Physical aging of confined glasses

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The properties of glasses confined to the nanometre length-scale can deviate substantially from those found in bulk samples. Physical aging, the structural relaxation of glasses toward equilibrium, leads to time-dependent mechanical, electrical, optical properties, etc. This article highlights experimental work on the impact of confinement on the physical aging of molecular and polymeric glasses, a topic that is both scientifically interesting and technologically important. Experimental observations, as well as challenges and future work, are discussed.

1. Introduction

Glasses are non-equilibrium, amorphous materials.[1,2] Consequently, annealing (aging) in the glassy state leads to a continual evolution of thermodynamic properties towards equilibrium.[3–9] The relaxation of thermodynamic properties, *e.g.*, volume or enthalpy, with annealing time is a phenomenon termed structural recovery. The time-dependent thermodynamic properties result from the molecular-scale relaxations (structural rearrangement) of molecules towards structural equilibrium.[3,4,6] The accompanying changes in mechanical, optical, and electrical properties that are influenced by structural recovery are termed physical aging. Here, the terms structural recovery and physical aging will be used interchangeably.

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Physical aging is known to occur in all glasses and is of enormous technical importance.[3–9] The time-dependent glassy-state properties greatly impact the desired materials' performance and useful lifetime.[8] Fig. 1a displays the temperature dependence of volume or enthalpy for a typical glass-forming liquid.[1] The glass transition temperature (T_g), which can be defined as the intersection of the liquid and glass portions of the volume (enthalpy) versus temperature curve, is an important material characteristic as properties (viscosity, modulus) change dramatically as the transition temperature is approached.[1] Above T_g (dotted line labeled T_g in Fig. 1a), the material is in equilibrium. Quenching of the material to an annealing temperature T_a (dotted line labeled T_a in Fig. 1a) results in the formation of a glass with excess thermodynamic properties compared to that of the equilibrium liquid if the glass transition did not intervene.[1] Subsequently, isothermal annealing leads to the relaxation of excess thermodynamic properties

with time, *i.e.*, structural recovery.[4] The change in material properties with annealing time is sigmoidal on a logarithmic timescale with three distinct regions: an initial plateau, a power law, and an equilibrium plateau, as illustrated in Fig. 1b.[10,11] The slope of the power law region provides a measure of the rate of physical aging.[3,4,10] The rate of physical aging is dependent on molecular structure as well as the magnitude of $T_g - T_a$.[6,8] Although it has been investigated for more than half a century, a complete understanding of physical aging remains a scientific challenge and is more than ever of technical importance.[10,12] (The reader is referred to ref. 3–9 for further information on physical aging.)

Nanotechnology demands the use of glasses confined to the nanometre length-scale (see Fig. 2 for types of confinement geometries). Examples range from the development of novel nanocomposites as advanced materials[13] to ultrathin membranes for gas separation.[14] The use of glasses confined to the nanometre length-scale can be problematic, as some material properties are size dependent.[15–18] It has become evident that significant changes in physical aging, thus the time-dependent glassy-state properties, can be significantly impacted by confinement.[14,19–23] Thus, our understanding of physical aging in materials in the bulk state may not directly transfer to the confined state.

This Highlight aims to provide a summary of recent experimental work that has been undertaken to characterize and understand the effects of confinement on physical aging. Section 2 briefly discusses confinement effects on T_g in order to discuss potential origins of

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(a)

