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The effect of physical aging on the viscoelastoplastic response of glycol modified poly(ethylene terephthalate)

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ABSTRACT

For most amorphous polymers, their long term viscoelastic behaviour is greatly affected by physical aging, referring to the transition of their non-equilibrium structure towards equilibrium. This, in turn, affects their thermomechanical properties. In this study, we successfully applied a constitutive model, originally developed for semi-crystalline polyesters to assess the impact of physical aging on stress relaxation and creep in two glycol modified poly(ethylene terephthalate) grades, (poly(ethylene-co-1,4-cyclohexylenedimethylene terephthalate) (PECT) and poly(ethylene-co-2,2,4,4-tetramethyl-1,3-cyclobutanediol terephthalate) (PETT). Both copolyesters are subject to annealing at T_g-20 °C for up to 504 h and subsequent uniaxial stress relaxation tests and, for PECT, creep tests. The results show that the annealing time has a significant influence on the viscoelastic behaviour increasing the resistance to creep and stress relaxation. The effect of physical aging on model parameters is described and analysed while it is found that the concentration of active polymer junctions decreases exponentially with annealing time. Generally, PETT and PECT showed almost identical viscoelastic behaviours at 30 °C, suggesting that the chemical structure of the glycol unit (2,2,4,4-tetramethyl-1,3-cyclobutanediol and 1,4-cyclohexylenedimethanol) does not have significant effect on their viscoelasticity. However, when stress relaxation is tested at increased temperatures, the structural effects are more apparent, demonstrating higher activation energies for PECT than those for PETT, describing the rate of the rearrangement of interchain interactions. Physical aging is also found to decrease these activation energies from 326.6 to 128.1 kJ mol^{-1} for PECT and from 262.7 to 78.5 kJ mol^{-1} for PETT.

1. Introduction

Polyesters are one of the most important classes of plastics [1], especially driven by the commodity plastic poly(ethylene terephthalate) (PET) [2–4], which has been extensively used in various industrial applications, including food packaging, textiles, and medical devices, due to its excellent mechanical and physical properties. However, the low impact strength of polyesters [5,6] and poor resistance to stress cracking and creep [7] have limited their use in engineering applications. To overcome these limitations, researchers have developed glycol-modified PET (PETG) by replacing part of the ethylene glycol (EG) with other glycol moieties, leading to higher impact strengths, better optical transparency [8], improved barrier properties [9] and higher chemical resistance than native PET [10]. The most frequently used glycol modification is the incorporation of 1,4-cyclohexylenedimethanol (CHDM) into PET backbone [10–12] (Fig. 1a), leading to ternary copolyesters with low crystallization rates, and hence enabling production of amorphous polyester with improved optical transparency (92% transmittance) [8]. Generally, when CHDM is copolymerized with aliphatic diols such as ethylene glycol and common diacids such as terephthalic acid, the glass transition temperature (T_g) is increased [13] and the backbone is rendered more resistant to hydrolysis [14] with respect to PET. Furthermore, the flexible nature of the CHDM unit increases the toughness of the polyester compared to a diol such as EG. PET modified with CHDM (PECT) is a promising polyester for high-end consumer products and applications where PET is not suitable due to poorer mechanical and thermal properties. Another promising diol, 2,2,4,4-tetramethyl-1,3-cyclobutanediol (TMCD), has more recently been

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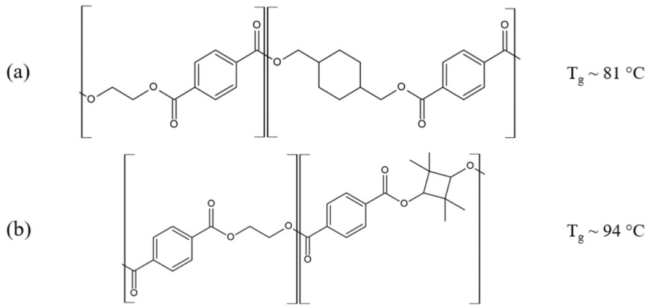

Fig. 1. Chemical structure of (a) poly(ethylene-co-1,4-cyclohexylenedimethylene terephthalate) (PECT) and (b) poly(ethylene-co-2,2,4,4-tetramethyl-1,3-cyclobutanediol terephthalate) (PETT) along with their corresponding T_g's.

used to modify PET (Fig. 1b) [15–17]. Due to the more sterically hindered structure of the substituted cyclobutyl ring, the incorporation of TMCD into the PET backbone increases the T_g even further [18] in respect to both PET and PECT, enabling higher application temperatures. Similar to PECT, PETT crystallizes very slowly compared to PET, and thus amorphous and optical transparent parts are easily produced [8].

Despite many advantages of PETGs, their long-term viscoelastic behaviour remains difficult to predict, especially due to the influence of physical aging on their viscoelasticity. Physical aging is a phenomenon occurring in amorphous polymers due to the molecular structure being frozen in a non-equilibrium state with a high potential energy [19,20], at temperatures below their T_g's. As a result, their molecular structure continuously approach thermodynamic equilibrium or move from one local energy minimum to another by gradual molecular rearrangements [21–23]. These structural changes significantly affect their mechanical and physical properties over time, including changes in stiffness, tensile strength, ductility [24,25] and viscoelastic behaviour [26], which affects the long-term performance and reliability of the material. During physical aging, the viscoelastic material becomes stiffer and hence the compliance decreases compared to the unaged one [27]. This effect has previously been explained by free volume theory [26,28], as a decrease in free volume towards its equilibrium value leading to hindered mobility of chain segments and thereby a higher E-modulus [26]. The effect of aging on creep behaviour can be seen as shifts on creep compliance versus time curves, where increased physical aging leads to shifting of the timescale towards longer time and thus increased resistance to creep.

Apart from physical aging, crystallization might also occur in some polyesters when temperature is increased. This is especially seen in PET and polyesters with linear and highly regular backbones, allowing formation of crystalline domains with closely packed chains and repeating structures. Often, in injection moulded samples with fast cooling, the polymer is not allowed to crystallize fully or the formed crystallites may be of poor quality. Depending on the timescale and storage-/application temperature, recrystallization or refinement of crystalline domains may occur, which would change many of the same properties as physical aging such as increase in tensile strength and stiffness along with embrittlement [29]. However, the incorporation of CHDM or TMCD in specific levels is known to reduce the crystallization rate significantly compared to PET. Polyesters with CHDM/EG and TMCD/EG composition of 30/70 have previously been found to show no crystalline peaks when scanned with DSC before and after aging at T_g-20 for 24 h [30]. Therefore no formation of crystallites are expected at these temperatures. However, it is important to mention, that small spherulites and nuclei can be difficult to detect with DSC.

