



# Optimizing physical aging in poly(ethylene terephthalate)-glycol (PETG)

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## ABSTRACT

Amorphous glassy polymers are widely used as structural materials. However, their mechanical properties continuously evolve with physical aging, which significantly influences their applications. In this work, we investigate the effects of aging on stress response of poly(ethylene terephthalate)-glycol (PETG). The PETG specimens are either quenched or annealed around or below the glass transition temperature ( $T_g$ ) for a period of time. The uniaxial compression tests are then performed at  $T_g - 40^\circ\text{C}$  and strain rate 0.001/s. The quenched polymers exhibit the smallest yield strength and strain softening, indicating that negligible structural relaxation occurs for the quenched condition. For annealed polymers, the yield strength increases with aging time. The results also show that there exists an optimal temperature to achieve the highest structural relaxation rate, which is around  $T_g - 20^\circ\text{C}$ . Compared with annealing at a single temperature, annealing at multiple temperatures in discrete steps is a more efficient method for structural relaxation. The same experiments are also performed on specimens with 30% predeformation. The optimal aging temperature does not change with predeformation. However, at the same annealing condition the yield strength of specimens with 30% predeformation is around 5 MPa less than that of undeformed specimens.

## 1. Introduction

When cooled around the glass transition temperature ( $T_g$ ), an equilibrium polymeric liquid gradually departs from its equilibrium state. This nonequilibrium structure continuously evolves towards equilibrium with annealing. This process is known as structural relaxation, which is also named as physical aging [1]. When polymer ages, the thermomechanical properties and macroscopic responses change with time. Thus, fully understanding physical aging plays a vital role when using polymers as structural materials. However, physical aging is a strong nonlinear process. The aging rate depends on temperature and the nonequilibrium structure itself [2], which results in complexity for both experimental characterization and constitutive modeling aging effects.

Structural relaxation can be measured using different techniques [3–7]. The pioneering work of Kovacs [8] measured the volume change of PVAc equilibrated at a certain temperature after instantly jumping from various temperatures, which illustrated many important features of physical aging. Differential scanning calorimetry (DSC) can measure the enthalpy relaxation during physical aging [9,10]. In a typical DSC test, materials are cooled from an equilibrium state to the glassy state at a certain cooling rate and then annealed for a different period of time at

low temperatures. The heat flow is measured during the heating process to investigate the effects of different cooling rates or annealing time on the magnitude and location of enthalpy overshoot. Broadband dielectric spectroscopy is also employed to describe structural relaxation of polymers [11]. The dielectric permittivity is measured and compared for polymers with different aging time [12]. Structural relaxation can also be characterized through measuring the gas permeability [13]. Cui et al. [14] found the permeability of polyimide thin films was decreased by an order of magnitude after 1000 h of aging.

Mechanical tests, due to the simplicity, are widely used to measure structural relaxation [15,16]. Struik [17] found the creep compliance shifted to larger time regions for a series of polymers. Sell and McKenna [18] investigated the yield stress of epoxy glasses subject to quench and isothermally aging up to 1000 h. The results showed that with aging, the yield strength increased 1.8 times over the longest period of aging time. Aging is also found to influence the deformation localization behaviors. A ductile to brittle transition is observed for various polymers with aging [19]. Zhang et al. [20] performed uniaxial tension tests on poly(ethylene terephthalate)-glycol (PETG). It was found that the localization type changed from necking for quenched polymer to shear banding for annealed polymers. Cailloux et al. [21] demonstrated that the failure behaviors of branched poly(lactic acid)

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showed a strong dependence on physical aging.

The evolvement of mechanical properties with aging can be either beneficial or detrimental to the applications of polymers. On one side, physical aging can increase the yield strength of polymers. On the other side, aging may induce an earlier failure of some amorphous polymers. Thus, accurately characterizing the aging rate is extremely important. The driving force for physical aging increases with decreasing temperature. However, at a sufficient low temperature, the low molecular mobility limits the relaxation. Thus, it may exist a certain optimal temperature to achieve the most sluggish structure state. Pye and Roth [22] used an ellipsometry to measure the thickness change during aging for polymer films. The results showed that there existed a peak in aging rate with temperature. Choi et al. [23] adopted a constitutive model to investigate the influence of aging temperature on the shape-memory behaviors of amorphous thermosets. The simulation results showed that the optimal aging temperature to tune the shape-memory response is around 20 °C below  $T_g$ . However, a complete investigation on optimizing the aging effects of amorphous polymers on mechanical response is still in its infancy. This work aims to perform a series of experiments to describe the effects of annealing time and temperature on the stress response of undeformed and predeformed amorphous polymers.