(b)
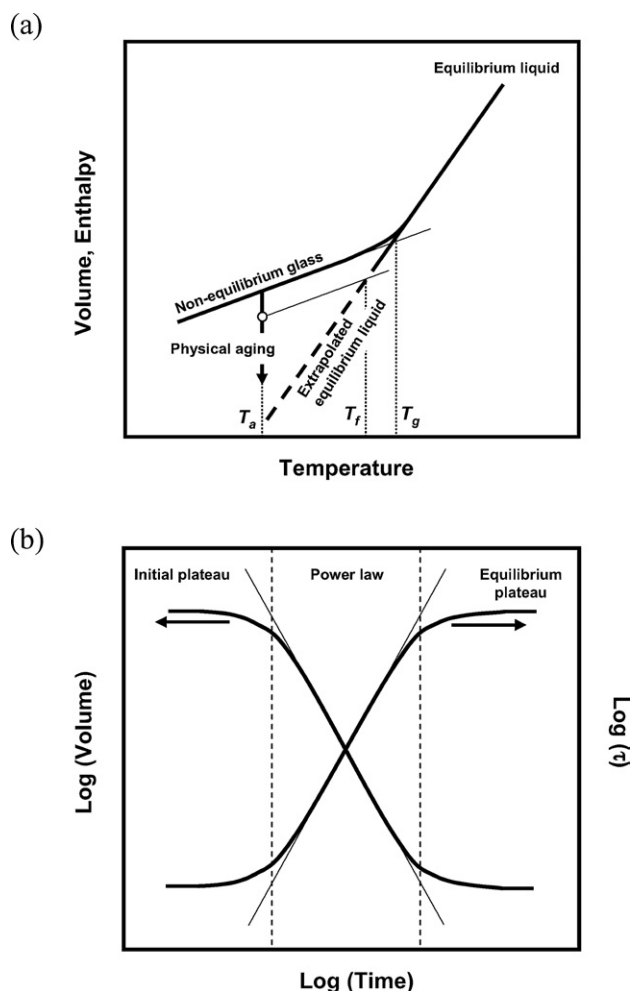
Fig. 1 (a) Temperature dependence of volume or enthalpy of an amorphous glass-forming polymer. Below T_g, the polymer is in a non-equilibrium glassy state. Isothermal annealing at T_a leads to spontaneous relaxation (structural recovery or physical aging) in the glassy state. See text for a description of T_f. (b) Sigmoidal relaxation behavior of volume or relaxation time constant as a function of physical aging time in the glassy state. Three different regimes can be observed: initial plateau, power law, and equilibrium plateau.

(a)   (b)   (c)   (d)   (e)

Polymer   **Inorganic**
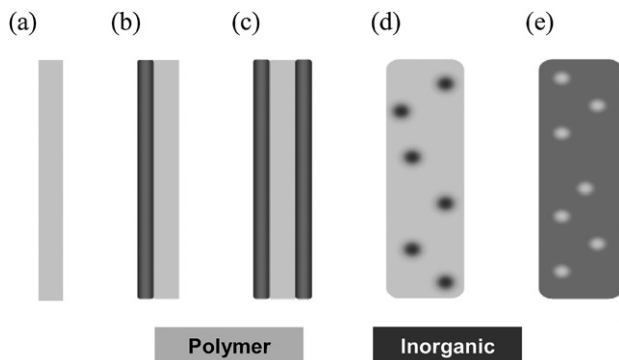
Fig. 2 Illustrations of commonly used geometries to physically confine polymer or molecular glasses to the nanometre length-scale: (a) thin free standing polymer film, (b) thin polymer film supported on one side, (c) thin polymer film supported on two sides, (d) nanofiller dispersed in polymer (nanocomposite), and (e) molecular glass-former filled in nanometre sized controlled pore glass.

confinement effects on physical aging. In Sections 3 and 4, a summary of selected work, revealing the diversity of confinement effects on aging, and discussions are presented, respectively. Lastly, conclusions and outlook are given in Section 5. Although this article covers experimental work, it is important to emphasize that considerable insight will result if the intriguing and important problems to be discussed are tackled from a combined experimental,[14,19–23] computational[24–27] and theoretical perspective.[28,29]

2. Confinement effects on the glass transition temperature

The T_g of molecular liquids and polymers can deviate substantially from the bulk T_g with confinement to the nanometre length-scale.[15,30–36] As the confining dimension is decreased below a critical value, e.g., film thickness in polymer films, interparticle spacing in polymer nanocomposites, diameter in molecular glass-former filled controlled pore glass, an increasingly large fraction of material is in direct contact with interfaces. The deviation in T_g with confinement can be explained as a result of (or lack of) interfacial interactions between the polymer and the interface.[15,31,33–36] Attractive interactions between the polymer and interface (substrate) can lead to an enhancement in T_g[15,33,35,36] while a repulsive or free/soft interface can lead to a reduction in T_g with confinement.[15,33–36] By altering the interfacial interactions it is possible to systematically change the T_g of a confined molecular liquid or polymer.[33,36] The author refers the reader to thorough reviews[37,38] for detailed information regarding confinement effects on T_g. The subject is briefly mentioned here to set the stage for the remainder of this Highlight.