Poor resistance to creep is a general challenge in polyesters, especially in applications at increased temperatures and long periods of use where design flexibility and durability of products are compromised. Similarly, stress relaxation can become an issue in strained designs, where stress is essential to maintain a given functionality in e.g. press- or snap fits. A possible way to enhance creep and stress relaxation properties of polyesters can be to accelerate physical aging through thermal treatment. In so doing, the long term viscoelastic behaviour can be tailored to fit certain product requirements. However, to predict the necessary aging time and temperature to obtain a polyester with the desired viscoelastic properties, suitable models are needed.

A classic way to describe the effect of physical aging on creep is by the double-logarithmic shift rate, μ, described by Eq. (1) [27].

$$\mu = -\frac{d\log(a_{t_e})}{d\log(t_e)} \tag{1}$$

where a_{t_e} denotes aging time shift factors and t_e describes the aging time at a given temperature. Another common way to shift creep and stress relaxation curves is by the time-temperature superposition principle. The response function in stress relaxation experiments is often represented by the stretched exponential of Kohlrausch-Williams-Watts (KWW) equation in Eq. (2).

$$S(t) = S_0 e^{-(t/\tau_0)^{\beta}} \tag{2}$$

where $S(t)$ is the stress response (or creep compliance), S_0 is the initial response, τ_0 is the characteristic relaxation time and β is the shape parameter. Changes in temperature from T_o to T leads to a change in relaxation time, and the resulting shift is described by $a_t = \tau_{T_0}/\tau_T$. Since physical aging causes a change in timescale for the viscoelastic response, time-aging time shift factors can also be described within the context of the KWW function as $a_t = \tau_{0,t_{e0}}/\tau_{0,t_e}$. These superposition methods can be powerful in predicting long term responses from short term tests, but they do not bring much further understanding of influence of chemistry and morphology. Furthermore the methods can be challenged in describing long term results accurately. J.L. Sullivan demonstrated that prediction of long term creep from short term creep data using a simple shift method led to large overestimations near and below T_g [31]. He explained this observation by the fact that long term creep proceeds much slower relative to short term creep in glassy polymer due to physical aging over time, which alters the properties during long tests [31]. Hutchinson et al. showed the effect of physical aging of PMMA at 125 °C (T_g-20 °C) for up to 120 h on low strain creep response and found that excellent superposition could be achieved by horizontal and vertical shifts [32]. They also found that shift rates for creep did not correspond to the ones found from DSC analysis of enthalpy relaxation, suggesting a more complicated relationship between the two types of relaxation governed by more than change in free volume. A more recent study by Nunes et al., investigating the effect of physical aging on the viscoelastic behaviour of epoxy resins, also employed a time-temperature superposition method and found that the shift rate does not depend on aging temperature at times up to 700 min, whereas the shift rate increases with temperature at longer aging times [33]. They found, that additional aging dependent functions were needed in the viscoelastic model to describe the divergences. This study further demonstrates the complexity of physical aging in polymers. Histova et al. tested the effect of a mineral filler on the creep response of a polyester before and after physical aging was induced [34]. They interpreted experimental results using a generalised Maxwell equation (Maxwell-Gourevich equation) and found that physical aging especially influenced the model parameter related to rubberlike elastic deformation. By assuming the physical sense of the model, they conclude, that physical aging causes significant changes in the structural elements that determine the rubberlike response.

In 2008 a constitutive model was presented, which was able to correctly describe observations in relaxation tests of high density polyethylene at various temperatures and to distinguish effects of constraints on polymer chains imposed by crystallites from effects of temperature on E-modulus [35]. This model was derived for semi crystalline polymers

Table 1
Moulding parameters for tensile bars of PETT and PECT.

	Moisture content [%]	Drying temp. [°C]	Drying time [h]	Melt temp. [°C]	Injection pressure [bar]	Mould temp. [°C]	Cooling time [s]
PETT	0.03	80	8	295	1150	80	20
PECT	0.02	80	8	272	800	60	26

and we believe it offers the possibility to describe the effect of physical aging on viscoelastic behaviour and to isolate the effects on the polymer network related to network homogeneity (distribution of crystallites and/or free volume) and chain interactions.

Even though several studies prove successful modelling of the effect of physical aging on stress relaxation and creep in amorphous polymers [26,34,36], the effect of chemical structure is not fully established. A recent study of star-shaped polystyrene showed that the aging rate decreases with increasing molecular stiffness [37]. Furthermore, an early study of linear polymers (cellulose acetate butyrate ester and polyimide Kapton-H) suggested, that physical aging is slowed down by rigidity of the main chain but not hampered [38]. The structural relaxation also depends on the amount and nature of intermolecular interactions between chains, and thus making the effect of chemical structure a complex subject. The main focus of this work is the effects of physical aging on viscoelastic properties in polyesters with different backbone rigidity.

The objectives of this work are: a) to investigate the effect of chemical structure of glycol modified PET on physical aging behaviour; b) to evaluate the effect of physical aging on stress relaxation and creep in amorphous glycol modified PET, c) to utilise a constitutive model to describe changes in the polyesters caused by physical aging. In this work, PETT and PECT (both with 30% glycol modification and similar molecular weights) are thermally treated to accelerate their physical aging. The constitutive models previously presented [35,39] will be used to characterize stress relaxation and creep behaviour in the two copolyesters and evaluate the effect of annealing time. The laws and methodology for determination of the model parameters are given as well in [35,39].

2. Materials and methods

2.1 Materials

Granulate of poly(ethylene-co-2,2,4,4-tetramethyl-1,3-cyclobutanediol terephthalate) (PETT) (GMX201, Eastman, USA), and poly(ethylene-co-1,4-cyclohexylenedimethylene terephthalate) (PECT) (GN007, Eastman, USA) were injection moulded (Arburg 470E 600–290 Arburg, GER) to tensile test specimens (1BA, ISO 527–2:2012) under conditions listed in Table 1.

Chemical structures and glycol ratios have previously been confirmed by hydrogen- and carbon nuclear magnetic resonance spectroscopy and infrared spectroscopy [30]. Average molecular weights were estimated from gel permeation chromatography as 14.0 and 14.8 kDa for PETT and PECT [30], respectively. Both injection moulded materials were found to be amorphous by DSC, showing neither melting nor crystalline peaks (Fig. S8 and S9).

