weight ratios in the aerospace and automotive industry.\(^1\) One of the most widely used polymers in demanding end-use applications is poly(ether ether ketone) (PEEK); mainly owing to its excellent mechanical properties, wear, and chemical resistance, as well as dimensional stability in a wide range of loading and environmental conditions.\(^2\) Moreover, the biocompatibility of PEEK has created new possibilities in the medical industry as an alternative to the metal framework in dental and orthopedic applications.\(^3\) PEEK is a semicrystalline thermoplastic aromatic polymer which, due to the presence of rigid ketone linkages, has a relatively high glass transition ($T_g = 143^\circ$C) and melting temperatures ($T_m = 334^\circ$C).\(^4\) PEEK has the ability to form crystals, although the overall crystallinity is rather low; and is typically in a range of 0–48% depending on processing conditions and molecular weight.\(^5\) The presence of the crystalline phase provides additional improvement in both the mechanical and the chemical resistance of PEEK. Addition of reinforcing fibers (glass, carbon) allowed for a further improvement in mechanical performance, and, as a result, carbon fiber reinforced PEEK grades are currently positioned as weight
saving alternatives to metals (with weight savings up to 80% when compared with steel according to the PEEK producers).\[6\]

The use of injection molding as a processing technique has facilitated the manufacturing of complex-shaped parts both from unfilled and short fiber reinforced PEEK in a cost and time-efficient manner. Cooling and flow conditions during processing largely affect the resulting crystalline morphology and thermodynamic state of the amorphous (glassy) phase. It is reported in literature that PEEK chains form orthorhombic unit cells which serve as building blocks for lamellae\[7\] that are geometrically arranged in spherulites with a typical size of 5–10 μm.\[8\] The lamellar thickness and the final degree of crystallinity are determined by processing conditions and are known to affect the yield stress, modulus, the yield stress kinetics, and long-term performance of the material.\[9\]

It is well known that the amorphous part of semicrystalline polymers is not in thermodynamic equilibrium upon cooling below the glass transition temperature.\[10–12\] Despite the fact that the mobility of polymer chains is greatly restricted below the glass transition temperature, it is essentially nonzero and small changes in chain conformation are still possible. This nonequilibrium state triggers a continuous evolution of thermodynamic parameters in a gradual approach to equilibrium; the material is said to undergo physical aging (to distinguish it from chemical aging due to molecular degradation).\[10\] Such a persistent strive to achieve equilibrium affects polymer properties: relaxation times will increase and, as a result, the viscoelastic and viscoplastic properties (yield stress, elastic modulus, creep rate, etc.) will evolve in time. The rate of physical aging is determined by molecular mobility, which can be accelerated by two important physical stimuli: temperature\[13,14\] and applied stress.\[15–18\] An increase in temperature will lead to a temperature-induced increase in molecular mobility which will accelerate physical aging. The aging process is thermoreversible, which implies that when heated above its glass transition temperature, and equilibrium is restored, the effect of thermal history and physical aging is erased.\[10\] Stress-induced mobility has a similar effect on the aging kinetics: when applied stress results in a small strain deformation, the aging process is accelerated while under higher applied stresses, the induced plastic flow effectively counteracts and reverses the effect of physical aging, a process known as strain softening.\[19\] Consequently, the combined effect of stress and temperature has a pronounced effect on the aging process and, as a consequence, on the yield stress of the polymer. With an increase in yield stress, the material’s lifetime in the plasticity-controlled failure region under both under static and cyclic load will improve.\[20\] On the other hand, it will lead to a more pronounced strain localization and possibly even embrittlement.\[21\]

Next to the increase in yield stress as a result of physical aging, there may also be a contribution of molecular orientation (strain hardening). In glassy polymers, molecular dynamics simulations on rapidly quenched samples indicated a dominant role of molecular orientation in yield stress evolution under constant stress loading.\[22\] However, in experiments on slow cooled (SC) samples, with a higher initial yield stress, the deformation during creep loading was observed to be too small for any substantial contribution of molecular orientation.\[23\] In case of semicrystalline polymers, this might be different, since crystallographic texture evolution can already lead to pronounced strain hardening at very low strain levels, and may, therefore, also contribute to yield stress evolution\[24–26\]

Since the material experiences the combined effect of applied stress and temperature during characterization experiments as well as service life, its mechanical properties are subject to evolution in the course of time. This phenomenon is usually referred to as progressive aging, and was identified as the main cause for the occurrence of a so-called endurance limit in polymer glasses.\[2,18,20,29–36\] The endurance or fatigue limit is defined as a stress level below which a material is assumed to withstand load indefinitely without failure. Examples of the endurance (fatigue) limit under static and cyclic load for compression molded PEEK at two test temperatures (23 and 70°C) are shown in Figure 1a. At lower applied stresses and higher temperatures, an apparent flattening of the lifetime curves is observed for both loading cases and test temperatures. Endurance limits are sometimes regarded as a material property in subsequent failure or damage analysis.\[37\] For polymer glasses, the stress level of the endurance limit is known to be caused by progressive yield stress evolution, and it will, consequently, depend on processing conditions and thermomechanical history. As a result, it cannot be used as a design parameter, since the apparent endurance limit will vary for different processing and loading conditions. Despite PEEK being a semicrystalline polymer, the question arises whether, similar to polymer glasses, this onset of the endurance limit is also related to yield stress evolution. Additionally, it should be noted that the observed endurance limit only applies to a single failure mechanism, in this case plasticity-controlled failure, implying that failure is only transferred to another failure mechanism, slow crack growth, as will be discussed next.

It is well established\[38–40\] that long-term failure of thermoplastics is controlled by two stress dependent failure mechanisms: plasticity-controlled and slow crack growth, which mechanism is dominant is determined by loading conditions and timescale (see Figure 1b). If the applied stress is sufficiently high, the failure is triggered by a critical amount of accumulated plastic deformation, therefore, failure is plasticity controlled. The typical characteristics of
plasticity-controlled failure is that the time to failure in cyclic loading is frequency independent, whereas lifetime, when compared with that under static load at the same maximum applied stress, shifts toward longer time (due to the oscillating nature of the applied load more time is needed to accumulate the same amount of critical plastic deformation).[41,42] At lower applied stresses, the dominant failure mechanism is slow crack growth: stable growth of cracks originating from processing-induced defects.[43–47] Slow crack growth is driven by applied stress and can be strongly accelerated when a high amplitude cyclic load is applied. Once the crack reaches a critical length, failure occurs in a typically brittle manner.

Material characterization is typically based on performing crack-growth experiments that are normally limited to relatively short times (10⁶ s). For many polymer systems, both glassy and semicrystalline, unfilled and fiber reinforced, it has been demonstrated that, at the same value of the maximum load, application of a high amplitude cyclic load will promote crack-growth and drastically reduce the failure time compared to that observed in static loading.[42,48] In the case of polymers with a very high resistance to crack growth, it is, nevertheless, not uncommon that crack-growth dominated failure is not observed during characterization experiments; a prime example being the absence of crack-growth dominated failure in current polyethylene (PE) pipe grades during certification testing.[49,50] The fact that crack-growth dominated failure is not observed during static tests of over a year only implies that the material is very crack resistant; it will definitely appear at lower loads and longer loading times. Consequently, an endurance limit observed in plasticity-controlled failure is nothing more than that; below the endurance threshold no plasticity-controlled failure will occur, but crack-growth dominated failure is still inevitable. In the case of PEEK, the resistance to crack growth, even at high amplitude cyclic loading, may be very high,[51] and, specifically at elevated temperature, the plasticity-controlled regime may cover loading times relevant to engineering application. Hence, the accurate prediction of the occurrence of endurance limits within the plasticity-controlled regime is still of the utmost importance.