3. Confinement effects on physical aging

Although the first reports of size effects on physical aging date back to the early 1990s,[19,39] a large amount of work has been undertaken recently.[14,20–23,40–57] The scope of the majority of these studies was to characterize and understand the change in the rate of physical aging with confinement. Confinement effects on physical aging have been investigated in

molecular glasses in nanopores, supported polymer films, unsupported polymer films (polymeric membranes), and polymer nanocomposites, and will be highlighted in that order subsequently.

3.1 Molecular glasses in nanopores

Calorimetry measurements revealed that the enthalpy recovery of ortho-terphenyl (o-TP) confined in nanopores was drastically different from that of the bulk.[20,39] In the experiments, o-TP was aged for different times in nanoporous glasses with mean diameters of 11.6, 22.5, and 47.9 nm. *Via* calorimetry studies, structural recovery was observed as an enthalpy overshoot upon heating through T_g. Fig. 3a and b show the development of enthalpy overshoot curves for o-TP in the bulk and confined in 11.6 nm diameter nanopores. Over the same aging time, there was a reduction in the development of enthalpy overshoot curves for the confined o-TP compared to the bulk. The observation suggested a reduction in the rate of structural recovery with confinement for the molecular glass o-TP.[39] However, a plot of $T_f - T_a$ versus aging time (where T_f is the fictive temperature and $T_f - T_a$ is a measure of the departure from equilibrium and equals zero at equilibrium) revealed (see Fig. 3c) that the confined glass aged to a different equilibrium state than the bulk. The fictive temperature of an aged glass, as indicated by the open circle in Fig. 1a, is the temperature at which it would reach the equilibrium line upon heating along the glass line.[20] (The reader is referred to ref. 20 for the method to determine T_f

from data presented in Fig. 3a and b.) For the bulk glass, $T_f - T_a$ approached a value of zero while for the confined glass, $T_f - T_a$ approached a non-zero value.[20] It was concluded that confined o-TP vitrified under isochoric conditions leading to the formation of negative pressures that altered the equilibrium enthalpy or structure.[20] Thus, while structural recovery appeared slower in the confined glass, it reached equilibrium on a shorter timescale than the bulk.

3.2 Supported polymer films

The effect of film thickness on the physical aging of polystyrene (PS) films supported on silicon was determined *via* ellipsometry.[21] Films were annealed at 150 °C for 24 h in vacuum to remove residual solvent and allow thermal equilibrium. Subsequently, films were aged at T_a ($T_a = 80$ °C) for 7 days. *Via* ellipsometry, physical aging was observed as an expansivity overshoot upon heating through T_g. Fig. 4 shows the development of aging overshoot curves for several films aged at 80 °C for 7 days. With decreasing film thickness there was a reduction in the development of aging overshoot curves and an absence of aging (no observed overshoot) for the 10 nm thick film.[21] Interestingly, for all film thicknesses investigated (10, 18, 30, 66 and 174 nm), expansivity overshoot curves exhibited peaks near $T \approx 100$ °C (bulk T_g of PS), while the T_gs of the 10, 18 and 30 nm thick films were substantially reduced compared to the bulk. As pointed out in the study, this result suggested a spatial distribution of T_gs within the films that

would result in a spatial distribution of physical aging rates, since the aging rate is dependent on the relative difference $T_g - T_a$.[21]

Poly(methyl methacrylate) (PMMA) and PS films supported on silica were used to investigate the effects of polymer-substrate interactions on the physical aging of thin films.[23] The fluorescence from dye molecules either doped into or covalently bonded (labeled) to the polymer was used to monitor aging. Physical aging leads to an increase in the fluorescence intensity of the dye molecules. The increase in intensity is due to a densification of the nanoscale medium surrounding the dye molecule, with a slightly denser environment yielding a higher intensity due to a reduced rate of nonradiative decay.[23] When annealed slightly below the bulk T_g, aging was absent in a 20 nm thick PS film,[23] a result consistent with earlier observations on thin PS films.[21] When PMMA was annealed slightly above the bulk T_g, a 20 nm thick film exhibited aging while a bulk film did not age.[23] The ability to suppress or induce aging in ultrathin polymer films was attributed to interfacial effects altering the T_gs of the films.[23] When annealed deep in the glassy state (T_a = bulk T_g − 87 K), confinement minimally impacted the physical aging of PS films but greatly impacted the physical aging of PMMA films.[23]

