



Experimental characterization of the thermoviscoelastic response of PA 6 under UV exposure

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ABSTRACT

In engineering applications, the mechanical performance of polymers can be significantly influenced by environmental factors such as heat, moisture, and ultraviolet (UV) radiation. Although UV exposure is generally associated with material degradation, some studies report non-monotonic changes in mechanical properties during early stages of aging. In this work, moisture-equilibrated polyamide 6 (PA 6) is subjected to controlled short-term and long-term UV exposure and characterized by gel permeation chromatography (GPC), differential scanning calorimetry (DSC), and dynamic mechanical analysis (DMA). The combined experimental approach provides complementary information on molecular, thermal, and thermoviscoelastic material changes induced by UV exposure. Short-term UV exposure results in a pronounced increase in storage modulus, while spatially unresolved GPC analysis of material spanning the entire sample thickness reveals only minor changes in number- and weight-average molar mass. DSC likewise indicates only minor changes in crystallinity. With increasing exposure time, spatially unresolved GPC analysis reveals a progressive reduction in molar mass, accompanied by a decrease in stiffness and changes in the thermoviscoelastic response. Temperature-frequency sweeps and master curve construction based on extended time-temperature superposition indicate that UV exposure affects the effective relaxation behavior within the investigated temperature-frequency range. The findings provide experimental insight into the evolution of UV-induced aging effects in PA 6 and may support future efforts in modeling long-term thermoviscoelastic material behavior.

1. Introduction

Polymers are widely used in engineering applications, from load-bearing structural components [1] to less critical parts in machinery or consumer products. Their mechanical performance can, however, be significantly affected by environmental factors such as heat, moisture, and ultraviolet (UV) radiation. While all of these factors may influence the material behavior, they differ in their physical roles. UV radiation is typically associated with degradation processes that alter the material itself. Temperature and moisture may also influence the material state directly while additionally representing environmental conditions under which the material response is observed and characterized. Early studies on photodegradation mechanisms, such as those by Bolland and Gee [2], established the role of radical autoxidation in oxidative polymer degradation. An extensive overview of photodegradation effects across different polymer classes is given by Fox [3]. Subsequent investigations demonstrated that UV irradiation can promote molecular-level degradation reactions, including chain scission processes and associated chemical modifications [4,5], which were linked to macroscopic deterioration such as embrittlement and loss of ductility [6,7]. Environmental

aging involves processes acting at different structural levels, ranging from molecular changes to the macroscopic mechanical response [8,9]. In practice, degradation rates and severities are often accelerated by combined environmental actions, e.g., temperature, oxygen, humidity, and radiation [10,11].

A common conceptual distinction in the literature separates reversible physical aging from irreversible chemical aging [12]. Physical aging is typically associated with molecular rearrangements without a change in chemical structure, whereas chemical aging is characterized by irreversible changes of the polymer's chemical constitution [13,14]. While both types of aging may occur simultaneously, the distinction is useful for interpreting time-dependent property changes and separating mobility-driven effects from chemically driven degradation as reported by Jöhlitz [14]. For chemically aging systems, modeling approaches based on internal variables have been proposed to represent the evolution of long-term degradation and network-related effects in a thermodynamically consistent framework [13].

In contrast to the common expectation that UV exposure necessarily leads to a consistent deterioration of mechanical performance,

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some studies report non-monotonic changes in mechanical properties during the initial stages of environmental exposure [15–17]. In semicrystalline polymers, short-term exposure has been associated with changes in tensile properties, which have been discussed in the context of structural reorganization and morphology-related effects prior to long-term degradation. For PA 6-based nanocomposites in particular, Dulebová et al. [18] reported an increase in tensile strength after UV aging, accompanied by a reduction in impact strength, indicating a tendency towards both strengthening and embrittlement. Similarly, Li et al. [10] observed changes in the tensile and creep behavior of PA 6 under combined UV exposure and mechanical loading, with higher tensile strength and reduced creep strain reported at the early stages of exposure.

These initial strengthening effects are generally temporary. As UV exposure increases, degradation processes accumulate, leading to an overall deterioration of mechanical properties [19,20]. Becerra and d'Almeida [15] identified a threshold UV dose in polyethylene below which stiffening effects dominated and above which pronounced property degradation occurred. Due to the limited penetration depth of UV radiation [21], chemical modifications induced by photo-oxidative degradation, including changes in molecular weight and the formation of oxygen-containing functional groups, are predominantly surface-localized and contribute to macroscopic deterioration [5,22]. Correspondingly, surface-sensitive observations emphasize gradients of degradation from the surface into the bulk, while prolonged thermal or oxidative exposure can lead to bulk degradation affecting the structural performance [8]. As a result, accumulated degradation processes acting across different length scales lead to a progressive deterioration of mechanical performance, including reduced ductility, tensile strength, stiffness, toughness, and fatigue resistance [19,20,23,24]. In the present work, such degradation gradients are not resolved on a spatial scale. Instead, the experimental analysis focuses on the overall structural response obtained from spatially unresolved measurements, i.e., measurements providing integral responses without spatial resolution. Within this framework, the structural scales and degradation mechanisms discussed in the literature serve as a conceptual basis for interpreting the observed effective responses rather than as individually resolved material states. UV-induced degradation of polymers can be regarded as a multiscale phenomenon. Photooxidative processes may initiate molecular-scale changes such as chain scission or chemical modifications [25], which can subsequently influence morphological features and moisture-dependent material behavior [26]. Because UV-induced degradation is often localized near the exposed surface, degradation gradients and surface-related damage mechanisms may develop [27]. The cumulative effect of these processes ultimately manifests itself in macroscopic property changes such as altered stiffness, damping behavior, strength, or fatigue performance [28].

While such degradation phenomena are often discussed separately at individual structural scales, recent studies have demonstrated that combining complementary experimental techniques such as dynamic mechanical analysis and differential scanning calorimetry can provide valuable insight into the coupling between microstructural changes and mechanical response in polyamides under hygro-thermal histories, cf. [29], even when spatially unresolved characterization techniques are employed.

Originality. Previous studies have examined UV-induced changes in mechanical, thermal, and molecular properties. However, combining insights from complementary experimental methods remains difficult in practice. In particular, it is still challenging to relate changes in molar-mass characteristics and thermal behavior, including overall crystallinity, to the macroscopic thermoviscoelastic response.

This work combines dynamic mechanical analysis (DMA), gel permeation chromatography (GPC), and differential scanning calorimetry (DSC) to comparatively assess molecular, thermal, and thermoviscoelastic responses of moisture-equilibrated PA 6 under UV exposure.

The combined experimental approach enables a qualitative comparison of trends across complementary characterization techniques, particularly with respect to the transition from initial stiffening to long-term changes in the relaxation behavior. In addition, master curves based on the time-temperature superposition (TTS) provide a framework for discussing the evolution of the effective thermoviscoelastic response within the investigated temperature-frequency range.

Outline. Section 2 describes the investigated material, conditioning and UV exposure, sample preparation, and experimental procedures. Section 3 summarizes the analytical framework for time-temperature superposition. Section 4 presents and discusses the results starting from molecular changes (GPC), followed by thermal response and overall crystallinity (DSC), and finally the macroscopic viscoelastic response (DMA and TTS), interpreted in terms of effective macroscopic responses under surface-dominated UV aging. Section 5 provides a brief summary and conclusions.

2. Experimental setup

2.1. Sample preparation

This study uses rectangular samples with dimensions of $80 \times 10 \times 2 \text{ mm}^3$. The samples were water-jet cut at the Institute of Engineering Mechanics, Karlsruhe Institute of Technology (KIT), from injection-molded plates manufactured at the Fraunhofer Institute for Chemical Technology ICT, Pfaffzettel, Germany, and were conditioned in a standard atmosphere (ATM-23/50), cf. [30], which is relevant for industrial applications that require specific levels of water absorption. All experimental results and interpretations presented in the following are restricted to this specific sample geometry and thickness. According to ISO 291 [30], ATM-23/50 corresponds to a temperature of 23°C and a relative humidity (RH) of 50%, resulting in terms of PA 6 to an equilibrium moisture content between 2.5 and 3.0 wt%. For PA 6, achieving this moisture equilibrium may require extended conditioning times of up to one year for a sample with a thickness of 2 mm [31]. In this study, the samples were stored in a climatic chamber (Mettmert ICH110 L) under ATM-23/50 conditions for at least one year to ensure equilibrium. Additional details are provided in [32,33].

After reaching the moisture equilibrium level, the samples were exposed to additional UV radiation under the same ATM-23/50 conditions. The UV exposure was conducted in the Mettmert ICH110 climate chamber equipped with a Havelis Sylvania F30W/T8/BL368 fluorescent lamp. This lamp predominantly emits UVA radiation, peaking at a wavelength of 365 nm, with an average UVA irradiance of $79.1 \mu\text{W}/\text{cm}^2$ (315–400 nm) at a distance of 1 m from the bare lamp. The UVB component (280–315 nm) was $0.11 \mu\text{W}/\text{cm}^2$ under the same conditions. The distance between the lamp and sample surfaces was approximately 20 cm. The exposure conditions were a black panel temperature of 23°C , a relative humidity of 50%, and total exposure times of 30 d and about 5 months, corresponding to total UVA doses of approximately $51 \text{ MJ}/\text{m}^2$ and $256 \text{ MJ}/\text{m}^2$, respectively. The applied UV doses correspond roughly to several months up to about one year of natural outdoor UV exposure, depending on geographic location and environmental conditions [34].