The paper will be arranged as follows. The experimental method section will mainly discuss the protocol for aging process and the main setup for the uniaxial compression tests. The following section presents the main results, focusing on the effects of aging temperature and aging time on the yield strength. The paper ends with main conclusions.

## 2. Experimental method

### 2.1. Material and sample preparation

The material used in this study is PETG, which was directly provided by McMaster-Carr Supply Co and used as its in-received condition without further chemical modification. For the dynamic temperature sweep tests, the large PETG film was cut to a rectangular shape with size 15 mm × 5 mm × 1.59 mm. For the uniaxial compression tests, the PETG rod was machined to a cylinder with 9.5 mm in diameter and 10 mm in height. The surface of cylindrical specimens were further polished by a sand paper.

### 2.2. Dynamic temperature sweep tests

The dynamic temperature sweep test was used to determine the glass transition region of PETG. The film specimen was subject to a 0.2% dynamic strain and heated from 20 °C to 130 °C at 2 °C/min on a DMA Q800.

### 2.3. Uniaxial compression tests

The uniaxial compression tests were performed on both undeformed and predeformed specimens. An illustration for the main experimental procedure can be found in Fig. 1. For the undeformed condition, the

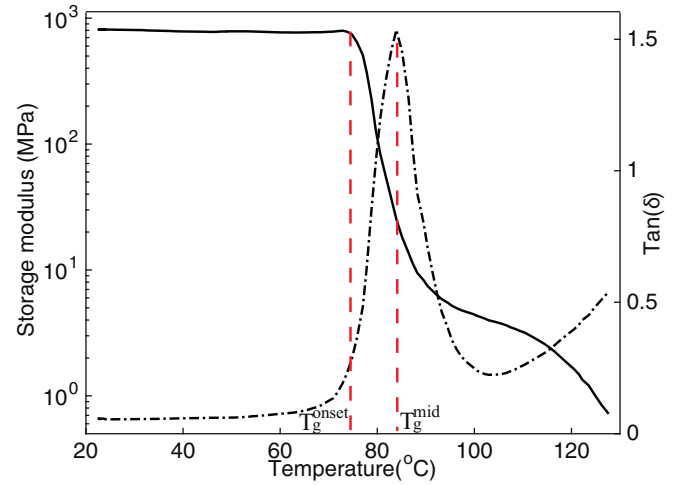


Fig. 2. The storage modulus and  $\tan \delta$  of PETG measured using the dynamic temperature sweep test.

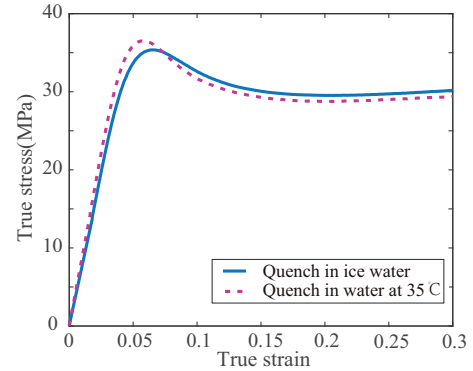


Fig. 3. Comparing the stress response of the specimens quenched in ice water or water at 35 °C.

specimens were first placed in an oven set at 100 °C for 30 min to remove previous thermal history. The quenched specimens were obtained either transferring the specimens from the oven to ice water or water set at 35 °C. For annealed condition, the oven temperature was lowered to a predetermined value, i.e., 75 °C, 65 °C, 55 °C and 45 °C, and kept isothermally for 1 h, 3 h, 10 h and 30 h respectively. In general, it took the oven around 5 to 10 min to stabilize at the setting temperature. Another approach was also employed to obtain the annealed specimens. The fully thermally rejuvenated specimens was subject to a temperature decrease in discrete steps from 75 °C to 45 °C. The discrete step was chosen as either 5 °C or 10 °C. At each temperature, the specimens were kept isothermal for a certain period time varying from 0.5 h to 4 h. After the thermal treatment, the specimens were moved to an Instron 3367 testing machine equipped with an environmental chamber set at 35 °C