Fluorescence spectroscopy allowed for the ability to monitor physical aging at distinct locations within a polymer film at or near interfaces[40] to test an earlier hypothesis that there existed a spatial distribution of local physical aging in thin
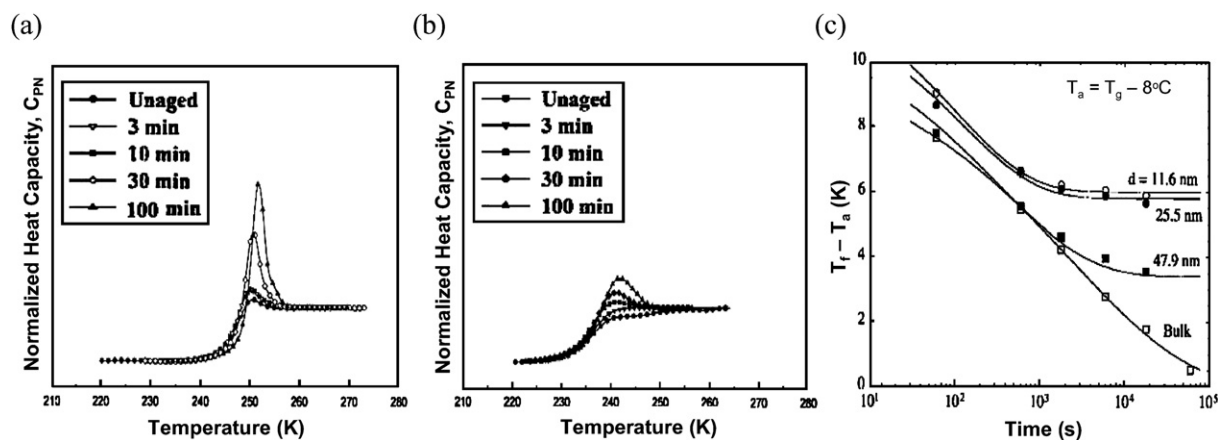
Fig. 3 Development of enthalpy relaxation curves as a function of aging time for o-TP in the (a) bulk state and (b) confined in 11.6 nm diameter pores. (c) Evolution of structural recovery for o-TP monitored *via* $T_f - T_a$. (Reprinted with permission from ref. 20.)
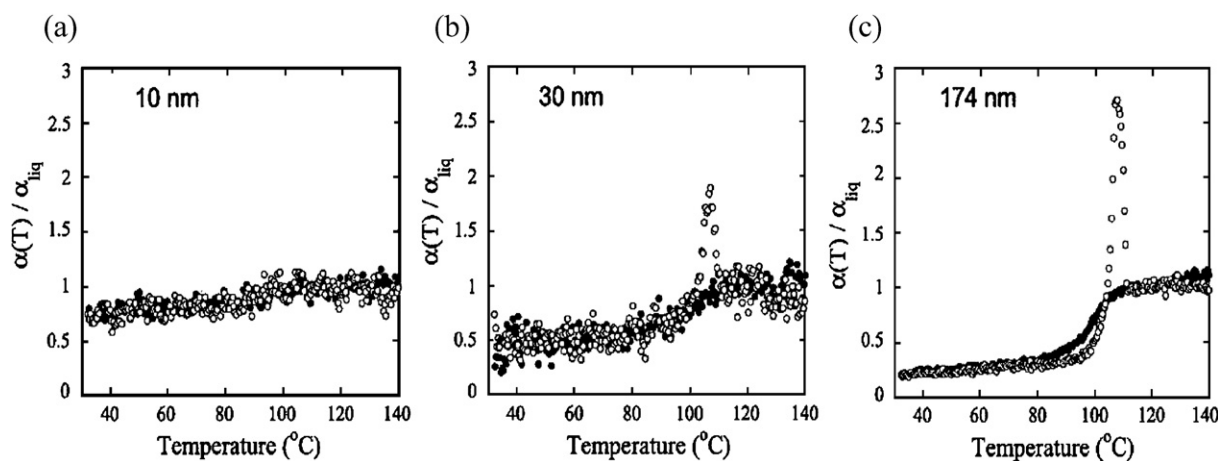
Fig. 4 Normalized expansivity of ultrathin PS films aged at 80 °C for 7 days upon heating (open symbols) and cooling curves from the melt (closed symbols). (Reprinted with permission from ref. 21.)