2.2. Gel permeation chromatography (GPC)

Gel permeation chromatography (GPC), also known as size exclusion chromatography (SEC), was used to determine the molar mass distribution of the investigated PA 6 samples. The characteristic quantities evaluated comprise the number-average molar mass M_n , the weight-average molar mass M_w , and the dispersity $\text{Đ} = M_w/M_n$ [35, 36].

In this study, GPC analysis was used to assess UV-induced changes in the molar mass characteristics of PA 6. GPC measurements were

performed on dissolved material and therefore reflect integral molar-mass characteristics without spatial resolution. Approximately 8 mg test portions were cut to the required mass by reducing their in-plane dimensions, while the original sample thickness of approximately 2 mm was retained. Consequently, the analyzed material extended across the entire sample thickness, but the measurements were not position-resolved in the thickness direction.

The SEC used is from the PSS Agilent 1260 Infinity II series, with an HPLC pump. The SEC is equipped with an RI detector (Knauer RI230). A guard column is used and the measurement columns (100, 300, 1000 Å PSS PFG 7 µm) were calibrated using monodisperse linear PMMA standards with peak molar masses between 102 and 981 000 g/mol. Hexafluoroisopropanol (HFIP) was used as the eluent with a flow rate of 1 mL/min at 25 °C. To start the measurement, 100 µL of the sample solution with a concentration of 1 mg/mL was injected onto the columns, using an autosampler.

2.3. Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) is a thermal analysis technique commonly used to investigate the thermal transitions and properties of polymeric materials. DSC analysis was performed using a Mettler Toledo DSC 1. The DSC samples were cut by reducing the lateral dimensions of the rectangular samples while retaining the sample thickness of 2 mm. Thus, the DSC measurements include both surface-near and inner regions and provide a mass-normalized integral thermal response across the sample thickness without resolving possible surface-to-core gradients. Measurements were carried out using PA 6 sample masses ranging from 4.838 to 9.978 mg [37]. The temperature ranged from -80 °C to 250 °C using a heating and cooling rate of 10 K/min to determine changes in thermal behavior associated with UV exposure. The heat-flow signals were normalized by the respective sample mass and are presented in W/g.

The degree of crystallinity was evaluated according to [38,39]

$$\chi_c = \frac{\Delta H_m}{\Delta H_m^0} 100\%, \quad (1)$$

where ΔH_m denotes the measured melting enthalpy and ΔH_m^0 represents the melting enthalpy of a fully crystalline PA 6 reference. Here, a value of $\Delta H_m^0 = 230 \text{ J g}^{-1}$ is adopted from the literature [40, p. 15].

2.4. Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis (DMA) is a common method for evaluating the thermoviscoelastic behavior of materials. In this study, measurements were performed using a GABO Eplexor® 500N DMA device in tension mode. The storage modulus E' , loss modulus E'' , and loss factor $\tan \delta$ were evaluated from the phase-shifted stress-strain response under harmonic loading [41]

$$E' = \frac{\Delta \sigma}{\Delta \epsilon} \cos(\delta), \quad E'' = \frac{\Delta \sigma}{\Delta \epsilon} \sin(\delta), \quad \tan \delta = \frac{E''}{E'}. \quad (2)$$

Here, the quantities $\Delta \sigma$, $\Delta \epsilon$, and δ denote the stress amplitude, the strain amplitude, and the phase shift, respectively.

The test parameters used within this work for the DMA measurements in tension mode are summarized in Table 1. The selected temperature range covers the glassy regime, the glass transition region, and the rubbery regime of moisture-equilibrated PA 6 while remaining below temperatures at which significant thermal degradation is expected. During each frequency sweep, the temperature was held constant. Between consecutive measurement temperatures, separated by 5 K, the temperature was increased at a rate of 1 K/min.

Table 1

DMA test parameters for time and temperature-frequency sweeps of PA 6.

Test parameter	Time sweep	Temperature-frequency sweep
Static strain	$\epsilon_0 = 0.1\%$	$\epsilon_0 = 0.1\%$
Dynamic strain	$\Delta \epsilon = 0.05\%$	$\Delta \epsilon = 0.05\%$
Frequency	$f = 5 \text{ Hz}$	$f \in [0.5, 50] \text{ Hz}$
Temperature	$\theta = 23 \text{ °C}$	$\theta \in [-100, 150] \text{ °C}$

3. Thermoviscoelasticity – fundamentals

3.1. Time-temperature superposition (TTS)

When considering linear viscoelastic material behavior, the current stress can be computed from the strain history via the Boltzmann superposition integral

$$\sigma(t) = \int_0^t R(t-s) \dot{\epsilon}(s) ds, \quad (3)$$

with the relaxation modulus $R(t)$. This equation holds for temperature-independent processes. For temperature-dependent problems of thermorheologically simple materials, the validity of the time-temperature superposition (TTS) is often assumed, giving

$$\sigma(t) = \int_0^t R(z(t) - z(s)) \dot{\epsilon}(s) ds, \quad (4)$$

$$z(t) = \int_0^t \frac{dw}{a_\theta(\theta(w))}, \quad (5)$$

$$z(s) = \int_0^s \frac{dw}{a_\theta(\theta(w))}. \quad (6)$$

If we consider a fixed temperature θ , the integral simplifies to

$$\sigma(t) = \int_0^t R\left(\frac{t-s}{a_\theta(\theta)}\right) \dot{\epsilon}(s) ds. \quad (7)$$

This means that relaxation effects occur on a reduced time scale t/a_θ depending on the temperature. For isothermal problems, the following relation holds for the relaxation modulus

$$R(t, \theta) = R(t/a_\theta, \theta_{\text{ref}}) = R(10^{(\log t - \log a_\theta)}, \theta_{\text{ref}}). \quad (8)$$

A change in temperature leads to a shift of the relaxation modulus alongside the logarithmic time axis with respect to the relaxation modulus given at a reference temperature θ_{ref} . Thus, a_θ is called (horizontal) shift function. Taking into account that the frequency has the dimension of an inverse time, a similar relation holds for storage and loss modulus,

$$E^{(\cdot)}(f, \theta) = E^{(\cdot)}(f a_\theta, \theta_{\text{ref}}) = E^{(\cdot)}(10^{\log f + \log a_\theta}, \theta_{\text{ref}}). \quad (9)$$

In this case, the reduced frequency is given by $f a_\theta$. The advantage of TTS is that experiments at different temperatures and for limited time (or frequency) ranges, by shifting, can be combined to master curves with broader time (or frequency) ranges. For a more detailed discussion of TTS, see, e.g., [42,43].

3.2. Extended time-temperature superposition

In some cases, TTS is not sufficient to model temperature-dependent viscoelastic behavior of a polymer [44]. However, applying additional vertical shifts alongside the logarithmic modulus axis can be a valid extension of TTS, see [32,45] for PA 6. Then, the following relation holds for storage and loss modulus

$$E^{(\cdot)}(f, \theta) = b_\theta E^{(\cdot)}(f a_\theta, \theta_{\text{ref}}), \quad (10)$$

$$\log E^{(\cdot)}(f, \theta) = \log b_\theta + \log E^{(\cdot)}(10^{\log f + \log a_\theta}, \theta_{\text{ref}}). \quad (11)$$

The temperature-dependent vertical shift function is denoted by b_θ .

The horizontal shift factor a_θ describes changes in the characteristic frequency scale, whereas the vertical shift factor b_θ is introduced as

an empirical factor to compensate for residual temperature-dependent offsets in the modulus level after horizontal shifting. It provides a phenomenological representation of combined temperature-dependent effects that are not captured by a_θ and is not assigned to a distinct physical mechanism. Since a common multiplicative change in the storage and loss moduli cancels in their ratio, see Eq. (2), the vertical shift does not affect the loss factor.

Accordingly, the extended TTS procedure described in [32,45] is applied to the temperature-frequency sweeps considered in this work. The horizontal and vertical shift factors are determined sequentially from the loss factor and the storage modulus, respectively. First, a_θ is determined from the loss factor to align the characteristic frequency ranges. Subsequently, b_θ is determined from the storage modulus to compensate for the residual offsets in the modulus level. Both shift factors are computed using an arc length minimization method.

4. Results

4.1. Gel permeation chromatography (GPC) of PA 6 samples

Fig. 1 illustrates the molar mass characteristics of PA 6 before and after artificial UV exposure, as obtained from GPC analysis. Fig. 1(a) shows the molar mass distributions $w(\log M)$ for the different exposure conditions. Fig. 1 (b–d) present the number-average molar mass M_n , the weight-average molar mass M_w , and the dispersity $\mathcal{D} = M_w/M_n$. Individual measurements are shown as symbols, and the horizontal lines indicate the group median for each exposure condition.