In this study, the long-term performance of PEEK is investigated by studying the deformation kinetics and the way it is affected by the temperature- and stress-induced yield stress evolution. A series of thermomechanical tests were carried out at different temperatures to study the combined effect of applied stress and temperature on yield stress evolution of PEEK polymer. The influence of applied stress was studied in compression, tension, and tension-tension fatigue. The effect of physical aging of the amorphous part of PEEK and texture development of the crystalline part is described by a logarithmic evolution law, using an effective time approach to translate the response to arbitrary thermomechanical conditions. The obtained yield stress evolution is subsequently combined with the Eyring flow theory to describe its influence on the deformation kinetics. Then, employing a critical accumulated plastic strain concept, the time-to-failure of PEEK under both static and cyclic load is predicted and the yield stress evolution is connected directly to the apparent endurance or fatigue limit (delayed plasticity-controlled failure).

2 | METHODS

2.1 | Materials and specimen preparation

The material used in this study is a PEEK (KETASPIRE KT-820), provided by Solvay Speciality Polymers, Alpharetta,
GA both in the form of granules (used for producing compression molded samples) and injection molded tensile bars according to the ASTM D638 Type I standard. For compression molding, granules were first dried under vacuum at 150°C for 4 hr. The melt temperature was set at 360°C while pressure (maximum applied force was 150 kN, time of application 2 min) was applied in a stepwise manner. A stainless steel mold was covered with aluminum foil and put in the press. During the molding process vacuum was applied. Three cooling methods were used to produce samples with different degree of crystallinity: quenched samples (Q) were cooled in a bucket with ice water. Since PEEK crystallizes relatively fast, amorphous sheets of 0.5 mm thickness could be obtained. Isothermally crystallized (IC) samples were kept at 175°C for 5 min, before cooling down quickly (between cold molds) to room temperature. This method mimics the injection molding process where the mold temperature is set at 175°C. The timespan of 5 min is sufficient to reach the maximum crystallinity at this temperature.[52] SC samples were cooled down at the slowest rate inside the compression molding machine by shutting it off and allowing it to cool down from 360°C to room temperature. Cylindrical samples for compression testing were machined from SC and IC plates with dimensions 4 × 4 mm².

2.2 | Mechanical testing

Tensile and creep tests were performed on a Zwick Z010 Testing Machine, equipped with a 10 kN load-cell and temperature chamber. Deformation kinetics were studied by measuring the strain rate and temperature dependence of the yield stress at strain rates ranging from 10^−5 to 10^−1 s⁻¹ and temperatures ranging from 23 to 130°C. The yield stress has been determined as either the maximum stress (when a clear peak is visible) or as the intersect of two tangents to the preyield and postyield parts of the stress–strain curve.[53] Static fatigue experiments (creep tests) are performed under constant force loading for a wide range of engineering stresses; the stress is applied in 10 s and subsequently kept constant until failure. Cyclic fatigue experiments were performed on a servo-hydraulic MTS Testing System, equipped with a 25 kN load cell, applying a sinusoidal load until failure. Compression tests were performed on a Zwick 1475 equipped with 100 kN load cell and a temperature chamber. Friction between the sample and steel plates was reduced by applying poly(tetrafluoroethylene) (PTFE) tape (3M 4580) to the sample and PTFE spray (Griffon TF089) onto the steel plates. True strain rate control was used, under the assumption of incompressibility, and true stress and true strain signals were recorded.

2.3 | Thermomechanical testing

The applied thermomechanical protocol to study the combined effect of applied stress and temperature on the yield stress evolution (physical aging) was as follows: first, preloads σₐ applied for a predefined period of time τₛ with either constant or sinusoidal load signal at a specific testing temperature Tₛ, second, the unloading stage with a rest period of τ_r = 5 min, and finally the measurement of the yield stress under an applied engineering strain rate of 10^−3 s⁻¹. A schematic of the applied thermomechanical protocol is shown in Figure 2.

3 | RESULTS AND DISCUSSION

3.1 | Influence of processing conditions on the mechanical response

Processing conditions strongly affect the yield stress and the deformation kinetics of a polymer material: in semicrystalline polymers, the cooling rate during processing influences both the crystalline phase (degree of crystallinity, size of spherulites, and lamellar thickness),[9,54,55] as well as the amorphous phase (thermodynamic state or the “age” of the amorphous phase).[31,56] As an example, Figure 3a shows the effect of three different processing conditions, SC, IC at 175°C (IC), and quenched (Q) on the stress–strain response of PEEK. It is clear that the different cooling rates significantly affect modulus, yield stress and strain at break of the material. During a constant strain rate (tensile) test, the increasing stress induces the onset plastic flow due to increased molecular mobility.[57–59] At the yield point (open markers in Figure 3a), the plastic flow within the polymer ε_p matches the strain rate ε_e experimentally applied.[60]

Similar to the tensile tests, when a constant stress is applied to a material (creep test), stress also induces molecular mobility that results in steady plastic flow. A higher stress leads to a higher mobility, resulting in a higher creep rates and a shorter time-to-failure; see Figure 3b for PEEK IC. The evolution of the plastic flow rate during a creep test can be studied using a so-called Sherby–Dorn plot where the creep rate is plotted as a function of strain[61] (see Figure 3c). Three distinct regions can be recognized: primary creep (a region of decreasing creep rate), secondary creep (a plateau region with a constant plastic flow rate), and tertiary creep (region of increasing plastic flow rate). When the plastic flow rate
during secondary creep is plotted versus the applied stress (filled markers in Figure 3d), it is clear that the kinetics of plastic flow during secondary creep test (solid markers) exactly matches the strain rate dependence of the yield stress (open markers). This equivalence between both steady states was first demonstrated on polycarbonate (PC) by Bauwens-Crowet et al.\cite{60} and implies that, in principle, the plastic flow rate during secondary creep can be predicted directly from tensile experiments.

The stress and temperature dependence of the plastic flow rate can be described by Eyring’s flow theory,\cite{62} according to Equation (1):

$$\dot{\varepsilon}_{pl}(\sigma, T) = \dot{\varepsilon}_0 \cdot \exp\left(-\frac{\Delta U_d}{RT}\right) \cdot \sinh\left(\frac{\sigma V^*}{kT}\right)$$

where $\dot{\varepsilon}_0$ is a rate factor, $\sigma$ is the applied stress, $V^*$ is the activation volume, $k$ is the Boltzmann’s constant, $T$ is the absolute temperature, $\Delta U_d$ is the activation energy, and $R$ is the universal gas constant.\cite{60,62} The index “d” refers to the fact that these parameters are related to the deformation kinetics, in contrast to the aging kinetics used further on. At the yield point, conditions $\dot{\varepsilon}_{pl} = \dot{\varepsilon}$ and $\sigma = \sigma_y$ hold, therefore, Equation (1) can be rewritten as:

$$\sigma_y(\dot{\varepsilon}, T) = \frac{kT}{V_d} \cdot \sinh\left(\frac{\dot{\varepsilon}}{\dot{\varepsilon}_0} \cdot \exp\left(\frac{\Delta U_d}{RT}\right)\right)$$