2.2 Tensile test

Tensile test specimens were fixed with the inlet in the lower pneumatic grip in a universal testing machine (Z005, ZwickRoall, GER) with a 25 mm gauge length extensometer (180102/2008, ZwickRoell, GER) controlled by testXpert II (Zwick, GER). E-modulus and yield strength were evaluated with speed of 1 mm/min until evaluation of E is completed, and an increased speed of 100 mm/min after that, respectively, at 23 ± 2 °C (Fig. S2 and S3, Table S1 and S2).

2.3 Thermal treatment

Tensile specimens were annealed in an oven at T_g-20 °C (61 and 74 °C for PECT and PETT, respectively) for 0.5, 1, 2, 4, 8, 16, 24, and 504 h. After thermal treatment, all samples were stored at room temperature for a least 24 h before testing.

2.4 Creep tests

A series of creep tests were performed on samples of PECT annealed for 0–24 h at T_g-20 °C in a Kappa Multistation (ZwickRoall, GER) with a non-contact strain measurement (videoXtens) and external temperature unit controlled and monitored by testXpert III (ZwickRoall, GER). The samples were subject to an applied stress of 28.6 MPa corresponding to an initial strain of 1.5% for 24 h at 30 °C. A loading speed of 1 mm/min was used.

2.5 Stress relaxation tests

Uniaxial stress relaxation tests were performed on samples in a Kappa Multistation (ZwickRoall, GER) with a non-contact strain measurement (videoXtens) controlled and monitored by testXpert III (ZwickRoall, GER). One series of relaxation tests was performed at 30 ± 3 °C (samples aged 0.5–24 h). Another series of tests was performed at 30, 40, 60, and 70 ± 3 °C (samples aged 0 and 504 h). All tests were performed with loading speed of 1 mm/min and samples were strained at $\epsilon = 1.5\%$ for 24 h.

2.6 Theoretical model

The physical relationships implied in the constitutive model is based on arbitrary three dimensional deformations with small strains (with straight forward extension to finite deformations). The strain tensor for macro-deformation at time $t \geq 0$ is denoted $\widehat{\epsilon}(t)$ and is given by:

$$\widehat{\epsilon}(t) = \widehat{\epsilon}_s(t) + \widehat{\epsilon}_e(t) \tag{3}$$

Where $\widehat{\epsilon}_s(t)$ describes the strain tensor for sliding of junctions and $\widehat{\epsilon}_e(t)$ is the strain tensor for elastic deformation. For the plastic flow in the polymer network, it is assumed that the rate of strain tensor for sliding junctions is linearly related with the rate of strain tensor for macro deformation according to Eq. (4), where ϕ describes the phenomenological relation described in Eq. (5).

$$\frac{d\widehat{\epsilon}_s(t)}{dt} = \phi \frac{d\widehat{\epsilon}(t)}{dt} \tag{4}$$

$$\phi = 1 - \exp(-\alpha e_e^{\beta}) \tag{5}$$

where, α and β are constants. A homogenization concept is used to account for local density fluctuations and inhomogeneous distribution of crystallites (for semi-crystalline polymers as PET). According to this concept the polymer is modelled as an inhomogeneous network of strands bridged by entanglements between chains, so-called junctions. The network is non-affine, which means, that junctions slide under deformation with respect to their reference position. To determine the inhomogeneity, Σ, of the equivalent network by fitting experimental observations, Eq. (6) is assumed [40].

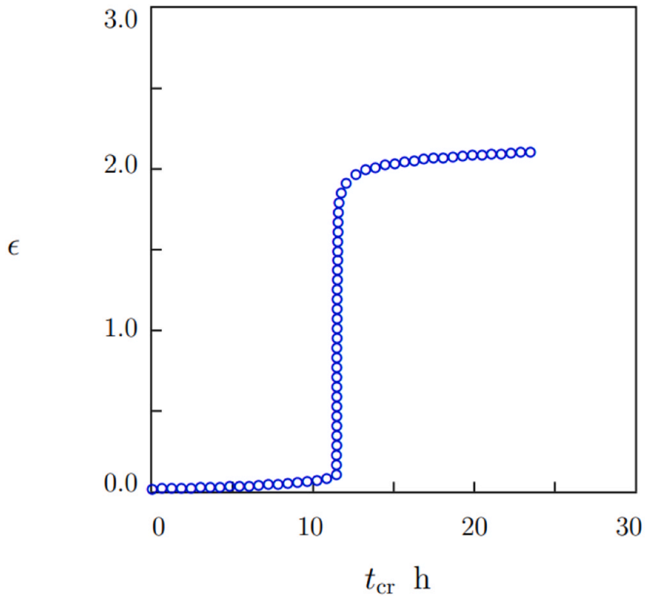

Fig. 2. Tensile strain ϵ versus creep time t_{cr}. Circles: experimental data in creep test with stress $\sigma = 28.6$ MPa at T = 30 °C on non-aged PECT.

$$f(\nu) = f_0 \exp\left(-\frac{\nu^2}{2\Sigma^2}\right) \quad (\nu \geq 0), f(\nu) = 0(\nu < 0) \tag{6}$$

where ν describes the dimensionless energy of inter-chain interaction at a reference temperature. For a given temperature, the energy of inter-chain interactions, V, is given by:

$$V = a\nu \tag{7}$$

where $a(T)$ describes the effect of temperature on V. The rate of activation of polymer chains, which due to e.g. crystallinity did not take part in the rearrangement, Γ, is related to V by the Eyring equation [41]:

$$\Gamma = \gamma \exp(-V) \tag{8}$$

where γ is the attempt rate, which is independent of deformation and whose temperature dependency can be described by the Arrhenius equation, Eq. (9).

$$\gamma = \bar{\gamma} \exp\left(-\frac{E_a}{RT}\right) \tag{9}$$

Where $\bar{\gamma}$ is a constant, E_a is the apparent activation energy, and R is the universal gas constant. The Eqs. (3)–(9) offer a set of stress-strain relationships to allow modelling with the seven adjustable parameters with the following physical meaning:

E is the modulus describing the linear elastic response.
κ describes the concentration of temporary active junctions
Σ indicates the inhomogeneity of the polymer network
α and β reflects the plastic flow of junctions
γ is the attempt rate of separation of polymer chains
a describes thermally-induced changes in the energy of interactions between chains.

For a more detailed derivation and description of the modelling, we refer to the two previous works [35,39].