As shown in Fig. 1(a), the normalized distributions reveal a slight shift towards lower molar masses with increasing UV exposure time. This trend is reflected in the characteristic molar mass parameters shown in Fig. 1(b) and (c). Compared to the UV-unexposed samples, the number-average molar mass M_n decreases by approximately 5%–15% after short-term UV exposure and by about 10%–18% after prolonged exposure. The weight-average molar mass M_w shows a similar but less pronounced decrease of about 3%–7% for short-term exposure and 7%–12% for long-term exposure. The stronger decrease in M_n compared to M_w , in combination with the moderate increase in $\mathcal{D}$ observed in Fig. 1(d), indicates the formation of low-molecular-weight fragments. Such a trend is typically associated with chain scission processes that occur during UV-induced degradation.

Although a progressive decrease in both M_n and M_w is observed with increasing UV exposure time, the absolute reductions remain considerably smaller than the corresponding changes observed in the macroscopic thermoviscoelastic response. Mild cross-linking cannot be completely excluded based on the present data. However, since all investigated samples remained fully soluble during GPC sample preparation and analysis, the absence of insoluble fractions suggests that network formation most likely did not occur. Furthermore, the measured molar mass distributions do not exhibit pronounced high-molecular-weight tails or additional peaks that would indicate network formation. Instead, the distributions shift gradually towards lower molar masses with increasing UV exposure time.

4.2. Differential scanning calorimetry (DSC) of PA 6 samples

Figs. 2 to 4 present the results from DSC of PA 6 samples. DSC thermograms were recorded at a heating and cooling rate of 10 K/min. The curves show the specific heat flow as a function of temperature. Each graph displays three thermal cycles: first heating (red curve), cooling (blue curve), and second heating (green curve). The melting and crystallization enthalpy, ΔH_m and ΔH_c , respectively, were obtained by baseline correction followed by integration of the corresponding peaks in the DSC thermograms.

The melting and crystallization peaks are clearly observable for all samples under consideration. The thermograms of the first heating exhibit variations in the melting peak shape with UV exposure, whereas

the normalized melting enthalpy ΔH_m remains within a comparable range for all exposure conditions (Figs. 2–4). The peak shape variations reflect differences in the distribution of melting transitions and may indicate changes in the organization of the crystalline domains. However, DSC does not resolve the underlying crystalline or lamellar morphology, and the origin of these variations therefore cannot be identified from the present measurements. The mean values for the melting enthalpies during the second heating also remain within a comparable range across the investigated exposure conditions (63.3 to 65.6 J/g). Accordingly, the repeated measurements do not indicate a systematic exposure time dependence of the difference between the first and second heating cycles. The first heating reflects the thermal response influenced by the crystalline structure established during processing and conditioning and potentially modified during subsequent UV exposure, whereas the second heating reflects the crystalline structure formed during the preceding controlled cooling step after the initial thermal history has been largely erased. This observation describes the thermal response of the pre-existing and subsequently recrystallized states but does not provide direct information on their crystalline morphology. Additional information on repeated DSC measurements, including the corresponding mean values and standard deviations of the characteristic thermal quantities, is provided in Appendix B and Table B.3.

With respect to crystallization upon cooling, the DSC thermograms indicate that crystallization remains clearly observable for all investigated exposure conditions. While individual measurements show slight variations in the magnitude of the crystallization enthalpy ΔH_c , the repeated DSC measurements summarized in Appendix B and Table B.3 indicate that these variations remain comparatively small. Thus, UV exposure does not suppress crystallization upon cooling within the investigated exposure range. The degree of crystallinity, based on DSC data, shows only limited variation with UV exposure. Considering the repeated measurements, the mean melting enthalpy during the first heating cycle remained between 70.8 and 72.4 J/g, while the mean degree of crystallinity ranged from 30.8 to 31.5%. These comparatively narrow ranges are consistent with the scatter observed across the repeated measurements in Table B.3. Hence, the DSC results do not indicate pronounced changes in the overall crystalline fraction of PA 6 due to UV exposure.

In addition to the melting and crystallization enthalpies discussed above, Table 2 summarizes the melting temperature θ_m and degree of crystallinity χ_c obtained from the first heating cycle, together with the crystallization temperature θ_c obtained during cooling. Both characteristic temperatures remain nearly unchanged with increasing UV exposure time.

While the glass transition temperature can in principle be estimated from DSC measurements, its determination is comparatively sensitive to the evaluation procedure because the associated baseline change is weak and broad for the material under consideration. Since DMA provides substantially higher sensitivity to segmental mobility and glass-transition-related phenomena, this work primarily discusses glass transition effects based on the DMA results presented in Section 4.3.

To summarize, according to the DSC results, UV aging affects the thermal response of PA 6 without causing pronounced changes in the characteristic thermal transition temperatures or the degree of crystallinity. These observations suggest that the dominant UV-induced modifications are not associated with substantial changes in the overall crystalline fraction. Possible structural changes may therefore be related to more accessible polymer regions, such as amorphous or inter-lamellar domains. The implications of these changes for the mechanical response are addressed in the DMA analysis.

4.3. Dynamic mechanical analysis (DMA) of PA 6 samples

4.3.1. Time sweep

To assess the reproducibility of the DMA response, time sweep measurements were performed on five samples for each investigated

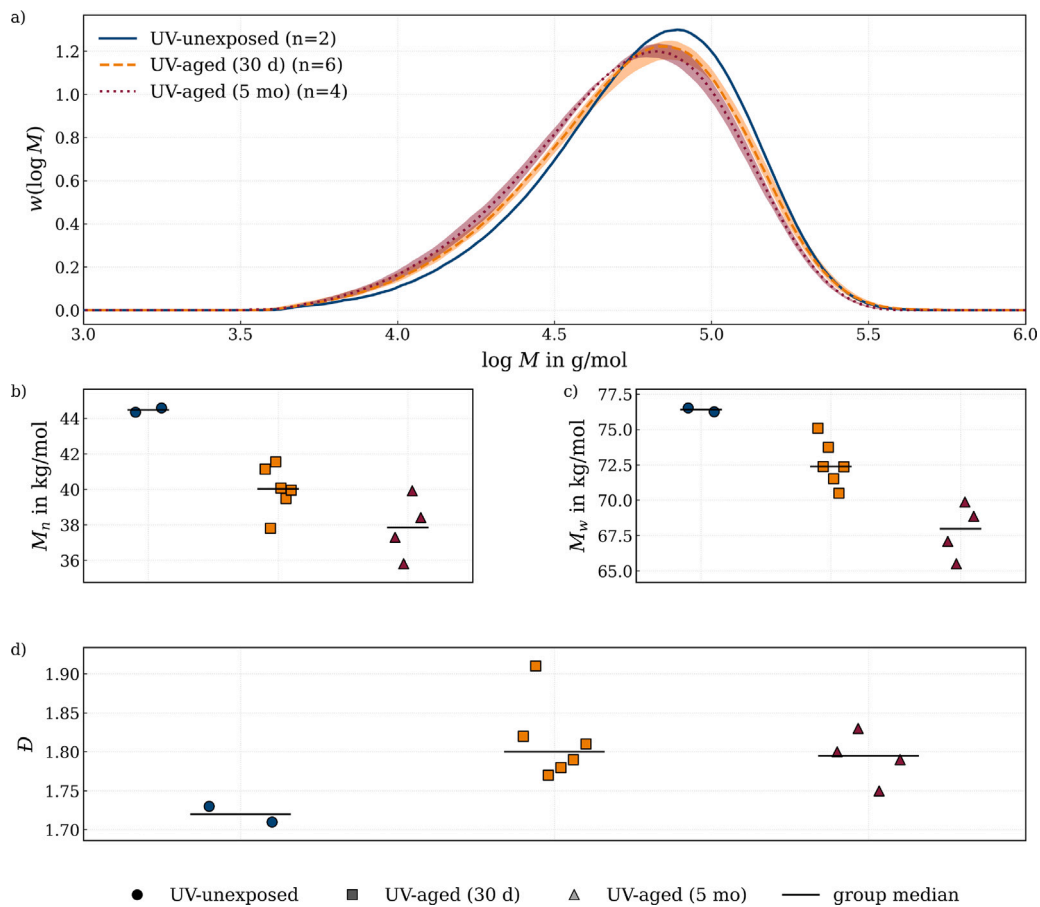


Fig. 1. Gel permeation chromatography (GPC) results of PA 6 before and after UV exposure. Numbers in parentheses denote the number of samples considered for each exposure condition. (a) Molar mass distributions $w(\log M)$ obtained from GPC analysis. For visualization purposes, the molar mass distributions were normalized such that $\int w(\log M) d(\log M) = 1$. The solid lines represent the median distributions of each exposure condition, while the shaded bands indicate the range of individual measurements within the respective group. (b–d) Number-average molar mass M_n , weight-average molar mass M_w , and dispersity $\bar{D} = M_w/M_n$ of the investigated samples. Individual measurements are shown as symbols, and horizontal lines denote the group median. The numbers in parentheses indicate the number of samples analyzed per condition.