At high applied stresses, one can assume $\sinh^{-1}(x) \approx \ln(2 \cdot x)$ and making use of $R = N_A \cdot k$, Equation (2) can be rewritten as:

$$\sigma_y(\dot{\varepsilon}, T) = \frac{kT}{V_d} \cdot N_A \cdot \ln\left(\frac{2\dot{\varepsilon}}{\dot{\varepsilon}_0} + \frac{\Delta U_d}{N_A \cdot V_d}\right)$$

The strain rate dependence of the yield stress for different processing conditions shows a linear relation with
logarithm of strain rate as shown in Figure 3d, while the change in the processing conditions (cooling rate) only shifts the deformation kinetics; the slope remains identical. The deformation kinetics of the IC and SC samples were further explored using tensile and creep tests at different temperatures. The strain rate dependence of the yield stress is presented in Figure 4a,c for IC and SC compression molded samples, respectively. The solid lines are fits employing the Eyring equation (Equation (2)) using the parameters listed in Table 1. Please note that both the activation volume \(V^*\) and energy \(\Delta U_d\) of the deformation kinetics of PEEK do not depend on processing conditions, the only parameter that changes is the pre-exponential factor \(\dot{\varepsilon}_0\). This observation is in line with those previously reported in literature concerning the influence of processing conditions on deformation kinetics of polymers: Bauwens-Crowet et al.\[60\] and Klompen et al.\[23\] showed that for polymer glasses a change in \(\dot{\varepsilon}_0\) accurately describes the effect of the thermodynamic state. For semicrystalline polymers, van Erp et al.\[9\] demonstrated that there is a linear relation between the logarithm of the rate constant \(\dot{\varepsilon}_0\) and the crystallinity in \(\alpha\)-isotactic polypropylene while both activation volume (the slope of the strain rate dependence of the yield stress) and energy (temperature dependence) of deformation remain largely unaffected by the changes in crystallinity and/or lamellar thickness.

The stress dependence of the time-to-failure of the SC and IC samples was studied in static loading conditions. The results, measured at various temperatures, are presented in Figure 4b,d. The solid lines in these figures are time-to-failure predictions based on the concept of a critical level of accumulated plastic strain \(\varepsilon_{cr}\). In this approach, it is assumed that the applied stress induces a steady rate of plastic flow within the material \(\dot{\varepsilon}_{pl}\) which can be estimated with the Eyring equation (Equation (2)) and parameters in Table 1. The accompanying plastic deformation will trigger failure once the accumulated strain reaches a critical level.\[20,31,63\] The critical strain was determined by plotting the minimum plastic flow rate during secondary creep versus time-to-failure for IC (open markers) and SC (filled markers) for different temperatures and applied stresses. Line is a fit using Equation (4). (f) Yield stress evolution for IC samples under creep load \(\sigma_a = 50\) MPa and \(T = 90^\circ\text{C}\), measured at \(10^{-3}\text{ s}^{-1}\). [Color figure can be viewed at wileyonlinelibrary.com]
rate during secondary creep (as determined from Sherby–Dorn plots) versus the corresponding time-to-failure\textsuperscript{[64]} (see Figure 4e). A linear relation with the slope of \(-1\) in a double logarithmic plot is found; consequently, the time-to-failure under a static load can be determined from:

$$t_f = \frac{\varepsilon_{cr}}{\varepsilon_{pl}} \tag{4}$$

It is observed that the critical strain shows some variation with differences in processing condition and test temperature; in this case the deviations are small and we make use of a single, average value for the critical strain. Predictions of time-to-failure for different temperatures using the critical strain concept are shown in Figure 4b,d for IC and SC samples, respectively.

In Figure 4b,d, it can be observed that the results of slow tensile tests and creep tests with a long time-to-failure, especially at higher test temperature, deviate markedly from the prediction based on the Eyring equation. These deviations are characteristic for the effect of yield stress evolution; the combined effect of temperature and applied stress accelerates physical aging of the glassy amorphous phase and promotes texture development of the crystalline phase, which, from mechanical properties perspective, result in a continuous increase of the yield stress in time and, as a result, failure will be delayed. The gradual increase in yield stress can easily be studied by stopping the creep test at different loading times, and determine the yield stress with a subsequent tensile test. An example is presented in Figure 4f, where the yield stress evolution is shown for the IC material subjected to a creep load of $\sigma_a = 50 \text{ MPa}$ at $90^\circ\text{C}$. Samples were unloaded at various loading times and yield stresses were obtained after unloading to 0 MPa and subsequently the yield stress is measured at a strain rate of $10^{-3} \text{ s}^{-1}$. It is obvious that the yield stress evolution is substantial: a 15 MPa increase in little more than a day (25% increase).

### 3.2 Yield stress evolution: Background

As is clearly shown in Figure 4f, the onset of the endurance limit, witnessed by the apparent flattening toward longer test times, is accompanied by the onset of a gradual increase of the yield stress. For polymer glasses, the yield stress evolution, in this case solely related to progressive physical aging, was investigated extensively by Klompen et al.\textsuperscript{[23]} As discussed above, the only parameter in the Eyring formulation that depends on the thermodynamic state (“age”) of the material is the pre-exponential factor $\dot{\varepsilon}_0$. As illustrated in Figure 5a, a decrease in $\dot{\varepsilon}_0$ implies that the strain rate dependence of the yield stress shifts toward lower strain rates, whereas the slope and the temperature dependence remain the same. As a consequence of the semilog characteristic, the logarithmic shift along the strain rate axis translates directly to an increase of the yield stress at a fixed rate ($\sigma_y(t) = \sigma_y^0 + \Delta \sigma_y(S_a(t))$, or vice versa (see Figure 5a). It is therefore sufficient to monitor the evolution of the yield stress at a single “fixed” strain rate, since it can be directly translated to the evolution of the pre-exponential factor $\dot{\varepsilon}_0$. To facilitate a direct translation Klompen et al.\textsuperscript{[18,23]} proposed to modify the pre-exponential factor $\dot{\varepsilon}_0(t)$ to make it time dependent in a following way:

| Material (processing conditions) | $\dot{\varepsilon}_0$ (s\(^{-1}\)) | $V^*_d$ (nm\(^3\)) | $\Delta U_d$ (kJ/mol) | $\varepsilon_{cr}$ (–) |
|---------------------------------|-----------------------------|------------------|----------------------|------------------|
| PEEK (IC at 175°C)             | $5.0 \times 10^{34}$       | 2.54             | 347                  | 0.035            |
| PEEK (SC)                      | $3.0 \times 10^{32}$       | 2.54             | 347                  | 0.035            |

Abbreviations: IC, isothermally crystallized; PEEK, poly(ether ether ketone); SC, slow cooled.

\[\text{FIGURE 5} \quad \text{(a) Effect of the state parameter } S_a \text{ on yield stress kinetics. (b) Schematic of the yield stress evolution for different initial states } \dot{\varepsilon}_0.\]
\[ \dot{\varepsilon}_0(t) = \dot{\varepsilon}_{0,\text{ref}} \cdot \exp\left(-S_u(t_{\text{eff}})\right) \]  

(5)

where \(\dot{\varepsilon}_{0,\text{ref}}\) is the pre-exponential factor for an unaged material and \(S_u\) is a state parameter that is representative for the thermodynamic state of the material. It has a clear physical definition; it is the horizontal shift between the aged material and the reference state (unaged, or rejuvenated state) as demonstrated in Figure 5a.