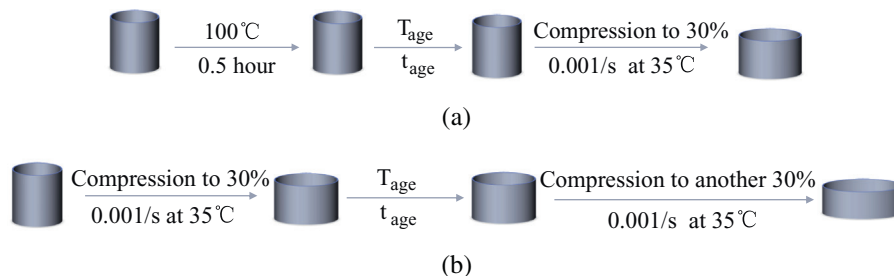


Fig. 1. An illustration for the experimental procedure of (a) undeformed specimens, and (b) predeformed specimens.

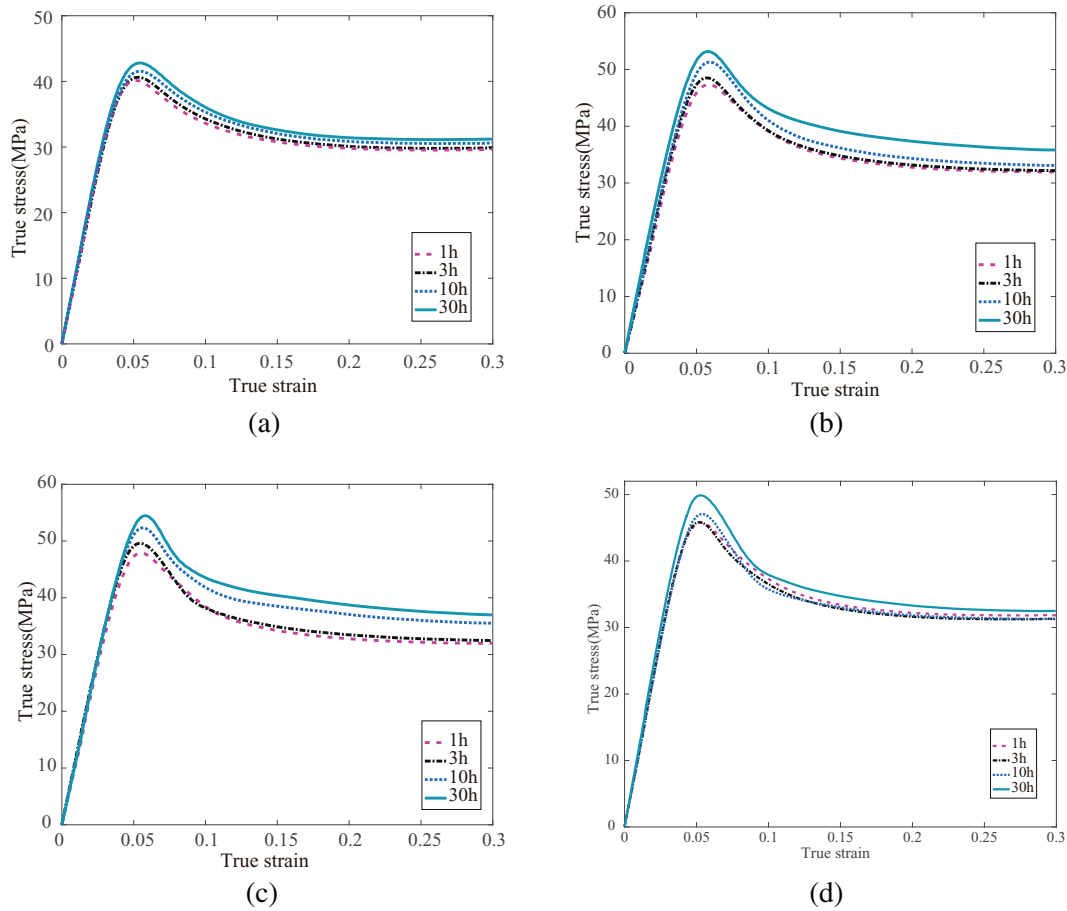


Fig. 4. The stress response of specimens annealed at a)75 °C, b)65 °C, (c)55 °C, and (d)45 °C.