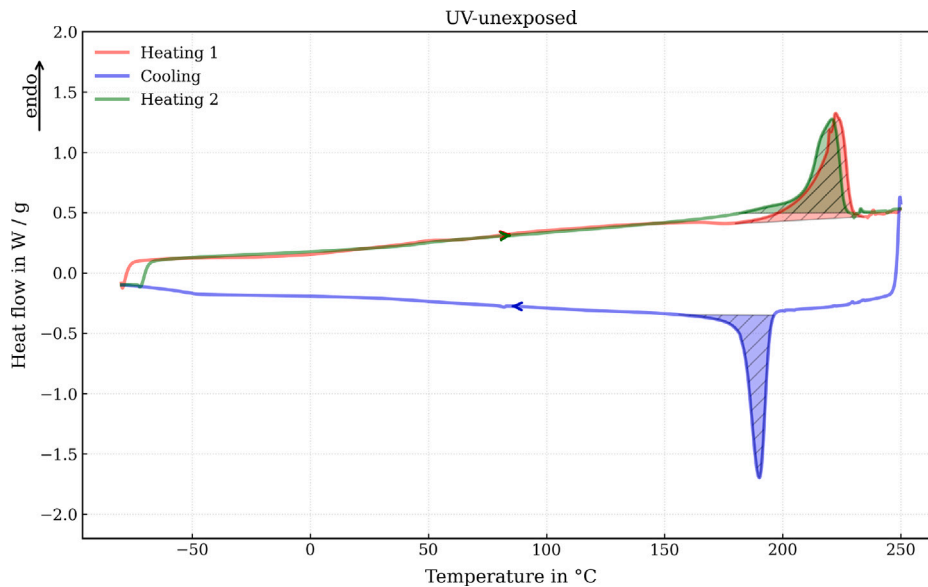


Fig. 2. DSC thermogram of PA 6 without UV exposure. The specific heat flow is shown as a function of temperature for three consecutive DSC cycles: first heating (red), cooling (blue), and second heating (green). The hatched areas highlight the melting and crystallization peak regions. The melting peak during heating and the crystallization peak during cooling are clearly visible. Measurements were performed in the temperature range from -80°C to 250°C using a heating and cooling rate of 10 K/min .

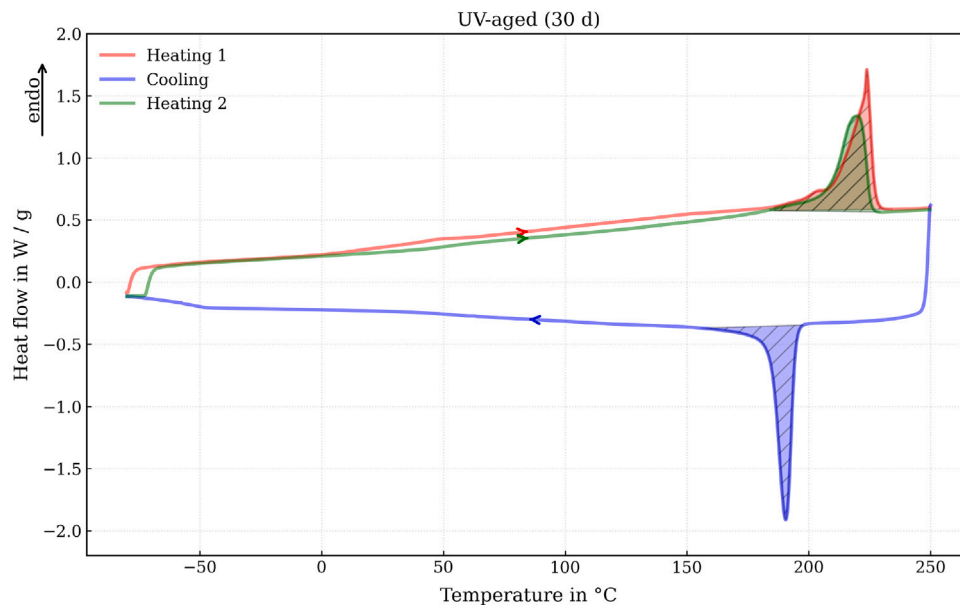


Fig. 3. DSC thermograms of PA 6 after short-term UV exposure (30 days). The specific heat flow is shown as a function of temperature for three consecutive DSC cycles (first heating, cooling, second heating). The hatched areas highlight the melting and crystallization peak regions. The characteristic melting and crystallization peaks remain visible, while variations in the shape of the melting peak from the first heating are observed compared with the UV-unexposed reference sample.

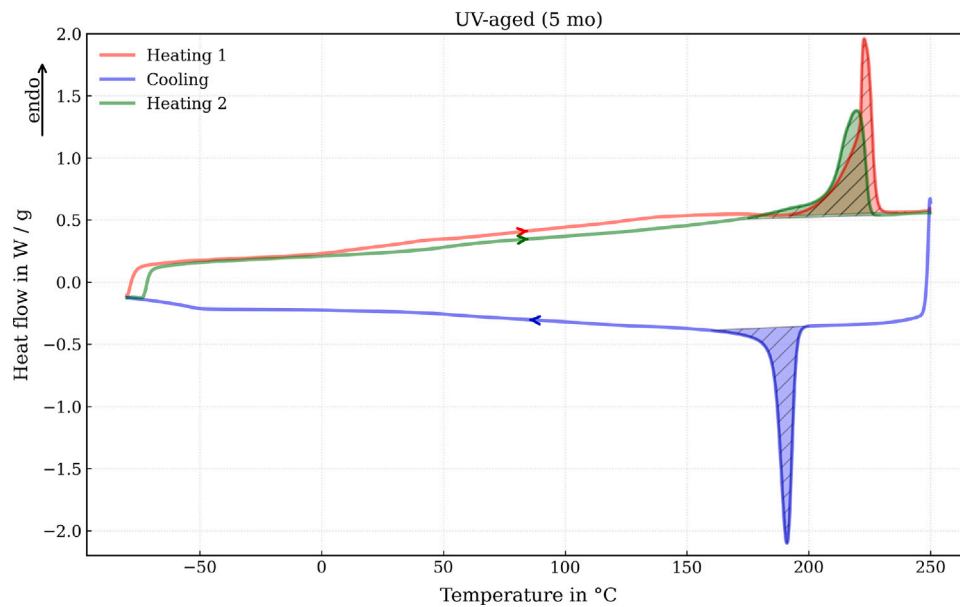


Fig. 4. DSC thermograms of PA 6 after prolonged UV exposure (5 months). The specific heat flow is shown as a function of temperature for three consecutive DSC cycles (first heating, cooling, second heating). The hatched areas highlight the melting and crystallization peak regions. Melting and crystallization peaks remain visible for all cycles, while the first-heating melting peak exhibits a modified shape compared with the UV-unexposed reference.

Table 2

Melting temperature θ_m and degree of crystallinity χ_c obtained from the first heating cycle, and crystallization temperature θ_c obtained during cooling, for the thermograms shown in Figs. 2–4.

Quantity	UV-unexposed	UV-aged (30 d)	UV-aged (5 mo)
θ_m	221 °C	222 °C	222 °C
θ_c	191 °C	191 °C	192 °C
χ_c	31.4%	28.4%	32.5%

UV exposure condition. During these tests, temperature and frequency were kept constant while the storage modulus was recorded over ten consecutive measurement cycles. For each sample, the mean storage modulus was calculated from the corresponding ten measurements. The resulting sample-specific mean values were subsequently used to assess the stability of the response and to quantify the sample-to-sample variability. The parameters of the tests are summarized in Table 1.

In Fig. 5, the storage modulus for the individual samples is depicted. Herein, each symbol represents the mean value of the ten measurements for each sample. Per condition, five samples were tested. The horizontal lines indicate the mean value and the vertical error bars

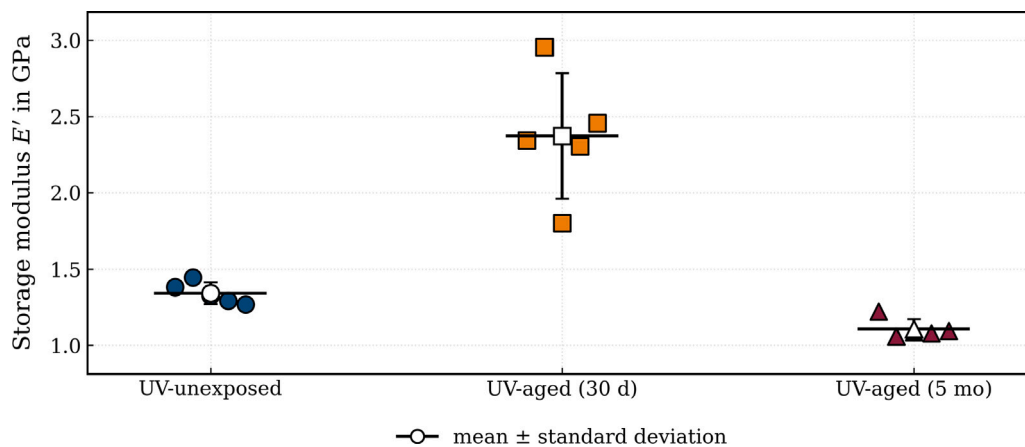


Fig. 5. Storage modulus obtained from DMA time sweep tests at constant temperature and frequency. Each symbol represents the mean storage modulus of a single sample, calculated from ten consecutive measurements during the time sweep test. Five samples were investigated for each exposure condition. The horizontal lines indicate the mean storage modulus of the respective exposure condition, and the vertical error bars denote the standard deviation of the measurements within each group. Short-term UV exposure (30 d) results in a pronounced increase in stiffness. In contrast, prolonged exposure (5 mo) leads to a decrease in storage modulus compared to the unexposed reference.

denote the standard deviation within each exposure group. The measurements reveal three characteristic stages of mechanical response: an unexposed reference state, a stiffened state after short-term exposure of about 30 days, and a mechanically degraded state after long-term exposure of more than 5 months. For the unexposed samples, the mean storage modulus of approximately 1300 MPa reflects the stiffness of the material in its baseline state. The relatively small scatter indicates a consistent mechanical response among the tested samples.