Klompen et al.\(^{[23]}\) further proposed a logarithmic relation to describe the evolution of the yield stress as shown in Figure 5b. The initial value of \(S_u\), determined by the thermal history during processing, is linked to a unique value of the initial age \(t_0\):

\[ \sigma_y(t) = \sigma_{y,0} + c \cdot \ln\left(\frac{t + t_a}{t_0}\right) \]  

(6)

where \(\sigma_{y,0}\) is the plateau stress level. As demonstrated by Klompen et al.\(^{[23]}\) combination of Equations (3), (5), and (6) leads to an equivalent expression for the evolution of \(S_u\):

\[ S_u(t) = c_0 + c_1 \cdot \ln\left(\frac{t + t_a}{t_0}\right) \]  

(7)

where \(c_0\) and \(c_1\) are constants, \(t_0 = 1\) s, and \(t_a\) determines the initial age (thermodynamic state as a result of processing; a glassy material processed at different cooling rates has different initial ages but the yield will follow the same evolution as was demonstrated by Klompen et al.\(^{[23]}\))

Knowing the evolution of state parameter \(S_u\), one can calculate the time-dependent pre-exponential factor \(\dot{\varepsilon}_0(t)\) using Equation (5). It should be noted that \(\dot{\varepsilon}_{0,\text{ref}}\) cannot be experimentally determined, since, regardless of processing conditions, the resulting thermodynamic state never corresponds to a completely rejuvenated case. Instead, since the pre-exponential factor of as-received material is known (\(\dot{\varepsilon}_{0,\text{AR}}\) corresponds to a specific initial age \(t_a\)), it can be used to determine a reference \(\dot{\varepsilon}_{0,\text{ref}}\) in the following way:

\[ \dot{\varepsilon}_{0,\text{AR}} = \dot{\varepsilon}_{0,\text{ref}} \cdot \exp\left(-c_1 \cdot \ln\left(\frac{t_a}{t_0}\right)\right) \]  

(8)

To account for the accelerated effect of temperature and applied stress, the effective time approach \(t_{\text{eff}}\) is used:

\[ t_{\text{eff}}(T, \sigma) = \frac{1}{a_T(T) \cdot a_\sigma(\sigma, T)} \int_0^t dt \]  

(9)

where \(a_T\) and \(a_\sigma\) are the temperature and stress acceleration factors with respect to the reference temperature \((T_{\text{ref}})\) and stress level \((\sigma_{\text{ref}})\), respectively. The temperature shift factor uses the time–temperature superposition principle in combination with an Arrhenius-based temperature activation and can be written as:

\[ a_T(T) = \exp\left(\frac{\Delta U_d}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{ref}}}\right)\right) \]  

(10)

where \(T\) is the temperature and \(\Delta U_d\) is the activation energy of aging. While the stress acceleration factor (at \(\sigma_{\text{ref}} = 0\) MPa), can be expressed as an Eyring-type shift function based on the time–stress superposition (TSS) as proposed by Tervoort et al.\(^{[65]}\) for stress activation of yielding and by Klompen et al.\(^{[23]}\) for stress activation of aging:

\[ a_\sigma(\sigma, T) = \frac{\sigma_{\text{ref}}^V}{\sinh \left(\frac{\sigma \sigma_{\text{ref}}^V}{kT}\right)} \]  

(11)

where \(V^*\) is the activation volume of aging. Therefore, the resulting formulation of the Eyring equation describing the effect of the time-dependent yield stress evolution on the plastic flow rate can be written as:

\[ \dot{\varepsilon}_p = \dot{\varepsilon}_{0,\text{ref}} \exp\left(-c_1 \cdot \ln\left(\frac{t + t_a}{t_0}\right)\right) \cdot \exp\left(-\frac{\Delta U_d}{RT}\right) \cdot \sinh\left(\frac{\sigma V^*}{kT}\right) \]  

(12)

and for the evolution of the yield stress (deformation kinetics):

\[ \sigma_y = \frac{kT}{V_d^*} \sinh^{-1}\left(\frac{\dot{\varepsilon}}{\dot{\varepsilon}_{0,\text{ref}}} \cdot \exp\left(c_1 \cdot \ln\left(\frac{t + t_a}{t_0}\right)\right) \right) \cdot \exp\left(\frac{\Delta U_d}{RT}\right) \]  

(13)

### 3.3 Thermal treatments: Temperature-activated yield stress evolution

First of all, we will study yield stress evolution in the absence of stress. In this case, texture evolution will not contribute to yield evolution, and only the effect of temperature-activated physical aging is studied. For this purpose, a set of injection molded samples was prepared and subjected to temperature annealing at different annealing temperatures \((T_{\text{Ua}})\) and various annealing times (\(t\)). After annealing, the yield stress was measured at an applied strain rate of \(10^{-3} \text{ s}^{-1}\), results at two test temperatures are presented in Figure 6. Figure 6a shows that an
increase in the annealing temperature leads to a marked acceleration of the physical aging effect. After an annealing for 10^6 s (12 days), a considerable effect of temperature-induced physical aging is observable at high annealing temperatures (at 110 and 130°C) as shown in Figure 6b. Therefore, both the annealing time and temperature have a significant influence of the yield stress of PEEK.

Struik\(^{[66–68]}\) already established that below the glass transition temperature (for PEEK \(T_g\) = 143°C) the same principles used for glassy polymers (time-temperature and TSS in an effective time approach) are also applicable to describe physical aging of semicrystalline polymers. Therefore, we approach the yield stress evolution in PEEK as proposed by Klompen et al.\(^{[23]}\) with the exception that we study the evolution at five different temperatures, and, hence, we regard the evolution of the ratio of the yield stress to the test temperature. In this case, the influence of temperature on the slope of the strain rate dependence, which translates directly to the yield stress evolution, disappears since:

\[
\frac{\sigma_y(\dot{\varepsilon}, T)}{T} = \frac{k}{V_d} \ln \left( \frac{2\dot{\varepsilon}}{\dot{\varepsilon}_0} \right) + \frac{\Delta U_d}{N_A V_d} \frac{1}{T} \quad (14)
\]

Figure 7 presents the evolution of the ratio of yield stress over temperature as a function of annealing time; the symbols indicate different annealing temperatures, the colors represent the testing temperature. For each testing temperature, the results from different annealing temperatures were shifted horizontally to construct a master curve. It should be noted that at lower annealing temperatures \((T_a = 50°C \text{ and } T_a = 70°C)\), the effect of temperature annealing is rather small even at the longest measurement times. As a result, the required shift cannot be determined accurately. Consequently, these two were ignored in the determination of the activation energy for aging \(\Delta U_a\), and the testing temperature of 90°C was chosen as the reference temperature (therefore, \(a_T(90°C) = 1\)).

To determine the activation energy \(\Delta U_a\), the \(a_T\) shift factors were plotted versus the inverse temperature and Equation (10) was fitted to the high temperature data where the effect of aging is noticeable (see Figure 8a). Next, the yield stress as a function of effective time was described using Equation (13). Parameters to describe the deformation kinetics of the injection molded samples (\(\dot{\varepsilon}_0, \Delta U_d, \text{ and } V_d^\alpha\)) were determined by fitting the data using Equation (2) as shown in Figure 8b, where the experimental data at longer times and higher temperatures, which is affected by yield stress evolution (indicated by the gray area), is ignored for the fit. To determine the parameters of the yield stress evolution (\(c^T_1\) and \(t_a\)), the shifted data in Figure 7 was fitted using nonlinear least square optimization assuming logarithmic dependence of the yield stress on effective time, where \(c^T_1\) determines the slope of the time-dependent yield stress evolution, and \(t_a\) is the time of the deflection of the curve from an initial time independent plateau. Parameters, describing the deformation and yield stress evolution, are presented in Tables 2 and 3, respectively. The quality of the obtained description of the experimental data supports the suitability of the approach proposed by Klompen et al.\(^{[23]}\) to describe accurately the temperature annealing in semicrystalline PEEK.