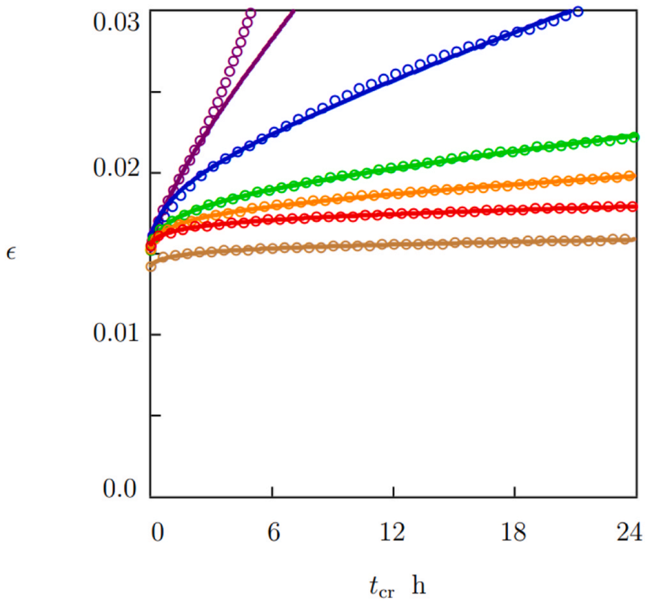

Fig. 3. Tensile strain ϵ versus creep time t_{cr}. Circles: experimental data in creep test with stress $\sigma = 28.6$ MPa at T = 30 °C on PECT samples aged at T = 61 °C for various times t_a: violet - $t_a = 0$, blue - $t_a = 1$, green - $t_a = 4$, orange - $t_a = 24$, red - $t_a = 168$, brown - $t_a = 504$ h. Solid lines: results of numerical analysis.

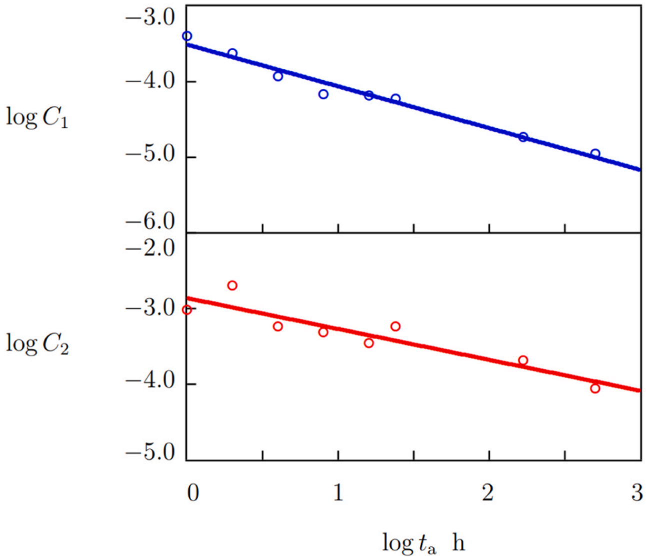

Fig. 4. Parameters C_1 and C_2 versus annealing time t_a. Circles: treatment of observations in creep test with stress $\sigma = 28.6$ MPa at T = 30 °C on PECT samples aged at T = 61 °C. Solid lines: results of numerical analysis.

3. Results and discussion

3.1 Effect of aging on creep resistance of PECT

A set of creep experiments have been performed to investigate the creep resistance in PECT. A relatively high stress of 28.6 MPa is applied to achieve an initial strain of 0.015, corresponding to the strain used in stress relaxation tests. The resulting creep curve of unaged PECT is shown in Fig. 2, where prominent creep is observed in both the primary and secondary creep range. Following, it is seen that tertiary creep leads to pronounced necking, which results in development of a new equilibrium state, while rupture is avoided in the 24 h test time. This phenomena could be caused by chain alignment causing strain hardening in

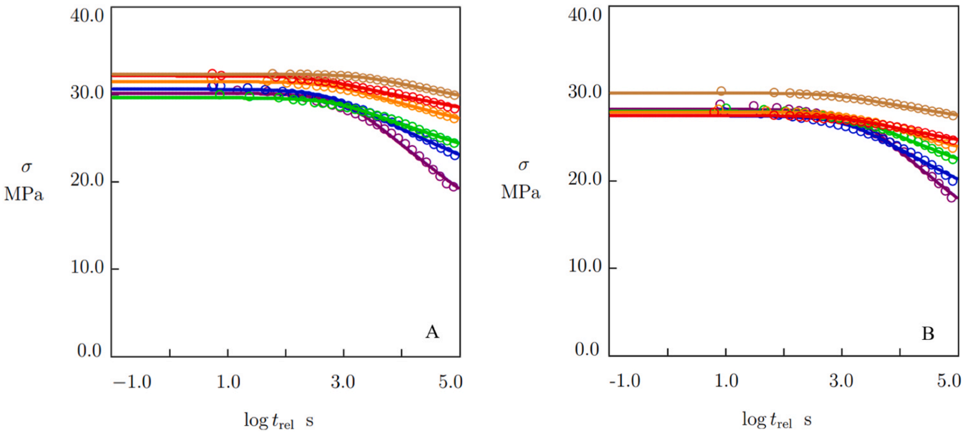

Fig. 5. Tensile stress σ versus relaxation time $t_{\rm rel}$. Circles: experimental data in stress relaxation test with strain $\epsilon = 0.015$ at T = 30 °C on (A) PETT and (B) PECT samples annealed at T_g–20 °C for various times t_a: violet - $t_a = 0$, blue - $t_a = 1$, green - $t_a = 4$, orange - $t_a = 24$, red - $t_a = 168$, brown - $t_a = 504$ h. Solid lines: results of numerical analysis.

the final stage. However, the geometry of the sample might also influence the measurement, as the neck reaches a thicker part of the sample at very high strains, allowing the cross sectional area to increase (see Fig. S11). These hypotheses need further confirmation leaving the observation yet unexplained.

To assess how the creep resistance of PECT changes with time, accelerated physical aging (annealing sub-T_g for various amounts of time t_a) is conducted, and creep curves of unaged and annealed samples are compared in Fig. 3. To fit the experimental data in these creep curves, the material parameter responsible for the viscoelastic response is firstly found from stress relaxation experiments. The viscoplasticity can then be evaluated from creep data, since the latter reflects both viscoelasticity and –plasticity, whereas stress relaxation only reflects viscoelasticity.