films.[21] This was achieved by the selective placement of a dye-labeled polymer layer within a multilayer film of neat polymer. The effects of interfaces on the physical aging of PMMA at T_a = bulk T_g − 87 K are illustrated in Fig. 5. Physical aging was greatest in the middle layer (representing bulk behavior), reduced by nearly a factor of two at the air-polymer interface, and near completely suppressed at the substrate-polymer interface.[40] When annealed at T_a = bulk T_g − 5 K (data not shown), the middle layer and the substrate layer aged similarly, while there was an absence of aging at the air-polymer interface. Trilayer geometry measurements conducted at T_a = bulk T_g − 87 K, in which aging was monitored at known distances away from the air-polymer and substrate-polymer interfaces,

revealed a distribution in physical aging rates extending some 200 nm from the interfaces.[40]

While many studies have reported reductions in aging rate with confinement, several studies have reported enhanced aging with confinement.[22,51] Dielectric relaxation spectroscopy (DRS) was used to monitor the combined dependence of film thickness and cooling rate on the physical aging of polycarbonate (PC).[22,51] *Via* DRS, a change in the dielectric permittivity was observed with aging time. Fig. 6 shows the impact of film thickness on physical aging of PC films annealed at 50 °C, quenched at rates of (a) 0.02 °C/s and (b) 60 °C/s.[51] Physical aging was enhanced with confinement. Additionally, the effects of confinement on aging were dependent on thermal history.

The faster the quench rate, the weaker the effects of confinement on physical aging. The combined thickness and cooling rate dependence on physical aging was explained by a fully diffusive mechanism of free volume holes to either external or internal surfaces.[22,51]

3.3 Unsupported polymer films

The consensus from the membrane literature is that glassy polymeric membranes exhibit enhanced physical aging with decreasing film thickness.[14,19,45,46,55–60] Polymeric membranes that have been investigated include polysulfone,[14,19,45,46] polyimides,[14,19,45,46,56,57] polynorbornene,[60] poly[1-(trimethylsilyl)-1propyne],[55] polyacrylate,[58] and poly(phenylene oxide)s.[14,45,46] Fig. 7 shows the impact of
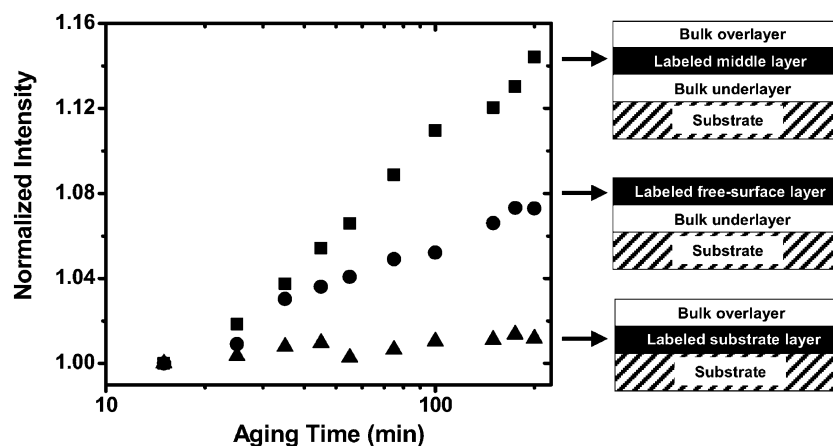
Fig. 5 Physical aging monitored by fluorescence in multilayer PMMA films. Normalized fluorescence intensity as a function of aging time (T_a = bulk T_g − 87 K) monitored exclusively in the middle of the film (squares), at the air-polymer interface (circles), and the substrate-polymer interface (triangles). The thickness of a labeled layer is 25 nm and the thickness of a bulk layer is 1000 nm.