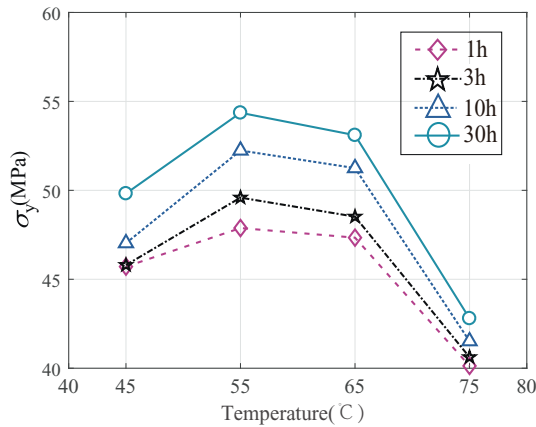


Fig. 5. The influence of the annealing temperature and time on the evolution of yield strength of undeformed specimens.

and kept for another 0.5 h to achieve a homogenous temperature field of the whole specimen. The specimens were compressed to 30% true strain at a true strain rate of 0.001/s. This relative low strain rate was chosen to make sure an isothermal condition during the compression process. The whole compression process took only 300 s. Thus, physical aging during the compression process was also negligible. To minimize the effects of friction, WD-40, a common lubricant, was used between the samples and compression platens. Visual observation indicated that the applied deformation was approximately homogeneous and no bulging was observed during the tests.

The predeformed specimens were obtained by deforming the

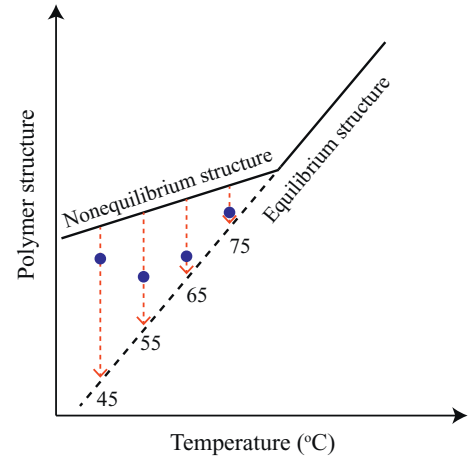


Fig. 6. An illustration to explain the physical mechanism of optimal aging temperature.

specimens at 35 °C and a true strain rate of 0.001/s followed by unloaded to zero stress. The specimens were then transferred into the oven set at 45 °C, 55 °C or 65 °C. At these three temperatures, the pre-deformed shape only showed slightly recovery. In comparison, a large fraction of predeformed shape is recovered when annealed at 75 °C. The aging time was chosen the same as the undeformed specimens. After annealing, the length of specimens were measured before moved back to the oven set at 35 °C. After kept for 30 min, the specimens were then subject to uniaxial compression for another 30% strain at a true strain rate 0.001/s. All the above tests were conducted at least twice. The