From the experimental curves presented in Fig. 3, it is clear, that aging has a large effect on creep resistance. Each creep curve is fitted separately with two parameters C_1 and C_2 and the effect of annealing time on these coefficients is presented in Fig. 4. The effect is described by linear dependencies in double logarithmic coordinates, where the observations and the simulated results coincide. The resulting modelled creep curves, describe the experimental data well, especially for highly aged samples, while it underestimates the strain in the unaged sample.

It has previously been hypothesised, that creep in PET involves the weakening and rearrangement of interactions between polymer chains rather than stretching of the backbone and thus is governed by the strength of secondary bonds [42]. As the strength of interchain interactions rely on Van der Waals forces it is plausible, that it increases during physical aging, causing greater creep resistance even if the macroscopic density remain the same, Table S3.

3.2 Stress relaxation in PETT and PECT with different annealing time

Fig. 5 shows the experimental and simulated stress response of PETT and PECT annealed at T_g-20 °C for different times. It is evident that preliminary annealing significantly decreases stress relaxation in both polyesters, which is also captured by the theoretical model. From the results shown in Fig. 5, the effect of annealing for PECT is similar to that for PETT.

Each of the curves in Fig. 5 is characterized by three parameters, since the parameter describing inhomogeneity, Σ, of the polymer network is independent of annealing time. This independency could arise from the hypothesis, that physical aging does not increase/induce ordered regions in the amorphous phase, which causes large density fluctuations, as in the case of (re)crystallization. However, physical aging could cause redistribution of free volume and thereby change the local fluctuations on a small scale. Fig. 6 shows E-modulus and the parameter γ (attempt rate of separation of strands) as function of annealing time. The simulations of both parameters, also illustrated in Fig. 6, is able to describe the values determined from fitting experimental data. The E-modulus increases weakly (logarithmically) with annealing time, which correspond well to results from tensile tests presented in Figs. S3–4 and from previous studies of the same polyesters

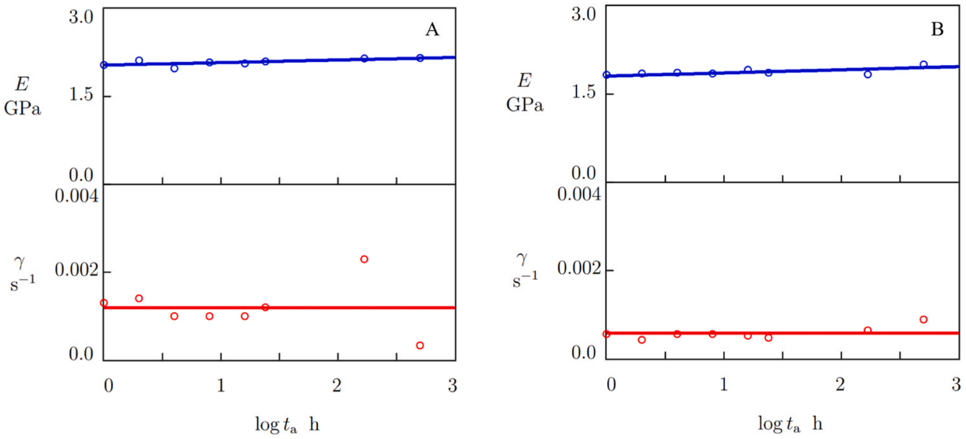

Fig. 6. Parameter E and γ versus annealing time t_a. Circles: treatment of observations in relaxation tests with strain $\epsilon = 0.015$ at T = 30 °C on (A) PETT and (B) PECT samples annealed at T_g–20 °C for various times t_a. Solid lines: results of numerical analysis.

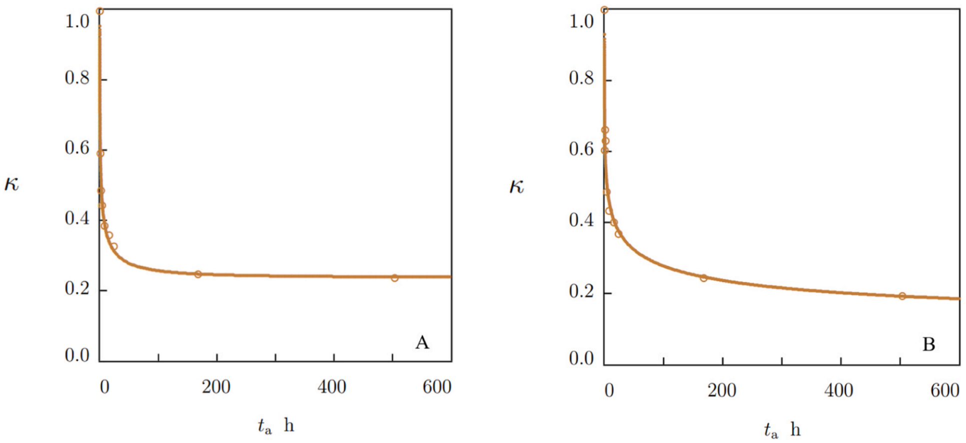

Fig. 7. Parameter κ versus annealing time t_a. Circles: treatment of observations in relaxation tests with strain $\epsilon = 0.015$ at T = 30 °C on (A) PETT and (B) PECT samples annealed at T_g–20 °C for various times t_a. Solid lines: results of numerical analysis.

[30]. The moduli of PETT and PECT differ only slightly showing that PETT is stiffer than PECT. This also consists with results from tensile tests, showing that E-modulus is 2.2 and 1.9 GPa for unaged PETT and PECT, respectively (Figs. S1–2, Table S1–2). The rate of rearrangement of interchain interaction and attempt rate of separation of strands, γ, is independent on annealing time and is twice as high for PETT as compared to PECT. Both observations are rather unexpected. The first suggests that the rate of rearrangements of chain interactions during stress relaxation is not influenced by physical aging, which contradicts the assumption, that molecular movement is prohibited in aged samples, since less free volume is available compared to that in unaged samples. This could suggest that physical aging redistributes free volume and changes the density on a scale that is much smaller compared to the mechanical response. Secondly, the chemical structure of PETT is more rigid compared to PECT, specifically with less flexibility in the TMCD unit of PETT compared to CHDM in PECT, which is manifested in the T_g difference between the two, where that of PETT is ~10 °C higher. The T_g difference implies that more energy is needed to initiate molecular mobility in PETT compared to PECT, and therefore it is notable, that the rate of interaction-rearrangement is found to be highest in PETT at the same temperature (30 °C). Our previous studies of physical aging rates, measured as enthalpy loss at T_g-20 °C, also suggested, that the enthalpy