After short-term UV exposure, the storage modulus increases compared to the UV-unexposed reference, reaching an average value of approximately 2400 MPa. The observed stiffening may be associated with changes in the semicrystalline morphology or mobility of amorphous regions. However, since no spatially resolved or spectroscopic characterization was performed, the present results do not allow the underlying structural contributions to be resolved directly.

With longer-term UV exposure, the storage modulus decreases again to values of about 1100 MPa, corresponding to a reduction of approximately 15% relative to the reference condition. In combination with the molar mass reduction observed in GPC, the decrease in stiffness might be indicative of chain scission becoming increasingly relevant with prolonged irradiation time.

4.3.2. Temperature-frequency sweep

For thermoviscoelastic material characterization, the applied temperature and loading frequency are varied, as summarized in Table 1. The material response is typically described by the storage modulus, the loss modulus, or the loss factor as a function of temperature.

Fig. 6 shows the storage modulus E' as solid lines, and the loss factor $\tan \delta$ as dashed lines, both depicted over the temperature. For clarity, only the material response at a frequency of 5 Hz is shown, which represents a typical frequency within the investigated range. Three environmental conditions are considered: samples without UV exposure, with short-term UV exposure of 30 days, and longer-term UV exposure of 5 months. All curves display the characteristic transitions of semicrystalline PA 6: a glassy plateau at low temperatures ($\theta < 0^\circ\text{C}$), a sharp drop in modulus around the glass transition region ($\theta_g \approx 20 - 30^\circ\text{C}$ for the moisture-equilibrated PA 6 considered in this study) which is accompanied by a maximum in $\tan \delta$, and a rubbery plateau at higher temperatures ($\theta > 80^\circ\text{C}$).

After short-term UV exposure, the storage modulus is approximately 25% higher in the glassy region compared to the unaged reference sample. This increase in stiffness occurs despite only comparatively small changes in the molecular and thermal quantities obtained from

GPC and DSC. In agreement with the DSC results presented in the previous section, the overall crystallinity remains largely preserved, indicating that the observed stiffening cannot be directly attributed to substantial changes in the crystalline fraction alone. Regarding the loss factor, the peak value is slightly lower for the UV-aged sample compared to the reference and shifted towards lower temperatures by about 10 K.

In contrast, prolonged UV exposure leads to a reduction of E' over the temperature. The loss factor remains nearly comparable to the reference state with respect to shape and magnitude but is only shifted by a few Kelvin towards higher temperatures. In combination with the reduction in molar mass observed by GPC, the decrease in stiffness is consistent with chain scission becoming increasingly relevant with prolonged UV exposure.

4.4. Master curves from temperature-frequency sweeps

The time-temperature superposition (TTS) principle was applied to temperature-frequency sweep data, presented in the previous section. This approach enables the creation of master curves that describe the thermoviscoelastic response over several decades of frequency. The detailed algorithm used for the horizontal and vertical shifting procedure has been described previously by [32], and the same methodology is applied here.

As already observed in [32,45], for PA 6, TTS is applicable in a limited range of temperatures and frequencies. Although the frequency sweeps were performed from 0.5 to 50 Hz, including frequencies above 10.8 Hz did not result in a consistent superposition of the isothermal data for all investigated UV exposure conditions. Therefore, the master curves were constructed using a frequency range from 0.5 to 10.8 Hz and a temperature range from 0°C to 60°C , allowing a consistent comparison between the different exposure conditions. The stepwise construction of a master curve is shown exemplarily in Fig. 7 for the sample that was not exposed to UV radiation. The dotted curves represent the original DMA measurements obtained at different temperatures (initial state), where the color scale indicates the corresponding temperature. Starting from the initial state, the datasets are shifted horizontally on the basis of the loss factor (step I). However, systematic temperature-dependent offsets remain between the storage modulus datasets for all investigated UV exposure conditions, as shown in Figs. 7, A.10 and A.11. For semicrystalline PA 6, such offsets may arise from the different temperature dependencies of the amorphous and crystalline contributions to the effective modulus. Since these contributions

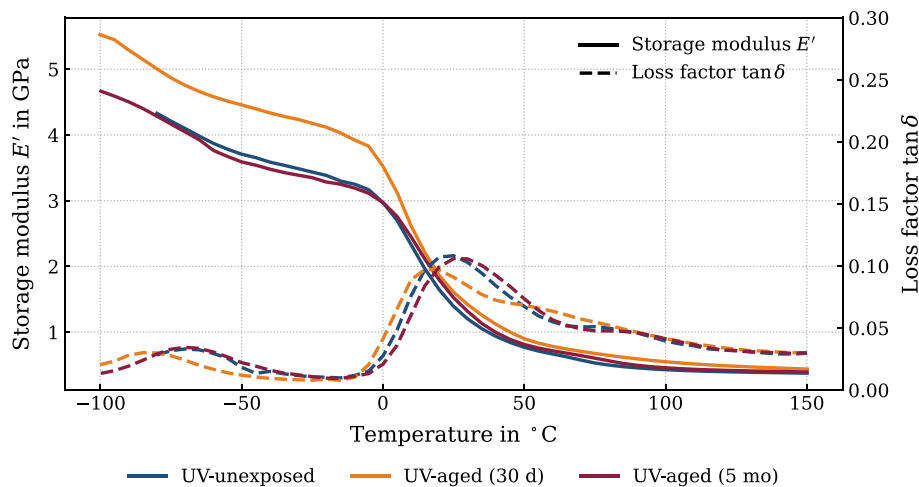


Fig. 6. Temperature-dependent DMA response of PA 6 under different UV exposure conditions. The storage modulus E' (solid lines) and the loss factor $\tan \delta$ (dashed lines) are shown as a function of temperature at a loading frequency of 5 Hz. All curves exhibit the characteristic viscoelastic transitions of semicrystalline PA 6, including the glassy plateau at low temperatures, the glass transition region marked by a peak in $\tan \delta$, and the rubbery regime at higher temperatures. Short-term UV exposure (30 d) results in an increased storage modulus over a wide temperature range and a shift of the $\tan \delta$ peak towards lower temperatures. In contrast, prolonged UV exposure (5 mo) leads to a reduction in storage modulus, while the loss factor remains largely comparable to the unexposed reference with respect to shape and magnitude but is shifted by a few Kelvin towards higher temperatures.

cannot be separated based on the present measurements, b_θ is applied in step II as an empirical correction for the remaining offsets. Thus, the measured response is not represented by horizontal TTS alone. For all samples, the reference temperature is set to 25 °C. Fig. 8 shows the obtained master curves of storage and loss modulus for the three UV aging states, as well as those of the loss factor. The corresponding horizontal and vertical shift factors are plotted in Fig. 9.

From the plots, the following observations can be made. First, it should be noted that the shift factors of the samples with $t_{UV} = 30$ d and $t_{UV} = 5$ mo at 20 °C appear to be outliers, see Fig. 9. A plausible explanation is that the curve segments at 20 °C and 25 °C are located near the maximum of the loss factor, where the determination of unique shift factors becomes increasingly sensitive. Possible errors in the horizontal shift then directly influence the vertical shift, leading to outliers in the corresponding plot. At the reference temperature (25 °C), all shift factors are by definition equal to one. Nevertheless, the observed deviation is restricted to a narrow temperature range around the maximum of the loss factor and does not affect the overall trend of the shift factors or the resulting master curves.

Below the glass transition, the shift factors for all three conditions show no substantial differences. In this range, the master curves of the sample not subjected to UV and the sample with $t_{UV} = 30$ d differ mainly in terms of a vertical shift, i.e. the master curves of the loss factor overlap, while the master curves of the moduli differ in terms of an offset in the vertical direction, see Fig. 8. When comparing the sample not subjected to UV and the sample with $t_{UV} = 5$ mo, the difference between the master curves of both modulus and loss factor is given by horizontal shifts.

The horizontal shift between the sample not subjected to UV and the sample with $t_{UV} = 5$ mo is also present above the glass transition temperature up to 50 °C. In contrast, the difference between the sample that was not subjected to UV and the sample with $t_{UV} = 30$ d can no longer be represented by a shift in this range as the curve shapes differ.

Regarding the thermoviscoelastic response of PA 6 and the influence of UV exposure, the following conclusions can be drawn.