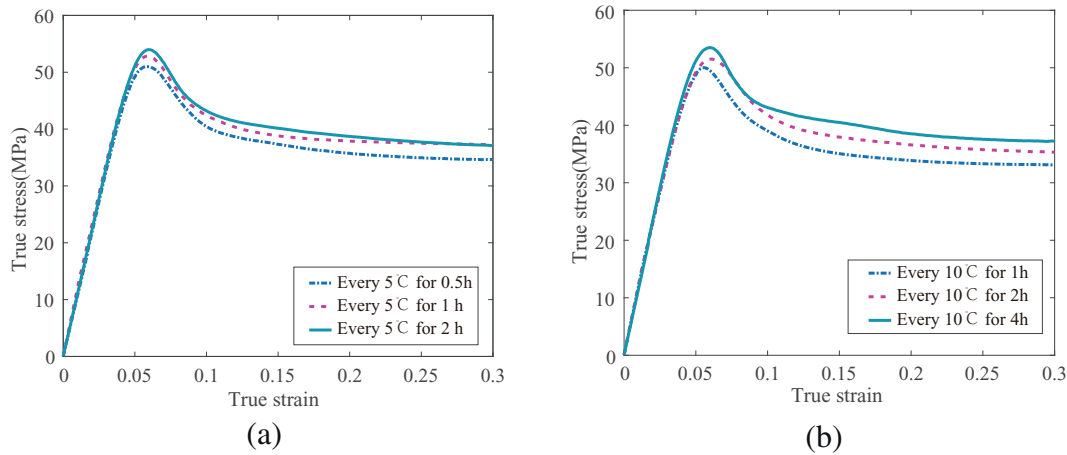


Fig. 7. The stress response of specimens annealed at every a) 5°C, and b) 10 °C for a certain amount of time.

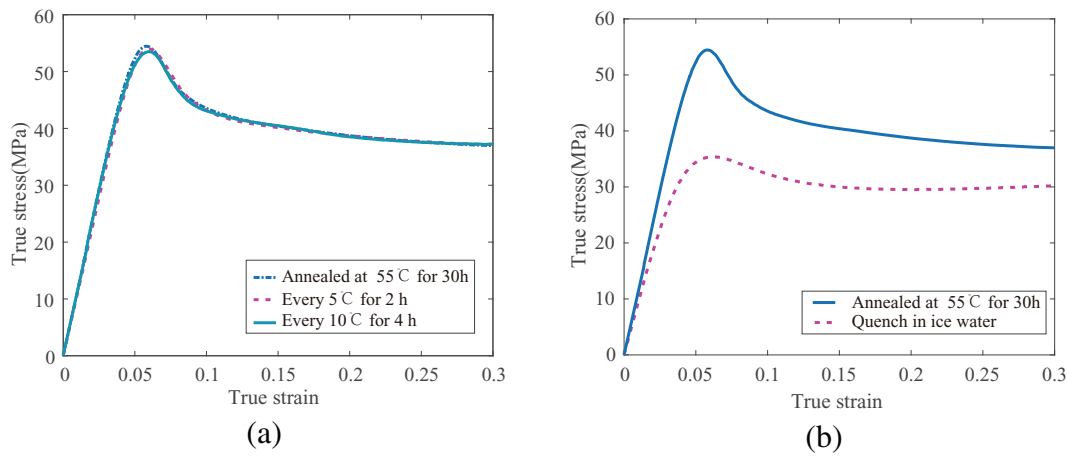


Fig. 8. Comparison the stress response of polymers a) annealed at three different conditions, and b) quenched in ice water and annealed at 55 °C for 30 h.

results were found to be remarkably reproducible. Thus, in the following section, we do not put an error bar on the results.

### 3. Results and discussions

PETG is a transparent amorphous thermoplastic. The PETG films and rods used in this work are provided by a commercial supplier. Thus, we use the dynamic temperature sweep test to characterize the glass transition region of the obtained materials. As shown in Fig. 2, the PETG films exhibits the typical glass transition behaviors of thermoplastics. A sharp storage modulus change occurs around 75 °C to 95 °C. The onset glass transition temperature  $T_g^{\text{onset}}$  is defined as the end temperature of glassy plateau, which is around 75 °C. The middle glass transition temperature  $T_g^{\text{mid}}$  is obtained from the location of  $\tan \delta$  peak with the value of 84 °C. The storage modulus continuously decreases at high temperature. The  $\tan \delta$  exhibits a upturn above 100 °C. These indicate PETG is transited into a viscous liquid at high temperature. In our previous work [20], we also used DSC tests to characterize the obtained polymers. The glass transition region measured during DSC scan is consistent with the results from dynamic temperature sweep tests.

The uniaxial compression tests are used to obtained the stress response of specimens with different thermal treatments. Sell and McKenna [18] also investigated the effects of physical aging on the yield strength of epoxy polymers. The compression tests were run at the aging temperature. Different from this, in our setup, all the specimens are deformed at the same temperature. This provides a direct

comparison of structural relaxation rate of different conditions. Fig. 3 compares the stress response of two quenched specimens. For both specimens, only a slight strain softening can be observed. This is because structural relaxation is ceased during the quenching process. The yield strength of specimens quenched in ice water is slightly smaller than the specimens quenched in water at 35 °C. This may be caused by the relaxation of some processes with fast modes at 35 °C, while those processes are nearly frozen in ice water.