3.4 Thermomechanical treatment: Stress-activated evolution

In this section, we will study the combined effect of applied stress and elevated temperature using the thermomechanical protocol described in Section 2. As shown in Figure 2, the applied stress (\(\sigma_a\)) is kept constant for a predefined annealing time (\(t\)) at a specific annealing temperature \((T_a)\), after which the material is unloaded to
zero stress and kept at this condition for 5 min, followed by a tensile test at an engineering strain rate of $10^{-3}$ s$^{-1}$.

During this treatment, creep deformation will occur, which may lead to an additional contribution to the yield stress evolution by strain hardening (texture evolution). The range of applied stresses and annealing times for each test temperature has to be chosen with care, since a too small stress will not induce any noticeable yield stress evolution whereas a too high stress may cause failure before the unloading stage. The yield stresses after different preloads and annealing times for one annealing temperature ($T_a=90^\circ C$) are presented in Figure 9a,b. Please note that in this specific experimental protocol the testing temperature $T$ is always equal to the annealing temperature $T_a$. From these results, it is evident that the applied stress accelerates the yield stress evolution: the higher the applied stress, the more pronounced the increase in the yield stress (see Figure 9a). However, as the applied stress increases to a critical level, at 90$^\circ$C approximately at 45 MPa, stress activation stagnates and a further increase in the stress level will not lead to further

![Figure 7](image1.png)  
**FIGURE 7** Ratio of the yield stress to temperature for several annealing temperatures ($T_a$), measured at different temperatures ($T$) versus the annealing time ($t_a$), and the master curve constructed by horizontally shifting the data according to the time–temperature superposition (TTS). Markers represent experimental data; lines are descriptions using Equation (13) with parameters listed in Tables 2 and 3 [Color figure can be viewed at wileyonlinelibrary.com]

![Figure 8](image2.png)  
**FIGURE 8** (a) The Arrhenius temperature shift factors versus inverse of the annealing temperature, line is a fit using Equation (10), and (b) yield stresses at different stain rates for different temperatures for injection molded samples, lines are descriptions using Equation (2) and parameters in Table 2 [Color figure can be viewed at wileyonlinelibrary.com]

| Deformation kinetics | $\dot{\varepsilon}_{0,AR}$ (s$^{-1}$) | $V^*_d$ (nm$^3$) | $\Delta U_d$ (kJ/mol) |
|----------------------|-----------------------------|-----------------|---------------------|
| 1.1 x 10$^{34}$      | 2.54                        | 347.0           |

Abbreviation: PEEk, poly(ether ether ketone).
The exact physical reason for this phenomenon is unclear. Similar observations have been made on a polymer glass, polyphenylsulfone (PPSU), which, additionally, also displayed a stress level where rejuvenation sets in ref. [29]. During physical aging, small changes in chain conformation will lead to a denser molecular stacking, thus increasing the intermolecular interaction. An increase in mobility may increase the rate at which densification occurs, but a further increase in the rate of changes in molecular conformation may actually counteract the aging process, eventually leading to rejuvenation. The fact that rejuvenation is not observed in PEEK at higher applied stresses may imply that there is a contribution of strain hardening that counteracts it.

Similar to Figure 7, the experimental data, for stresses below as well as above the stagnation level, were

**TABLE 3** Model parameters describing yield stress evolution of PEEK. Yield stress evolution parameters were determined at $T_{\text{ref}} = 90^\circ C$

| Yield stress evolution | $c_1^T$ (temperature) ($-$) | $c_1^\sigma$ (stress + temperature) ($-$) | $\Delta U_a$ (kJ/mol) | $t_a$ (s) | $V_a$ (nm$^3$) |
|------------------------|-----------------------------|------------------------------------------|-----------------------|-----------|----------------|
|                        | 1.01                        | 1.54                                     | 182.0                 | $5.0 \cdot 10^5$ | 1.1            |

Abbreviation: PEEk, poly(ether ether ketone).

**FIGURE 9**
(a) Thermomechanical testing:
(a) and (b) Yield stresses measured at $T_a = 90^\circ C$ for different preloads ($\sigma_a$) and loading times ($t$), and
(c) master curve constructed by horizontally shifting data to the minimum applied stress according to the time–stress superposition (TSS). Dashed lines are a guide to the eye.
(d) Corresponding shift factors for different applied stresses [Color figure can be viewed at wileyonlinelibrary.com]

**TABLE 4** Applied stresses in MPa ($\sigma_a$) for different measurement temperatures ($T$) corresponding to the markers in Figure 10

| Temperature ($T$) | 50°C | 70°C | 90°C | 110°C | 130°C |
|-------------------|------|------|------|-------|-------|
| $\sigma_a$        | 35   | 30   | 20   | 15    | 10    |
| $\sigma_a$        | 45   | 35   | 25   | 20    | 15    |
| $\sigma_a$        | 50   | 50   | 35   | 30    | 25    |
| $\sigma_a$        | 60   | 55   | 40   | 35    | 30    |
| $\sigma_a$        | 65   | 60   | 45   | 40    | 35    |
| $\sigma_a$        | —    | —    | 50   | 45    | 40    |
| $\sigma_a$        | —    | —    | 52   | 50    | 45    |
| $\sigma_a$        | —    | —    | 54   | 52    | 47    |

acceleration of the yield stress evolution. This is shown in detail in Figure 9b. The exact physical reason for this phenomenon is unclear. Similar observations have been made on a polymer glass, polyphenylsulfone (PPSU), which, additionally, also displayed a stress level where rejuvenation sets in ref. [29]. During physical aging, small changes in chain conformation will lead to a denser molecular stacking, thus increasing the intermolecular interaction. An increase in mobility may increase the rate at which densification occurs, but a further increase in the rate of changes in molecular conformation may actually counteract the aging process, eventually leading to rejuvenation. The fact that rejuvenation is not observed in PEEK at higher applied stresses may imply that there is a contribution of strain hardening that counteracts it.

Similar to Figure 7, the experimental data, for stresses below as well as above the stagnation level, were
shifted horizontally to form a master curve, presented in Figure 9c, with the minimum applied stress as a reference stress (hence \( \sigma_r = 1 \)). The related shift factors for each creep preload stress are presented in Figure 9d which shows the respective shift factors \( a_\sigma \) as a function of the stress/temperature ratio. The gray line in Figure 9d represents the Eyring-based stress shift factor from Equation (11). This expression represents the stress shift for a reference stress of 0 MPa. For a stress shift to a reference level other than 0 MPa, the shift factor from Equation (11) has to be adapted using Equation (15) as follows:

\[
a_{\sigma,ref}(\sigma, T) = \frac{a_\sigma(\sigma, T)}{a_\sigma(\sigma_{\text{ref}}, T)}
\]

which will give a shift factor value equal to 1 at the reference stress, and is presented in Figure 9d as the dashed colored line. The factor separating the intersects of both expressions with the y-axis exactly equals the stress shift at the reference stress \( a_\sigma(\sigma_{\text{ref}}, T) \).