- Short-term UV exposure (30 d): The master curves exhibit an elevated modulus level accompanied by a reduced loss factor. This indicates a stiffer viscoelastic response. Furthermore, at low reduced frequencies corresponding to temperatures above the glass transition, the curve shapes differ which indicates changes in

the relaxation behavior that cannot be represented by horizontal and vertical shifting.

- Long-term UV exposure (5 mo): The difference compared to the unexposed state is mainly given by a horizontal shift. This indicates a time shift in the effective relaxation behavior while its shape remains similar.
- Applicability of TTS: Extended time-temperature superposition is limited to the investigated temperature and frequency range. Outside this range, smooth master curves of both storage modulus and loss factor cannot be obtained by horizontal and vertical shifting.

4.5. Discussion of results

Based on the molecular, thermal, and effective thermoviscoelastic responses obtained from GPC, DSC, and DMA, two distinct stages are observed in the UV-induced aging of PA 6.

During the initial stage, GPC reveals only minor reductions in number- and weight-average molar mass, while DSC indicates no substantial change in crystallinity. At the same time, DMA measurements show a pronounced increase in stiffness, particularly in the glassy regime, accompanied by a reduced loss factor. The comparatively small changes in molar mass detected by GPC and in crystallinity determined from the thickness-integrated DSC measurements contrast with the pronounced change in effective stiffness. Since the methods characterize different sample volumes and the surface-to-core gradient is not resolved, these observations are compared qualitatively. Possible contributing factors discussed in the literature include physical aging, local moisture variations, residual-stress relaxation, or surface-localized oxidation effects, although the present measurements do not allow these contributions to be resolved individually.

With long-term UV exposure, the measured decrease in molar mass is consistent with chain scission becoming increasingly relevant. This decrease is accompanied by reduced stiffness and a shift in the thermoviscoelastic response. At the same time, DSC suggests that the overall crystallinity remains comparatively stable, indicating that the observed change of the thermoviscoelastic response cannot be attributed solely to changes in crystalline fraction.

A combined evaluation of the GPC, DSC, and DMA results shows that the applied characterization techniques provide complementary information on the molecular, thermal, and thermoviscoelastic response

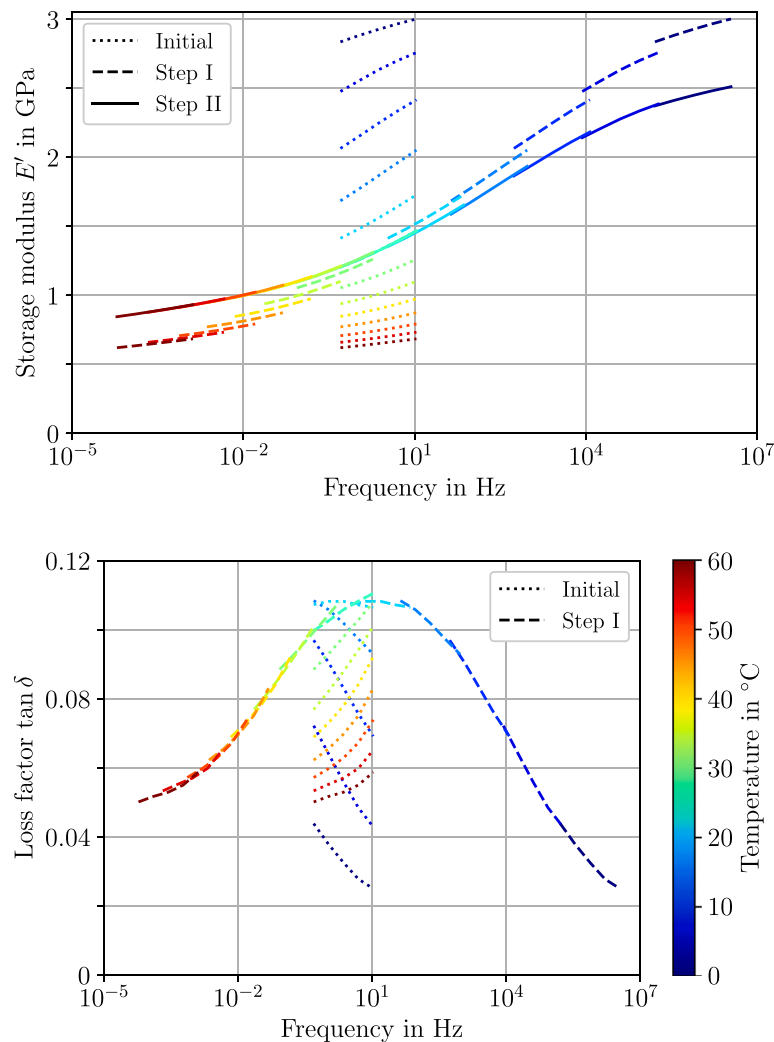


Fig. 7. Illustration of the master curve construction based on DMA temperature-frequency sweep data. The dotted curves represent the original, unshifted measurements obtained at different temperatures, where the color indicates the test temperature ranging from 0°C (blue) to 60°C (red). In a first step (Step I), the individual datasets are shifted horizontally along the frequency axis according to the TTS principle. Since horizontal shifting alone does not yield a smooth master curve for the storage modulus, an additional vertical shift is applied in a second step (Step II). The resulting aligned datasets form the continuous master curve using 25°C as reference temperature.

of PA 6. The observed differences between the molecular, thermal, and thermoviscoelastic responses illustrate the complexity of UV-induced aging and underline the value of a combined experimental characterization. While the present measurements do not directly resolve local degradation processes, the combined observations capture the transition from initial stiffening to long-term changes in the viscoelastic response.

5. Summary and conclusion

The present study shows that UV exposure leads to a time-dependent and non-monotonic evolution of the thermoviscoelastic response of moisture-equilibrated PA 6. While short-term exposure is associated with pronounced stiffening, prolonged exposure results in a shift of the thermoviscoelastic material response. The combined application of GPC, DSC, and DMA provides complementary information on the molecular, thermal, and thermoviscoelastic behavior of the material. Taken together, the results indicate that different characterization techniques capture different aspects of the UV-induced material changes and therefore provide distinct information for their assessment. Beyond

the changes in modulus level, the master curve analysis based on extended time-temperature superposition indicates that UV-induced aging also affects the effective relaxation behavior within the investigated temperature-frequency range.

At the same time, the present results do not allow a unique identification of the underlying structural mechanisms. In particular, the applied integral characterization techniques do not resolve local microstructural changes or the spatial distribution of UV-induced degradation, which is expected to be predominantly surface-localized in the investigated samples. Future studies should therefore complement the present integral characterization with position-resolved spectroscopic measurements to identify thickness-dependent chemical changes and with WAXS and SAXS measurements to characterize crystal structure and lamellar organization, respectively. Such complementary investigations may provide further insight into the mechanisms underlying the observed transition from initial stiffening to long-term changes in relaxation behavior.

The presented results highlight the value of considering molecular, thermal, and thermoviscoelastic observations jointly when assessing UV-induced aging effects in PA 6. Such a combined perspective may be relevant for the development and validation of material models

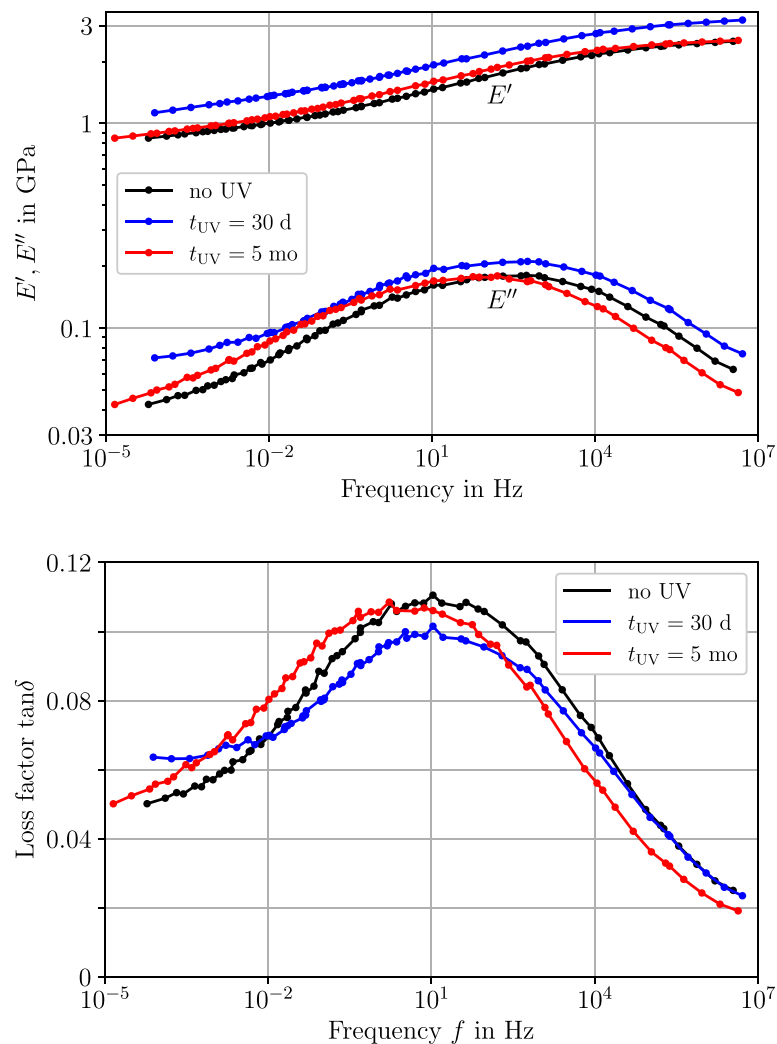


Fig. 8. Comparison of the master curves for all three UV radiation states: UV-unexposed samples (no UV), UV-aged for 30 days ($t_{UV} = 30$ d), UV-aged for 5 months ($t_{UV} = 5$ mo). Storage and loss modulus are depicted on the top and the loss factor on the bottom. For all curves, a reference temperature of 25 °C is used. Note that the vertical axis of the modulus plot is scaled logarithmically.

intended to describe long-term material behavior under environmental exposure.