Fig. 4 plots the stress response of undeformed polymers annealed at different temperatures. All the stress response shows the typical viscoplastic deformation with yielding and strain softening. At each annealing temperature, the yield strength increases with aging time. The highest annealing temperature chosen was 75 °C, which was the onset glass transition temperature. As shown in Fig. 4-a, the yield strength of polymers annealed for 1 h and 30 h does not show much difference when annealed at 75 °C. Also the yield strength of specimens annealed at 75 °C is smallest than annealed at the other three temperatures, as shown in Fig. 5. The increase of yield strength after 30 h annealed at 45 °C is also insignificant. In comparison, when annealed at the two middle temperatures, the yield strength difference between 1 h and 30 h is around 7 MPa. Fig. 5 also shows the yield strength exhibited a peak at 55 °C. This observation is similar to the observation of volumetric relaxation demonstrated by Pye and Roth [22]. The mechanism behind this phenomena is straightforward. When annealed at  $T_g^{\text{onset}}$ , the structure is trapped at a higher energy state even though the equilibrium structure can be reached at a short period of time. An extremely low annealing temperature, such as 40 °C below  $T_g^{\text{onset}}$  in our setup,

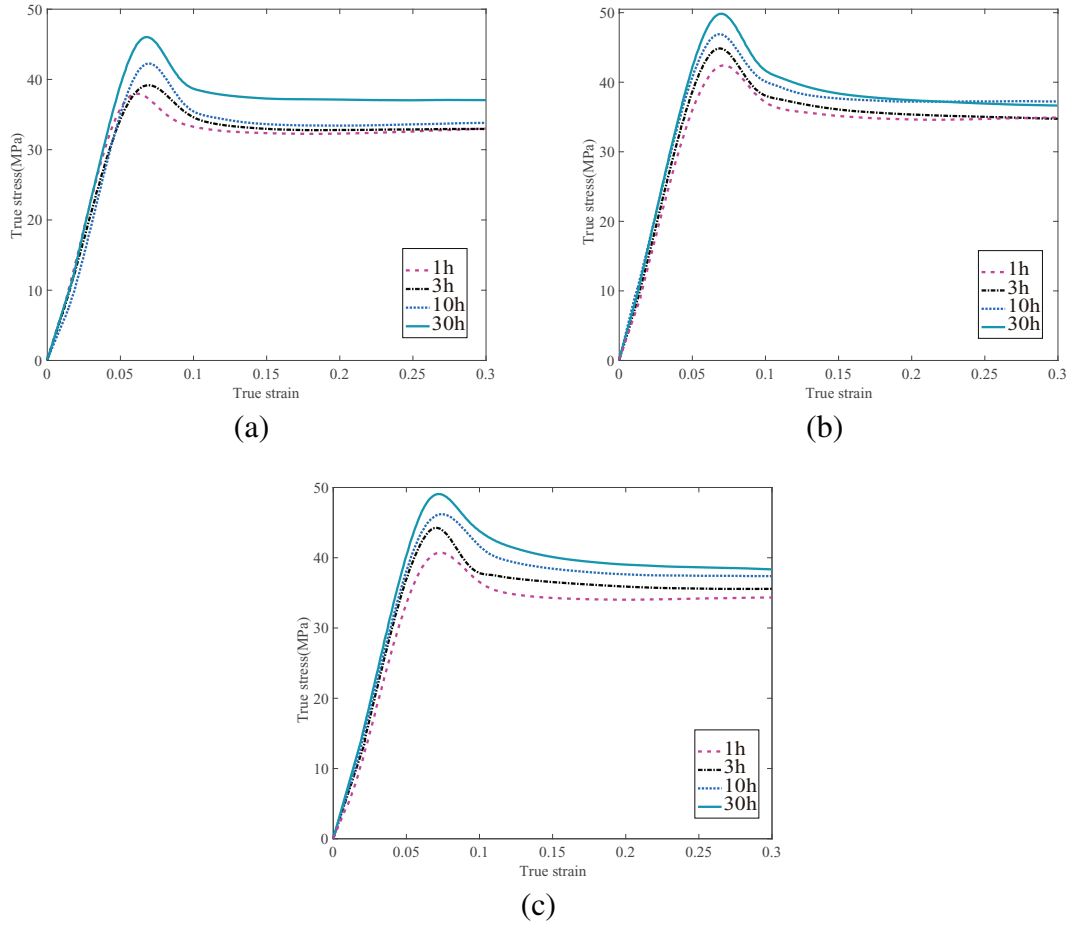


Fig. 9. Stress response of PETG with 30% predeformation and annealed at (a) 65 °C, (b) 55 °C, and (c) 45 °C for different amounts of time.