Similarly, master curves for other annealing temperatures were constructed as shown in Figure 10. Resulting shift factors for each applied stresses are plotted in Figure 11a. Please note that the minimum applied stress is different for each annealing temperature and, for a proper comparison, one needs to correct the shift data to a reference of zero stress. To achieve this, the obtained shift factors of the different annealing temperatures are first fitted using Equation (15). In the fitting procedure, the stagnation phase is neglected. By fitting the low stress data only, the activation volume for aging \( V^*_a \) can be determined. The difference between the activation volume related to deformation kinetics \( (V^*_d = 2.54 \text{ nm}^3) \) and that related to stress accelerated aging \( (V^*_a = 1.1 \text{ nm}^3) \) is striking. Similar differences have been observed in PC.\(^{[23]}\)

| Temperature \((T)\) | 23°C | 50°C | 70°C | 90°C |
|---------------------|------|------|------|------|
| \( \sigma_a \) (MPa) | 65   | 45   | 30   | 35   |
| \( \sigma_{a,\text{min}} \) (MPa) | 70 | 50 | 45 | 50 |
| \( \sigma_{a,\text{ref}} \) (MPa) | 75 | 55 | 45 | 50 |
| \( \sigma_{a,\text{ref}} \) (MPa) | 80 | 60 | 55 | 56 |
| \( \sigma_{a,\text{ref}} \) (MPa) | — | — | 60 | 58 |

**TABLE 5** Maximum applied stresses in cyclic loading case (sinusoidal wave, \( R = -1 \), and frequency \( f = 1 \) Hz) in MPa \( (\sigma_a) \) for different measurement temperatures \((T)\) corresponding to the markers in Figure 17 master curve.

**FIGURE 10** Ratio of the yield stress to temperature measured at different temperatures \((T)\) versus the annealing time \((t)\) under applied stress \((\sigma_a)\), and the master curve constructed by horizontally shifting the data according to time–stress superposition (TSS). Data are shifted first to the minimum applied stress \((\sigma_{a,\text{min}})\), followed by a shift to zero stress level. Markers represent experimental data; lines are descriptions using Equation (13) with parameters listed in Tables 2 and 3. Values of the applied stresses \((\sigma_a)\) are presented in Table 4 for each measurement temperature \( T \) [Color figure can be viewed at wileyonlinelibrary.com]
poly(vinyl chloride)\textsuperscript{20} and PSU\textsuperscript{29} In the view of Eyring, the activation volume represents the volume involved in the molecular events taking place. Following that reasoning, the differences could be rationalized by the fact that plastic deformation requires a cooperative segmental motion that will require a larger volume than in the case of aging, which is related to very local segmental motion that will require a larger volume than the fact that plastic deformation requires a cooperative multiplied by the slope of the Equation (10), as a result of the temperature change, can be combined to a single one at a reference temperature of 90°C. Here, it should be noted that a yield stress at a certain temperature can be translated directly to the full yield kinetics (strain rate and temperature dependence) for the thermodynamic state it represents. This is clarified in Figure 13a, where it is shown that a measured yield stress can be directly translated to the yield kinetics if the kinetics of the reference state are known (as in our case). As a result, each yield stress, measured at a certain strain rate and a certain temperature, can thus be translated to the corresponding yield stress values measured at an arbitrary rate and an arbitrary temperature using the Eyring flow kinetics.

In the present case, we use this method to translate the master curve data of all temperatures to 90°C, the reference temperature (all at the same strain rate of 10\textsuperscript{−3} s\textsuperscript{−1}). This can be done by applying a vertical correction \(\Delta \sigma_y \) that principally consists of the horizontal shift \(\ln(\sigma_y, T, ref)\), defined by Equation (10), as a result of the temperature change, multiplied by the slope of the \( \frac{\Delta \sigma_y}{T} \) ratio versus \(\ln(\dot{\varepsilon})\), or:

\[
\frac{\Delta \sigma_y}{T} = k \frac{\Delta U_d}{R V_d} \left( \frac{1}{T_{ref}} - \frac{1}{T} \right)
\]

where \(\Delta \sigma_y\) is the yield stress difference at two measurement temperatures: \(T\) and \(T_{ref}\), the reference temperature. The master curves, shifted to the reference temperature, are presented in Figure 12a, representing the yield stress evolution at various annealing temperatures \(T_a\), but all “measured” at \(T_{ref} = 90°C\). Next, the data for different annealing temperatures are shifted horizontally until the collapse and form a combined master curve for yield stress evolution at zero stress and a reference temperature of 90°C (as shown in Figure 12b). The corresponding temperature shift factors \(a_{T, ref}\) are plotted

\[
a_{\sigma,0}(\sigma, T) = \begin{cases} \frac{\sigma V_a}{kT} \sinh \left( \frac{\sigma V_a}{kT} \right) & \text{if } \sigma \leq \sigma_{stag} \\ \frac{\sigma_{stag} V_a}{kT} \sinh \left( \frac{\sigma_{stag} V_a}{kT} \right) & \text{if } \sigma > \sigma_{stag} \end{cases}
\]
versus the inverse temperature in the Arrhenius plot in Figure 13b. For comparison, shifts factors that were determined in temperature annealing case (as in Figure 8a) are plotted as well. Since the slope of lines is proportional to the activation energy of aging $\Delta U_a$, it can be concluded that the activation energy of aging can be assumed the same in the case of thermal treatments as well as thermomechanical treatments.

In order to determine the stagnation stresses ($\sigma_{stag}$) for other temperatures, stagnation stresses are plotted versus test temperature (see Figure 14). Stagnation stresses are shown to be linear with respect to temperature. Experimentally applied stresses during static thermomechanical protocol are both below and above stagnation level (as indicated by vertical bar). For a proper description of observed behavior in a constitutive framework, one needs to supplement the yield stress evolution with the correct values of the stagnation stress. In the scope of this work these stress levels for different temperatures can be determined experimentally and taken into account using Equation (16).

![Figure 12](wileyonlinelibrary.com) Data shifted to 0 MPa (as shown in the right part of Figure 10): (a) Shift to one reference temperature using $\Delta U_d$ according to Equation (17) and (b) master curve constructed by further horizontal shift [Color figure can be viewed at wileyonlinelibrary.com]

![Figure 13](wileyonlinelibrary.com) (a) Schematic illustration of the shift to the same reference temperature. (b) Arrhenius plot showing temperature shift factors both in the case of temperature annealing and combined effect of applied stress and temperature. Lines are fit using Equation (10) [Color figure can be viewed at wileyonlinelibrary.com]

![Figure 14](wileyonlinelibrary.com) Stagnation stresses under static applied load. Lines are a guide to the eye. Vertical bars indicate the range of experimentally applied stresses under static conditions [Color figure can be viewed at wileyonlinelibrary.com]

### 3.5 Role of strain hardening in yield stress evolution

The master curve obtained using thermal treatments without application of stress (Figure 7) will solely be
governed by temperature-activated aging. The master curve based on thermomechanical treatments, including application of stress (Figure 10), may also contain a contribution of strain hardening. The contribution of the latter can be verified by a direct comparison of both master curves at $T_{\text{ref}} = 90^\circ C$, which is presented in Figure 15. From this figure, it is very clear that the two master curves are not identical; the thermomechanical treatment evidently shows a stronger evolution of yield stress with time than the thermal treatment. The master curve obtained from thermomechanical treatments is also fitted using Equation (13) to determine the parameters describing yield stress evolution under both temperature and applied stress.

