



Physical aging of polystyrene films tracked by gas permeability

Thomas M. Murphy, B.D. Freeman, D.R. Paul*

Department of Chemical Engineering, The University of Texas at Austin, Austin, TX 78712, United States

ARTICLE INFO

Article history:

Received 31 October 2012

Received in revised form

28 November 2012

Accepted 2 December 2012

Available online 6 December 2012

Keywords:

Physical aging
Gas permeability
Confinement

ABSTRACT

Most studies using gas permeation to characterize physical aging in thin polymer films have focused on polymers of interest as membrane materials, such as polysulfone (PSF) and Matrimid. Many other physical aging studies, using techniques other than gas permeation, focus on polystyrene (PS). In this work, physical aging in bulk PS films and PDMS-coated thin PS films was studied using well-established gas permeation techniques. The ~400 nm PS films aged slightly faster than bulk PS. However, the difference between rates of aging in thin and thick films was much less than that reported in PSF and Matrimid films of similar thicknesses. The ~800 nm films aged in a manner generally similar to bulk PS. Comparison of the normalized oxygen permeability of ~400 nm films of PS, PSF, and Matrimid revealed that a ~400 nm PS film experiences a slower decline in relative permeability than a PSF or Matrimid film does. Unlike what has been observed previously in studies of PSF and Matrimid films, PS films do not appear to show aging behavior that is strongly dependent on film thickness or highly accelerated relative to bulk. Because it would be difficult to use the results of PS aging studies to predict the aging behavior of typical gas separation polymers, we suggest that PS is not a good model for the aging behavior of commercially useful gas separation membrane materials.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

Physical aging generally refers to spontaneous property changes that occur over time in a non-equilibrium glassy material as it approaches equilibrium via structural rearrangement [1]. In bulk polymer glasses at typical service temperatures, these changes are usually slow and continue almost indefinitely [2]. At elevated temperatures, however, aging is typically more rapid, and equilibration is possible over accessible experimental timescales. Much of the recent literature regarding physical aging in polymers has focused on aging in confined geometries. Interest in this area of study stems from the wide variety of applications that utilize polymers in confined geometries, such as gas separation membranes and nanocomposites, among others [3–8].

A significant portion of the literature on aging of confined polymers has focused on aging in glassy materials that are of interest as gas separation materials, such as polysulfone (PSF) and various polyimides (notably Matrimid) [4,5,9–21]. Typically, the polymers of interest have T_g s greater than 150 °C (often much higher) [4,9,11,15]. These studies are normally conducted at near-ambient temperatures (35 °C, most often), and gas permeability

is measured over the course of weeks or months. Researchers using gas permeation techniques have generally observed accelerated or enhanced physical aging with decreasing film thickness. The thickness at which noticeable modifications in the aging behavior begin has been observed to be on the order of a few microns, which is much greater than the thickness typically associated with the onset of T_g depression in thin films (by roughly an order of magnitude or more, for many polymers) [22,23].

Huang and Paul used gas permeability measurements to study freestanding PSF, Matrimid, and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) films with thicknesses ranging from bulk down to 400 nm [4,16,24–26]. They observed an acceleration of aging with decreasing film thickness in all polymers studied. In a study of the temperature dependence of aging as assessed by gas permeability, Huang and Paul observed that the difference between the aging rates of 400 nm and 3.6 μ m PSF films was greater for films aged at 35 °C than for films aged at 45 °C or 55 °C [16]. Increasing the temperature increased the aging rate at each thickness but decreased the sensitivity of aging rate to film thickness. For the thinnest films considered (400 nm), the difference in the aging rates at the three temperatures considered was small. A study of PPO films aged at different temperatures showed similar results [25]. Rowe et al. used a PDMS coating technique to enable gas permeation studies of PSF and Matrimid films as thin as ~18 nm [5]. They observed that the initial permeability decreased as

* Corresponding author. Tel.: +1 512 471 5392; fax: +1 512 471 0542.
E-mail address: drp@che.utexas.edu (D.R. Paul).

film thickness was decreased incrementally from 465 nm to 20 nm. For a 20 nm PSF film, the initial oxygen permeability was approximately 30–40% less than that of a bulk or 465 nm PSF film, indicating that the thinner film had already achieved a denser, lower-free volume state by the time the first measurement could be made [5]. The properties of the ultrathin films strongly deviated from those of bulk films, and these deviations were said to be consistent with the ideas of enhanced mobility of near-surface material and T_g depression in the thinnest films. In general, gas permeation aging studies have observed that by the time the films reach 100 h of aging time, thinner films typically show most of the following characteristics relative to thicker ones: lower absolute permeability values, higher selectivities, faster rates of permeability decline, and slighter greater rates of increase in selectivity [4,5,24]. In some cases, the rate of permeability decline may not continue to increase with decreasing thickness. For example, the thinnest films studied by Rowe et al. (20 nm PSF and 18 nm Matrimid) show a slower rate of permeability decline than some of the thicker films, but they have absolute permeability values that are significantly lower. This finding indicates that, for the thinnest films, which would be expected to have depressed T_g , rapid aging occurring in the first hour may result in a highly “aged” film that has a reduced driving force for physical aging and thus a slower rate of permeability decline.