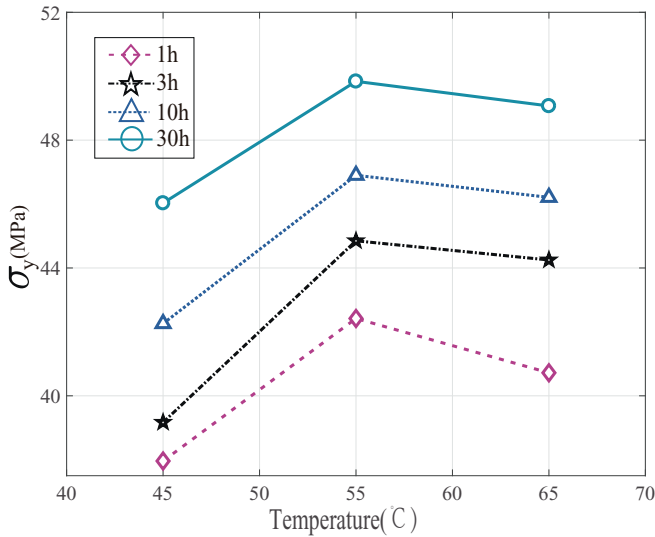


Fig. 10. The influence of the annealing temperature and time on the evolution of yield strength of preformed specimens.

results in a low relaxation rate. Thus, structural relaxation is also limited in this case. We also provide an illustration to explain the above physical mechanism in Fig. 6. When annealed at 55 °C, polymers obtain the most sluggish structure. This is caused by a balance between the distance departure from the equilibrium state and the relaxation rate.

We also adopt another aging protocol. The polymers are annealed in

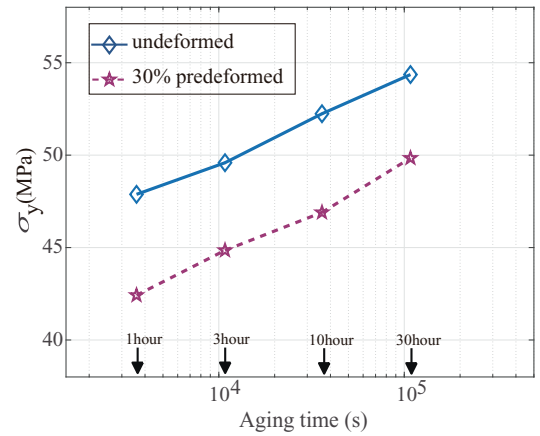


Fig. 11. Comparing the yield strength of undeformed and preformed specimens aged at 55 °C.

discrete steps at multiple temperatures for a certain period. As shown in Fig. 7, the yield strength increases with aging time at each step. Fig. 8-a compares the yield strength of annealed at three different conditions: annealed at 55 °C for 30 h, every 5 °C for 2 h, and every 10 °C for 4 h. The stress responses of the specimens annealed at these three conditions are almost identical. The total annealing time at multiple temperatures is around 16 h. Compared with 30 h annealed at a single temperature, the aging procedure in discrete steps is proven to be a more efficient method to achieve maximum structural relaxation. When annealing at a certain temperature, structural relaxation only involves with some



relaxation processes, which have the relaxation time smaller or comparable with experimental time scale at the chosen annealing temperature. In comparison, when annealed at multiple temperatures, more relaxation processes have the chance to relax towards equilibrium.

In our setup, the quenched specimens exhibit the lowest yield strength, indicating minimum structural relaxation occurred. In comparison, specimens annealed at 55 °C for 30 h have the maximum structural relaxation, exhibiting the largest yield strength. Fig. 8-b compares the stress response of specimens under these two conditions. As shown, the yield strength increased from 35 MPa for quenched polymers to 55 MPa for annealed polymers. This shows that the mechanical performance of amorphous polymers can be remarkably changed by aging effects.