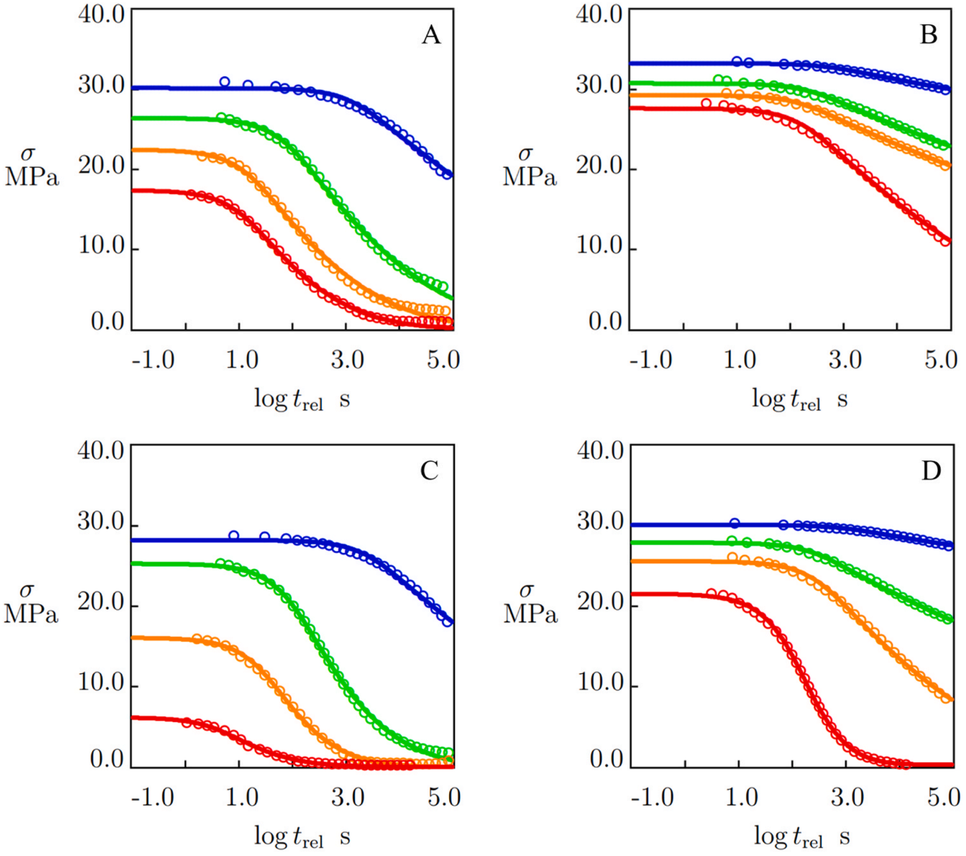

Fig. 8. Tensile stress σ versus relaxation time t_{rel}. Circles: experimental data on (A) non-aged PETT (B) PETT aged for 504 h at T_g–20 °C (C) non-aged PECT and (D) PECT aged for 504 h at T_g–20 °C in stress relaxation test with strain $\epsilon = 0.015$ at temperatures T = 30 (blue), T = 50 (green), T = 60 (orange) and T = 70 (red) °C. Solid lines: results of simulations.

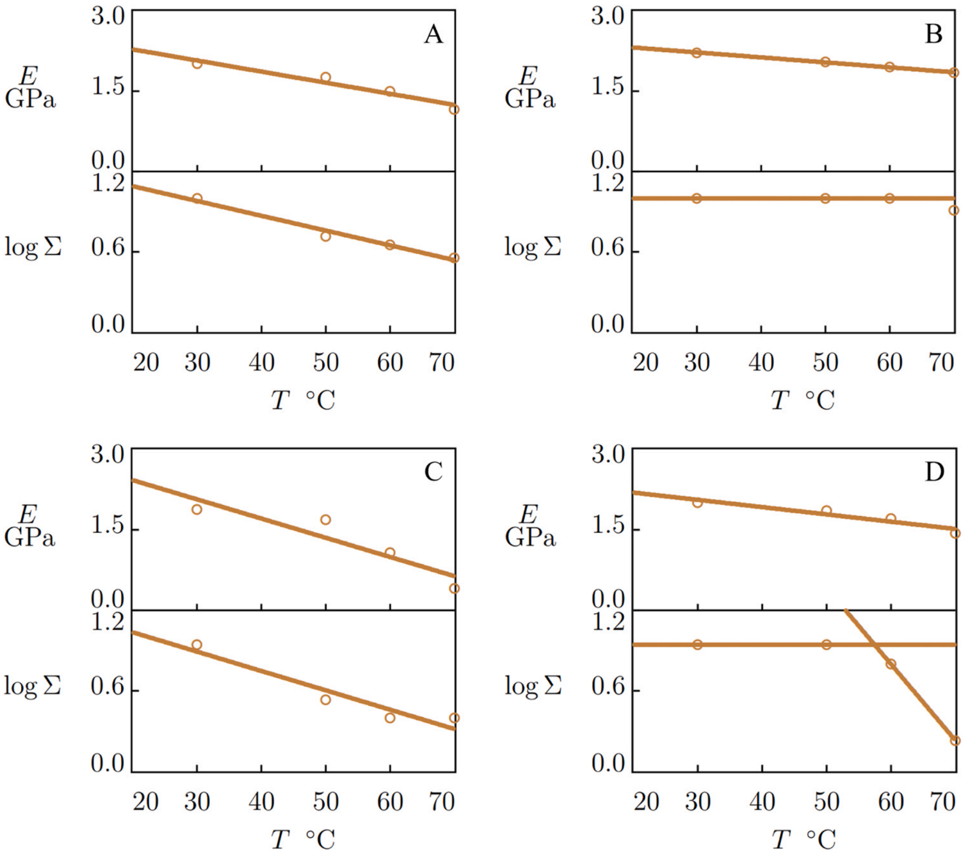

Fig. 9. Parameter E and Σ versus temperature T. Circles: treatment of observations on (A) non-aged PETT (B) PETT aged for 504 h at T_g–20 °C (C) non-aged PECT and (D) PECT aged for 504 h at T_g–20 °C in stress relaxation test with strain $\epsilon = 0.015$. Solid lines: results of simulations.

relaxation occurs faster in PECT than in PETT at the same temperature relative to T_g, suggesting that structural relaxation should occur faster in PECT [30]. However, even when the backbone of PETT is more sterically hindered, the nature of the intermolecular forces in the two polyesters is the same. Therefore, the fitted/simulated values of γ, could imply that the mechanism taking place during stress relaxation of these polyesters does not involve steric crowding and might be predominantly governed by Van der Waals forces and hydrogen bonding.