(a)

(b)
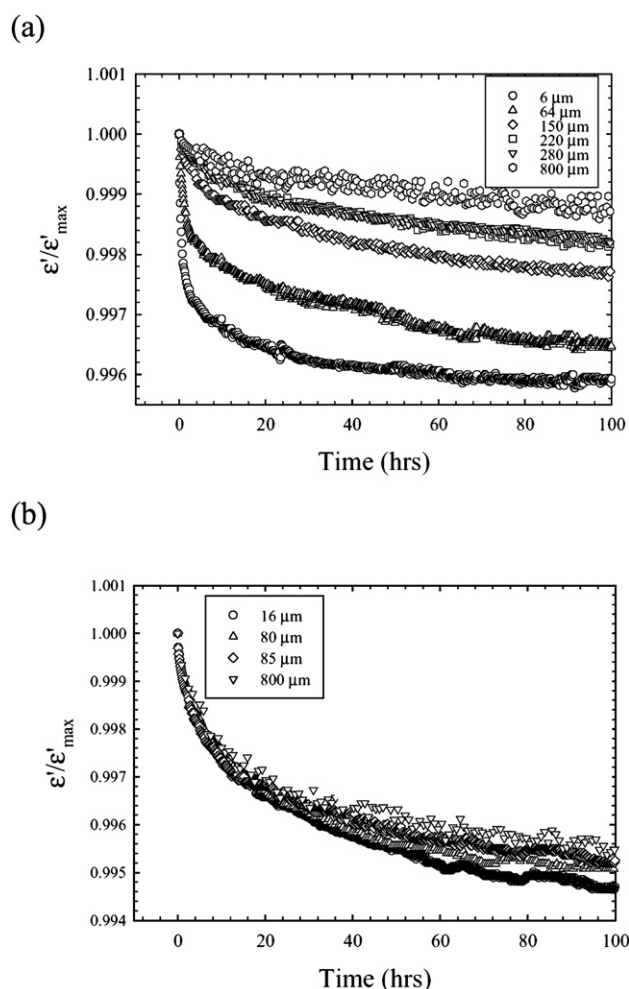
Fig. 6 Physical aging of polycarbonate films monitored by dielectric relaxation spectroscopy. Normalized permittivity of thin films aged for 100 h cooled to $T_a = 50\ ^\circ C$ at (a) 0.02 and (b) 60 $^\circ$C/s. (Reprinted with permission from ref. 51.)

film thickness on the physical aging of polysulfone measured *via* oxygen permeation studies.[14] Decreasing film thickness below ∼3.6 μm leads to enhanced physical aging. The enhanced physical aging with decreasing film thickness has also been observed *via* refractive index studies for polysulfone and a poly(phenylene oxide).[45] Models based on either the thickness dependence of T_g[60] or free volume loss[59] were developed to explain the observed experimental results.

3.4 Polymer nanocomposites

The effects of confinement on the physical aging of polymers are not unique to the thin film geometry and have also been observed in polymer nanocomposites.[41–44,49,50] In fact, thin films could be considered model systems for nanocomposites for which the thickness of a thin film is related to the average interparticle distance of nanoparticles in a polymer matrix.[42] For an epoxy/clay nanocomposite, enthalpy relaxation was reduced by nearly a factor of four with the incorporation of ten parts per hundred clay compared to the neat epoxy.[49,50] The reduction in aging with the addition of clay was rationalized assuming a layer with reduced mobility at the organic-inorganic interface.[50] Fluorescence studies have shown that the physical aging of PMMA[41–43] and poly(2-vinyl-pyridine)[42,43] deep in the glassy state could be suppressed almost completely using silica nanoparticles that have an attraction with the polymer. When nanoparticles did not possess an attraction with the polymer, such as in the case of PS

and silica nanoparticles, aging was not suppressed.[43]

4. Discussion

As highlighted above, confinement can have a dramatic impact on the physical aging of molecular and polymeric glasses. The impact of confinement on aging is dependent on several factors such as molecular structure, type of confinement, interactions with interfaces and aging temperature.