CRediT authorship contribution statement

Loredana Kehrer: Writing – original draft, Visualization, Investigation, Formal analysis, Conceptualization. **Valerian Hirschberg:** Writing – original draft, Investigation. **Johannes Keursten:** Writing – original draft, Visualization, Investigation. **Thomas Böhlke:** Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Master curves

In Figs. A.10 and A.11, the master curves resulting from horizontal and vertical shifting are depicted. Here, the temperature of 25 °C is considered as reference temperature for the shifting procedure.

Appendix B. Repeated DSC measurements

To provide additional information regarding the repeated DSC measurements, Table B.3 summarizes the characteristic thermal quantities obtained for the investigated exposure conditions. The table reports the corresponding mean values and standard deviations and thereby documents the scatter observed between individual measurements. For the UV-unexposed condition, two measurements were available, whereas six and four measurements were available for the UV-aged (30 d) and UV-aged (5 mo) conditions, respectively.

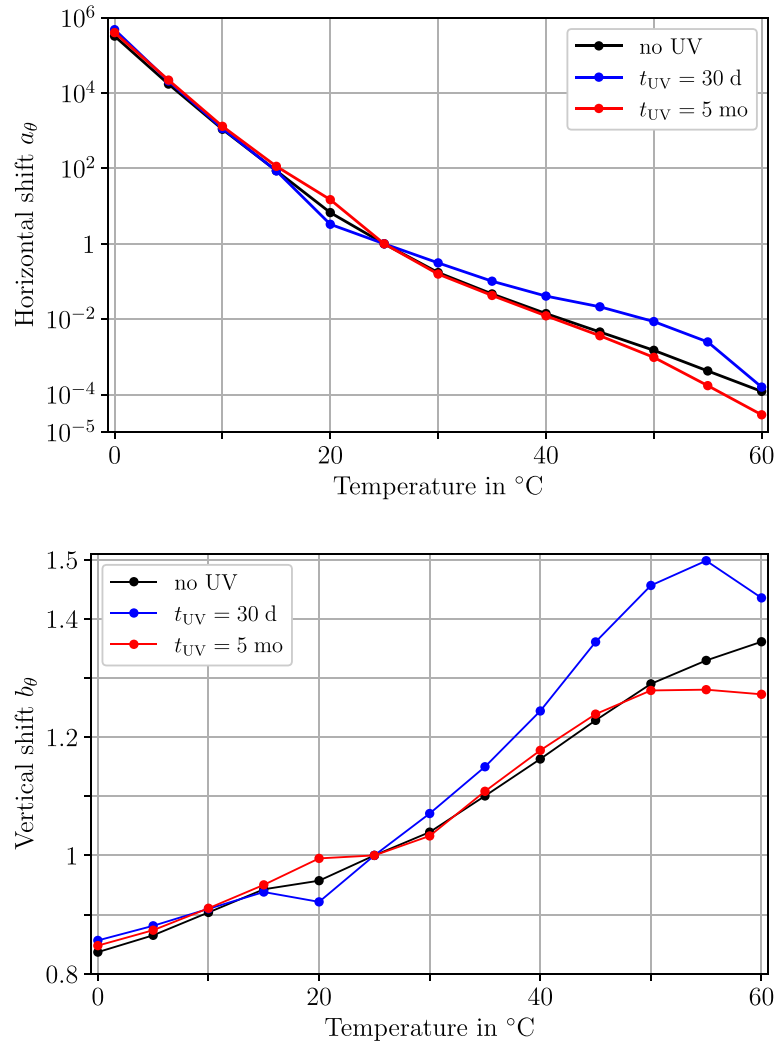


Fig. 9. Comparison of the determined temperature-dependent shift factors for all three UV radiation states: UV-unexposed samples (no UV), UV-aged for 30 days ($t_{UV} = 30$ d), UV-aged for 5 months ($t_{UV} = 5$ mo). The horizontal shift is depicted on the top in logarithmic scaling, the vertical shift on the bottom in linear scaling.

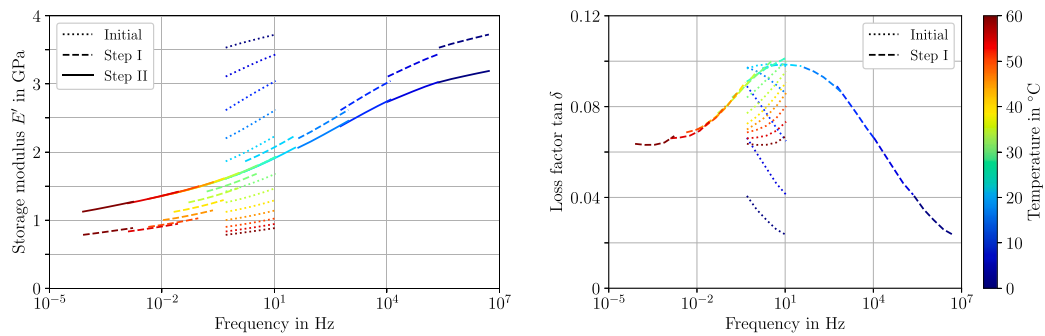


Fig. A.10. Master curve construction (ATM with UV radiation, $t_{UV} = 30$ d).

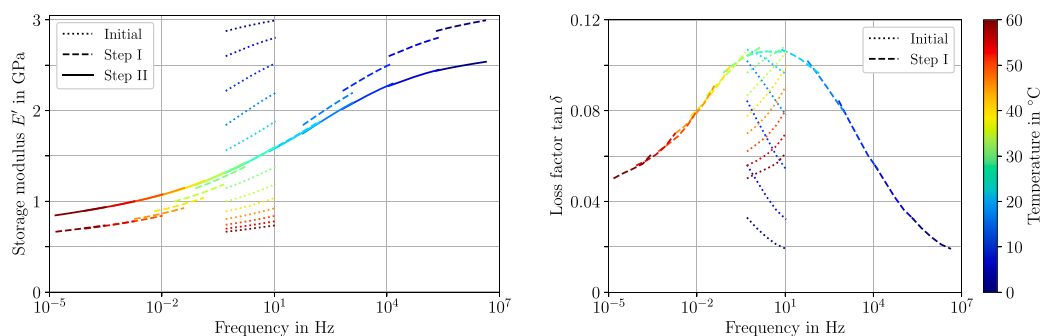


Fig. A.11. Master curve construction (ATM with UV radiation, $t_{UV} = 5$ mo).

Table B.3

Mean values and corresponding standard deviations obtained from repeated DSC measurements of the UV-unexposed ($n = 2$), UV-aged (30 d, $n = 6$), and UV-aged (5 mo, $n = 4$) samples. Thermal quantities are reported as mean $\pm$ standard deviation, whereas sample masses are reported as the range of the individual measurements. The subscripts 1 and 2 denote values obtained from the first and second heating cycles, respectively. The melting temperature θ_m refers to the first heating cycle, whereas θ_c refers to the cooling cycle.

Quantity	UV-unexposed	UV-aged (30 d)	UV-aged (5 mo)
ΔH_{m1} in J/g	72.4 ± 0.3	72.4 ± 4.1	70.8 ± 2.6
ΔH_{m2} in J/g	63.7 ± 2.8	65.6 ± 12.6	63.3 ± 14.1
ΔH_c in J/g	-69.1 ± 0.3	-70.4 ± 1.1	-70.5 ± 2.2
θ_m in $^{\circ}\text{C}$	222.9 ± 1.6	222.8 ± 0.9	222.4 ± 0.7
θ_c in $^{\circ}\text{C}$	191.6 ± 0.8	191.7 ± 0.3	192.2 ± 0.4
χ_{c1} in %	31.5 ± 0.1	31.5 ± 1.8	30.8 ± 1.1
χ_{c2} in %	27.7 ± 1.2	28.5 ± 5.4	27.5 ± 6.1
Mass range in mg	6.028–9.702	4.838–9.978	5.115–6.950

Data availability

Data will be made available on request.