In addition to undeformed specimens, specimens with predeformation were also used to investigate the effects of annealing temperature on mechanical response. The predeformation was induced by compressing the polymers in its glassy state. During the unloading and annealing period, around 5%–7% strain was recovered. However, when annealed around or above 70 °C, most of the deformed shape was recovered. Such a phenomena is known as shape-memory effects [24]. Thus, different from undeformed polymers, only three annealing temperatures were chosen for predeformed specimens. As shown in Fig. 9, the yield strength of oriented polymers also increased with annealing time. The polymers exhibited a smaller yield strength when annealed at 45 °C than annealed at 55 and 65 °C. Fig. 10 summarizes the yield strength of predeformed polymers under various aging conditions. At the same annealing time, the maximum yield strength occurred at 55 °C, which was consistent with the observation for undeformed polymers. The yield strength of both undeformed and predeformed polymers annealed at 55 °C is shown in Fig. 11. The yield strength increased linearly with logarithm of time for both conditions. The slope of undeformed and predeformed specimens was close, indicating that the aging rate was not affected by predeformation. The rate of physical aging strongly depends on the structural relaxation spectrum [23]. The breadth of spectrum, representing the broad distribution of the relaxation processes, controls the aging rate. In general, in the short time region a narrower spectrum results in less structure relaxation, while in the long term region a narrower spectrum induces more structural relaxation. For PETG, it is found the optimal temperature does not change with predeformation, which indicates the predeformation does not change or only slightly changes the shape of structural relaxation spectrum.

However, it is also found the absolute value of yield strength for predeformed polymers is around 5 MPa lower than that of undeformed polymers in the same aging condition, which suggests the mechanical deformation influences the microstructure of PETG. Applying mechanical deformation on amorphous polymers can induce an opposite effect of physical aging, known as mechanical rejuvenation [25–29]. With physical aging, the nonequilibrium structure of amorphous solids evolves towards the equilibrium state, which leads to a decrease in energy, entropy and molecular mobility. In contrast, the mechanical deformation drives the structure of amorphous solids away from equilibrium. During rejuvenation, a fraction of work is stored in the amorphous solids, which can be measured using differential scanning calorimetry [28,30]. Using optical photobleaching technique, Lee and Ediger [31] can directly measure the change of molecular mobility during aging and rejuvenation processes, which clearly shows a decrease in molecular mobility with aging and an increase in molecular mobility when applying deformation. While aging can induce a ductile to brittle transition, rejuvenation effects are able to increase the ductility of amorphous polymers [32] and metallic glasses [26]. Here, for amorphous thermoplastics PETG, we find that mechanical predeformation can substantially reduce the yield strength compared with undeformed polymers, such an effect is similar to the rejuvenation effect.

#### 4. Conclusions

Physical aging plays an essential role on the mechanical performance of amorphous solids. Various works from both experimental and modeling perspectives have been performed to understand aging behaviors in polymers. The most widely used model is based on Tool's fictive temperature theory. This model is able to qualitatively and quantitatively describe the effects of physical aging on the volumetric and enthalpic relaxation. Modeling the mechanical response of polymers with different thermal treatments is a more challenge task. Only a few models have been developed to describe this phenomenon [25,33]. However, those models are not fully calibrated for various aging conditions. In this work, we perform a complete investigation to obtain the mechanical response of both undeformed and predeformed amorphous polymers under different aging conditions. The polymers show little structural relaxation during the quenched condition since limited strain softening is observed during uniaxial compression tests. When annealed below  $T_g$ , the yield strength and the magnitude of strain softening increase with aging time. Annealing temperature also influences the aging rate. The results show there exists an optimal annealing temperature with maximum structural relaxation. When annealed time is the same, the polymers exhibited the largest yield strength when annealed at 20 °C below the onset glass transition temperature. The aging rate does not change with predeformation. However, at the same thermal treatment, the yield strength is around 5 MPa less for the predeformed specimens. The experimental observations in this work can deepen our understanding of physical aging, and also provide a useful guide for developing models to describe the aging effects on mechanical response.

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