The effect of annealing on the third model parameter κ is shown in Fig. 7. As E-modulus and γ are almost unaffected by physical aging, much of the explanation, provided by the model, for the decreased stress relaxation in annealed samples, seem to be found in this coefficient. κ decreases strongly with annealing time described by the stretched exponential function $\kappa = \exp(-(t_a/t_{a0})^m)$ with m = 0.33 for PETT and m = 0.23 for PECT. Describing the concentration of temporary active junctions, κ is 1 in unaged samples of both PETT and PECT and hence all junctions are active and able to slide during the stress relaxation experiment on unaged samples. After annealing for 24 h, κ decreases to roughly 0.2 in both polyesters, meaning that ~80% of the junctions have become locked and resists sliding as stress is applied. This observation implies, that the strength and/or amount of secondary bonds increases during physical aging adding to the hypothesis, that these interactions governs the stress relaxation. This agrees with the idea of physical aging as a densification process or a rearrangement of the polymeric segments into a structure with stronger intermolecular interactions, where free volume is decreased and molecular movements inhibited. However, based on the observations of γ, which is unaffected by annealing, the rate of breakage and formation of interchain interactions during stress relaxation is maintained in spite of physical aging. This could suggest, that physical aging causes local densifications, where the entanglements are strongly locked not allowing them to slide, while the rate of rearrangement of bonds remain the same without separating the chains. κ seems do decrease slightly faster in PETT compared to PECT, suggesting that the rigid nature of TMCD causes faster formation of locked junctions in the matrix compared to CHDM.

3.3 Thermal effects

Experimental data obtained at temperatures up to T_g for non-aged samples and samples aged for 504 h at T_g-20 °C are presented in Fig. 8. The stress drops faster the higher the temperature, but is maintained to a significantly higher degree in aged samples compared to the unaged. At increased temperatures, especially at 70 °C, the stress is relaxed much faster in PECT than in PETT. This is because, the temperature is in close proximity to T_g of PECT (81 ºC from DSC, Fig. S8 66 °C from dynamic mechanical analysis, Fig. S6). At T_g the storage modulus drops significantly as the material starts to soften leading to fast stress relaxation. Furthermore, a sample is rejuvenated, when kept above T_g for a period of time, since the material is able to obtain an equilibrium state. However, to completely rejuvenate a sample, it is necessary to reach the equilibrium in a liquid-like state, and thus the temperature would need to reach at least the offset of the T_g. This might explain why the initial stress at 70 °C is still three times as high for the aged PECT as for the unaged, suggesting an effect of physical aging, at least on a short timescale.

The effect of temperature on the obtained model parameters are presented in Figs. 9–11. E-modulus decreases linearly with temperature in both copolyesters, where the rate of decay is higher in unaged samples compared to the aged by twice. The decay rate is similar in both materials but is slightly steeper for PECT in both unaged and aged samples. The decrease in E-modulus with increasing temperature is expected, as higher temperature means that the molecules have more kinetic energy,

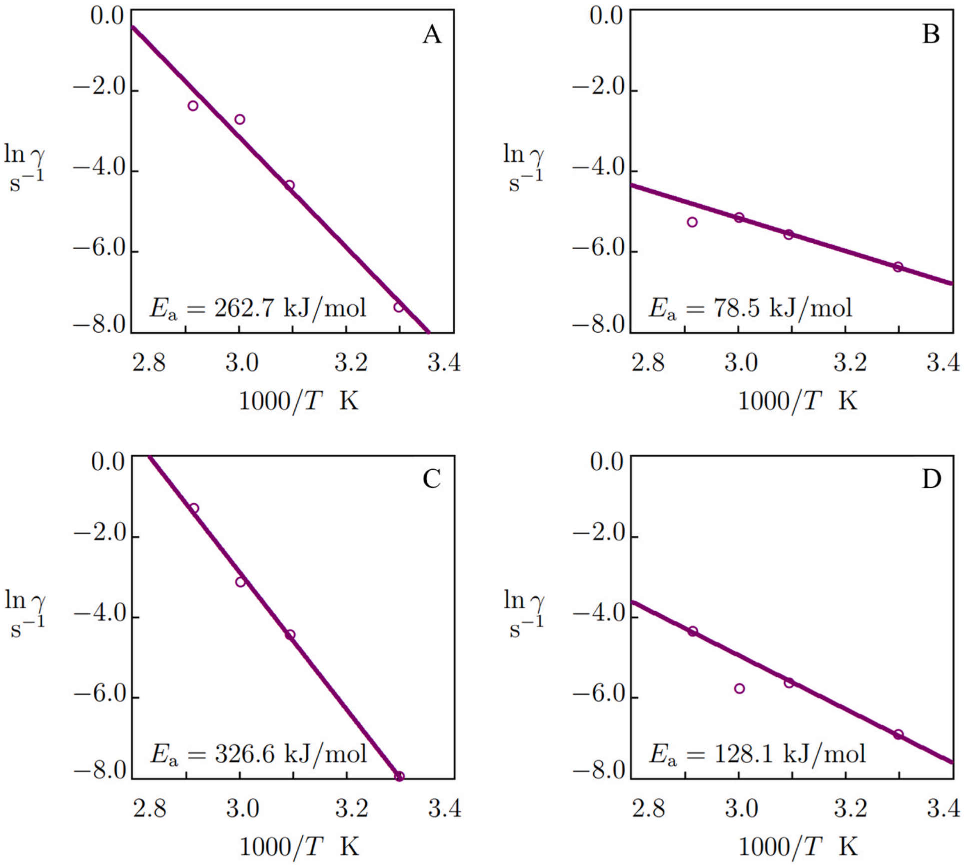

Fig. 10. Parameter γ versus temperature T. Circles: treatment of observations on (A) non-aged PETT (B) PETT aged for 504 h at T_g–20 °C (C) non-aged PECT and (D) PECT aged for 504 h at T_g–20 °C in stress relaxation test with strain $\epsilon = 0.015$. Solid lines: results of simulations.