Rowe et al. also characterized the aging behavior of polysulfone (PSF) films using variable energy positron annihilation lifetime spectroscopy (PALS) [27]. The results indicated that free volume decreased throughout the film during physical aging, as expected. A 450 nm film was observed to undergo accelerated aging when compared to a bulk sample, which is in agreement with previous studies of PSF films that used gas permeation techniques [4]. Additionally, Rowe et al. observed reduced *ortho*-positronium lifetimes at lower implantation energies, suggesting the existence of smaller free volume elements in the near-surface region of the film (within the first 50 nm). In contrast, variable-energy PALS studies of PS films by Cao et al. and Algers et al. showed an increase in *o*-Ps lifetime at low implantation energies [28,29]. Rowe et al. suggested that the near-surface regions of PSF films age more rapidly than bulk and that the enhanced mobility offered by a free surface allows that region of the film to reach a lower free volume state more quickly than bulk. Using established correlations, the *o*-Ps lifetime was used to calculate the fractional free volume (FFV), and the FFV was then used to calculate the oxygen permeability. The permeability values calculated from the PALS aging data (with no adjustable parameters) were then compared to data gathered independently using gas permeability measurements over time. For films of 50 nm, 125 nm, and ~450 nm, there was remarkably good agreement between the two sets of data [27].

Another important body of literature has focused on aging in polymers like polystyrene (PS), which is perhaps the most commonly used polymer in studies of the glass transition and physical aging in confined geometries. In many of these studies, aging has been characterized using ellipsometry, dielectric spectroscopy, fluorescence spectroscopy, or DSC [8,30–36]. These studies often investigate aging at temperatures that are closer to T_g than the temperatures used in the gas permeation studies.

Pye et al. used an ellipsometry procedure developed in their laboratories [32] to study aging in thin PS films and observed that a ~30 nm film aged at a slower rate than a ~2400 nm film at all temperatures considered [31]. The difference between the aging rates of the two PS films depended on the aging temperature. For the aging temperatures they considered, there was generally a larger difference between the aging rates of thicker and thinner films when the aging temperature was a greater distance from T_g . The difference in aging rates did not correspond merely to a shift in

the aging rates to lower temperatures due to T_g depression in the ~30 nm film, which they found to be consistent with the idea of a gradient in dynamics across the film.

Koh and Simon studied the aging of stacked ultrathin PS films using DSC [37]. They observed that the T_g broadened and decreased with decreasing film thickness. An aging rate was defined as the rate of change in the fictive temperature (T_f) with respect to the logarithm of time ($-dT_f/d \log t_a$). When aged at the same distance from T_g , bulk and ultrathin films (62 nm) showed similar aging rates, but the time required to reach equilibrium was slightly greater for the 62 nm films than it was for bulk. When aged at the same temperature, however, the ultrathin films had reduced aging rates compared to bulk yet required a shorter time to reach equilibrium. They note that their results suggest the possibility that at aging temperatures that are more than 15 °C lower than T_g (i.e., $T_g - T_a > 15$ °C), the ultrathin films may begin to show greater aging rates and shorter equilibration times than bulk when aged at equivalent distances from T_g . Using the equilibration time as the criteria for comparing the aging responses of the various films, the ultrathin films were said to undergo accelerated aging. A recent DSC study by Boucher et al. found that even PS films with thicknesses in the range of hundreds of nanometers demonstrated accelerated aging (as judged by the time required to reach equilibrium) when aged at 358 K or 369 K [35].

Priestley et al. studied the physical aging of PS supported on a non-attractive silica substrate by measuring changes in the peak fluorescence intensity of chromophore-doped PS films [38]. When aged at 32 °C ($T_{g,bulk} - 71$ °C), the aging response of a 20 nm film was similar to that of a 500 nm film. However, when aged at 93 °C ($T_{g,bulk} - 10$ °C), the 20 nm film showed no aging while the 500 nm film aged more rapidly than it did at 32 °C. The absence of aging in the 20 nm film aged at 93 °C was said to arise from T_g depression, which caused the 20 nm film to be above its T_g and in equilibrium at 93 °C.

There has been discussion in the literature about the possibility of fundamental differences in the aging of stiffer-backbone polymers like PSF or Matrimid and that of a polymer like PS, which has a more flexible backbone [32,34,39]. Gray et al. used ellipsometry to compare the aging behavior of PS and PSF films [34]. They measured the change in thickness of PS and PSF films quenched from above T_g in either a supported or freestanding state and then held at a given aging temperature (65 °C for PS, 100 °C for PSF). For both PS and PSF, 400 nm and 1000 nm films that were supported during the quench showed essentially identical aging behavior. The physical aging of PS films quenched while supported was then compared to that of films quenched in a freestanding state (i.e., mimicking the annealing procedure used in many of the gas permeation aging studies). They observed that 1260 nm and 600 nm films quenched in a freestanding state aged more slowly than supported-quenched films of similar thickness, despite undergoing much more rapid cooling through T_g . Upon reheating the freestanding-quenched films above T_g and then cooling in a supported state, the subsequent aging behavior was nearly identical to that of a film originally quenched in a supported state. The difference in aging rates between supported-quenched and freestanding-quenched films was much less in the 600 nm film than in the 1260 nm film. The aging rates of freestanding-quenched PS films exhibited a noticeable thickness dependence at these length scales. This finding differs from what was observed in supported films, which did not show any thickness dependence in their study and were observed previously to have thickness-independent aging rates until becoming thinner than 100 nm [31]. They suggest that different quench conditions (i.e., freestanding versus supported) would lead to different types of stresses in the glassy film, which would in turn affect the aging rate.

Download English Version:

<https://daneshyari.com/en/article/5182561>

Download Persian Version:

<https://daneshyari.com/article/5182561>

[Daneshyari.com](https://daneshyari.com)