While briefly described in Section 2, confinement can dramatically impact T_g.[15,30–38] As physical aging is only possible below T_g and is dependent on $T_g - T_a$ (quench depth),[6] several experimentally observed confinement effects on physical aging can be related to confinement effects on T_g. The absence of physical aging for ultrathin PS films supported on silica aged slightly below bulk T_g is a result of a depression in the T_g of the films to a temperature lower than the aging temperature.[21,23] The observed presence of physical aging for ultrathin PMMA films supported on silica annealed slightly above bulk T_g is a result of an increase in the T_g of the films to a temperature above that of the annealing temperature.[23] Therefore, the shift in T_g with confinement, which has been shown to be tunable,[35,36] alters the conditions for which polymers undergo aging.

The absence of physical aging at the air-polymer interface of PMMA films, as indicated by fluorescence multilayer experiments, results from a reduced T_g at the free surface.[40] The results reveal a spatial distribution in physical aging across a film that is partially a consequence of changes in T_g near the interfaces.[34,40] The spatial distribution of physical aging is consistent with Fig. 4b.[21] One plausible reason why ultrathin PS films exhibit aging overshoot curves at bulk T_g while their T_gs are reduced compared to the bulk T_g value could be related to spatially distributed physical aging; only the portion of the film with a T_g near the bulk value experiences aging.[21,23] It is noted, that recently it has been observed that glasses formed by vapor deposition exhibit enthalpy overshoot curves far above the nominal T_g,[61,62] reminiscent of Fig. 4b. It may be worth asking if the result reprinted in
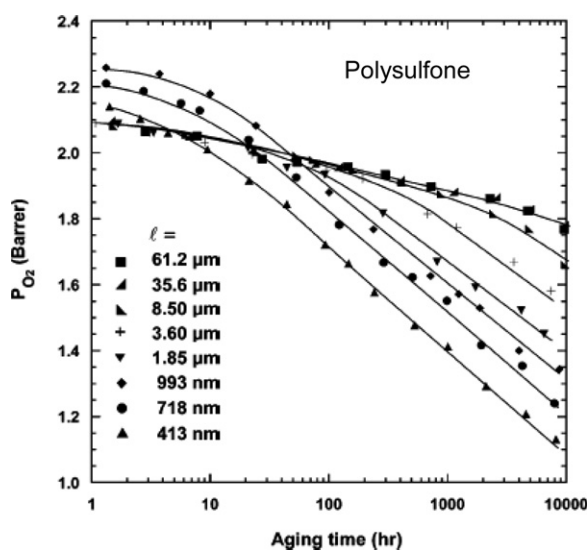
Fig. 7 The impact of film thickness on the physical aging of polysulfone membranes aged at 35 °C monitored *via* permeation measurements. The decrease in oxygen permeability with aging time is accelerated with decreasing film thickness below ~3.60 μm. (Reprinted with permission from ref. 14.)

Fig. 4b. and those in ref. 61 and 62 are at all connected.

Structural recovery of o-TP confined in nanopores (discussed in Section 3.1) was successfully modeled using a version of the Tool–Narayanaswamy–Moynihan–Kovacs–Aklonis–Hutchinson–Ramos (TNM-KAHR) models[63–66] that were adapted to incorporate vitrification under isochoric conditions.[20] The structural recovery data of the confined o-TP was modeled using macroscopic properties with a reduced T_g under isochoric conditions. Successful modeling of the data suggests that the deviations in aging with confinement are directly related to the change in T_g with confinement and isochoric structural relaxation.[20]

Some effects of confinement on aging cannot be explained by changes in T_g. The onset film thicknesses at which deviations in physical aging are observed are much greater than the onset film thicknesses at which deviations in T_g are observed for supported films[22,23,40,42,51] and unsupported films.[14,19,45,46,60] For example, the difference in onset film thickness at which deviations in T_g and physical aging are observed for PC and polysulfone is an order of magnitude.[14,67] It has also been reported that interfaces (air-polymer interface and polymer-silica interface) impact aging on a greater length-scale than T_g.[40] Though experimentally

observed, the reason(s) why physical aging is affected by confinement and interfaces to much greater length-scales than T_g remains elusive.