References

- [1] G.W. Ehrenstein, S. Pongratz, Beständigkeit von Kunststoffen: Gegenüber Medien und Alterung, Carl Hanser Verlag, München, 2007.
- [2] J. Bolland, G. Gee, Kinetic studies in the chemistry of rubber and related materials. III. Thermochemistry and mechanisms of olefin oxidation, *Trans. Faraday Soc.* 42 (1946) 244–252.
- [3] R.B. Fox, Photodegradation of high polymers, *Prog. Polym. Sci.* 1 (1967) 45–89.
- [4] N. Grassie, N. Weir, The photooxidation of polymers. I. Experimental methods, *J. Appl. Polym. Sci.* 9 (3) (1965) 963–974.
- [5] D.J. Carlsson, D.M. Wiles, The photooxidative degradation of polypropylene. Part I. Photooxidation and photoinitiation processes, *J. Macromol. Sci. Part C: Polym. Rev.* 14 (1) (1976) 65–106.
- [6] N. Grassie, J. MacCallum, Thermal and photochemical degradation of poly (n-butyl methacrylate), *J. Polym. Sci. Part A: Gen. Pap.* 2 (2) (1964) 983–1000.
- [7] D.E. Mouzakis, H. Zoga, C. Galiotis, Accelerated environmental ageing study of polyester/glass fiber reinforced composites (GFRPCs), *Compos. Part B: Eng.* 39 (3) (2008) 467–475.
- [8] K.T. Gillen, R.L. Clough, Time-temperature-dose rate superposition: a methodology for extrapolating accelerated radiation aging data to low dose rate conditions, *Polym. Degrad. Stab.* 24 (2) (1989) 137–168.
- [9] A.V. Tobolsky, Properties and Structures of Polymers, Wiley, New York, 1960.
- [10] X. Li, X. Zhao, L. Ye, Stress photo-oxidative aging behaviour of polyamide 6, *Polym. Int.* 61 (1) (2012) 118–123.
- [11] X. Zhao, X. Li, L. Ye, G. Li, Stress-thermooxidative aging behavior of polyamide 6, *J. Appl. Polym. Sci.* 129 (3) (2013) 1193–1201.
- [12] J.M. Hutchinson, Physical aging of polymers, *Prog. Polym. Sci.* 20 (4) (1995) 703–760.
- [13] A. Lion, M. Jöhrlitz, On the representation of chemical ageing of rubber in continuum mechanics, *Int. J. Solids Struct.* 49 (10) (2012) 1227–1240.
- [14] M. Jöhrlitz, On the representation of ageing phenomena, *J. Adhes.* 88 (7) (2012) 620–648.
- [15] A. Becerra, J. d'Almeida, UV effects on the tensile and creep behaviour of HDPE, *Polym. Polym. Compos.* 25 (5) (2017) 327–332.
- [16] H.-C. Hsueh, J.H. Kim, S. Orski, A. Fairbrother, D. Jacobs, L. Perry, D. Hunston, C. White, L. Sung, Micro and macroscopic mechanical behaviors of high-density polyethylene under UV irradiation and temperature, *Polym. Degrad. Stab.* 174 (2020) 109098.
- [17] N.M. Ainali, D.N. Bikiaris, D.A. Lambropoulou, Joint physicochemical effects of UV-B irradiation on microplastics formation: The case of poly (vinyl chloride) and poly (methyl methacrylate), *Polym. Degrad. Stab.* 238 (2025) 111366.
- [18] L. Dulebová, F. Grešková, J.W. Sikora, V. Krasinskyi, Analysis of the mechanical properties change of PA6/MMT nanocomposite system after ageing, *Key Eng. Mater.* 756 (2017) 52–59.
- [19] J. Toháček, Z. Vrátníková, Polymer life-time prediction: The role of temperature in UV accelerated ageing of polypropylene and its copolymers, *Polym. Test.* 36 (2014) 82–87.
- [20] A. de Souza Rios, W.F. de Amorim Júnior, E.P. de Moura, E.P. de Deus, J.P. de Andrade Feitosa, Effects of accelerated aging on mechanical, thermal and morphological behavior of polyurethane/epoxy/fiberglass composites, *Polym. Test.* 50 (2016) 152–163.
- [21] K.T. Gillen, R.L. Clough, C.A. Quintana, Modulus profiling of polymers, *Polym. Degrad. Stab.* 17 (1) (1987) 31–47.
- [22] J. White, A. Shyichuk, Macromolecular scission and crosslinking rate changes during polyolefin photo-oxidation, *Polym. Degrad. Stab.* 92 (7) (2007) 1161–1168.
- [23] D.V. Ceretti, M. Edeleva, L. Cardon, D.R. D'hooge, Molecular pathways for polymer degradation during conventional processing, additive manufacturing, and mechanical recycling, *Molecules* 28 (5) (2023) 2344.
- [24] Z. Huang, H. Wang, A review on photochemical effects of common plastics and their related applications, *J. Polym. Sci.* 62 (6) (2024) 969–997.
- [25] Y. An, A. Padermshoke, T. Kajiwara, T. Van Nguyen, M. Yonemura, D.-I. Kato, H. Mokudai, T. Masaki, H. Masunaga, Y. Kobayashi, et al., Influence of ultraviolet light-induced photooxidation on the surface chemistry and biodegradability of aliphatic polyamide films, *Langmuir* 41 (25) (2025) 16150–16159.
- [26] P. Sharma, A. Sambale, M. Stommel, M. Maisl, H.-G. Herrmann, S. Diebels, Moisture transport in PA6 and its influence on the mechanical properties, *Contin. Mech. Thermodyn.* 32 (2) (2020) 307–325.
- [27] B.-H. Yang, S.-Y. Chang, Y. Zhang, F. Yang, S. Lee, Cracking in UV-irradiated poly (methyl methacrylate)/functionalized graphene composites: Solvent effect, *J. Polym. Res.* 31 (9) (2024) 274.
- [28] H. Lamni, M.N. Abdelaziz, G. Ayoub, X. Colin, U. Maschke, Experimental investigation and modeling attempt on the effects of ultraviolet aging on the fatigue behavior of an LDPE semi-crystalline polymer, *Int. J. Fatigue* 142 (2021) 105952.
- [29] D. Finazzi, G. Seychal, J.-M. Raquez, G. Robert, K. De Clerck, L. Daelemans, W. Van Paepegem, Study of the temperature-humidity equivalence and the time-temperature superposition principle in the finite-strain response of polyamide-6 and short glass fibre-reinforced polyamide-6, *Polym. Test.* 141 (2024) 108653.
- [30] ISO 291, Plastics – Standard atmospheres for conditioning and testing (ISO 291:2008(E)), 2008.
- [31] ISO 1110, Plastics – Polyamides – Accelerated conditioning of test specimens (ISO 1110:2019(E)), 2019.
- [32] L. Kehr, J. Keursten, V. Hirschberg, T. Böhlke, Dynamic mechanical analysis of PA 6 under hydrothermal influences and viscoelastic material modeling, *J. Thermoplast. Compos. Mater.* 36 (11) (2023) 4630–4664.
- [33] A. Dyck, L. Groß, J. Keursten, L. Kehr, T. Böhlke, Modeling and FE simulation of coupled water diffusion and viscoelasticity in relaxation tests of polyamide 6, *Contin. Mech. Thermodyn.* 36 (4) (2024) 935–953.
- [34] Atlas Material Testing Technology, Weather summary reports, 2021, URL <https://www.atlas-mts.de/-/media/ametekatlas/files/knowledgecenter/datatool/weathersummaryreports/2021.pdf>.
- [35] A. Striegel, W.W. Yau, J.J. Kirkland, D.D. Bly, Modern Size-Exclusion Liquid Chromatography: Practice of Gel Permeation and Gel Filtration Chromatography, John Wiley & Sons, Hoboken, New Jersey, 2009.

- [36] F.W. Billmeyer, Textbook of Polymer Science, John Wiley & Sons, Hoboken, New Jersey, 1984.
- [37] International Organization for Standardization, Plastics—Differential scanning calorimetry (DSC)—Part 3: Determination of temperature and enthalpy of melting and crystallization, 2025, ISO 11357-3:2025.
- [38] B. Wunderlich, Thermal Analysis of Polymeric Materials, Springer, Berlin, Heidelberg, New York, 2005.
- [39] G.W.H. Höhne, W. Hemminger, H.-J. Flammersheim, Theoretical fundamentals of differential scanning calorimeters, in: Differential Scanning Calorimetry, Springer, Berlin, Heidelberg, 2003, pp. 31–63.
- [40] G.W. Ehrenstein, G. Riedel, P. Trawiel, Thermal Analysis of Plastics: Theory and Practice, Carl Hanser Verlag GmbH & Co KG, München, 2004.
- [41] K.P. Menard, Dynamic Mechanical Analysis: A Practical Introduction, CRC Press, Boca Raton, 2008.
- [42] J.D. Ferry, Viscoelastic Properties of Polymers, Wiley, New York, Chichester, Brisbane, Toronto, Singapore, 1980.
- [43] H.F. Brinson, L.C. Brinson, Polymer Engineering Science and Viscoelasticity: An Introduction, Springer, New York, Heidelberg, Dordrecht, London, 2015.
- [44] R.H. Colby, Breakdown of time-temperature superposition in miscible polymer blends, *Polymer* 30 (7) (1989) 1275–1278.
- [45] J. Keursten, L. Kehr, T. Böhlke, Linear and nonlinear thermoviscoelastic behavior of polyamide 6, *Proc. Appl. Math. Mech.* 22 (1) (2023) e202200145.