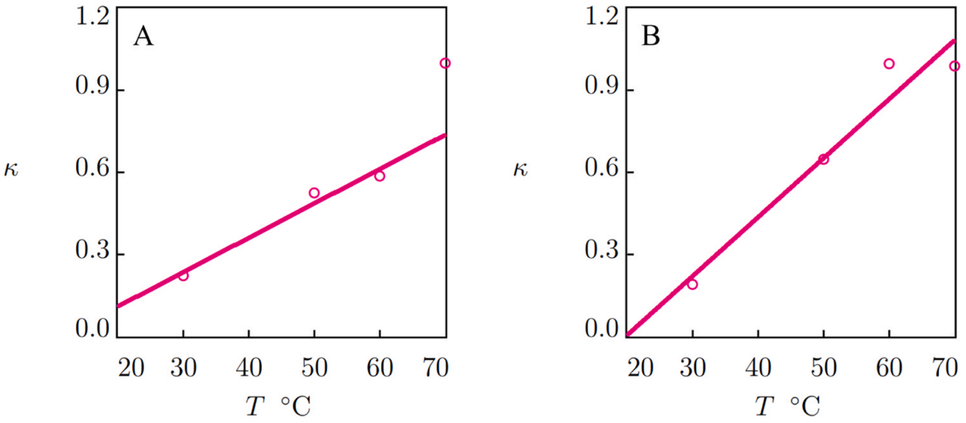

Fig. 11. Parameter κ versus temperature T. Circles: treatment of observations in stress relaxation test with strain $\epsilon = 0.01$ on samples of (A) PETT and (B) PECT aged for 504 h at T_g – 20 °C. Solid lines: results of simulations.

hence the secondary bonds have less effect. The network heterogeneity decreases linearly with temperature in unaged samples, suggesting that higher temperatures allow rearrangement of polymeric segments yielding a more homogenous network. However, for aged samples of both PETT and PECT, the inhomogeneity is unaffected by temperature until T_g is approached (seen for PECT around 60–70 °C in Fig. 9) where it suddenly starts dropping. The reason for the constant inhomogeneity in aged samples might be due to stronger molecular interactions in the aged samples compared to the unaged, and thus more energy is needed to allow further rearrangement of the polymer segments. As T_g is approached, enough thermal energy is provided to break/rearrange the intermolecular interactions and form a more homogeneous network. This consist well with previous observations in the model parameters, suggesting that physical aging forms locked junctions that are strong enough to resist sliding when the sample is strained. These junctions would most likely keep the polymer network fixed until the temperature approaches T_g and enough energy is provided to break the interactions.

The rate of rearrangement of temporary interactions can be described by an Arrhenius dependency (Eq. (9) Section 2.6) with activation energy as indicated in the figure. Aging causes a large decrease in activation energy in both copolyesters, but generally the values are higher for PECT than PETT suggesting a larger effect of temperature in

PECT, which also fits well with the experimental data. This observation also agrees with previous studies of enthalpy relaxation in PECT and PETT, where activation energies of 218–224 and 134–159 kJ mol^{-1} where found, respectively [30]. However, from the data shown in Fig. 6, it is seen, that the rate of secondary bond rearrangement is independent of annealing time, which questions the direct connection to the data presented here, where a difference in γ is clearly seen between unaged and aged samples.

Fig. 11 depicts κ as function of temperature. As κ describes the concentration of active junctions, a value of 1 means that all interactions between chains are temporary and can be broken easily during stress relaxation compared to locked junctions. In unaged samples all values for κ were 1 at any temperatures, and hence all junctions are active. In aged samples of both PETT and PECT, locked interactions are formed, probably due to rearrangement of polymer segments into conformations with stronger/more secondary bonds as previously discussed. However, when temperature is raised up to T_g, the locked junctions disappear, as seen for PECT, where κ reaches 1 at 70 °C.

Generally, observations of κ (concentration of active junctions), which strongly decreases with annealing time, and Σ (inhomogeneity of the polymer network), which is independent of temperature in annealed samples but significantly affected by temperature in unaged samples, suggest that stronger intermolecular interactions are formed during physical aging. The model also suggest that the secondary bonds have a larger effect on stress relaxation than stiffness of the polymer backbone, since the viscoelastic behaviour is almost identical in the two copolyesters but is greatly affected by annealing. Based on κ, the model suggests that the rate of physical aging is higher in PETT than PECT, as the decay in κ with annealing time is greatest for PETT. Furthermore, the model implies, that the attempt rate of separation of polymer chains is twice as high in PETT compared to PECT, suggesting more secondary bond rearrangement, which could enable faster structural changes. In our previous work, physical aging, especially manifested as enthalpy relaxation, occurred faster in copolyesters containing CHDM compared to TMCD. These earlier results combined with the results presented here imply, that the effect of physical aging cannot be explained by free volume theory alone, and that chemical structure also has an influence, which yet needs to be fully understood.

4. Conclusion

In this work we apply a constitutive model to describe the mechanical response in two glycol modified PET polymers, namely PETT and PECT, with different thermal history. The model uses a homogenization concept, which account for local density fluctuations in the polymer network, enabling the model to capture the structural development during physical aging. The results show that the model can predict the stress relaxation of PETT and PECT annealed for different durations with satisfactory precision. Furthermore, the model can describe creep in annealed PECT but underestimates the resulting strain in the unaged samples. The effect of physical aging on model parameters has been described, where κ is most strongly affected by aging. The concentration of active junctions decreases exponentially with annealing time, indicating that molecular configurations with stronger interchain interactions are formed during physical aging rendering the entanglements immobile when strained. Generally, PETT and PECT showed similar behaviours at 30 °C, suggesting that the chemical structure of the glycol unit (TMCD and CHDM) does not have significant effect on stress relaxation in the tested compositions. This also implies that PETT and PECT age with similar rates at T_g-20 °C, which contradicts previous work. When stress relaxation is tested at increased temperatures, the structural effects are more visible, demonstrating higher activation energies for PECT than PETT. The work presented here provides insights into how physical aging affects the viscoelastic response of polyesters, which is merely a small contribution to the future work of describing the complex non-equilibrium behaviour of amorphous polymers.

CRediT authorship contribution statement

Anne Therese Husth Weyhe: Conceptualization, Methodology, Investigation, Writing – original draft, Writing – review & editing. **Aleksey D. Drozdov:** Conceptualization, Methodology, Formal analysis, Writing – review & editing. **Jesper de Claville Christiansen:** Conceptualization, Supervision, Writing – review & editing. **Emil Andersen:** Conceptualization, Writing – review & editing. **Donghong Yu:** Conceptualization, Supervision, 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.

Data availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mtcomm.2023.107241.

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