Reductions in physical aging with confinement have been attributed to interfacial effects perturbing molecular mobility.[23,40–43,47–50] A recent study has suggested that the suppression of physical aging for ultrathin PMMA films supported on silica and silica-PMMA nanocomposites is partially related to the reduction in the strength of the β-relaxation process of confined PMMA.[41] A forty percent reduction in the strength of the β process of PMMA was observed with the addition of 0.4 vol% silica nanoparticles. The reduced strength of the β process was attributed to hydrogen bonding interactions between the ester side groups of PMMA (motions associated with the β process[68]) and the hydroxyl groups on the surface of the silica nanoparticles.[41]

Enhancements in physical aging with confinement have been explained by models[22,59] based on free volume loss during structural relaxation.[69] Two mechanisms of free volume reduction during aging are (i) free volume hole diffusion to the interface and (ii) lattice contraction.[59] A model assuming free volume loss through diffusion to the film surface (a thickness dependent effect) and

lattice contraction (a thickness independent effect) was developed to describe the thickness dependent effects of aging on the gas permeability of glassy membranes.[59] However, a recent study has suggested that lattice contraction is not a mechanism for free volume loss during aging and proposed a fully diffusive model to explain the thickness dependence of aging invoking not only free volume diffusion to the external surface but to internal surfaces created by low density regions.[22] While the above models describe well the enhancement of aging with confinement, it must be mentioned that there exists earlier experimental evidence against the notion of free volume diffusion.[70]

Of particular interest is why some glasses show a reduction in aging rate with confinement while others show an enhancement in aging rate with confinement. One possible explanation is related to interfacial effects. Polymers that exhibit attractive interactions with a substrate show a suppression in aging with confinement,[23,40–43,49,50] while unsupported films (no substrate effects) show an enhancement in aging with confinement.[14,19,45,46,60] However, interfacial effects do not explain all the observed experimental differences. For example, the reduction in physical aging at the air-polymer interface of PMMA films[40] and the enhancement in physical aging with confinement for unsupported films[14] cannot be explained by invoking only interfacial effects. As with confinement effects on T_g,[36,71–73] chemical structure appears to play a significant role in the way confinement impacts physical aging. The difference in the length-scale at which confinement affects aging for different polymers, greater than 1 micron for polysulfone and PC (rigid backbone)[14,22] and less than 300 nm for PMMA and PS (flexible backbone),[23] highlights this effect. Systematic studies investigating the role of chemical structure on the impact of confinement on physical aging are warranted. It is noted that with the vast difference in length-scales at which physical aging is affected by confinement it may be advantageous to distinguish between nanoscale and microscale effects.

A final point worth mentioning is the notion that the glassy state, *i.e.*, initial glassy state after quenching from above T_g to T_a and the equilibrium glassy state

after aging, is altered by confinement. Changes in the glassy state imply deviations in the instantaneous state of the glass (volume) and the departure from equilibrium, both of which would impact the rate of physical aging. A decrease in the glassy state thermal expansion coefficient of PS films supported on silica with confinement has been observed, suggesting both a change in the initial glassy state prior to aging and the departure from equilibrium.[32] Experimental evidence for a change in the equilibrium glassy state of confined glasses has also been reported, suggesting a deviation in the departure from equilibrium.[20] A connection between possible changes of the glassy state and physical aging of confined polymer should be of significant importance for future studies.

5. Conclusions and outlook

From the present Highlight and related literature, it is clear that confinement can have an enormous impact on the physical aging behavior of molecular glasses and polymeric glasses. The observations presented are important from both scientific and technological perspectives. Studying aging in confined geometries provides an opportunity to gain further understanding of the glassy state and the glass transition. Confined polymeric glasses range from thin films to nanocomposites and are of enormous technical importance in diverse fields ranging from microelectronics[74] to tissue engineering[75] to gas separations.[76]

From the work presented it should also be clear that many important observations and questions remain unanswered. In addition, the development of experimental approaches should aim to measure the full relaxation time distribution or the accompanying mechanical property changes during physical aging of confined glasses. Finally, simulations should be employed and theories developed to aid our understanding of confinement effects on the physical aging of glasses.

Acknowledgements

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