To demonstrate it more clearly, Equation (13) can be simplified by using that $\sinh^{-1}(x) \approx \ln(2x)$ for $x \gg 1$:

$$\sigma_y(t, \dot{\varepsilon}, T) = \frac{kT}{V_d} \ln \left( \frac{2\dot{\varepsilon}}{\dot{\varepsilon}_{0,\text{ref}}} \exp \left( \frac{\Delta U_d}{RT} \right) \right) + \frac{kTc_1}{V_d} \ln \left( \frac{t_{\text{eff}} + t_a}{t_0} \right)$$

(18)

$$= \sigma_{y,0}(\dot{\varepsilon}, T) + c \ln \left( \frac{t_{\text{eff}} + t_a}{t_0} \right)$$

(19)

Since the slope $c_1$ increases under applied stress form $c_1 = 1.01$ to $c_1 = 1.54$, it can be interpreted that there is an additional contribution that affects the yield stress evolution and results to an even further apparent increase in the yield stress at given conditions.

In the work of Klompen et al.,[23] where a similar comparison was made for glassy PC, such a difference was not observed. The deformations, observed during the thermomechanical treatment of PC, were at most 2–3%; apparently too small contribute significantly to yield stress evolution. In the case of PEEK, larger deformations were observed at the highest testing temperatures and loads, to a maximum of approximately 10%. This, and the fact that strain hardening may be more pronounced in a semicrystalline material like PEEK as a result of texture hardening, reorientation of the crystalline lamellae during deformation.[69] This can be visualized by studying the intrinsic
stress–strain response of PEEK in uniaxial compression, a loading geometry that inhibits strain localisation.\[^{[70]}\] To investigate the possible contribution of strain hardening to yield stress evolution, the thermomechanical treatments were also performed in compression (following above mentioned thermomechanical protocol as shown in Figure 2). Results of the compression tests, performed to determine the influence of the initial creep period, are presented in Figure 16. In Figure 16a, the compressive stress–strain curves after 30 hr of creep at 70°C and different stress levels are presented. At this temperature, the effect of physical aging is relatively small and it is clear that the increase in the apparent yield stress of the material is mainly due to strain hardening. It is also evident that the strain hardening is already quite strong at low strain levels; this is not uncommon in semicrystalline materials and is related to texture hardening.\[^{[69]}\]

In Figure 16b, results are presented for a preload of 45 MPa at 110°C for different times under load. At 110°C, the increase in strain softening unmistakably indicates that the effect of physical aging is much more pronounced, especially at longer loading times. To further elucidate, Figure 16c compares the compressive stress–strain curve, at 110°C, for the as-received material to that of a sample loaded with 45 MPa for 30 hr. The insert gives a detail zoom of the curves to specify: (a) the contribution of strain hardening, defined as the difference between the original yield stress (dotted line) and the stress level of the as-received stress–strain curve at the yield strain of the preloaded sample, and (b) the contribution of physical aging, being the difference between the yield stress after the thermomechanical treatment and the stress level of the as-received stress–strain curve at the yield strain of the preloaded sample. Unquestionably, Figure 16c illustrates convincingly that, in the case of PEEK, both physical aging, as well as strain hardening, contribute considerably to yield stress evolution.

### 3.6 Thermomechanical treatments: Stress activation in cyclic loading

Since load-bearing polymer products are usually subjected to loading histories with a strong cyclic component,\[^{[31]}\] we will also investigate the evolution of yield stress in cyclic fatigue. A cyclic load is typically expressed by three parameters: its maximum load, \( R = \frac{\sigma_{\text{max}}}{\sigma} \), and the frequency \( f \). Cyclic loading is known to affect both plasticity-controlled failure as well as aging kinetics. With respect to failure kinetics, it is observed that the time-to-failure under a cyclic load shifts toward longer loading times when compared to static loading at the same maximum stress (see Figure 1b), since the rate of accumulation of plastic deformation is lower than the one under a static load because of the oscillating nature of the load.\[^{[20,42]}\] Another important feature is that, in the plasticity-controlled region, the time-to-failure under cyclic load is typically frequency independent (under isothermal conditions).\[^{[31]}\] Moreover, the stress-activation acceleration of aging (\( \alpha_a \)) will be affected as a result of the cyclic variation of stress. If it is assumed that the acceleration is determined by the momentary value of the stress, the stress shift will also display a cyclic variation in time. This can be dealt with easily by defining an average stress shift per cycle\[^{[20]}\], which can be numerically determined by solving Equation (11) over a cycle and dividing it by the cycle time \( t_{\text{cycle}} \), or:

\[
\frac{1}{\alpha_{\sigma,\text{cyclic}}} = \frac{t_{\text{eff}}}{t_{\text{cycle}}} = \frac{1}{t_{\text{cycle}}} \int_0^{t_{\text{cycle}}} \frac{1}{\alpha_{\sigma}(\sigma(t), T)} \, dt
\]

With this approach, the stress activation during cyclic loading can be directly determined from the parameters for stress activation determined in static loading. Comparable to deformation kinetics, stress activation of the yield stress evolution (under the same maximum applied stress) is delayed under cyclic loading case due to the oscillating nature of the load and likewise frequency independent. Similar to the static loading case, the thermomechanical treatments were repeated for a cyclic loading case \( f = 1 \text{ Hz}, R = .1 \) at four measurement temperatures \( T = 23, 50, 70, \text{ and } 90^\circ\text{C} \) with maximum applied stresses according to Table 5. The data collected for the various maximum stresses were shifted to the data of the minimum \( \sigma_{\text{cyclic}} \) to form master curves for each testing temperature, presented in Figure 17. To shift the corresponding shift factors to zero reference stress, the shift factor for the reference stress was calculated by integrating Equation (11) per cycle according to Equation (20) assuming a constant activation volume of aging \( V_a^* = 1.1 \text{ nm}^3 \) both in static and cyclic loading conditions. The shift factors, corrected for zero reference stress, are shown in Figure 18a for the four test temperatures. Surprisingly, and in contrast to the observations in the static loading case (see Figure 11), there is no observable stagnation of the stress activation found for cyclic loading within the stress range experimentally applied. For instance, at \( T_{\text{ref}} = 90^\circ\text{C} \), for the highest cyclic applied stresses of 58 MPa, apparent yield stress keeps increasing, while at a static loading at a level of 45 MPa stagnation is observed. When the yield stress evolution under cyclic load is plotted together with the static case (as shown in Figure 18b), one can observe that both follow the same relation. The difference being only that the apparent absence of the stagnation of the yield stress evolution.
3.7 Lifetime predictions and endurance limit estimation

In the preceding sections, we have unambiguously established that both temperature and stress have a pronounced influence on the evolution of the yield stress. What remains is to establish that this evolution is responsible for the occurrence of the apparent endurance limit and that it can be quantitatively captured by it. To do so, the deformation kinetics and related times-to-failure are determined here over a range of temperatures for the injection molded samples used to study the evolution of yield stress, see Figure 19. The time-to-failure data clearly show the appearance of what is typically described as an endurance limit and the concept of critical strain will be used to predict the plasticity dominated time-to-failure as was explained and demonstrated in the first results section (see Equation (4) and Figure 4b).

To determine the respective values for the critical strain $\epsilon_{cr}$ at various temperatures investigated for the injection molded samples used here, the plateau creep rates during secondary creep as determined by Sherby–Dorn plots are evaluated as a function of the time-to-failure on double logarithmic axes (see Figure 19a,b). All curves in Figure 19a demonstrate a strict power-law behavior with a slope $-1$, indicating that each curve is well described by a single value of critical strain, irrespective of the occurrence of progressive aging. It should be noted that we observe a considerable variation in the critical strain as a function of temperature; similar observations were made on other semicrystalline polymers like PE. Hence, to improve the lifetime predictions, the critical strain has been optimized for each temperature. This allows the description of the time-to-failure under static load including the evolution of the thermodynamic state by effectively integrating Equation (12) where the plastic strain rate evolves as a result of temperature and stress induced progressive aging until the critical strain is reached (see solid drawn lines in Figure 19d):

$$\epsilon_{pl}(t) = \int_{0}^{t} \dot{\epsilon}_{pl}(\sigma, T, t_{eff}) dt \quad \text{with failure once} \quad \epsilon_{pl} = \epsilon_{cr}(T)$$

(21)

where $\epsilon_{pl}$ is the accumulated plastic strain, $\dot{\epsilon}_{pl}$ is the plastic flow rate depending on the thermomechanical history according to Equation (12), and $\epsilon_{cr}(T)$ is the critical plastic strain (at a given temperature as determined from Figure 19a) corresponding to failure. It is shown that the resulting description captures the experimental data well.

The same approach and parameters are now also used to describe the evolution of properties and predict the resulting time-to-failure for samples that are cyclically loaded. Note that under cyclic load with $R = .1$, a stagnation of yield stress evolution was not observed and the yield stress can evolve further. The resulting predictions are shown in Figure 20, and as might be expected the
critical strains established for static load also provide a good prediction for the failure under cyclic load, resulting in an accurate prediction of the apparent endurance (fatigue) limit level under cyclic loading conditions as well.

The apparent endurance limit, resulting from progressive aging, is demonstrated to be predicted well under both static and dynamic loading condition, when the evolution of the yield stress is properly accounted for and it can be safely stated that it is not an intrinsic material property. Knowing that progressive aging is at the core of the phenomenon and that the evolution of the yield stress depends both on the evolution of the yield stress over time, as well as on the initial level of the yield stress as it results from the molding process, warrants investigation of the influence of the shape of the loading signal and the initial state of the material on the level of the apparent endurance limit. These effects are studied using compression molded samples, molded with a similar mold temperature as the injection molded samples, that is, \( T = 175^\circ C \). It is first demonstrated in Figure 21 that the temperature- and stress-dependent evolution of the yield stress of these samples is equivalent to that observed in injection molded samples. Next, samples that were IC at \( T = 175^\circ C \) are used to predict the apparent endurance limit as it evolves under different load signals resulting in a change in the stress activation (Equation (20)). Triangular, sinusoidal, and square signal (at \( R = .1 \) and two test frequencies \( f = 1 \) and \( 0.1 \) Hz) are evaluated and the results are shown in Figure 22a, and the apparent fatigue limit is shown to be noticeably affected by the shape of the load signal since both the stress activation (\( a_{\sigma} \)) and the rate of the accumulation of plastic deformation are loading history dependent. Prediction and experiment are again shown to be in good agreement.

Finally, the influence of initial state of the material on the level of the apparent endurance limit is demonstrated by showing the materials with two markedly different initial states as obtained by isothermal crystallization (IC at \( 175^\circ C \)) and SC, resulting in different values for the reference rate constant \( \dot{\varepsilon}_{0,AR} \) (see Figure 22b). The resulting level of the apparent endurance limit is shown to be significantly impacted by this change in initial yield stress level.

It is unequivocally demonstrated that the endurance limit reported in literature is not to be regarded as an intrinsic material parameter, but rather a result of processing, use and characterization induced evolution of the thermodynamic state of the amorphous phase of the material and concurrent texture development of the crystalline phase, that is, progressive aging. Therefore, the phenomenon is more correctly termed an apparent endurance limit that can be well predicted by the presented framework based on established models.

### 3.8 Characterization procedure

To facilitate the broader use of the framework developed and explored in this study a characterization procedure describing all necessary steps to determine the required model parameters is provided in the following summary:

- tensile tests performed at different strain rates for different temperatures allow determination of the parameter capturing the deformation kinetics: \( V_d, \Delta U_d, \) and \( \dot{\varepsilon}_{0,AR} \). Note: longer tests at higher temperature are to be excluded because of the progressive aging.
performing thermomechanical tests at one strain rate at different temperatures (for different annealing times $t_a$ and different applied stresses $\sigma_a$), and using TSS to shift the stress-annealing curves first to the minimum applied stress, and subsequently to zero stress, provides the shift factors used to construct the master curve, that are captured with an Eyring-type stress shift (Equation (11), providing the value of the activation volume of aging $V^*_a$); the master curves shifted to zero stress at different temperatures are then fitted with Equation (13), and the yield stress evolution parameters are determined ($c_1^*$, and $t_a(T)$); by shifting the data to one reference temperature using Equation (17) vertically, and then horizontally to construct one master curve, allows one to determine the value of activation energy ($\Delta U_a$) by employing Equation (10);
plotting the plateau creep rate versus the time-to-failure of static load experiments is used to determine the temperature-dependent critical strain ($\varepsilon_{cr}(T)$); Equation (21) with the thus obtained parameters describing the deformation kinetics, yield stress evolution of the plastic flow together with the values of critical strain finally allow to predict the apparent endurance limit both under static and cyclic load.

The presented characterization and modeling approach is shown to predict the apparent endurance limit in PEEK under both cyclic and static load. It is expected that the framework can be used broadly as a first approach to study similar phenomena in other semi-crystalline polymers.

FIGURE 22 Compression molded poly(ether ether ketone) (PEEK): (a) Comparison of the time-to-failure at $T = 70^\circ C$ for a static and cyclic preloads with different shapes of the loading signal (triangular, square, and sinusoidal). Load ratio $R = .1$ and $f = 1$ and 0.1 Hz. Markers are experimental data; lines are fit using Equation (21) with parameters listed in Tables 3 and 6. Shift factors and effective time are calculated by using Equation (9). (b) Effect of processing conditions on the endurance limit (IC is isothermally crystallized at $175^\circ C$ and SC is slow cooled). Lines are a guide to the eye [Color figure can be viewed at wileyonlinelibrary.com]

4 | CONCLUSIONS

Temperature and applied stress induced structural changes in PEEK polymer and are shown to accelerate physical aging and promote texture development of the crystalline phase. Extensive experimental work has been done to study the yield stress evolution under the combined effect of applied stress and temperature. Acceleration of the yield stress evolution by temperature was described using time–temperature superposition that follows an Arrhenius type relation. Stress activation was described by introducing an Eyring type shift factor and employing TSS. Under static load, the activation by stress shows a stagnation limit, while under a cyclic load with $R = .1$ stresses required for stagnation were not reached. This information was combined with the Eyring equation to describe the time-dependent plastic flow. Together with the critical strain concept, it allows the description of the time-to-failure both under static and cycle load. As a result of the yield stress evolution, the failure in the plasticity-controlled region is markedly delayed and manifests itself in an apparent endurance limit. This limit is, therefore, not a material property but depends on temperature, processing conditions, and loading history and is not a reliable design parameter: apparent flattening of the stress–lifetime curve under cyclic load does not mean that failure is avoided.

ACKNOWLEDGMENTS

This work is part of the Research Program of the Dutch Polymer Institute DPI, Eindhoven, the Netherlands, project number #786t. The authors would like to thank Solvay for providing material for this research. The authors would also like to thank Janneke Govers, Job Dickens, and Mike van Zwieten for their efforts and contributions within the experimental work.

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